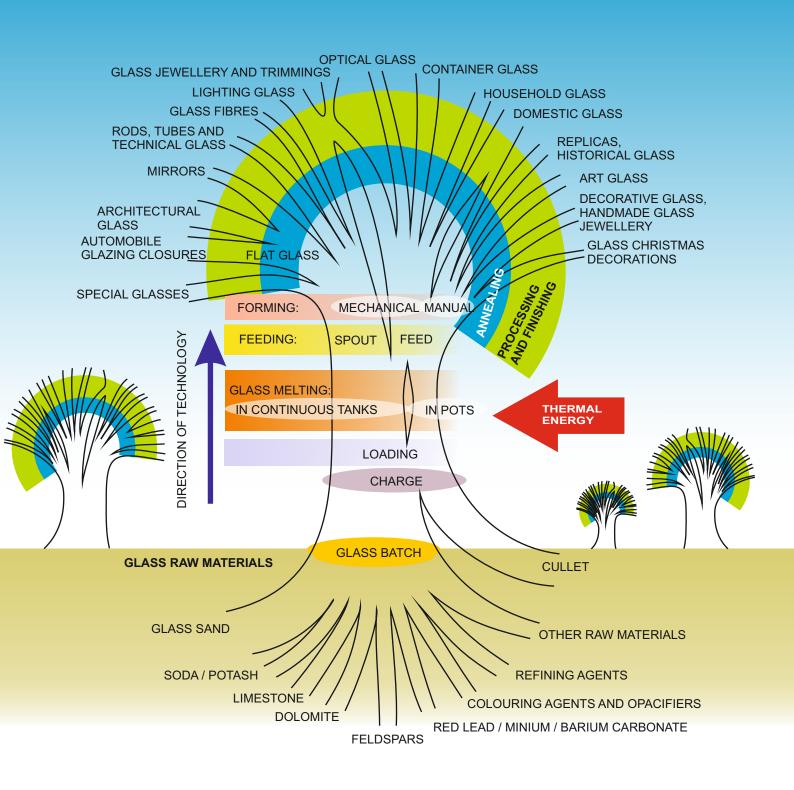**TECHNICAL UNIVERSITY OF LIBEREC**
DEPARTMENT OF GLASS PRODUCING MACHINES AND ROBOTICS

AUTOMATIC GLASS PRODUCTION TECHNOLOGY

Vlastimil Hotař, Vladimír Klebsa, Barbora Nikendey Holubová, Ivo Matoušek

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AUTOMATIC GLASS PRODUCTION TECHNOLOGY

The textbook was drawn up on the basis of experience in teaching of subject "Glass Technology" for future graduates of engineering studies at the Department of Glass Producing Machines and Robotics. It is based on current knowledge in the field and mentions some trends in glass technology.

The textbook is intended for the subject "Automatic Glass Production Technology" for students of the 1st year of postgraduate master study programme N0715A270018, N0715A270019 - Machines and Equipment Design and N2301 - Mechanical Engineering, specialization Glass Producing Machines and Robotics.

Contents

Acknowledgement

Preface

The textbook is intended for the subject "Automatic Glass Production Technology" for students of the 1st year of postgraduate master study programme N0715A270018, N0715A270019 - Machines and Equipment Design and N2301 - Mechanical Engineering, specialization Glass Producing Machines and Robotics.

The aim is to familiarize students with the basics of existing glass technology with emphasis on the equipment and machines used. The scope of the textbook corresponds to the current diversity of glass production and includes basic information about technologies.

The content of study texts is first devoted to the definition of glass and glass melt, the structure and classification of glass. The properties of glass and glass melt and raw materials for glass production follow. In the next part, the textbook is structured on the basis of technological operations from the beginning of production up to final adjustments, i.e. from glass batch preparation, through loading, melting, feeding, forming, annealing to processing and finishing. The last chapters are briefly devoted to defects and quality control.

The study assumes knowledge of chemistry, physics and mathematics at the level of mechanical bachelor and engineer.

1 Introduction
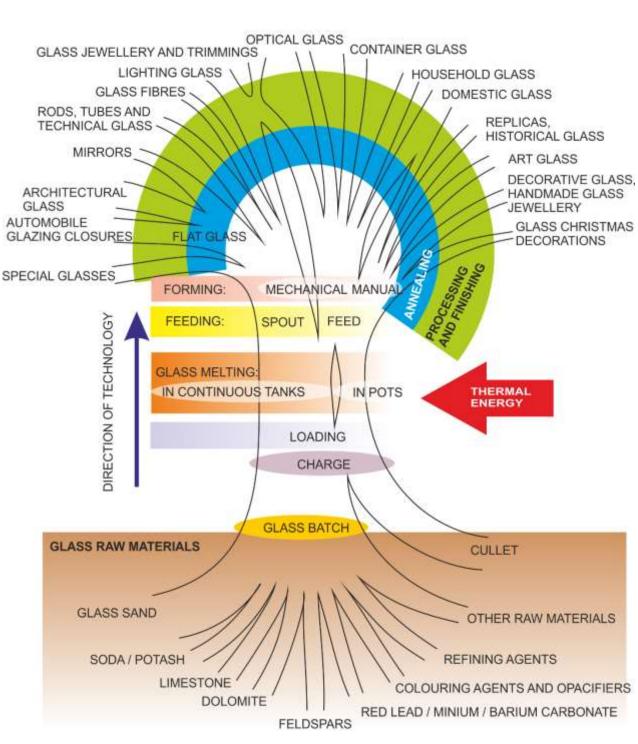
The range of current glass production is allowed by fully automated machines and equipment, advanced technologies and complicated lines. Modern glass producing facilities are automated, often robotic, clean, produce large volumes, and modern glassmakers often sit in the control room at computers.

In the past, glass production underwent major changes not only in technology, but also in the perception of glass as a material. Over the course of two millennia, glass has transformed from a unique material, balanced with gold, into a common material. In ancient history, glass products were considered an exclusive commodity, which was the prerogative of only prominent and wealthy individuals. As technology improved, glass became cheaper and more affordable. Glass gradually began to replace some materials, such as stoneware in the case of container glass, which was completely replaced (not only) by glass over time. Glass began to be used as an imitation of precious and semi-precious stones, until a specific branch was finally set up: glass jewellery affordable for anyone. Progressive changes in technology underlie this transformation, such as the invention of glass-blowing pipe in the first century BC, mechanization that made production more efficient, the introduction of simple machines at the beginning of the industrial revolution, automatic machines such as the Owens bottle machine from the early 20th century, up to high-performance lines, enabling the production of available glass products. Over time, glass lines become very expensive, but thanks to large production volumes, they make it possible to produce relatively cheap products that are competitive with other materials.

Advances in glass industry have been and are influenced by the development of technologies, both glass technologies and technologies that are used for machines and equipment and are not directly related to glass technology. The main impulses for research, development and deployment of new and often revolutionary machines have been and are efforts to introduce technologies that will enable the production of the product in larger volumes, often at lower unit prices and possibly also lead to increased qualitative properties of glass products.

Common glass technology can be shown by the glass technology tree (Fig. 1.1). Similar basic raw materials are mostly used and in the case of the most common glasses the main raw material is glass sand. These glasses are referred to as silicate glasses. Other important raw materials are soda, potash, limestone and others. A mixture of glass raw materials without cullet is called a ***glass batch*** and together with cullet a ***glass charge***. The preparation of the charge is followed by loading into melting units, melting and feeding of the glass melt. The forming of the glass melt, its annealing and finishing of glass products follow. The production of individual products differs in the composition and amount of the glass melts required, in the feeding and forming technologies, in the amount of cooled products and in a wide range of subsequent processing, finishing and use. As it appears from Fig. 1.1, there is a whole range of glass products with a wide range of uses, from purely technical applications to purely design products.

Most glass technologies are based on the basic principle of production of glass products, Fig. 1.2. The future product must go through individual phases of technology and, in view of the above, it is always possible to encounter the use of equipment and machines. Machines and equipment often differ fundamentally for individual products, although the basic principle remains the same.

GLASS TECHNOLOGY TREE

Fig. 1.1 Glass technology tree
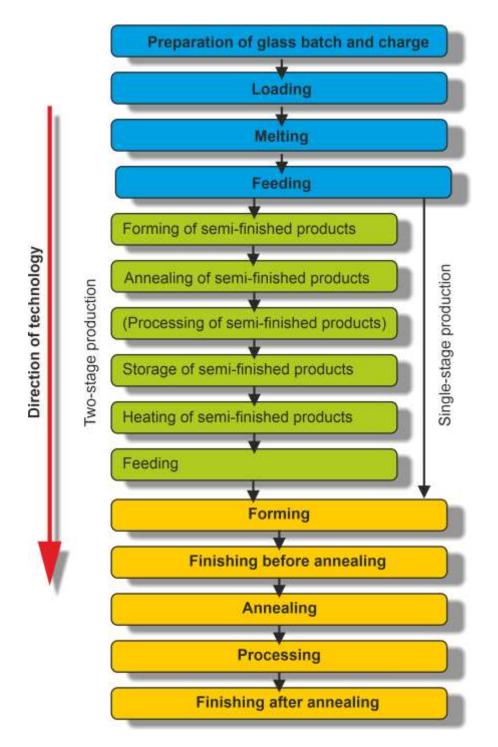
Fig. 1.2 Basic principle of glass technology with the division of single-stage and two-stage production

In general, production can also be divided into single-stage and two-stage production. Two-stage production is characterized by the production of semi-finished products, which are cooled, stored, so-called primary production. The semi-finished product is then further processed by reheating to a plastic state, or even melted, then dosed and finally reformed. This principle of production is characteristic especially for older technologies, special technologies and low-volume technologies, where it does not pay to choose single-stage production for a small number of products.

In single-stage production, the intermediate operation of annealing the semi-finished product is omitted, therefore lower costs can be generally achieved, as energy for annealing and reheating is saved, production time is shortened, the costs of subsequent forming, handling and storage are reduced. Single-stage production is modern production and is designed for large volumes of products. From a technological point of view, it is not always possible to introduce single-stage production for a certain type of products. At present, it is also not flexible enough and is therefore not suitable for small volumes of products.

A very important technological step is the melting itself. In principle, glass factories work on two basic principles of melting technologies. These are periodic - discontinuous melting (in day-tank and pot furnaces) and continuous melting (in continuous tank furnaces). For pot melting and day-tank melting, the melting cycle is repeated in daily cycles. In the case of continuous tanks (glass melting units, GMU), the process is continuous, without interruption (for more information see Chapter 7.6). These two basic principles differ not only by the melting itself, but also by the loading of charge, feeding and forming of the glass melt. This is also related to different mechanization, automation, different machines and equipment. They also clearly differ in terms of production volume and variety of products.

2 Basic terms

Glass is a special material due to its behaviour, structure, properties and production and, after all, methods of use. Glass is a solid substance, distinguishing between the basic states of matter - solid, liquid, gaseous and plasma.

2.1 Crystalline, liquid and glassy states

Crystalline substances are characterized by a periodically recurring internal structure. This periodicity can also manifest itself over a "long-range", and then we speak of a single crystal. Another characteristic of crystalline substances is that, when heated above the melting point, they form a melt, mostly of relatively low viscosity. These substances with a regular internal structure have certain defects (lattice defects), which are characterized, classified and to some extent used. These are point, line (dislocation), surface (block boundaries in a mosaic structure) and volume defects.

Unlike crystalline substances, the glassy state represent a disordered grouping of basic building blocks (molecules or ions) affecting mainly mechanical properties. These substances gradually lose their strength when heated (glasses do not have a sharp melting point, but so-called liquidus temperature), soften and gradually begin to behave as highly viscous liquids, whose viscosity decreases with increasing temperature. A characteristic property of substances in the glassy state is the existence of a glass transition region, which can also be called a region of glass transition - vitrification. However, in a detailed study of the internal structure of glass, it is possible to find localized regions with a certain degree of regularity of the internal arrangement. It is a regularity at the so-called "short-range", in other words - their degree of internal regularity shows the so-called short-range arrangement. In addition to glass, other substances also show similar characteristics, such as asphalt, wax, a number of high-molecular substances, but also metals in the amorphous state, i.e. metal glasses, etc. When trying to briefly summarize the knowledge about the glassy state, which is difficult to study, requiring modern methods and constantly ongoing, it is possible to use the definition formulated by E. D. Zanotto [35]: "*Glass is a nonequilibrium, non-crystalline condensed state of matter that exhibits a glass transition. The structure of glasses is similar to that of their parent supercooled liquids (SCL), and they spontaneously relax toward the SCL state. Their ultimate fate is to solidify, i.e., crystallize.*" This definition is for those who understand the meaning of glass transition.

2.1.1 Glass transition region

Most inorganic substances form a melt of very low viscosity when heated above the melting point, and crystallize upon gradual heat removal. Other substances gradually soften and turn into highly viscous melts, which can be easily super-cooled and do not crystallize with increasing viscosity, but glass is formed. This can be demonstrated by the volume and temperature dependence of both types of substances (Fig. 2.1).

As the melt is cooled, the volume decreases continuously from point 1 to point 2 (solidification temperature). In the case of crystalline substances in point 2, spontaneous crystallization occurs with sufficiently slow annealing. The temperature drop stops and the volume of the substance changes rapidly due to the phase transformation (crystallization). As soon as all the melt turns into crystals (point 3), their volume further decreases to point 4.

In the case of glass solidification, the initial course is the same up to point 2. However, in point 2, crystallization does not occur and the volume decreases continuously up to point 5. In the section between points 2 - 5, it is a super-cooled liquid. From point 5 to point 6, a change in the behaviour of the substance is evident, the volume of which decreases more slowly. The temperature T_g corresponding to point 5 is called the glass transition temperature or also the vitrification temperature. In technical glass terminology, the melt above the temperature T_g is called glass melt, below the temperature T_g the term glass is used.
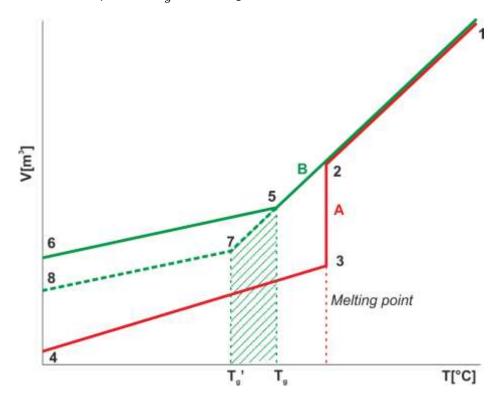
Fig. 2.1 Schematic representation of the change in volume with temperature: A - solidification with crystallization (1-2-3-4), B - glass solidification: - slow cooling (1-5-7-8), fast cooling (1-5-6)

If the melt in point 1 cools significantly more slowly without crystallization, the behaviour of the substance under examination will change only at a slightly lower temperature (point 7), which is indicated $T_g{'}$. The final volume of the system in point 8 will therefore be smaller than in point 6, which corresponds to higher cooling rate. From this course, it can be concluded that the properties of glass below the glass transition temperature T_g depend on its thermal history. The range of temperatures between T_g' and T_g is called the glass transition interval or also the vitrification interval. The rate of cooling and thus the glass transition also affect most properties (to varying degrees, more significantly, for example refractive index).

2.2 Glass classification

Several aspects can be applied to the classification of glasses. For the purposes of this textbook, the following aspects are chosen: chemical composition, method of production and purpose of use.

2.2.1 Classification by chemical composition

According to its chemical composition, glass forms two large groups of substances. On the one hand, there are organic glasses (e.g. polymethyl methacrylate), on the other hand, there are inorganic glasses, Fig. 2.2. These will be dealt with in more detail in this text, because inorganic glasses form the material basis of the most glass commodities produced. Glass can be formed under certain circumstances by elements (S, Se, P, As), oxides, halides, chalcogenides and metals, but the widest industrial use belongs to glasses made of oxides, i.e. oxide glasses.
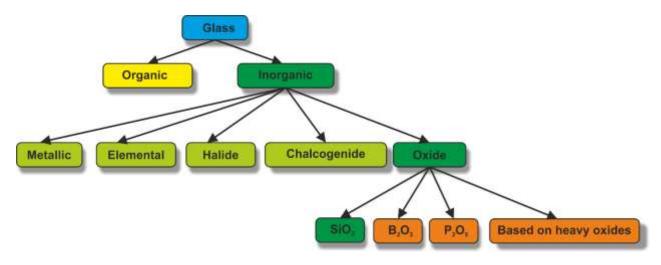
Fig. 2.2 Classification of glasses by chemical composition

Some oxides can form glass on their own, these are glass-forming oxides. These include, in particular, silicon dioxide (SiO_2), boron trioxide (B_2O_3), phosphorus pentoxide (P_2O_5), and some others. Other oxides can form glass only in combination with other oxides (so-called conditional glass formers or intermediates e.g. aluminium oxide, Al_2O_3); in addition, other oxides can participate in the structure of glass, they can be called modifiers, the presence of which affects the structural network and final properties of glass (Na_2O, K_2O, CaO, MgO, PbO and more). Glasses are thereby considered to be a multi-component system, where the main component is glass-forming oxide (silicate), other components are modifying oxides. According to the number of oxides (components) we distinguish one-component glasses consisting of one oxide (it must be glass-forming oxide), an example is quartz glass (silica glass) consisting of almost only silicon dioxide, and multi-component glasses consisting of two or more oxides, at least one of which must be glass-forming oxide. These glasses are the materials for production of the vast majority of glass commodities.

In the following, the term glass will refer to silicate glasses, in which the main glass-forming oxide is silica (silicon sioxide), according to which we distinguish the class of silicate glasses.

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2.2.2   Classification by method of production

This section is limited to a list of the most commonly used production technologies according to which the product groups are called. They are cast, pressed, drawn, blown glasses, glass jewellery and some others.

2.2.3   Classification by purpose of use

At this point, the application areas of the produced glasses will be mentioned, very roughly speaking, according to the relevance of use in practice.

Container glasses: wide- and narrow-neck glass containers made of coloured (usually green and brown) or clear, so-called "white" glass.

Architectural glasses: simple window glass, insulating glass (thermal insulation and/or noise reduction), flat glass provided with functional coatings, all-glass elements (doors, etc.), formed architectural glass (glass blocks, bent glass), fire and safety glass (also laminated with film), decorative (stained, sandblasted, embossed), walking glass, mirrors and more.

Glass fibres: insulation fibres (thermal, acoustic and electrical insulation materials), tubular skylights, reinforcing textile fibres (textiles for the production of glass laminates, etc.).

Automobile glazing closures: bent, laminated and tempered glass.

Domestic glassware: drinking, cooking, decorative glass.

Chemical glass: a very wide range of laboratory supplies, single-purpose apparatuses.

Technical and optical glass: lighting glass, incandescent light bulbs, lenses for optical systems, spectacle glasses, displays and screens.

Special glasses: clear and opaque quartz glass, foam glass, bioactive glass, glass for vitrification of radioactive waste, glass-crystalline materials, etc.

Artistic and decorative glass, glass jewellery, figurines, sculptures, etc.

2.3   Glass structure

Opinions on the structure of glass have undergone a long development. Basic ideas were formulated by Zachariasen (random network theory) and Lebedev (crystallite theory). Zachariasen's theory assumes the existence of a structural lattice created by basic structural elements, which are silicon-oxygen tetrahedrons, SiO_4^{4-}, Fig. 2.3. This structural network, in contrast to the structure of crystalline SiO_2 is irregular, as the structure of disordered melt has "frozen". Modifiers (especially alkali metal and alkaline earth metal oxides) generate non-bridging oxygen and seek to build an advantageous coordination sphere. Their presence causes the breaking of some bonds between the oxygen and silicon atoms, causes the irregularity of the network of tetrahedrons and allows the formation of cavities in which the cations of said metals are located.
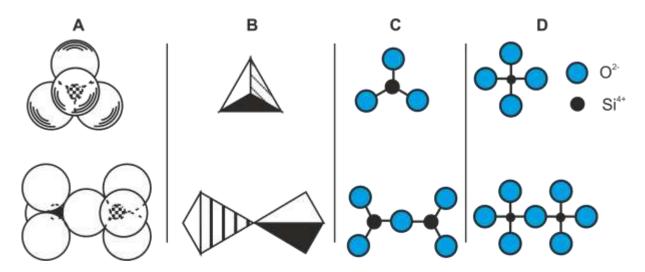
Fig. 2.3 Representation of a tetrahedron, SiO_4^{4-}, possible representation of one tetrahedron and two tetrahedrons connected by bridging oxygen, A - by means of a model, B - schematic representation with indication of tetrahedron position, C - surface representation with non-indicated oxygen in the axis perpendicular to the page, D - surface representation with all oxygen in plane

It follows from the foregoing that the basic structural unit of silicate glasses is the tetrahedron, SiO_4^{4-}, with a silicon atom in its centre of gravity and oxygen atoms in its four vertices. The individual tetrahedrons are connected to each other by their vertices, i.e. the oxygen atom, which is common to two adjacent tetrahedrons (so-called bridging oxygen, Fig. 2.3). In the case of the presence of other cations (sodium, potassium, calcium, etc.), the bridging oxygen bond is interrupted and a negative charge remains on the non-bridging oxygen, compensated by the respective cations. This loosens the network of tetrahedrons and disrupts the oxygen bridges. The presence of non-bridging oxygen results, among other things, in a reduction in the melting temperature. The comparison of the structure of crystalline SiO_2 (1), vitreous SiO_2 (2) and soda-silica (3) glasses is shown in Fig. 2.4.
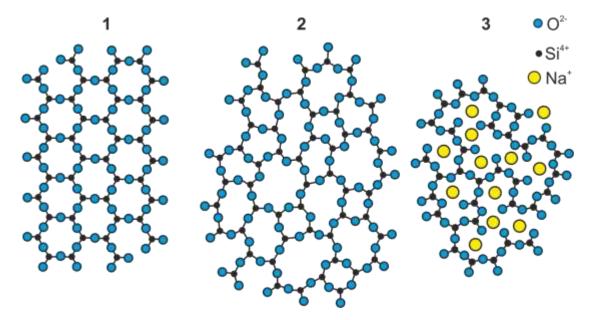
Fig. 2.4 Structure of crystalline SiO_2, vitreous SiO_2 and soda-silica glass

Stevels also studied the structure, introducing four structural parameters, X, Y, Z and R, which assessed, among other things, the "strength" of glass structure. According to Stevels, the Y parameter indicates the mean number of bridging oxygen per tetrahedron and its size (more frequent interconnection of tetrahedrons, SiO_4, in the structure) also increases the melting temperature of the respective glass. The parameters introduced by him are as follows:

X…   mean number of non-bridging oxygen per tetrahedron (generally polyhedron),
Y…   mean number of bridging oxygen per polyhedron,
Z…   mean number of all oxygen per polyhedron (i.e. coordination number of the cross-linker),
R…   ratio of the total number of oxygen to the total number of cross-linkers (silicon).

The following relations apply between these four structural parameters:

$X + Y = Z$
$X + \frac{1}{2}Y = R$ (2.1)

Which may be rewritten into the following relations:

$X = 2R - Z$
$Y = 2Z - 2R.$ (2.2)

If the basic polyhedrons are tetrahedrons (e.g. SiO_4^{-4}), the value is $Z = 4$. The R parameter can be easily calculated from molar composition of glass. If the values of the Z and R parameters are known, it is possible to calculate the remaining parameters, i.e. X and Y, using the above-mentioned relations.

Example:
Molar composition of glass: $2Na_2O.CaO.6SiO_2,$
because it is silicate glass $Z = 4$
the R parameter from the definition $R = \frac{15}{6} = 2,5$
from the relation $X = 2R - Z = 5 - 4 = 1$
from the relation $Y = Z - X = 3$

The value of the parameter $Y = 3$ says that three oxygen atoms in one polyhedron are bridging on average. This example is simple. For most industrial glasses, the value of the Y parameter is not integer (e.g. for glass composition $Na_2O.4SiO_2$), some ions may behave abnormally and the calculated values may be distorted.

The mean number of bridging oxygen per polyhedron (i.e. the value of the parameter Y) has a significant effect on many properties of glass. From structural point of view, it is clear that increasing parameter value Y represents a stronger and more compact interconnection of polyhedrons in the structure of glass, which may mean, for example, that glass of similar composition but with higher parameter value Y has a higher melting temperature. Several examples are summarized in the table for illustrative purposes. The glasses under examination will be close in terms of their chemical composition (from qualitative point of view), but the changing ratio of oxides will affect the value of the parameter Y, i.e. some properties of glass.

Table 2.1 Influence of the Y parameter on selected properties of glass

Glass composition	Y	Melting temperature [ºC]	$\alpha \times 10^6$ [K^{-1}]
SiO_2	4	2000	0.7
$Na_2O.2SiO_2$	3	1250	14.6
$Na_2O.SiO_2$	2	1050	22.0

α … mean linear coefficient of thermal expansion

Another idea of the structure of glass was formulated in the so-called crystallite theory (Lebedev), which assumes the random presence of small regions of increased regularity of arrangement in the structure (Fig. 2.5). This theory was later modified, on the basis of further research, in the sense that the inner regions with a regular arrangement and the outer, completely chaotic, regions are interconnected by a deformed structure in which the regularity of the arrangement decreases from the centre of the crystallites to the outer region.
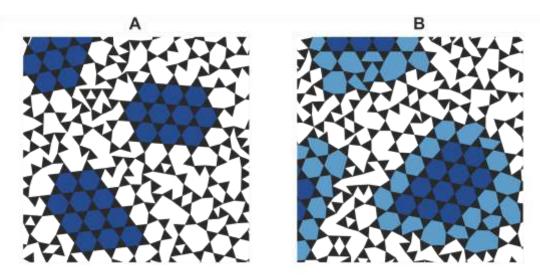
Fig. 2.5 Surface representation of the structure of quartz glass: A - according to crystallite theory, B - according to modified crystallite theory

3   Properties of glass and glass melt

The term "properties of glass and glass melt" includes a wide range of parameters defining glass and glass melt in terms of thermal, mechanical, electrical, optical and chemical properties. This chapter provides only the description of the most important properties, shortened to the scope of knowledge required for a mechanical engineer. More detailed information can be found in the bibliography, (see Bibliography).

3.1   Viscosity

The viscosity is a property of substances in the liquid state, i.e. substances that can flow. Viscosity is an important property of glass and glass melt and its knowledge is important in production. The fact that even the glass itself is described by high viscosity may seem unusual, but it corresponds to reality.

From technological point of view, glass melt is referred to as a Newtonian fluid. The rate of deformation is then directly proportional to the strain that causes deformation. If the solid body moves in a liquid medium at a certain velocity, the surface layer of glass melt on the body has the same velocity and the other layers are braked with the outer layers due to tangential stress - a velocity gradient is created across the layers, Fig. 3.1. The layers of liquid medium cease to be affected by the body only at a certain distance from the body. The sum of all stresses (tangential stresses) in the individual layers represents the total braking force F_x [N], which acts to reduce the velocity of the outermost layer to zero. In different liquid media, this resistance to flow is generally different. For glass melts, the internal resistance F_x is directly proportional to the velocity gradient (tangential stress) and the friction surface S_x [m^2] according to the relation

$$F_x = \eta S_x \frac{\Delta v_x}{\Delta y} \ , \quad (3.1)$$

where η is the constant of proportionality, which is called the coefficient of viscosity, the *dynamic viscosity*.
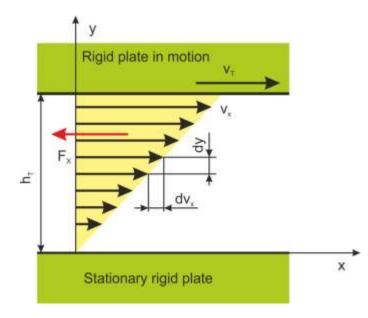
Fig. 3.1 Schematic representation of the velocity gradient in a viscous fluid

If the resistance F_x is related to the surface S_x, a relation is obtained for the tangential (shear) stress $(\frac{F_x}{S_x})$, which is proportional to the change in velocity in the direction perpendicular to the direction of motion according to the Newton's law

$$\tau_{xy} = \eta \frac{dv_x}{dy} \quad . \qquad (3.2)$$

Thus, the dynamic viscosity represents the internal resistance to flow of the glass melt. The unit of dynamic viscosity in the SI system of units is Pa·s ($kg.m^{-1}.s^{-1}$). In the older literature, the Poise (P) unit was used almost exclusively, according to the SI system of units corresponding to dPa·s, which is ten times smaller than Pa.s. Because the viscosity is very strongly temperature dependent and varies from melting temperatures to annealing temperatures by many orders of magnitude (from 10^1 to $10^{13.5}$ Pa.s), its logarithm is often given. Therefore, it is always necessary to take this fact into account when studying and taking over numerical values of viscosity from the older literature.

Furthermore, it is possible to define the *kinematic viscosity* ν, which represents the ratio of the dynamic viscosity and the density ϱ

$$\nu = \frac{\eta}{\varrho} \; . \qquad (3.3)$$

The unit of kinematic viscosity has the dimension $m^2 \cdot s^{-1}$. If the reader encounters only the term "viscosity", it means the dynamic viscosity. The reciprocal of the **viscosity** is called the **fluidity**, a measure of the ease of flow.

With increasing temperature, glass undergoes a transition from the glassy (solid) state smoothly to the plastic to liquid state in the glass transition interval and becomes glass melt. The measure of "plasticity" of the glass melt, i.e. the ability to flow, is the dynamic viscosity. For conventional silicate glasses, the described behaviour (depending on the chemical composition) begins to manifest itself above a temperature of about 400 to 550°C.

Knowledge of the temperature course of viscosity is important practically in all areas of glass technology. The relationship between temperature and viscosity for glasses is characterized by the so-called viscosity curve, the typical course of which is shown in Fig. 3.2.

Under normal conditions, the viscosity curve is mainly influenced by the chemical composition of glass. From technological point of view, a distinction is made between "short" glasses with a steep course of the viscosity curve and "long" glasses with a gradual course of the viscosity curve, Fig. 3.3. The indication comes from the history when the glassmaker had a longer processing time for glass with a gradual course of the viscosity curve. Another technical distinction is between "hard" glasses, the viscosity curve of which is placed higher on the graph of dependence, and "soft" glasses, the viscosity curve of which lies at the bottom of the graph, Fig. 3.3. At a given temperature, "soft" glasses have a lower viscosity and are therefore softer than glasses with the viscosity curve placed above.

In addition to the course of the viscosity curve, which is an important characteristic of each glass melt, so-called reference points of viscosity are defined, which correspond to a different temperature for each glass melt. These are the following viscosity reference points:

- melting point 10 Pa·s,
- working point 10^3 Pa·s,

- liquidus temperature/flow point 10^4 Pa·s,
- Littleton softening point $10^{6.6}$ Pa·s,
- deformation temperature t_d 10^{10} Pa·s,
- annealing point 10^{12} Pa·s,
- glass transition temperature T_g $10^{12.3}$ Pa·s,
- strain point $10^{13.5}$ Pa·s.
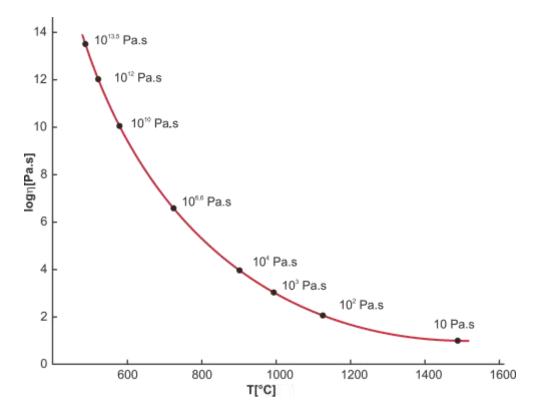
Fig. 3.2 Viscosity curve (unspecified composition)
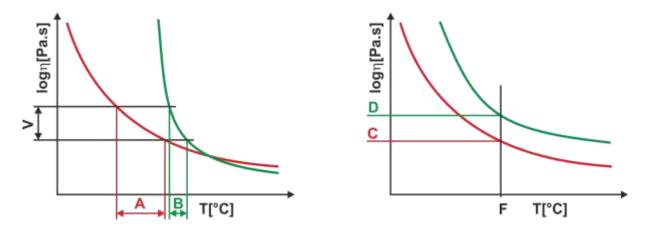
Fig. 3.3 Viscosity curves of different types of glasses: V - viscosity interval for glass processing, A - interval of processing temperatures of "long" glass, B - interval of processing temperatures of "short" glass, C - viscosity of "soft" glass at a given temperature F, D - viscosity of "hard" glass at a given temperature F

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Technologically significant points and regions of glass processing are shown in Fig. 3.4. Viscosities below 10^2 Pa·s are important for glass melting, 10^2 to 10^8 Pa·s for forming and product deformation (10^9 to $10^{11.5}$), and 10^{12} to $10^{13.5}$ for annealing.
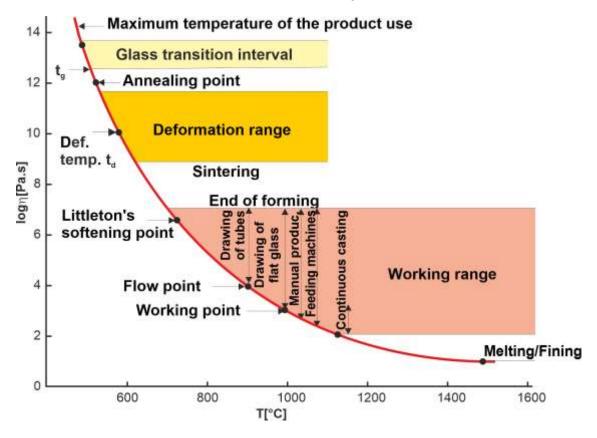
Fig. 3.4 Technologically significant points and regions of glass processing (viscosity in Pa·s)

Experimental methods for determining the entire viscosity curve are usually instrument demanding and time consuming, therefore it is often possible to encounter the calculation of the viscosity curve using empirical relations that simplify the calculation and require the measurement of only a few viscosity points. We most often encounter the calculation using the Vogel-Fulcher-Tammann equation (abbreviated to V-F-T equation), the use of which requires the determination of three pairs of temperature-viscosity points and the calculation of the course of the viscosity curve is sufficiently accurate.

$$log\, \eta = A + \frac{B}{T-C}, \qquad (3.4)$$

where η - is the dynamic viscosity (Pa·s),

T - is the absolute temperature (K),

A, B, C - are the constants.

Another possibility is to make the calculation directly from the chemical composition of glass melt. Due to the fact that the effect of individual oxides differs and does not have an additive character, i.e. it is influenced by the mutual interactions of these oxides, it is necessary to evaluate the effect of individual oxides for a predetermined region, e.g. by the method of empirical additivity

factors (Lakatos-1972 /Beerkens-1997 method) and to determine the appropriate regression relations for calculating the constants of the used relation. In general, higher silicon dioxide content increases the viscosity of glass melt, while higher content of modifying oxides, e.g. alkali metal oxides, decreases the viscosity.

3.1.1 Viscosity measurement

Relative methods for measuring the viscosity of glass melt require calibration of the viscometer using known viscosities of other substances (oil, glycerol, syrup). We use absolute methods to measure quantities from which the viscosity can be calculated directly. Due to the wide range of viscosities, several types of viscometers are used for measurement. The most commonly used are the viscometers using falling sphere/bubble rise (measurement of low viscosities in the range of 10^1 to 10^4 Pa·s), concentric cylindersmargules rotating cylinders (measurement of low viscosities in the range of 10 to 10^5 Pa·s), glass fibre elongation viscometer (measurement of medium and high values of viscosity in the range of 10^7 to 10^{14} Pa·s), Littleton softening point ($10^{6.6}$ Pa·s), penetration viscometer (for measuring high values of viscosity in the range of 10^7 to 10^{13} Pa·s), viscosity above 10^{13} Pa·s can also be measured using the beam-bending method. Even glass still has the defined viscosity at room temperature, which is, however, extremely high (> 10^{20} Pa.s) and is manifested, for example, by deformation of improperly placed tubes and rods during long-term storage. The selected methods of viscosity measurement are described below.

Falling-sphere method. A modified measurement procedure consists in suspending a platinum sphere on a thin platinum-rhodium fibre, which is fixed to one scale beam. A counterweight is placed on the opposite scale bowl Z to adjust the rate of fall (or rise) of the sphere so that its trajectory is monitored only in the range of a few millimetres. The rate of fall is measured using a suitable optical or electronic device. The method is suitable for measuring viscosities of glass melts in the range of 10^1 to 10^4 Pa.s. The measuring method is not absolute, but calibration must be performed before measurement. The method is based on the knowledge that the ratio Z/v is constant at constant viscosity regardless of the size of the counterweight. By plotting the dependence of log η against log Z/v we obtain a linear dependence, and for the viscosity and the rate of braked fall of the sphere, the following relation applies

$$log\,\eta = a + b\,log\,Z/v \quad (3.5)$$

where Z is the mass of the weight [g],

v – is the rate of fall of the sphere [m·s^{-1}],

a, b – are the instrument constants calculated from calibration measurements,

η – is the coefficient of dynamic viscosity [dPa·s].

Concentric-cylinder method. This is an absolute method of measuring viscosity on a rotary viscometer, in which one of the concentric cylinders rotates around its own axis and the other one is fixed. The inner cylinder is made of platinum or PtRh alloy. If the inner cylinder rotates, the force required to rotate it is measured at the set constant speed. In the case of rotation of the outer cylinder (cylindrical crucible), the inner cylinder is suspended on a torsion fibre. The method is suitable for measuring the viscosities of glass melts in the range of 10 to 10^5 Pa.s.

The following relation applies to the calculation of viscosity

$$\eta = \frac{M\left(\frac{1}{r_1^2 - r_2^2}\right)}{4\pi h_s . \omega} = A\frac{M}{\omega} , \qquad (3.6)$$

where M - is the moment of force [N.m],

r_1, r_2 - are the radii of cylinders [m],

h - is the shear layer height [m],

ω - is the angular velocity [s^{-1}],

A - is the instrument constant, including geometric dimensions of the specific arrangement.

Glass fibre elongation method. It is an absolute method and can be used for measuring viscosities in the range of 10^7 to 10^{14} Pa·s. A fibre of circular cross-section is drawn from the glass melt, which is fastened between suitable rods and placed in the axis of a vertical electric furnace, the temperature of which is stabilized at a certain value. In this case, one rod is firmly attached, the force exerted by the suspended weight is applied to the other rod in the direction of its longitudinal axis. Due to the weight and the effect of the viscous flow, the fibre elongates at a certain rate

$$v = \frac{\Delta L}{\Delta t} \qquad (3.7)$$

The coefficient of dynamic viscosity can be determined from the elongation rate v

$$\eta = \frac{4}{3}\frac{mgl}{\pi v d^2} \cdot 10 \quad (3.8)$$

where m is the mass of the weight with a rod [kg],

l - is the length of fibre [m],

d - is the diameter of fibre [m],

g - is the gravitational acceleration [9.81 m·s^{-2}],

v - is the elongation rate of fibre [m·s^{-1}].

Littleton softening point ($10^{6.6}$ Pa·s). The determination is carried out by measuring the elongation rate of the glass fibre with a diameter of 0.55 to 0.75 mm and a length of 235 mm suspended in a vertical furnace without load. The furnace is heated at a constant rate of 4 to 6°C·min^{-1} and the Littleton softening point is the temperature at which the rate of spontaneous elongation of the fibre is exactly 1 mm per minute under these conditions.

Penetration method. The method makes it possible to measure the viscosity of glasses in the range of 10^7 to 10^{13} Pa·s. The measurement is performed on a glass disc with a diameter of 30 mm and a thickness of 3 mm with a polished front surface. The sample is placed in a vertical electric furnace and kept at a constant temperature. A metal specimen, the end of which is formed by the hemisphere with a diameter of 3 mm, is pressed into the polished surface of the glass sample with a known force F. The depth of indentation l for a period of time τ is measured using an electronic or optical device.

Viscosity is calculated from the relation

$$\eta = \frac{9F}{32\sqrt{2rl^3}} \cdot \tau, \quad (3.9)$$

where F is the acting force [N],

τ - is the time [s],

l - is the depth of indentation [m],

r - is the radius of the specimen [m],

η - is the coefficient of dynamic viscosity [Pa·s].

This is an absolute method when using a spherical specimen.

Beam-bending method. The beam or rod is embedded or supported at two ends and subjected to the force applied from above or below. The viscosity calculation is based on the relation

$$\eta = \frac{gl^3}{144In}\left(m + \frac{\varrho Sl}{1,6}\right), \quad (3.10)$$

where η is the viscosity [Pa·s],

g - is the gravitational acceleration (9.81 m·s^{-2}),

I - is the cross-sectional moment of inertia [m^4],

n - is the mean beam bending speed [m·s^{-1}],

m - is the mass of the weight [kg],

l - is the span of supports [m],

ϱ - is the density of glass [kg·m^{-3}],

S - is the cross-section of the beam [m^2].

The moment of inertia I is calculated from the relation, for the rod

$$I = \frac{\pi r^4}{4}, \quad (3.11)$$

for the beam:

$$I = \frac{bh^3}{12}, \quad (3.12)$$

where b is the width of the beam [m],

h - is the height of the beam [m],

r - is the radius of the rod [m].

3.2 Surface tension

The surface tension is the resultant force that tends to minimize the surface area of liquids - melts. The surface tension is denoted by the Greek letter γ and has the unit $N \cdot m^{-1}$, while the surface tension of $1\ N \cdot m^{-1}$ has the liquid in which the force of 1 N acts over the length of 1 m of perpendicular section through the surface. In general, the following formula applies

$$\gamma = \frac{dF}{dl} \qquad (3.13)$$

where dF is the force acting perpendicular to the section through the surface area,

dl – is the length of virtual section through the liquid surface area.

Usually, the surface tension of glass melt is expressed in the unit a thousand times smaller, i.e. $mN \cdot m^{-1}$.

The surface tension is explained by the action of cohesive forces. Each particle (molecule) of liquid is subjected to attractive cohesive forces exerted by adjacent particles. The nature of cohesive forces can be explained by electrostatic attraction and repulsion of molecules. The interaction is only short-range and decreases with a much higher power (usually the sixth power). The attractive action of each particle can thus be limited to a very small spherical space in the centre of which the particle in question is located. This space is called the sphere of molecular action and its radius ρ_m is called the radius of molecular action. Inside the liquid, the interaction of molecules is in equilibrium and the resultant of forces is zero. Molecules with a distance from the surface smaller than ρ_m of their spheres form the surface layer of liquid. Each molecule located in this layer is again affected by adjacent molecules of liquid, but because there are no more molecules of liquid above the liquid surface, the resultant of forces is non-zero. The resultant of attractive forces between gas molecules (above the surface area) is much smaller than the resultant of the action of liquid molecules from the inside and the resulting attractive force is directed inside the liquid. The result is a force that ensures that the liquid is shrunk into the minimum surface area, i.e. the surface tension.

In glass technology, the effects of surface tension can be encountered in the field of melting, fining, feeding, forming and heat treatment of glass.

Surface tension is an additive property, which can be used in an approximate calculation from the known chemical composition of glass and knowledge of additive constants. Among the more common oxides, the surface tension is increased by, for example, calcium oxide (CaO), magnesium oxide (MgO); potassium oxide (K_2O), lead(II) oxide (PbO), boron trioxide (B_2O_3) act in the opposite direction. The surface tension of glass melts is not much affected by temperature - its dependence on temperature is given in Fig. 3.5.

A number of methods are used for measuring the surface tension:

- drop-weight method,
- sessile droplet method,
- maximum bubble pressure method,
- fibre elongation method,
- ring method, etc.

The fact that the surface tension is not much affected by temperature is exploited in its experimental determination using the *fibre elongation method*, which is relatively simple.
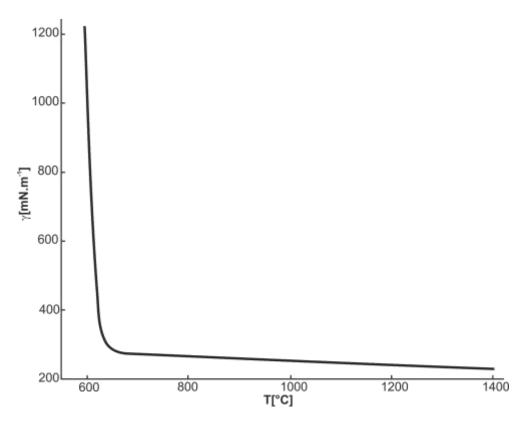
Fig. 3.5 Dependence of surface tension of glass melt on temperature of flat glass

Fibre elongation method. A glass fibre with a diameter of about 0.6 mm and a length of about 80 mm is suspended so as to be in the axis of a spiral made of platinum wire. After heating the spiral with resistance heat, the fibre first shortens due to surface tension and enlarges (swells) at the point of maximum temperature. As the temperature is further increased, the weight of the fibre overcomes the surface tension and the lower part, including the enlarged part, falls off.

At a suitably selected rate of heating and the correct length of fibre, the fibre enlarges. The enlarged part is separated from the waste end of the fibre at the original diameter and weighed. The surface tension is calculated from the relation

$$\gamma = \frac{2gM}{\pi d}, \qquad (3.14)$$

where M is the mass of the dropped-off part of fibre [kg],

g - is the gravitational acceleration [9.81 m·s^{-2}],

d - is the diameter of fibre [m].

The scheme of the method is shown in Fig. 3.6.
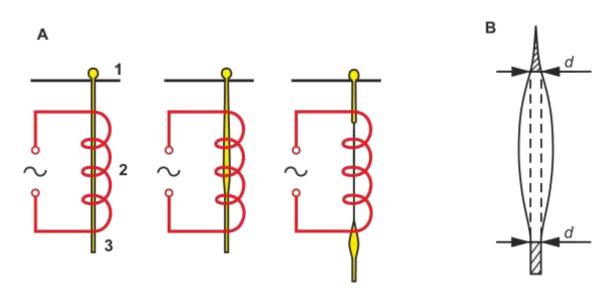
Fig. 3.6 Scheme of surface tension measurement of glass using the loaded fibre method: A - representation of the method, 1 - holder with a hole for suspending the fibre, 2 - heating spiral, 3 - suspended fibre, B - separation of the elongated end of the dropped-off part of fibre

3.3   Glass crystallization

Substances in the amorphous state, including glass, are in other words in the metastable supercooled liquid. This means that they are characterized by higher value of internal energy than substances in the crystalline state. Thermal exposure at a suitable temperature leads to crystallization and thus to transition to a stable, crystalline state. Crystallization, in other words also devitrification, is mainly influenced by the following properties:

- rate of nucleation (N_R), which represents the number of the crystalline nuclei formed in the volume unit of glass per time unit,
- crystal growth rate (K_R), which represents the geometric growth of the size of crystalline nuclei [$\mu m \cdot h^{-1}$],
- liquidus temperature (T_L), there can be no crystalline phase above this temperature.

The correlation between the two above-mentioned rates and thus the easy understanding of the possibility of the formation of a crystalline phase (devitrification) is shown in the scheme in Fig. 3.7.

Just below the liquidus temperature, nuclei are virtually absent (subcritical annealing interval u between the liquidus temperature T_L and the beginning of the N_R curve), unless the glass melt has cooled (even for a short time and temporarily) below the temperature of the high-temperature beginning of the N_R curve. If the temperature of glass melt is maintained in the interval u for a longer period of time (without prior annealing), devitrification virtually cannot occur. The presence of nucleation nuclei itself is possible on the basis of two mechanisms:

- ***Heterogeneous nucleation,*** the growth of crystals takes place subsequently at foreign crystallization centres (boundary areas of imperfectly dissolved grains, areas of contact of the glass melt with the refractory material, surface contamination of the melt, etc.).

- **_Homogeneous nucleation:_** crystal nuclei are formed by separation from the melt based on thermodynamic equilibrium between the components present in the melt.
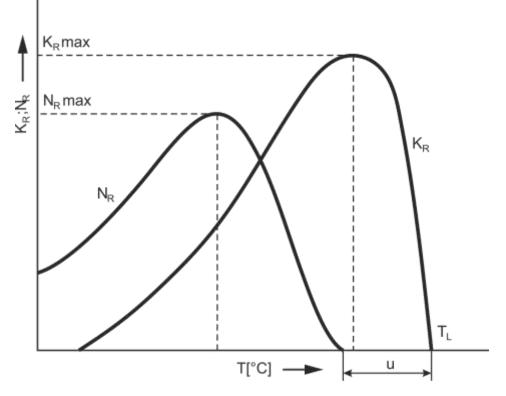
Fig. 3.7 Dependence of the rate of nucleation and the crystal growth rate on the temperature

Fig. 3.8 Glass crystallization: A – clear glass pressing rod without visible crystallization, B – fragment of glass from a tank furnace with appreciable crystallization after heterogeneous nucleation, C - opal pressing rod with crystallisation after homogeneous nucleation

The goal of glass technology is (in most cases of technology) to minimize heterogeneous and homogeneous nucleations. Nucleation itself is not a problem, but the growth of crystals, which are visible from a certain size and cause opacity and cracking of glass, is essential. Crystallization is minimized the easier:

- the lower the rate of nucleation is,
- the larger the range of the subcritical cooling interval u is,
- the further the maximum values of temperature are set apart.

In some cases, however, crystallization preceded by a homogeneous nucleation is desirable. By adding a suitable nucleating agent it is possible to induce crystallization in almost all types of glasses (Chapter **Chyba! Nenalezen zdroj odkazů.**). In some cases, crystalline opacity is formed, which causes the opacity of glass (opaque or light scattering glass). Another case concerns glass-crystalline materials (glass-ceramics), which have specific properties, such as zero or negative thermal expansion. The aim can also be to improve mechanical properties. Many properties of the original glass are improved by controlled crystallization, including strength, hardness and heat resistance. In addition to increasing the strength, a clear reduction in brittleness is important for glass-crystalline materials. In all cases, homogeneous nucleation and crystallization are influenced by the composition of glass (addition of nucleating agents) and thermal conditions during the so-called quenching (controlled crystallization).

The following procedures are used for determining the crystallization properties:
- gradient furnace method,
- method of direct microscopic observation in heat chamber,
- method of rapid cooling of the sample.

3.4 Other thermal properties

Knowledge of thermal properties is important in solving technological problems of production, in thermal engineering calculations, in the use of glass products at increased temperatures and also in solving the automation and control of glass production. In the following text, thermal expansion, specific heat, thermal shock resistance and thermal conductivity will be discussed.

3.4.1 Thermal expansion

The thermal expansion (dilatation) can be defined as a change in the dimensions of a glass specimen with a change in temperature at a constant pressure. When changing the linear dimensions, it is a matter of linear expansion; when changing the volume dimensions, it is a matter of volume expansion. In terms of quantity, we characterize thermal expansion most often by the coefficient of thermal expansion (linear, volume), which has the dimension [K^{-1}] or [ºC^{-1}].

The coefficient of linear thermal expansion α is defined by the relation

$$\alpha = \frac{1}{l_0}\frac{dl}{dT}, \qquad (3.15)$$

where l_0 is the length of the measured sample at the reference temperature T_0.

dl - is the elongation of the measured sample when its temperature is changed dT.

The coefficient of volume expansion β is defined by the relation

$$\beta = \frac{1}{V_0}\frac{dV}{dT}, \qquad (3.16)$$

where V_0 is the volume of the measured sample at the reference temperature T_0.

dV – is the increase in volume of the measured sample when its temperature is changed dT.

The *coefficient of volume expansion β* can be simply expressed for solids with an isotropic lattice, as well as for glasses, due to the low value of α, as follows

$$\beta = 3\alpha \quad . \qquad (3.17)$$

Equation (3.15) defines the so-called *true coefficient of linear thermal expansion,* which indicates the relative change in length of a specimen when its temperature is changed by dT at a given temperature T. However, for small temperature intervals α can be considered as a constant, so the so-called *mean linear coefficient of thermal expansion* can be defined by the relation

$$\alpha_{T_2 - T_1} = \frac{1}{l_0} \cdot \frac{\Delta l}{\Delta T} \quad (3.18)$$

where T_1, T_2 are the initial and final temperatures [°C],

Δl - is the change in length when the temperature is changed by $\Delta T = T_2 - T_1$,

l_o - is the initial length of the sample.

The *mean linear coefficient of thermal expansion* indicates the relative change in length of the sample of glass being measured when the temperature is changed by 1°C in the temperature range (T_2, T_1). The temperature range is usually set at 20 to 300°C in order to compare the thermal expansion of glasses of different chemical compositions. The temperature dependence of linear expansion is graphically represented by the curve of thermal expansion (dilatation curve of glass, Fig. 3.9).
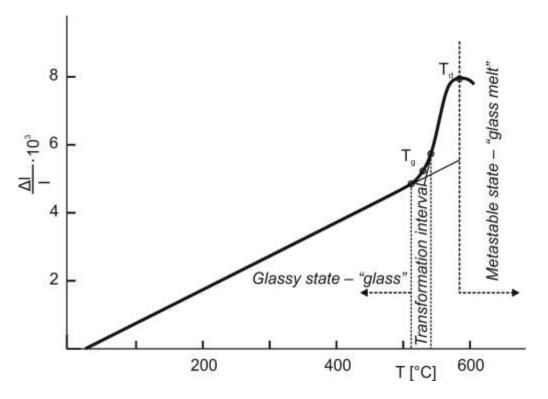
Fig. 3.9 Thermal expansion/dilatometric curve of soda-lime-silica glass: T_g – glass transition temperature, T_d – dilatometric softening point (deformation temperature)

The glass transition temperature T_g is approximately in the middle of the interval. It is determined from the dilatation curve measured at a heating rate of 10°C·min^{-1} and corresponds to a viscosity of 10$^{12.3}$ Pa·s. The deformation temperature T_d is usually defined by the bend of the curve of thermal expansion and corresponds to a viscosity of approximately 10^{10} Pa·s.

The course of the dilatation curve (Fig. 3.9) is approximately linear for stress-free glass (well cooled) up to the glass transition temperature T_g. This is followed by a steeper course of the dilatation curve up to the temperature of dilatometric softening point (deformation temperature T_d), when the measured glass sample is deformed by the pressure applied by pressure device. For glass with internal stress (poorly cooled), we observe a bend of the dilatation curve approximately 100°C below the transition temperature. These findings are illustrated in Fig. 3.10.

The temperature range for which α is defined is usually between 20 and 300°C. A conversion can be made for another range (below temperature T_g). How does the mean coefficient of linear thermal expansion change with temperature for Simax glass and soda-lime-silica glass is shown in Table 3.1.

As follows from the above, the mean coefficient of linear thermal expansion depends on the chemical composition of glass. Quartz glass shows the lowest thermal expansion, the thermal expansion of some selected glasses is given in Table 3.2. As the data shows, the thermal expansion of glasses is most significantly reduced by the increased content of silica (SiO_2), while the increased content of alkali metal oxides (Na_2O and K_2O) and others acts conversely.

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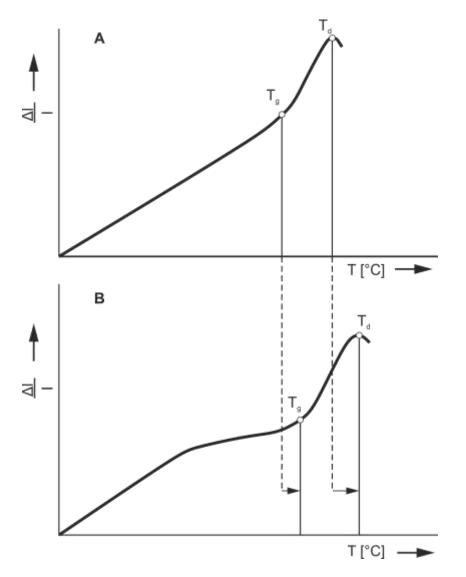
Fig. 3.10 Dilatation curve of well and poorly cooled glass: A - well annealed glass, B - poorly annealed glass (rapid cool)

Table 3.1 Mean coefficient of linear thermal expansion of glass α for Simax glass and soda-lime-silica glass for different temperature ranges

$\Delta T = (T_2 - T_1)$ [°C]	α [°C^{-1}]	
	Simax glass	**Soda-lime glass**
20 – 100	3.16×10^{-6}	8.06×10^{-6}
20 – 200	3.24×10^{-6}	8.33×10^{-6}
20 – 300	3.20×10^{-6}	8.67×10^{-6}
20 – 400	3.14×10^{-6}	8.91×10^{-6}
20 – 500	3.07×10^{-6}	-

Table 3.2 Thermal expansion of selected glasses for the temperature range from 20 to 300°C

Glass	α [°C^{-1}]
Quartz	$0.6 - 0.8 \times 10^{-6}$
Simax	3.2×10^{-6}
Eutal (for glass fibres)	4×10^{-6}
Flat glass	$8 - 9 \times 10^{-6}$
Container glass	9×10^{-6}
Lead crystal	9.4×10^{-6}

Dilatometers are used for determining thermal expansion, and in operation methods of comparing two laminated, joined or sealed glasses are used.

3.4.1.1 Dilatometers

According to the method of measurement, we distinguish between direct, interference and differential dilatometers.

Pushrod dilatometer

A sample of glass to be measured is placed in a quartz glass tube which is sealed at the lower end and placed in a vertical electric furnace. Using a rod, the change in length of a sample is transmitted to the indicator, the temperature is measured with a thermocouple. The sample elongates when heated as well as the quartz tube and the rod made of quartz glass. The change in length of the lower part of the tube is registered by the indicator in the opposite direction to the elongation of the sample of the same length. The change in length of the upper part of the tube is compensated by elongation of the rod by the same length and therefore the change is not shown on the indicator. Thus, the total length of the sample reduced by the elongation of the lower part of the tube is recorded on the indicator. The changes in length can be read, for example, using a dial indicator or electronically. The measurement in a horizontal furnace is based on a similar principle, but the thermal expansion of the quartz rod and the tube must be subtracted from the measured data.

Interference dilatometer

The measured sample is inserted between two polished plates of quartz glass or sapphire. The measurement of the change in length is based on the measurement of interference fringes. As the dimensions of the sample change during heating, the two interference plates also move relative to each other and the interference fringes move. The actual measurement consists in counting the interference fringes that pass through the reference point marked on the upper interference plate in the course of the change in temperature from T_1 to T_2.

Differential dilatometers

These dilatometers differ from direct dilatometers in that the change in temperature is determined from the change in length of the metal standard, which has the same dimensions as the sample of glass to be measured and is placed in a quartz glass tube next to the glass sample. The elongation of the sample is then compared to the change in length of the standard and their changes in length are usually recorded graphically.

3.4.1.2 Operational control

The following methods are used for the operational control of the thermal expansion of glasses:

- ring test,
- double-thread method,
- surface sealing method.

Ring test

It is used mainly in the production of flashed and cased glasses and consists in blowing and annealing a sandwich cylinder from both glasses with a diameter of about 80 to 100 mm. A ring 20 to 40 mm high is punched out of the cylinder and cut cross fire ly. Depending on the ratio of expansion of the two glasses, the cases shown in Fig. 3.11 may arise.
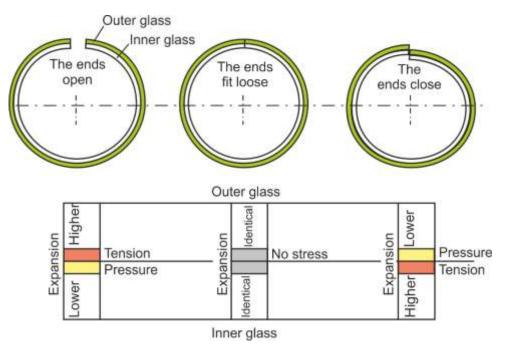
Fig. 3.11 Ring method of thermal expansion test

Double-thread method

It consists in building the rods of the two tested glasses and drawing them into the thread. After annealing, an arc is formed in which the glass with greater expansion shrinks more and will be on the inside of the arc.

Surface sealing method

It is used in the inspection of sealing glasses. It consists in building two glasses in the form of rods or prisms, one of which is usually standard. After annealing, they are ground in plane-parallel so that the weld is perpendicular to their surface, and the specific path difference in weld is measured using a polarizing apparatus with a precision compensator and a calibration graph of

the dependence of the specific path difference on the difference of expansion of both glasses is drawn.

3.4.1.3   Thermal shock resistance

The thermal shock resistance (sometimes also the resistance to sudden changes in temperature) is the ability of glasses to withstand a thermal shock in a certain temperature range without breaking. It is given by the largest temperature difference ΔT [°C], by which the heated sample (product) can be cooled or the cold product can be heated without breaking.

The effect of thermal expansion is that upon sudden cooling, glass shrinks and a temporary stress is created. The lower the extensibility of glass, the lower the shrinkage and the higher its thermal shock resistance. When the glass product is heated rapidly, a compressive stress arises in the surface layer, and when it is rapidly cooled, a tensile stress arises. Since the tensile strength of glass is much lower than the compressive strength and the product breaks more easily when rapidly cooled, the thermal shock resistance is usually expressed by the resistance to cooling by the relation

$$\Delta T = T_1 {}_- T_2, \qquad (3.19)$$

where ΔT is the thermal resistance [°C],

T_1 - is the heating temperature of the sample [°C],

T_2 - is the ambient cooling temperature [°C].

Thermal shock resistance depends on the thermal expansion given by the chemical composition of glass, and for massive rapidly cooled glass is given by the relation

$$\Delta T = \frac{\sigma(1-\mu)}{\alpha E}, \qquad (3.20)$$

where σ is the tensile strength of glass,

μ - is the Poisson's ratio,

α - is the coefficient of linear thermal expansion,

E - is the Young's modulus of elasticity in tension.

A simplified relation can be used for the approximate calculation of thermal resistance

$$\Delta T = \frac{1000}{\alpha . 10^7}, \qquad (3.21)$$

which ideally applies to a 1 mm thick plate and to products of the same thickness, neglecting the effect of shape. The graphical dependence ΔT of α is shown in Fig. 3.12.
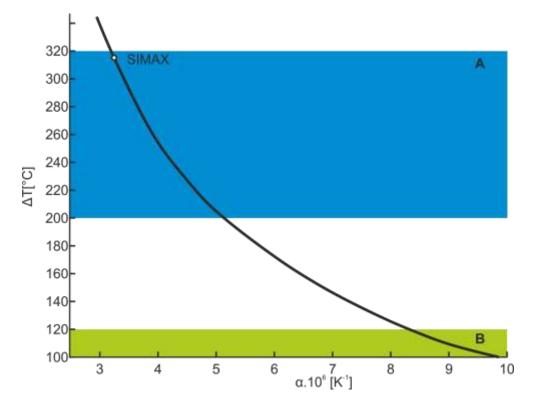
Fig. 3.12 Dependence of thermal shock resistance on thermal expansion for a 1 mm thick glass plate: A - heat-resistant glasses, B - soda lime silicate glasses

The internal stress in glass can be calculated (when heated or cooled at a constant rate, when evenly distributed internal stress stabilizes in glass) for the glass plate on the surface according to the relation

$$\sigma = \frac{1}{3} \cdot \frac{E\alpha}{a(1-\mu)} hd^2 \ , \qquad (3.22)$$

where σ is the stress [Pa],

E - is the Young's modulus of elasticity in tension [Pa],

α - is the coefficient of linear thermal expansion [K^{-1}],

a - is the thermal diffusivity [m^2·s^{-1}],

μ - is the Poisson's ratio [-],

d - is the half thickness of the plate [m],

h - is the rate of heating or cooling [K·s^{-1}].

The thermal resistance of glasses is also a function of the shape of the sample (product), homogeneity of glass, integrity of its surface, annealing (tempering), the nature of its edges, which can be burnt off or ground, etc. It is therefore not a purely material property.

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For example, for a quartz glass plate with a thickness of 1 to 2.5 mm, the value of thermal resistance is 1000 to 1100°C, a tube with a diameter of 10 to 30 mm of the same material has a resistance of 800 to 900°C.

According to thermal resistance, glass products are divided into three groups:

- glass products with low thermal resistance, to which $\Delta T < 100°C$ applies (including flat and container glass),
- glass products with medium thermal resistance, to which $100°C < \Delta T < 250°C$ applies (laboratory glass, pharmaceutical glass, etc.),
- glass products with high thermal resistance, to which $\Delta T > 250°C$ applies (cooking glass, all-glass apparatuses of large dimensions, quartz glass products, etc.).

3.4.1.4 Determination of thermal shock resistance

The principle of the method is to heat a sample of glass, or glass product, to a gradually increasing temperature followed by rapid cooling in a water bath with a temperature of about 20°C until the glass sample (product) is damaged (breaks, cracks appear, a piece is chipped off, etc.). Because, as mentioned above, this property of glass products, as well as mechanical properties, is influenced by a number of factors, it is necessary to use the minimum number of products specified in the standard for the test.

3.4.2 Specific heat capacity

The specific heat capacity (the term specific heat is used in the older literature) is important for the course of heat exchange processes during heating or cooling of glass melt. Knowledge of specific heat capacity is therefore important, for example, when compiling heat balances for the design of melting furnaces, it is also used especially in the field of forming, feeding and annealing of glass.

The specific heat capacity c_p [J·kg^{-1}·K^{-1}] (index p, indicates constant pressure) is defined by the amount of energy in the form of heat dQ, which causes the temperature of the substance to increase from temperature T to temperature $T + dT$, divided by the mass of the substance m and by increase in temperature dT, i.e.

$$c_p = \frac{dQ}{dT}\frac{1}{m}, \qquad (3.23)$$

where dQ is the energy increment [J],

dT - is the temperature increment [K],

m - is the mass of glass [kg].

It is thus a small amount of energy in the form of heat dQ needed to heat a unit amount of glass from temperature T to temperature $T + dT$. Different amount of energy in the form of heat is needed to increase temperature of the same amount of different substances in the same way.

The specific heat capacity of glasses, like other substances, is temperature dependent and increases with increasing temperature and asymptotically approaches a constant value. Therefore, the term of mean specific heat capacity $\bar{c}_p$ was introduced, which is defined by the relation

$$\bar{c}_p = \frac{\Delta Q}{\Delta T} \frac{1}{m}. \qquad (3.24)$$

If the dependence $c_p = f(T)$ is known, it is possible to make the calculation of mean specific heat capacity $\bar{c}_p$ [J·kg^{-1}·K^{-1}] for the interval $\Delta T = T_1 - T_2$

$$\bar{c}_p = \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} c \, dT, \qquad (3.25)$$

where $\bar{c}_p$ is the arithmetic mean of all values $f(T)$ in the interval ΔT.

The calculation of the amount of energy in the form of heat ΔQ [J], required to heat m [kg] of the amount of the substance by ΔT [K], is simplified if $\Delta Q = Q$

$$Q = \bar{c}_P m (T_2 - T_1). \qquad (3.26).$$

Due to the absolute values of the mean specific heat capacity of glasses, it is more preferable to use a smaller derived unit J·g^{-1}·K^{-1} and in the case of conventional industrial glasses, it is in the range of approximately 0.46 to 1.20 J·g^{-1}·K^{-1}. Compared to technical silicate glasses, the values of specific heat for clear quartz glass are lower, but higher than alkali-lead-silicate glass with the content of 22.3% PbO. The dependence of the mean specific heat capacity on temperature for selected glasses is shown in Fig. 3.13.
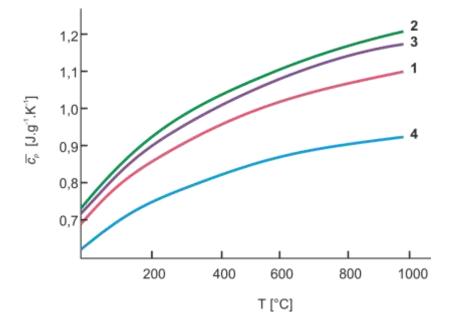
Fig. 3.13 Temperature dependence of mean specific heat capacity on temperature: 1 - clear quartz glass, 2 - soda lime silicate glass, 3 - borosilicate glass, 4 - lead glass with the content of 22.3% PbO

The measurement of specific heat capacity is performed using method calorimeter. The sample of glass is heated in a platinum crucible to the selected temperature and transferred to a water-filled calorimeter. After reaching a temperature equilibrium between the sample and the

calorimeter, the mean specific heat capacity is calculated from the quantity of heat transferred by the sample to the calorimeter. In modern practice, the heat capacity is with the aid of a differential scanning calorimeter (DSC): a small quantity of the unknown glass in an Al (or Pt) pan is heated such that its temperature rises at a predetermined rate. The DSC system adjusts the rate of heat input (dQ/dt) to obtain the required dT/dt and plots dQ/dt as a function of T. The change of dQ/dt relative to the "baseline" obtained by running an empty pan equals mCpdT/dt, where m is the mass of glass.

3.4.3 Thermal conductivity

The thermal conductivity can be defined on the basis of the relation

$$\frac{dQ}{d\tau} = -kA\frac{dT}{dx} \, , \qquad (3.27)$$

where dQ is the quantity of heat [Wh][1] that passes through the surface area A [m^2] within a period of time $d\tau$ [h],

$-\frac{dT}{dx}$ - is the temperature gradient [K·m^{-1}],

k – is the constant of proportionality – thermal conductivity of the given material [W·m^{-1}·K^{-1}].

Then, the specific thermal conductivity represents the quantity of heat Q, that, at steady state, passes per unit time τ [h] through a unit area A [m^2] of a flat wall, at a unit thickness d [m] and at a unit temperature difference ΔT [K] of the opposite surfaces. The following therefore applies

$$k = \frac{Q\,d}{A\,\Delta T\,\tau} \, . \qquad (3.28)$$

When thermal conductivity is mentioned here, it is appropriate to mention thermal energy that may basically propagate in three ways:

- by conduction, transfer of part of the kinetic energy between adjacent particles differing in mean kinetic energy, in this process the particles do not move, they only vibrate around their equilibrium positions, thermal energy is transferred by the substance at the nano level,
- by convection, in which the substance itself transfers energy at the micro to macro level,
- by radiation (emission), in which thermal energy is transferred by electromagnetic waves.

In the case of conduction, particles (molecules, ions) are important, which are in constant motion, the intensity of which increases with temperature. In solids such as glass, the particles are in a constant force field of other particles and the deflection of each of them therefore causes the deflection of adjacent particles. If the substance (body) does not have the same temperature everywhere, the interaction of the particles balances their kinetic energies, so that the warmer parts

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[1] watt-hour [Wh] = 3,600 joules [J]

of the body with higher energy of molecules are cooled and the colder parts of the body with lower energy of molecules are heated.

If the body is immersed in a bath of the temperature different from the temperature of the body, the energy exchange takes place until a steady state, when the whole body has the same temperature. If we keep two parts of the body permanently at unequal temperatures, the molecules in warmer parts have a permanently greater kinetic energy than the molecules in colder parts and the energy from warmer parts of the body is transferred to colder parts. In this case, the transfer of thermal energy takes place by heat conduction (in the first case by non-steady-state - non-stationary conduction, in the second case by steady-state - stationary conduction). Because this is an interaction between quanta of thermal energy, so-called phonons, this mechanism is called the phonon mechanism.

Heat transfer is greatly enhanced when parts of substances larger than molecules are in motion. Therefore, a convection is created in liquids or gases and the heat transfer takes place by convection. The convection caused only by the difference of densities in liquid is called natural convection, while the convection caused by the action of external forces is called forced convection.

Thermal radiation or emission is of a completely different nature, because it transfers thermal energy from one body to another without arranging the environment. The transfer of energy by radiation takes place even if the ambient temperature between the two bodies is substantially lower or higher than the temperature of the two bodies. This transfer of radiant energy takes place in final quantities, called photons, and the mechanism of energy transfer is called the photon mechanism.

In the case of silicate materials, including glass, all three mechanisms are involved in heat transfer, so the term "thermal conductivity" becomes comprehensively relevant and measurement methods are demanding.

In substances permeable to heat radiation, heat penetrates not only by conduction but also by radiation. The effective thermal conductivity k_{ef} is then the sum of the thermal conductivity by conduction k_v and the thermal conductivity by radiation k_z

$$k_{ef} = k_v + k_z \ . \qquad (3.29)$$

The radiant component of thermal conductivity k_z is minimal at temperature below 400°C. Below a temperature of 300°C, heat is transferred in glass only by conduction. At higher temperatures, the proportion of radiant component increases in colourless glasses.

The measure for the formation or compensation of temperature differences in glass is the *thermal diffusivity a* [m²·s⁻¹]. The correlation between thermal diffusivity and thermal conductivity is

$$a = \frac{k}{c_p \varrho} \ , \qquad (3.30)$$

where k is the thermal conductivity,

c_p – is the specific heat capacity,

ϱ - is the density.

Clear quartz glass shows the highest thermal conductivity of all technical glasses. At a temperature of 20°C, the specific thermal conductivity of clear quartz glass is 1.3816 $W \cdot m^{-1} \cdot K^{-1}$, which is approximately 20% higher than that of borosilicate glasses and approximately 50% higher than that of lead glass with the high content of lead. Due to the fact that quartz glass shows the highest thermal conductivity, its value decreases by exchanging SiO_2 for other oxides in glass. Depending on the effect of exchanging the same amount of different oxides, it is possible to compile a series of decreases in thermal conductivity

$$B_2O_3 \; < \; MgO \; < Al_2O_3 < ZnO < CaO < \; BaO < \; PbO < Na_2O < \; K_2O$$

The specific thermal conductivity of soda-lime-silica glass is then reported to be around 1 $W \cdot m^{-1} \cdot K^{-1}$.

Knowledge of thermal conductivity is important especially during melting and during forming. In the case of melting, it is the heat transfer by radiation from burners or from indirect electric heating. There is also heat dissipation from glass melt and furnace atmosphere through the GMU (Glass Melting Unit) lining. In the case of forming, heat is transferred from the glass melt to the surroundings (mainly by radiation) or mould (mainly by conduction). It is therefore important to know the thermal conductivity of other materials (GMU lining, mould material,…).

3.4.3.1 Methods for measuring the thermal conductivity

Methods for measuring the thermal conductivity can be divided into two basic groups:

- measurement at steady heat flow (steady-state methods),
- measurement at non-steady heat flow (non-steady state/transient methods).

The best known method of the first group is the so-called *plate method*. Its principle consists in that one surface of the size A of the measured flat plane-parallel plate (circular or square) is attached to the heater and the opposite surface of the plate to the cooler. The edge surfaces of the plate are either perfectly insulated or are provided with heated compensating strips, which prevent the exchange of heat with the environment. In a plate of defined thickness, a stationary temperature gradient is created between its hot and cold surfaces $\Delta T = T_1 - T_2$. In addition to the two temperatures, which must be constant during the measurement, the quantity of heat Q, entering the heater from the sample to be measured is measured (e.g. voltage U and current I keeping the heater at a constant temperature are measured). The specific thermal conductivity is calculated from the relation (3.28).

An example of the method of measurement at non-stationary heat flow is the so-called transient *hot wire method*, the principle of which consists in measuring the temperature rise T of a linear heat source (hot wire) of length l, located in the middle of the measured environment. If this linear heat source has a constant energy input Q, its temperature t will continue to rise over time τ the faster the lower the thermal conductivity of the surrounding environment. By plotting the values of temperature T against the logarithm of the measurement time $\ln \tau$, a line is obtained, the direction of which will be indirectly proportional to the specific thermal conductivity k of the measured glass. This method relates to the measurement of the so-called *true thermal conductivity* controlled by the mechanism of heat conduction, i.e. up to temperatures of maximum 500 to 600°C.

3.5 Density

The density ϱ is defined as the mass of the specific volume of a homogeneous substance at a given temperature

$$\varrho = \frac{m}{V}, \qquad (3.31)$$

where ϱ is the density [$kg \cdot m^{-3}$, $g \cdot cm^{-3}$] of a homogeneous body at a given temperature,

m - is the mass of the body [kg, g],

V - is the volume of the body [m^3, cm^3].

The density, as well as other properties of glass, depends on its chemical composition. Glasses of different chemical composition differ in the value of density depending on the atomic number, atomic mass and dimensions of ions introduced in the form of oxides into glasses. The density of most alkaline-lime-silicate glasses is around 2,500 $kg \cdot m^{-3}$, this value is regarded as mean value for commercial glasses. Only quartz glass and technical glasses containing a larger proportion of silica (SiO_2) and boron trioxide (B_2O_3), furthermore some glasses for metal sealing in vacuum electrical engineering have a relatively low density, between 2,200 and 2,300 $kg \cdot m^{-3}$. On the other hand, lead glasses and some others have a density greater than 3,000 $kg \cdot m^{-3}$, special glasses with transition elements (some optical and protective glasses against X-ray and gamma radiation) reach an exceptionally high density - 5,000 to 7,000 $kg \cdot m^{-3}$. Due to the high sensitivity of density to the composition of glass and its deviation, continuous monitoring of density fluctuations sometimes replaces the control analysis of glass and control analyses of glass batches.

Naturally, the density of glass also changes with temperature. For example, in the case of float flat glass, its density at normal temperatures is reported to be 2,400 to 2,500 $kg \cdot m^{-3}$ (depending on the composition). At temperatures above 1,400°C, the density is below 2,300 $kg \cdot m^{-3}$. It is assumed that the density of glass changes linearly at high temperatures.

The following methods are used for determining the density of glass:

- pycnometric method, which is used for direct determination in small samples: the mass of the sample is determined by weighing, the volume then indirectly from the mass of the water displaced by the sample from the pycnometer,
- hydrostatic double-weighing method, which is used for determining the density of larger pieces of glass, or even whole products,
- measurement in heavy liquids (sink-float method). This method is very fast and accurate and is used as an operating method to check the stability of glass composition on a daily basis. The sample and the standard of known density are heated at a uniform rate in a heavy liquid (mixture of α-bromonaphthalene and acetylene tetrabromide). Heating causes the density of liquid to gradually decrease and the samples to go down. The density of the sample can be calculated from the difference in temperatures at which the sample and the standard pass the reference mark on the measuring cylinder.

3.6 Mechanical properties

The mechanical properties of glass are important for the use of glass products in all areas. The most stringent requirements are the requirements for its use as a construction material. As will be further explained, the mechanical properties of glass depend mainly on the surface quality, shape and dimensions of the products and on the thermal history; the effect of glass composition is lower.

An analysis of the measurement of the strength of glass in the event of an impact, pressure and bending revealed that the cause of the glass breakage always involves tensile forces that arise under the action of any of the above stresses. Glass is generally ten to fifteen times less strong in tensile stress than in compressive stress. The results of measuring the strength of a number of samples of the same glass show considerable variance, which goes along with the practical experience in the use of glass in technology. The explanation of this phenomenon is based on the assumption of the existence of cracks on the surface of glass, which are the germ of incipient failure.

Based on fracture mechanics, the study of glass fracture is based on the assumption that glass is governed by Hooke's law up to fracture and the plastic deformation is limited only to the immediate vicinity of the crack root. Compared to metals, the ultimate strength at room temperature of glasses is thus lower than the elastic limit and at higher temperatures it is difficult to distinguish between plastic deformation and viscous flow.

Glass fracture is the process of crack formation and propagation. In case of glasses, the so-called Griffith cracks are assumed to be present in glass before loading. These cracks, with the size of the order of tens of nm, occur on the surface of glass during production and are therefore not properties of the material. When loaded, glass is first deformed elastically and, when critical tensile strength is reached, it is suddenly broken by brittle fracture emanating from the surface. The relationship between the length (or depth) of the crack and the strength of glass in the event of a failure can be expressed by the equation

$$\sigma = \sqrt{\frac{2E\gamma}{\pi a}} , \qquad (3.32)$$

where σ is the critical stress at which the fracture [Pa] occurs,

E - is the Young's modulus of elasticity in tension [Pa],

γ - is the surface tension [N·m^{-1}],

a - is the crack size [m].

The effect of surface quality can be demonstrated on the flexural strength (also known as bend strength) of flat glass after scratching with sandpaper with grains of silicon carbide of different sizes as given in Table 3.3. (The grain size is given in the number of mesh openings per inch, according to the FEPA standard, where higher value means finer grain.)

Table 3.3 Flexural strength of float flat glass 2.8 mm thick and its effect by scratching the surface

Scratching the surface with paper		Side	Flexural strength [MPa]	
Grain size according to FEPA	Specific grain size [μm]		Average value	Effect of scratching
Initial, intact sample	-	Non-tin Tin	238 117	1.00 1.00
No. 500	13.3 - 11.3	Non-tin Tin	73 77	0.31 0.66
No. 240	63 - 53	Non-tin Tin	32 31	0.13 0.25
No. 36	600 - 500	Non-tin Tin	19 18	0.08 0.15

The mechanical strength of glass is further reduced by structural inhomogeneities, whether in the form of crystals, striae, stones, bubbles or immiscible phases (Chapter 12).

Furthermore, it is fatigue that occurs in the course of long-term stress to glass, in which the stress is concentrated on the surface of cracks and the stress continues to increase over time until the strength of glass is exceeded. Fatigue is also affected by the corrosive effects of water vapour as well as increased temperature. With long-term loading, the effect of ageing also begins to show.

The mechanical properties of glass are also affected by annealing and, where appropriate, by tempering of the product (this is the effect of internal stress, Chapter 3.7).

The mechanical strength of glass is also affected by the shape and complexity of products. In general, large and shape-complex glass products have lower mechanical strength (and the variance of measured values is higher) than small and shape-simpler products. The measured strengths of lump glass are on average one tenth to fifteenth of the strength of glass fibres. It is assumed that a smaller number of cracks are found on the surface due to the short solidification time. The strength of fibres increases from fibres with a diameter of less than 1 μm and at 0.1 μm the strength of fibres approaches the theoretical value.

The effect of chemical composition on mechanical properties is lower than surface quality, surface fatigue, annealing, tempering, etc. In general, the strength of glass is increased by oxides, which increase chemical resistance (which indirectly affects the surface quality).

3.6.1   Elastic modulus and Poisson's ratio

The Young's modulus of elasticity in tension E [Pa] is determined by Hooke's law in the form of

$$E = \frac{\sigma}{\varepsilon} \quad , \qquad\qquad (3.33)$$

the shear modulus G [Pa] then

$$G = \frac{\tau}{\gamma} \quad , \qquad\qquad (3.34)$$

where σ is the tensile stress [Pa],

ε – is the relative elongation [-],

γ – is the relative displacement [-],

τ – is the shear stress [Pa].

The Poisson's ratio μ [-] is a constant of proportionality between the relative deformation in the direction of stress and the relative deformation in the direction perpendicular to the applied stress. It is determined by the relation

$$\mu = \frac{\varsigma}{\varepsilon} = \frac{E-2G}{2G} \, , \qquad (3.35)$$

where ς is the relative deformation in the direction perpendicular to the direction of stress [-],

ε – is the relative deformation in the direction of stress [-].

The following table shows the values of the modulus of elasticity in tension E, shear modulus G and Poisson's ratio μ of the most commonly produced glasses.

Table 3.4 Elastic modulus E, G and Poisson's ratio μ for the most commonly used glasses and several metals

Glass	E [MPa]	G [MPa]	μ [-]
Quartz glass (according to SÚ	73,089	31,509	0.16
Sodium-potassium crystal	66,851	27,458	0.217
Lead glass (21% PbO)	58,417	24,133	0.211
Flat glass	72,479	29,753	0.220
Simax glass	62,918	26,722	0.176
Metals			
Steel	200,000 – 220,000	70,000 – 85,000	0.28
Copper	120,000 – 130,000	42,000 – 47,000	0.34
Aluminium	66,000 – 68,000	26,000 – 28,000	0.33

The moduli of elasticity are affected by the composition of glass and connections with the strength of bonds, the tightness of particles in glass network, with the deformability of ions and thus also with ion relaxation, coordination number, etc., are assumed.

The moduli of elasticity of cooled glasses below the glass transition temperature T_g decrease with increasing temperature, with the exception of quartz glass, Pyrex and Simax glasses, where the moduli increase. In the range of temperatures above T_g, the values of moduli of glasses drop rapidly. Non-annealed and tempered glasses have lower moduli of elasticity in tension than cooled glasses, while the Young's modulus of elasticity E of tempered glass is about 7% lower.

The measurement of the Young's modulus of elasticity is performed using a number of methods. The following are only examples.

Static methods – the measurement of deflection of bars or plates under bending load is usually used. For bending with three linear edges, the deflection of the specimen is read at the point of maximum deflection under the central edge.

Dynamic methods – these methods are based on measuring the rate of propagation of ultrasonic waves through a sample, with the rate of propagation of ultrasound depending on the elastic properties of the environment and its density. These methods are more accurate than static methods and are divided into impulse and resonant methods.

3.6.2 Tensile, compressive, flexural and shear strength

When stressed at room temperature, glasses behave as brittle materials, which are deformed only elastically until they break, and plastic deformation can be neglected. In the range of elastic deformation, Hooke's law in the following form applies

$$\sigma = E \cdot \varepsilon \,, \qquad (3.36)$$

where σ is the stress [Pa], to which the following applies

$$\sigma = \frac{F}{A} \qquad (3.37)$$

E - is the Young's modulus of elasticity in tension [Pa],

ε - is the relative elongation [-],

F - is the external acting force [N],

A - is the surface area [m^2].

In the introduction, significant differences in the tensile strength of glasses, compressive strength (10 to 15 times higher than tensile strength) and flexural strength (also known as bend strength, 2 times higher than tensile strength) were mentioned. In the case of an ideal homogeneous microstructure and intact surface, the theoretical strength of glass would reach a bond strength of the order of 20,000 to 30,000 MPa. However, surface defects and structural inhomogeneities reduce the tensile strength of glass to 40 to 100 MPa and the compressive strength to 500 to 2,000 MPa. If the Griffith cracks in the surface layer of glass could be removed, glass would have a strength at least 10 times greater and would be close to the theoretical strength.

Tensile strength is measured by tensile testing, problems are mainly encountered in the clamping of specimens. Tensile strength means the maximum load that the test specimen can withstand during tensile testing, related to unit of its cross-section.

When measuring the compressive strength, samples in the shape of a cube, prism, cylinder, etc., are used for the measurement. The faces of samples, which are in contact with the jaws of the test device, are finely ground and polished. A larger number of samples is used for the determination. During the measurement, the samples are loaded between two parallel ground steel plates. Compressive strength is the load at which the test specimen is crushed.

Flexural strength is measured using the method of loading with three linear edges (maximum stress arises under the central edge on the surface opposite to that edge), using the method of loading with four symmetrically placed linear edges (maximum stress arises under the central edges on the surface opposite to these edges and is constant in the whole area between the central edges) or using the method of loading with two concentric circular edges of unequal diameter.

3.6.3 Impact toughness

Impact toughness can be characterized by dynamic flexural strength of glass. The impact flexural strength is defined by the work required to break the test specimen and related to the cross-section area. The break rate is of the order of 10^{-3} to 10^{-4} s.

The following impact tests are recognized:

- Charpy impact test,
- Izod impact strength test,
- steel ball impact test,
- swing bag impact test,
- headform impact test.

The specific type of test is usually chosen according to the purpose of use of the glass product and the tests are standardized for specific purposes.

3.6.4 Hardness

Hardness is the ability of a material's surface to retain its shape under concentrated mechanical load. The hardness of glass is quite high, it is comparable to the hardness of hardened steel. Due to its high hardness, glass is scratch-resistant during normal contact with other materials. In the Mohs scale of hardness, glasses occupy level 5 to 7.

Indentation methods are most often used for measuring the hardness of glass, usually according to Vickers or Knoop. The principle is to press a body of a defined shape and size into the surface of glass and the resulting indentation is measured and observed using a microscope.

The Vickers method is based on pressing a diamond pyramid into the surface of glass. The hardness value is then determined by the ratio of the applied load and the surface area of the indentation. Due to the very small loads applied (hundredths to several N) and small indentations, it is referred to as microhardness. For most glasses, the Vickers hardness (HV) ranges between 4,000 and 7,000 MPa. The hardest is quartz glass (7,000 MPa), harder are aluminosilicate and borosilicate glasses, the softest are glasses with high content of PbO; for flat float glass, the indicated value is 5,300 MPa.

3.6.5 Abrasion resistance

The measure of the abrasion resistance of glasses is represent with the amount of glass ground with a loose or bonded abrasive under constant, precisely defined conditions, i.e. at a certain speed of rotation of the grinding wheel at a constant pressure after running a certain path and using a standard abrasive of defined grain size (emery paper, diamond powder, silica sand). For bonded abrasive, synthetic corundum or a diamond wheel is usually used.

3.6.6 Internal pressure resistance

The strength of glass products against internal pressure resistance (internal overpressure or bursting strength) is determined for hollow products and tubes. The products are filled with water under pressure, which is gradually increased until the product ruptures. The rate of pressure increase and the duration of action are defined and are approximately 0.1 to 0.4 MPa·s^{-1}. The time

at prescribed values is 15 to 60 seconds, while the minimum measured internal overpressure is 1.5 to 2 times the operating pressure.

3.6.7 Strengthening, hardening and toughening of glasses

The reason for the small and often insufficient strength of glass is mainly its low tensile strength. An important factor that significantly reduces the strength of glass is the existence of surface defects (not only Griffith cracks). When trying to increase the strength of glass, it is necessary to focus on previous factors and remove or at least minimize their effects. The individual methods used will be characterized hereinafter.

3.6.7.1 Tempering

Rapid cooling of glass surface causes it to shrink and after cooling the whole product, a permanent compressive stress is produced in the surface layers. Cracks on the surface of glass are pressed by this tension, so more force is needed to enlarge them. The method is used in practice mainly in the production of safety glass (whether architectural, interior glass or automobile glazing closure), see Chapter 11.2.5.

3.6.7.2 Chemical strengthening by ion exchange stuffing

In this method, the compressive stress is induced by exchanging sodium cations for larger cations in the surface layer. An example is the exchange of the Na^+ cation for the K^+ cation (or another cation with a larger ionic radius) by immersing the glass in a melt of potassium salts.

3.6.7.3 Etching

This method uses the action of hydrofluoric acid and consists in removal of the surface layer of glass, in which defects are concentrated, which reduce the strength of glass. A mixture of hydrofluoric acid and sulphuric acid is usually used for etching.

3.6.7.4 Surface crystallization

Heat treatment of suitable chemical composition glass creates crystals in the surface layer (Chapter 3.3). The created crystalline phase has a negative thermal expansion (the volume of the product decreases with increasing temperature) or a thermal expansion lower than the base glass, therefore a compressive stress is generated in the surface layer during cooling.

3.6.7.5 Other procedures

In addition to the above procedures, we can encounter, for example the glazing of glass surface (glass or enamel), in which a layer is created with compressive stress on the glass surface. Another procedure is lamination - glass laminates are special products made of glass fibres bonded with a suitable organic resin (Chapter 11.4.1). Finally, the lubrication of glass fibres directly during their production also aims to increase their strength.

3.7 Internal stress

Mechanical strength is, among other things, a function of internal stress, which can be generated in the product by mechanical or thermal stress as well as imperfect annealing. During forming, the contact of the outer surface of the product with the mould results in a temperature gradient between the surface of the product and its inner layers due to the poor thermal conductivity

of glass. This temperature gradient results in the generation of stresses between differently warm layers of glass. The resulting stress would remain in glass without the technological process of "cooling", and therefore the glass products are subjected to technological process of controlled cooling, so-called annealing (Chapter 0).

By its nature, permanent or temporary internal stress can be generated in glass and glass melt.

3.7.1　Temporary internal stress

Assume that a glass plate (similar in composition to conventional flat glass produced by float technology) heated to a temperature of 400ºC, i.e. to a temperature where the glass still behaves as a solid, will be gradually cooled. The plate is cooled only from the bottom, to a temperature of 20°C, the section of the plate is shown in Fig. 3.14 A. For better explanation, it is appropriate to divide the plate into several imaginary layers, Fig. 3.14 B. When cooling this plate, low thermal conductivity of glass will cause the surface of the underside of the plate to cool faster than its inner layer and the surface of its upper side, Fig. 3.14 C. This generates a temperature gradient, the magnitude of which is related to the rate of cooling of the plate. At the same time, dilatation causes the lower layers of the plate to shrink mare than in the case of inner and upper layers. Since these layers with different temperatures cannot shift relative to each other (viscous flow is excluded at such low temperatures), a stress is generated in the plate, namely a tensile stress on the lower surface and a compressive stress on the upper surface of the plate. While maintaining the temperature gradient, the stress in the plate will persist until the bottom layer is cooled to the target temperature of 20°C, Fig. 3.14 D. As soon as the temperature continues to equalize between its inner and outer layers as the plate continues to cool, internal stresses will disappear throughout the plate, which is called **temporary stress**.

In most real cases, the entire surface of the plate is cooled and the temperature inside the plate is higher. Then there is a tensile stress on the surface of the plate (cooler part) and a compressive stress inside the plate. In the case of heating, the resulting stress will have the opposite character - i.e. tensile stress inside and compressive stress on the surface of the plate.

The magnitude of this stress depends mainly on the temperature gradient (3.4.3), then on the thermal expansion (Chapter 3.4.1) and also on the conductivity of glass (3.4.3). If the rate of temperature change is too high, the temporary stress may cause mechanical strength to be exceeded and the product to fail. In addition, rapid cooling is more dangerous for glass because tensile stress is generated in the surface layer, which can cause the development of surface cracks more easily than compressive stress.

3.7.2　Permanent internal stress

Suppose now that the same glass plate is cooled in the same way, but this time from a temperature of 550ºC (Fig. 3.15 A, B), at which the product appears solid, but a viscous flow is allowed between the layers in glass melt. If a temperature gradient is generated as a result of cooling of the glass plate (in the temperature range just below 550°C), its presence in the plate does not result in stress, as this stress is immediately equalized by the viscous flow of the layers of glass melt, Fig. 3.15 C.

If the rate of cooling is uniform, i.e. the temperature gradient generated is constant, then no stress will develop inside the plate until the bottom surface of the plate reaches 20 °C, Fig. 3.15 D.

Once the temperature of the plate begins to equalize (the temperature of the upper surface will approach the temperature of the lower surface), internal stress (compressive stress on the lower surface, tensile stress on the upper surface) begins to develop in the plate, which due to the high viscosity of glass cannot be compensated by deformation and remains in the product as a ***permanent stress***, Fig. 3.15 E. Thus, a permanent internal stress remains in the cooled plate, which is equal in its magnitude to the stress that was equalized by the internal viscous flow during cooling, but has the opposite sign (opposite character).

Permanent stress can only occur in glass when a temperature gradient has been generated at temperatures at which an internal viscous flow of the glass melt is possible and the appropriate temperature interval is called the annealing interval. The annealing interval is thus the temperature range in which the stress is equalized by viscous flow of the glass melt at a technologically acceptable time, but when no spontaneous deformation of the product occurs during this time. All stresses that arise in glass at temperatures below the lower limit of the annealing interval are temporary in nature, i.e. temporary stresses, and they last only until the temperature gradient disappears. However, they can be caused not only by a change in temperature, but also mechanically.

If the viscosity is low, this stress is equalized by viscous flow. If a viscous flow is not possible due to the high viscosity (lower temperature), this stress remains in the product even after it has been cooled. In order to minimize the amount of residual stress in glass, the glass products are subjected to controlled cooling – annealing, Chapter 0.
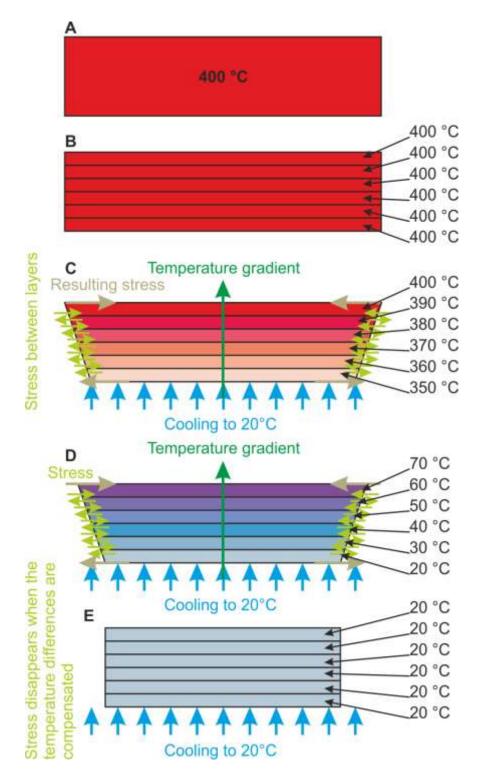
Fig. 3.14 Development of temporary stress in the section of a glass plate: A - section of the plate, B - imaginary division of the plate into layers, C - start of plate cooling, D - end of plate cooling, E - plate after temperature equalization
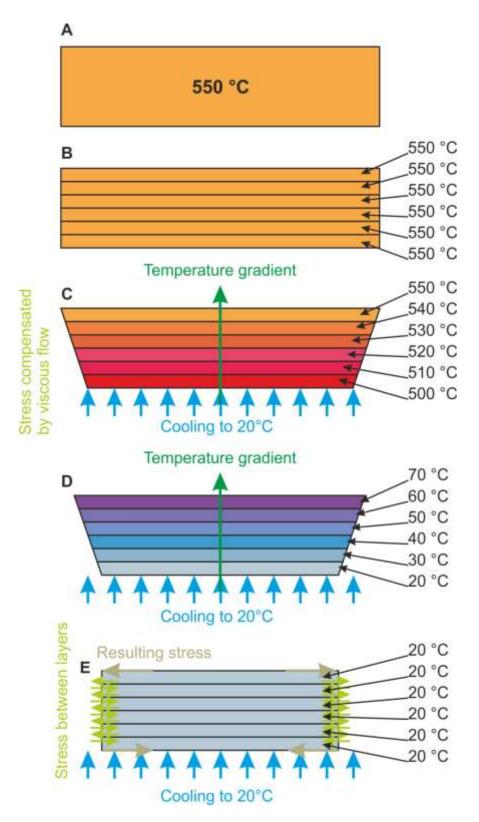
Fig. 3.15 Development of permanent stress in the section of a glass plate: A - section of the plate, B - imaginary division of the plate into layers, C - start of plate cooling, D - end of plate cooling, E - plate after temperature equalization

3.8 Electrical properties

Knowledge of the electrical properties of glass is important in their use in electrical engineering, electronics and other industries. Knowledge of the electrical properties of glass melt is then important in the electrical melting of glass or in the application of electric boosting. The electrical properties of glasses are mainly affected by chemical composition, temperature, heat treatment and crystallization.

Glasses are generally characterized by high electrical resistance, dielectric strength and low dielectric losses, while special glasses have significant semiconducting electrical properties, e.g. chalcogenide and halide glasses have electrical properties usable especially in modern electrical engineering.

3.8.1 Electrical conductance

The unit of electrical resistance R is the ohm [Ω], which is defined by the resistance of a conductor on which a voltage of 1V is generated when a current of 1 A flows through. The reciprocal quantity is electrical conductance G, the basic unit of which in the SI system is siemens.

Ionic conductivity with mass transport and **electron conductivity** without mass transport are distinguished. Most common types of glass melts are characterized by ionic conductivity, while the current carriers are most often cations of alkali metals (in particular Na, K). In non-alkali oxide glass melts, their action is replaced by cations of metals (Pb, Ba). There can be surface and bulk electrical conductivity.

The **surface conductivity** tends to be significantly higher than the bulk conductivity of the same glass and is caused by the condensation of a very thin layer of water vapour on the surface of glass, in which the alkaline components released by corrosion of glass dissolve. It is used at temperatures below 100ºC, especially in humid atmosphere, and is closely related to the chemical resistance of glass to water. The specific surface resistance ϱ_S is determined from the ratio of voltage and current flowing only through the surface of the measured sample.

The **bulk conductivity** is defined by the specific bulk resistance ϱ_V [Ω·m]

$$\varrho_v = R_v \cdot \frac{q}{h} \, , \qquad (3.38)$$

where R_v is the internal resistance [Ω],

q - is the cross-section of the sample [m^2],

h - is the length [m].

The **specific bulk resistance** ϱ_V is determined by the ratio of the current flowing through the bulk part of glass to the applied voltage and from the geometric dimensions of the test prism or cylinder.

As already mentioned, the vast majority of common glass melts are ionic conductors, where the carriers of electric current are the ions of alkali metals. These move in the melt due to the electric field of the networks of tetrahedrons, SiO$_4$.

Electrical conductance increases with increasing temperature. The chemically simplest glass melt - quartz glass melt, is characterized by excellent insulating ability even at high temperatures; in common glass melts, the electrical conductance below a temperature of about 1400°C changes by up to 15 orders of magnitude (see characteristics in Fig. 3.16).

A special phenomenon that accompanies the electrode heating of glass melt during electric melting (during direct heating of the glass melt) is the so-called thermal instability (deregulation effect). As a result, the warm, i.e. more conductive, areas of glass melt become more and more hot in the furnace as more and more current flows through them, while the colder areas become more and more cold. If the same voltage remained on the electrodes, the phenomenon would increase. The supply circuit must therefore be provided with either constant current or impedance regulation.
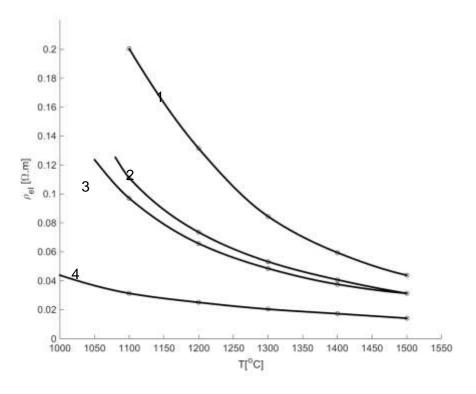
Fig. 3.16 Temperature dependence of specific bulk resistance of some glass melts: 1 - glass for the production of TV tubes, 2 - flat glass, 3 - white container glass, 4 - water glass

Regarding the influence of the chemical composition of glass, it has already been mentioned that the electrical conductance is most significantly reduced by the increasing content of silicon dioxide (SiO_2), while alkali metal oxides (Li_2O, Na_2O, K_2O) increase the conductance. Electrical conductance can be measured or calculated. The equation for electrical conductance is given from a number of empirical relations

$$log\ G = A - \frac{B}{T}, \qquad (3.39)$$

where T is the absolute temperature [K] and A, B are the constants that must be first determined. The formula also applies at high temperatures, but with different constants. The equation can be used in the intervals of 20 to 800°C and 1000 to 1450°C, with the exception of the glass transition interval.

An indicative calculation of the specific resistance can be made using the Borel equation, knowing the initial conditions

$$\varrho_m = \varrho_{15} \cdot \frac{15}{m} , \qquad (3.40)$$

where ϱ_m is the specific resistance of glass melt containing m molar % of Na_2O,

ϱ_{15} – is the specific resistance of glass melt containing 15 molar % of Na_2O.

When using the above equation for alkaline glasses with the composition of Na_2O-K_2O-CaO-SiO_2 it is necessary to substitute for m

$$m = Na_2O + \tfrac{1}{2}K_2O, \qquad (3.41)$$

where *m* is the molar % indicating the "fictitious" content of alkali (half the value of the concentration of K_2O corresponds to roughly twice the radius of the K^+ ion compared to the Na^+ ion, thus reducing its mobility by the network of tetrahedrons, SiO_4).

In glass melts with mixed alkalis and high total alkali content (above 10 mol%), an anomalous behaviour is applied where the specific resistance of glass melt is significantly higher than would correspond to the linear dependence of specific resistance in equimolar replacement of alkali cations. The result is the course of the dependence of specific resistance of glass on equimolar replacement of alkalis with a significant maximum. An even more significant maximum is manifested when measuring the specific resistance of similar glasses below the temperature T_g.

The value of TK 100 (temperature at which the specific resistance of glass is 100 MΩ·cm) is often given as a characteristic of glass melt, Table 3.5.

A number of methods have been developed to determine the magnitude of electrical conductance or resistance. As an example, let us mention the principle of the compensation four-probe method used for obtaining the basic data needed to design electric melting units. It is a measurement of dependence of the specific resistance of glass melt on the temperature at alternating voltage. The method is based on measuring the voltage drop that results from the flow of current between two platinum electrodes immersed in glass melt. The voltage drop is compensated by voltage drop generated on the ohmic resistor, through which current of the same magnitude and phase as the glass melt flows. Current is introduced into the glass melt by current electrodes and the voltage drop is detected by voltage probes.

Table 3.5 Selected glasses and their resistance

Glass	TK 100 [°C]	Specific resistance log $\varrho_{250\,°C}$ [Ω·cm]	Specific resistance log $\varrho_{350\,°C}$ [Ω·cm]
Heat-resistant glass (Kavalier Sazava)	250	8.0	6.6
E-glass (glass for glass fibres)	300	8.8	7.3
Quartz glass	450	12.3	10.5

3.8.2 Dielectric properties

When exposed to alternating current or an alternating electromagnetic field, dielectric properties related to the polarization of a dielectric are applied.

Capacitance C is the ability of a dielectric to accumulate an electric charge, the unit is farad [F]. It is determined by the relation

$$C = \frac{Q}{U} = \frac{2A}{U^2} \qquad (3.42)$$

where Q is the charge [C],

U - is the electric potential [V],

A - is the energy of electric field [W·s].

Relative permittivity ε indicates the degree of polarization of a dielectric induced by electric field; it is determined by the ratio of the capacitance of a capacitor using the examined material as a dielectric, compared with the capacitance of a capacitor that has vacuum as its dielectric.

$$\varepsilon = \frac{C}{C_0} \qquad (3.43)$$

where C is the capacitance of a capacitor with a dielectric [F],

C_0 - is the capacitance of a capacitor that has vacuum as its dielectric [F].

Loss factor $tg\,\delta$ expresses the losses that occur during polarization phenomena. For example, in an ideal capacitor connected to alternating voltage, the electric current overtakes the voltage by 90º, so that the shift between voltage and current will be less than 90° (Fig. 3.17). Dielectric losses correspond to that part of the energy which changes into heat when current flows through a real dielectric. Energy converted into heat is loss energy. The loss factor can be expressed as follows

$$tg\,\delta = \frac{I_p}{I_j} \qquad (3.44)$$

where $\qquad I_p$ is the vector of active (loss) current,

I_j - is the vector of capacitive (reactive) current.
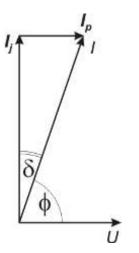
Fig. 3.17 Vector diagram of dielectric losses

The angle of dielectric losses δ is considered an important characteristic of insulators. The larger angle, the greater (under otherwise identical conditions) the dielectric losses. In the case of insulators, it is required that the angle of dielectric losses δ and thus the loss factor $tg\ \delta$ be as small as possible. Good insulators include those whose loss factor is of the order of 10^{-4} to 10^{-3}. Insulators with a loss factor of 10^{-2} to 10^{-1} are considered non-compliant.

Loss number p. The total losses in a dielectric depend on both the relative permittivity ε, and the magnitude of loss factor $tg\ \delta$ and are given by the relation

$$p = \varepsilon\ tg\ \delta \qquad (3.45)$$

The effect of glass composition on dielectric losses is dependent on different mechanisms over a wide range of frequencies, so that different maxima occur on the curves $tg\ \delta$. Like borosilicate glass, quartz glass is characterized by low losses. Examples of measured values of some glasses are given in Table 3.6.

Table 3.6 Selected glasses and their dielectric properties

Glass	Permittivity ε (1 MHz, 20°C)	Loss factor tg $\delta \cdot 10^4$
Heat-resistant glass (Kavalier Sazava)	4.6	40
E-glass (glass for glass fibres)	6.1	60
Quartz glass	3.8	1 to 2

3.8.3 Dielectric strength

The dielectric strength of glasses is defined as the ability of a dialectic to withstand the action of a high-voltage electric field without breaking and without losing insulating properties. Insulator breakdown is a physical process in which a discharge occurs. A discharge occurs when the critical electric field gradient is exceeded. It is a sudden phenomenon in which a perfectly conductive path

is created inside the insulator. The dielectric strength of a dielectric is defined by the field intensity E_p [V·m^{-1}], at which the breakdown occurred according to the relation

$$E_p = \frac{U}{k} \quad , \qquad (3.46)$$

where U is the voltage between electrodes [V],

    k - is the electrode spacing [m].

In practice, it is indicated in kV·cm^{-1} or kV·mm^{-1}. It depends very much on the shape of the electrodes and on the field intensity in tested material. A distinction is made between dielectric strength at DC voltage and dielectric strength at AC voltage of a certain frequency. We distinguish the following types of breakdowns:

- purely electrical (intrinsic), which leads to the breaking of bonds between charged particles. All distorting effects (inhomogeneities, sample shape, electrode material, impurities, etc.) must be excluded,
- thermal, when heating occurs due to dielectric losses, the temperature increases (and thus dielectric losses and electrical conductance), until the resulting effect is a breakdown, which is manifested by melting glass,
- electrochemical: with long-term exposure to an electric field, irreversible chemical processes can take place.

Theoretically, the dielectric strength of glass is 10^7 to 10^8 V·cm^{-1} (i.e. 10^4 to 10^5 kV·cm^{-1}), the actual strength is usually one or more order of magnitude lower. It is influenced by temperature, chemical composition, duration of electric field, its frequency and thickness of the sample. For example, in a glass sample heated to 100°C, the dielectric strength changes significantly with the content of Na_2O. At zero content it was measured from 7 to 11×10^6 V·cm^{-1} (depending on the type of glass), at a content of 15 wt.% of Na_2O it drops below 2×10^6 V·cm^{-1}.

3.9 Optical properties

Significant and often decisive properties for the appearance of glass products are optical properties, glass is valued for its transparency, but also colour and refractive index. In glass industry, you can find the largest range of colours and shades used in jewellery production. However, the use of optical properties of glass for technical purposes, such as selectively transparent glasses coloured throughout the mass (car and architectural glass), tubular skylights, optical systems, as well as photosensitive, photoplastic, luminescent, laser, photochromatic, polychromatic and other special glasses cannot be neglected. Knowledge of optical properties is also important for the surface layers of glass, which change not only its chromaticity, but above all its transmittance for some components of electromagnetic radiation. An example is architectural glass with selective transparency.

To introduce this issue, it is appropriate to repeat the basic properties of electromagnetic radiation, which includes a wide range of radiation from gamma radiation, through X-rays and ultraviolet radiation, to visible radiation, infra-red radiation, microwaves up to radio waves, Fig. 3.18.

Light can be understood as an electromagnetic wave: each light wave has its electrical and magnetic components, both of which can be expressed by a vector. The wavelength (λ) of a

continuous light wave is the distance between successive wave peaks, amplitude (intensity), frequency is the number of waves transmitted per second, Fig. 3.19 A. The third basic property of light is the wave angle (polarisation), which can be very easily imagined as an electromagnetic wave oscillating in one plane of the same wavelength as seen in Fig. 3.19 A (monochromatic light). An example of non-polarized ("ordinary") light is the scheme shown in Fig. 3.19 B, where the electromagnetic waves of the individual components of light oscillate in different planes (in the given example, perpendicular to each other). The basic characteristic of light is its wavelength.

White light (daylight) is called light, which has all wavelengths represented in the visible region in the same proportion as sunlight, and the human eye perceives it as colourless.

The light visible to the human eye is in the wavelength range from 380 to 750 nm (

Table 3.7) and the different wavelengths are perceived by the human eye as different colours.
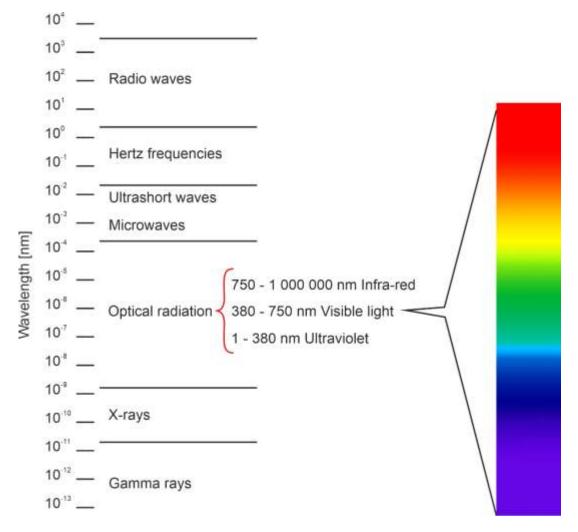
Fig. 3.18 and representation of the colour spectrum of visible radiation

Table 3.7 Visible spectrum

Colour	Wavelength λ (nm)	Frequency ν (Hz)	Energy (eV)
red	700	4.29×10^{14}	1.77
orange	600	5.00×10^{14}	2.06
yellow	580	5.17×10^{14}	2.14
green	525	5.71×10^{14}	2.36
blue	450	6.66×10^{14}	2.75
purple	400	7.50×10^{14}	3.10
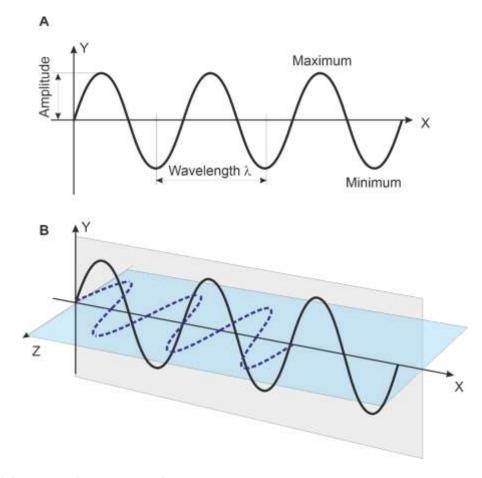
Fig. 3.19 Light as an electromagnetic wave

A region of shorter wavelengths than violet (380 nm) is referred to as Ultra-Violet (UV radiation). A region of longer wavelengths than red (750 nm) is referred to as Infra-Red (IR radiation).

The speed of light in vacuum is 299,792,458 meters per second, slightly lower is the speed of light in air. The speed of light in other materials is significantly lower, which results in optical phenomena during the transition from one environment to another, e.g. from air to glass.

During the interaction of light with glass, part of the radiation is reflected from the monitored glass object, part is absorbed, part causes secondary radiation emission in object material, part of the radiation can be transmitted and part of the radiation can be emitted by the object itself, Fig. 3.20. The following text describes some optical properties important for glass.

3.9.1   Reflection and refraction at the optical interface

When a ray of monochromatic light is incident from a medium of refractive index n' on the interface separating it from a medium of refractive index n (glass), it is generally divided into two rays. One remains in the medium of refractive index n' (reflected ray) - it is called a reflection, the other refracts in glass - it is called a refraction. The angle α, that the incident ray makes with the perpendicular erected at the point of incidence on the interface is the angle of incidence, β the angle of refraction and α' the angle of reflection (Fig. 3.21). According to the law of reflection, the angle of reflection is equal to the angle of incidence.

$$\alpha = \alpha' \qquad (3.47)$$
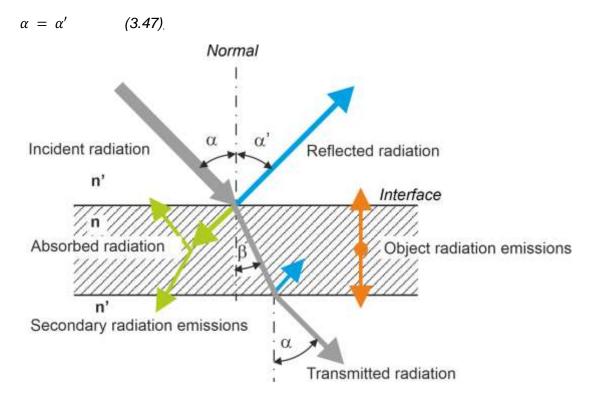
Fig. 3.20 Interaction of optical radiation at the interface

Refraction of light can be defined as the change in direction and speed of a ray of light when it passes through an optical interface. Mathematically, the ratio of refractive indices can be expressed as the ratio of the sine of the angle of incidence of a ray of monochromatic light and the sine of the angle of refraction of the same ray according to Snell's law:

$$\frac{\sin \alpha}{\sin \beta} = \frac{n}{n'} \qquad (3.48)$$

for $n' = 1$, the relation can be rewritten into the following form

$$n = \frac{\sin \alpha}{\sin \beta}. \qquad (3.49)$$

Because glass is usually surrounded by air, the refractive index of glass relative to air is most often given. If it is necessary to determine the refractive index of glass in a vacuum, the refractive index for air must be multiplied by a factor of 1.00027.

If the ray passes from an optically thinner medium to an optically denser medium, i.e. $n' < n$, then $\beta < \alpha$ the ray refracts to the perpendicular, Fig. 3.21 A. Conversely, if it passes from an optically denser medium to an optically thinner medium, i.e. $n > n'$, then $\beta > \alpha$ the ray refracts from the perpendicular, Fig. 3.21 B. In the latter case at a certain angle of incidence α_m, the angle of refraction is $\beta_m = 90°$. This is the so-called limiting angle of incidence or also critical α_m, at which the refraction still occurs. For angles of incidence greater than the limiting angle α_m, all light from the interface is reflected; this phenomenon is called **total internal reflection**.
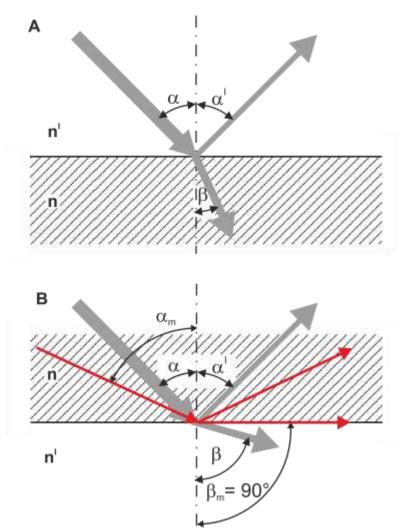
Fig. 3.21 Schematic representation of refraction and reflection: A – from optically thinner to optically denser, B – from optically denser to optically thinner

Reflection and refraction occur in the plane of incidence. The component of the ray that is reflected is given by reflectivity R and the component that is refracted and transmitted is given by transmittance T_R. In the case where light is incident and reflected in the direction of the normal (angle of incidence $\alpha \approx \alpha' \approx 0$), the following applies to reflectivity R_n

$$R_n = \left(\frac{n'-n}{n'+n}\right)^2. \qquad (3.50)$$

For ordinary glass in air, air $n' \approx 1$ and glass $n = 1.5$. Then about 4% of light is reflected. However, when light passes perpendicularly through a glass object (plate), the light is reflected both on the surface when entering the object and on the surface when leaving the object. The combination of both reflections R_g can be obtained approximately from the equation:

$$R_g = \frac{2R_n}{(1+R_n)}, \qquad (3.51)$$

and then about 7.7% of light is reflected according to the calculation. Even when using very clear glass (colourless, without absorption), only about 92.3% of perpendicularly incident light passes through the glass plate. For glasses with a higher refractive index, the amount of transmitted light is even smaller.

The reflectivity will increase with the angle of incidence and will also be affected by the polarization of radiation. After simplifying the Fresnel equations, for polarized light in the plane perpendicular to the plane of the image (Fig. 3.21) the reflectivity is given by the equation:

$$R_\perp = \left(\frac{n'\cos\alpha - n\cos\beta}{n'\cos\alpha + n\cos\beta}\right)^2 \quad (3.52)$$

and if the polarized light is in the plane parallel to the plane of the image, the reflectivity is given by the equation:

$$R_\parallel = \left(\frac{n'\cos\beta - n\cos\alpha}{n'\cos\beta + n\cos\alpha}\right)^2. \quad (3.53)$$

Using Snell's law:

$$\beta = arcsin\left[\left(\frac{n'}{n}\right)\sin\alpha\right] \quad (3.54)$$

reflectivity $R_\perp$ and $R_\parallel$ can be completely derived from the angle of incidence α. If the light is non-polarized, the following applies:

$$R = \frac{R_\perp + R_\parallel}{2}. \qquad (3.55)$$

The dependence of the reflectivity on the angle of incidence and the polarization of light is given in Fig. 3.22.
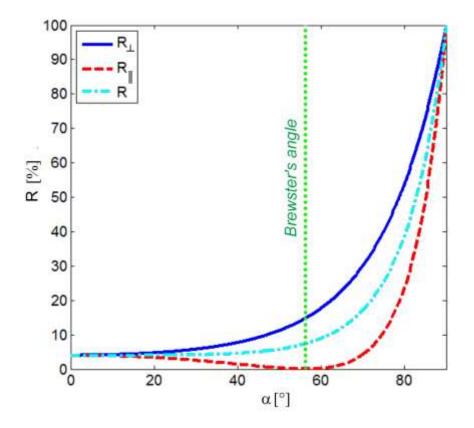
Fig. 3.22 Dependence of the reflectivity R (glass on air) on the angle of incidence α and polarization of light, for $n^{'} \approx 1$ and $n = 1.5$

If the incident light is polarized in the plane parallel to the plane of the image, the reflectivity $R_{\parallel}$ decreases up to the Brewster's angle, at which the light passes perfectly through the surface, then the reflectivity increases. The Brewster's angle α_B is defined by the relation

$$\alpha_B = arctan\left(\frac{n}{n'}\right). \qquad (3.56)$$

For the plane of the glass surface with a refractive index of 1.5 it is $\alpha_B = 56{,}31°$.

The refractive index depends on the chemical composition of glass, the temperature and the wavelength of the light incident on glass. Due to its dependence on the wavelength of incident light, it is necessary to state it while indicating the relevant wavelength.

In terms of chemical composition, the values of refractive index of conventional silicate glasses range from 1.48 to 1.56. The mean value used in the indicative calculations is 1.5. The refractive indices of selected glasses are given in Table 3.8.

Table 3.8 Refractive indices of selected glasses for the wavelength of 589.3 nm

Glass	Refractive index n
Soda lime silicate (flat and container glass)	1.52
Borosilicate (heat-resistant glass)	1.48
Lead silicate (30% PbO)	1.56
Lead crystal (24% PbO)	> 1.54
E-glass (glass for glass fibres)	1.55
Aluminosilicate	1.54
Quartz glass	1.46

The refractive index of light also changes with temperature, and in the case of silicate glasses this dependence is usually linear up to the glass transition interval, Fig. 3.23. If silicate glass (curve A) is cooled from the temperature T_2 at such a rate that an equilibrium state occurs at all times, the refractive index increases up to the temperature T_{MAX} when the refractive index is at its maximum value n_{MAX}. In the further course, the refractive index decreases according to curve A until it reaches the refractive index n_A at temperature T_1. If cooling takes place faster, that the structural transitions cannot follow the structural arrangement of higher temperatures, the refractive index changes with temperature according to curve B and at temperature T_1, glass will have the refractive index n_B. The refractive index is thus lower than during slow cooling and such glass is called *non-stabilized* glass. However, changes in the refractive index are in the thousands, which is significant when used in optics.

As already mentioned, the refractive index of glass also depends on the wavelength, an example of this dependence is shown on quartz glass, Fig. 3.24. This dependence implies an important property for glass - dispersion.
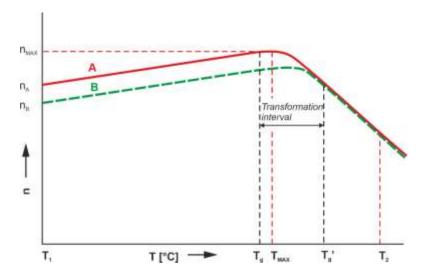
Fig. 3.23 Scheme of a change in the refractive index depending on the temperature (glass transition range modification)
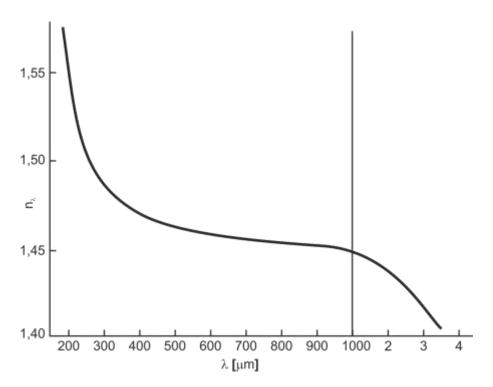
Fig. 3.24 Dependence of the refractive index on the wavelength, the so-called dispersion curve of quartz glass

3.9.2 Dispersion

Dispersion of light (also called chromatic dispersion or spectral decomposition of white light) is the decomposition of mostly white daylight according to its wavelength, i.e. colour. In general, the refractive index in a medium is higher for shorter wavelengths (representing, for example, blue colour) than for longer wavelengths (corresponding to red colour). For a beam that contains both components, the blue component will have a smaller angle of refraction than the red component when refracted at the air-glass interface. The white light beam consists of all the colours of the visible spectrum and, when refracted at the interface, decomposes into individual colour components to form a "rainbow spectrum". The decomposition of white daylight can be observed by means of a glass prism, Fig. 3.25.
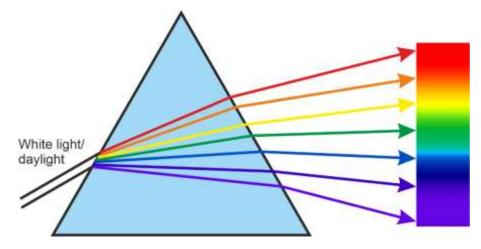
Fig. 3.25 Dispersion of white light in a prism
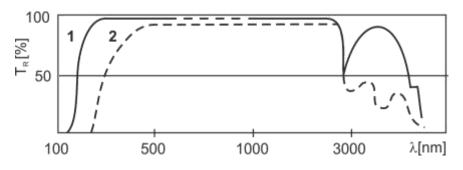
The dispersion of light can be encountered in everyday life in the form of a rainbow. For glass, the dispersion is valued especially in the case of decorative glass, glass jewellery components, light fixture components (e.g. pendants) and in optics, where it may be desirable or, conversely, undesirable.
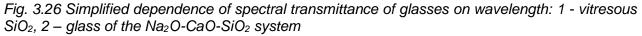
3.9.3 Absorption

The intensity of the light passing through glass decreases due to its partial absorption. The amount of light absorbed depends on the type of substance in which the absorption occurs and the wavelength of light. If the absorption occurs uniformly over the entire visible region of the spectrum, then the spectral composition of the light emerging from the substance does not change, i.e., there is no change in colour, but only decrease in light intensity. However, if light of only a certain wavelength is absorbed, then the light has a different spectral composition after passing through the test substance, in other words a colour change occurs. This phenomenon exists in coloured glasses, where this selective absorption is usually caused by a small addition of colouring component in glass matrix.

Quantitatively, the light transmittance of glass can be expressed by the so-called transmittance coefficient T_R, which is given by the ratio of the intensity of light emerging from (I) and light entering (I_O) the sample. It refers to the unit thickness, and when multiplied by hundreds, we obtain the light transmittance of glass in percentage. An example of the dependence of light transmittance on wavelength (spectral transmittance) is given in Fig. 3.26. Further examples are given in Fig. 3.27.

Conventional colourless flat and container glasses with the composition of Na_2O-K_2O-CaO-MgO-SiO_2 transmit optical radiation in the range $\lambda \approx 300$ nm (UV radiation) to $\lambda \approx 5,000$ nm (IR radiation). The production of some glasses is directly aimed at reducing or, conversely, increasing the absorption of light in the required range of wavelengths. The spectral transmittance of clear quartz glass is limited in the short-wave region by wavelength $\lambda \approx 160$ nm (ultraviolet region of the spectrum) and in the infra-red region of the spectrum by wavelength $\lambda \approx 5,000$ nm. Ultraviolet radiation with shorter wavelengths are transmitted through fluoride and phosphor glasses. X-rays are transmitted through lithium-beryllium-boron glasses. On the contrary, X-rays together with gamma radiation are absorbed by glasses containing a high percentage of heavy metal oxides, mainly PbO. Chalcogenide glasses do not transmit in the visible region due to the shift of the lower limit of transmittance in the IR region to $\lambda \approx 900$ nm but, depending on their composition, they transmit IR radiation up to $\lambda \approx 20,000$ nm.

Fig. 3.26 Simplified dependence of spectral transmittance of glasses on wavelength: 1 - vitresous SiO₂, 2 – glass of the Na₂O-CaO-SiO₂ system

The production of heat-absorbing glass is based on the strong absorption of infra-red radiation by the combination of Fe_2O_3 – FeO pigments. Such glass is most often used in the form of flat glass in means of transport and in construction to reduce the internal temperature caused by intense lighting in bright sunlight.

3.9.4   Scattering

Light scattering is defined as a change in the direction of light propagation that is scattered at different angles deviating from the original direction when it is incident on or passing through two media. Light scattering was observed by Tyndall as the light ray passed through micro-heterogeneous systems. This scattering manifested itself in the formation of the so-called light cone. The scattering effect is caused by the bending of light that occurs on the surface of colloidal particles. As an example of the Tyndall effect in glass, it is possible to describe the scattering of light on colloidal gold particles in the so-called golden ruby. Light scattering depends on the size of colloidal gold particles. If their size is in the range from 20 to 50 nm, scattering does not show and we get a beautiful purple colour. With a particle size in the range from 70 to 100 nm, a slight scattering can be observed, which is intense at particle sizes in the range from 200 to 500 nm, when the metallic lustre of gold particles already appears in the scattered light. Another example is light scattering in opalines. In this case, it is clear that the degree of light scattering caused by particles that are small compared to the wavelength depends on the wavelength of light - blue scatters more than red. As the particle size increases, the scattered light shows an increasingly intense bluish colour. In this case, transmitted light has a yellow to brown colour shade.

There can be three types of scattering centres:

- Rayleigh scattering,
- Raman scattering,
- Mie scattering (generally replaced with Rayleigh-Gans approximation theory).
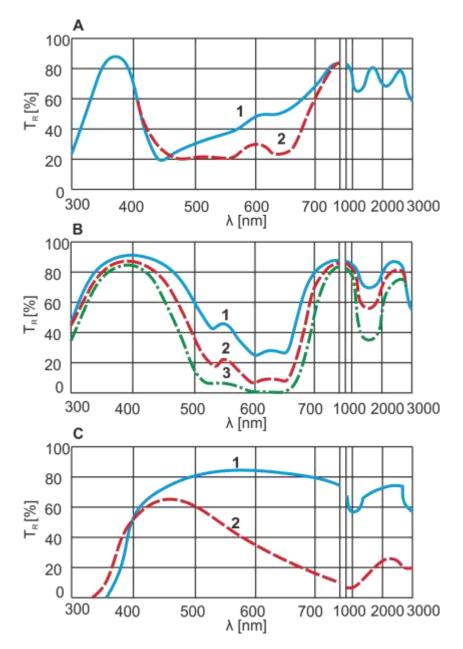
Fig. 3.27 Transmittance of a 2 mm thick glass plate,
A – with a composition of 0,25% NiO:
    1 – 75.3% SiO_2, 11.7% CaO, 13% Na_2O,
    2 – 70.6% SiO_2, 11% CaO, 18.4% K_2O,
B – with a composition of 70.6% SiO_2, 11% CaO, 18.4% K_2O:
    1 – 0.05 CoO,
    2 – 0.1% CoO,
    3 – 0.2% CoO,
C – with a composition of 75.3% SiO_2, 11.7% CaO, 13% Na_2O:
    1 – 2% Fe_2O_3 (oxidizing conditions),
    2 – 2% FeO (reducing conditions)

3.9.5 Luminescence

Luminescence is the ability of some substances to emit light when energy is supplied in any form other than thermal energy. Therefore, in order for luminescence to occur in glasses, there must be so-called luminescence centres in glass. These centres can be obtained by doping glasses, for example, with Mn^{2+}, Ce^{3+}, UO_2^{2+}. Luminescent glasses can be classified by method of excitation as follows:

- photoluminescent (excitation is performed by a source of ultraviolet or visible radiation, especially for substances with small and medium concentrations of luminescent centres) and
- thermoluminescent (excitation is caused by an increase in temperature after previous excitation).

In terms of duration, they are classified as follows:

- fluorescence (disappears after the end of luminescence excitation), and
- phosphorescence (luminescence lasts for a certain period of time even after the end of excitation).

3.9.6 Photosensitive, photoplastic, photochromic and polychromatic glasses

In the case of photosensitive glasses, when exposed to radiation of a certain wavelength (often UV radiation), a latent (invisible) image is first formed, which can be developed into visible by further processing. The essence of these glasses is the presence of the so-called photosensitive elements Au, Cu, Ag and possibly others, which are present in small concentrations. The principle is similar to photography.

In the case of photoplastic glasses, nuclei for the crystallization of silicates or fluorides are formed after exposure and subsequent heat treatment. The dissolution rate of the regions of crystallised mass in etching media (mainly in HF) then differs from the dissolution rate of original glass and thus a relief is created.

Photochromic glasses are glasses that are coloured by exposure to radiation of suitable wavelengths - colour centres are formed. After the interruption of exposure to activating radiation, discolouration occurs - destruction of colour centres. The colour centres of this glass are metastable. Halides of silver, copper, cadmium, as well as europium and cerium are mainly used in photochromic glasses. Photochromic glasses are used as UV protection on glasses or too intense visible radiation (Heliovar lenses for sunglasses).

A newer type of photosensitive glass is polychromatic glass. When exposed to UV radiation (300 nm), a latent image is first formed at room temperature, followed by first heat treatment at temperature of 450 to 500°C, then final exposure to UV radiation (300 nm) and subsequent thermal radiation at temperatures of 300 to 410°C. The result is glass products with permanently coloured patterns in glass mass.

3.9.7 Birefringence, polarization and interference of radiation

Glass is characterized by the fact that it is an isotropic substance, i.e. that its properties, including optical properties, are the same in all directions. If stress is present in glass, either due

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to imperfect annealing or due to the effects of external force, glass becomes optically anisotropic and birefringent. This means that light ray incident on the surface of such glass splits into two rays, ordinary and extraordinary, which are polarized in mutually perpendicular planes. As a result of the different velocities of the two rays as they pass through glass, a phase shift (path difference) occurs between them, the magnitude of which is directly proportional to the stress in glass. This phenomenon is used in practice to determine the magnitude of internal stress in glass using polarizing devices (Chapter 10.4).

In general, light radiation is defined as electromagnetic waves propagating linearly, with the maxima of individual waves forming a cylindrical envelope around the axis of direction of propagation. However, if oscillations of radiation are arranged in a certain way, we get linearly, elliptically or circularly polarized radiation in terms of arrangement. Light polarization can occur due to its reflection, refraction, absorption, or scattering.

Light interference occurs when two light rays pass through the medium in the same direction and oscillate in the same plane. As a result of their folding, the light wave may intensify, weaken or, in special cases, completely disappear.

3.10 Chemical resistance

Chemical resistance is an important property of glass, characterizing the extent of its ability to endure itself from corrosive effects of various external media. Glass corrosion is a result of the action of atmosphere, water, acids, alkalis and other chemicals. The quantitative content of some substances present in the extract also plays an important role at present, which is particularly relevant for products that come into contact with food products and medicaments. Therefore, resistance tests are performed according to internationally recognized standards.

3.10.1 Water resistance of glass

There are two effects of water. Either it is the effect of atmospheric humidity, then the process is called weathering, or it is the effect of excess water on glass, then the process is called leaching. In principle, the two processes differ in that in the first case the corrosion products remain on the surface and in the second case they are removed from the surface.

3.10.1.1   Effect of water on glass

The dynamic action of aqueous medium on the surface of glass generally results in an ion exchange of alkaline cations Na^+, K^+ or Li^+ present in glass for ions H^+ or H_3O^+ from aqueous medium. Divalent cations Ca^{2+}, Mg^{2+}, Ba^{2+}, Pb^{2+} and Zn^{2+} may also partially participate in this ion exchange. The result of this ion exchange is the formation of a layer of *hydrated silica gel* with Si-OH groups. As a rule, the extract of glass generally contains all its components, although usually in a proportion different from the original glass.

When water acts on the surface of glass, diffusion predominates, and the amount of leached alkaline components from glass, in relation to time, depends on the rate of passage through the layer of hydrated silica gel, which gradually intensifies. The reaction of the components of glass with water is fastest in the first phase of leaching, when the layer of gel is the thinnest. In the first hour, with a few exceptions, most of the total extract is leached, with a substantial part consisting

of basic components in which alkalis predominate. In a static medium, the pH of water increases with the amount of leached cations and the water then begins to act as an alkaline solution.

However, Si-OH groups (silanol groups) on glass surface are also formed in highly chemically resistant glasses (quartz glass, non-alkaline glasses) and are the cause of hydrophilic behaviour of untreated surfaces of glass products. The fresh fracture surface of glass reacts with water vapour to form Si-OH surface groups. Water molecules are then bonded to these groups via a hydrogen bridge, which can no longer be virtually removed by drying at normal temperatures. Gradual desorption of physically bonded water (150 to 200°C) and elimination of Si-OH groups occur at elevated temperature, releasing water and forming the original Si-O-Si bonds (above 400°C) Fig. 3.28.
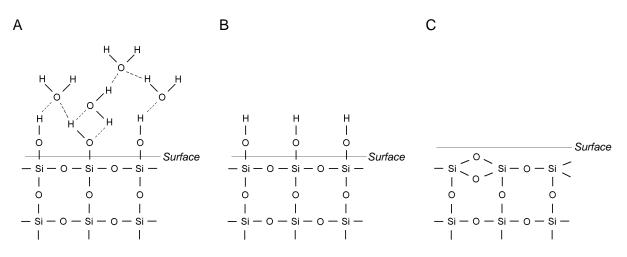
Fig. 3.28 Ratios on the surface of quartz glass depending on the ambient conditions: A - laboratory conditions, humid air; B - temperature around 200°C; C - temperature above 700°C

3.10.1.2   Effect of water vapour on glass

Atmospheric humidity causes "weathering" to occur on the surface of glass, with:

- formation of "water layer" on the surface of glass,
- release of alkalis from the surface of glass due to hydrolytic action,
- reaction of released alkalis with CO_2 from air to X_2CO_3,
- corrosive action of a highly concentrated solution of X_2CO_3 on the surface of glass to form corrosion products.

If frequent removal of alkalis from glass surface is ensured, a layer with a lower concentration of alkalis (higher concentration of SiO_2) is formed on the surface of glass, which further acts as a protective barrier against further leaching.

If moisture condensation and evaporation occurs alternately on the surface of glass, corrosion products may be concentrated in some parts of the surface and visual highlighting may occur, which may result in "matt" or "interference". In the extreme (but not rare) case, for example, improperly placed flat glasses will be glued together and degraded, because corrosion products can no longer be removed without traces otherwise than mechanically (by grinding and polishing).

The larger the glass surface (cullet, frit), the stronger the action of water vapour and generally moisture on glass can be observed. Because "water" in glass surface is bonded by adsorption forces, it cannot be removed on a large surface or by drying at laboratory temperature.

3.10.1.3   Determination of water resistance

The tests are based on leaching of:

- glass cullet in boiling water under normal laboratory conditions,
- glass cullet at elevated temperature and pressure in an autoclave.

The cullet tests use a screened fraction of freshly crushed glass (usually 0.3 to 0.5 mm) washed with acetone to remove dust particles. For ordinary glasses, the cullet is leached in distilled water at 98°C/ 60 minutes. For chemically resistant glasses (for example alkali borosilicate glasses of Pyrex type) heating in an autoclave at 121°C/ 30 minutes is used. The leachate from the inner surface of products (like bottles) is obtained in an autoclave (121°C/ 60 minutes).

The resulting leachate/solution is titrated with hydrochloric acid to determine the leached alkalis or, in special cases, quantifying the selected components in the solution. Depending on the consumption of HCl or the content of selected components, glass is then classified into the appropriate resistance class according to the relevant standards. There are five resistance classes for the standard cullet test at 98°C (HGB classes, best class I, worst class V).

3.10.2 Acid resistance of glass

The corrosive effect of acids on the surface of glass is similar to that of water, but alkaline dissolution of the layer of silica gel in alkaline glasses is excluded and the rate of corrosion of glass is defined only by the diffusion rate of alkali ions from glass into solution. The surface of corroded glasses is covered with a layer of silica gel with a content of SiO_2 of about 95%.

During corrosion of glasses by acids, some other components of glass are leached e.g. Al^{3+}, Ca^{2+} or Pb^{2+}, so that, for example, water-resistant glasses with a higher content of Al_2O_3 are more affected (extracted) with acids. The chemical nature of acids (excluding HF) has very little effect on the corrosion of glass. In addition to temperature, the concentration of H^+ ions, i.e. the pH of the medium, is decisive for the reaction rate. The reaction rate also affects the solubility or insolubility of the resulting reaction products on the glass surface, e.g., $BaSO_4$ or $PbSO_4$, which may reduce the reaction rate.

In general, the mechanism of action of acids on the glass surface can be described by the following processes:

- disruption of bonds between alkalis and basic glass-forming tetrahedrons $[SiO_4]^{4-}$,
- extraction of alkalis and formation of a layer of silica gel,
- reduction of the penetration of additional acid through this layer to the surface of the original glass.

Only hydrofluoric acid HF reacts chemically with the layer of silica gel, dissolves it, reveals another surface and the corrosion (dissolution) process continues. This forms the basis of the process of *chemical polishing and frosting of glasses*, Chapter 11.3.1.

3.10.2.1   Determination of acid resistance

To determine the acid resistance, products or polished cut-outs from products of regular geometric shapes are used, which are suspended in a bath of boiling solution of hydrochloric acid with a concentration of $c(HCl) = 6$ mol l^{-1} under reflux condenser for 3 hours. According to the older procedure, the difference in weight before and after the test was determined by weighing and the weight loss was converted to a surface area of 100 cm^2 of sample. A newer method is based on spectrophotometric determination of the content of components (Na_2O, K_2O, or CaO and SiO_2) in the leachate and again with conversion to a surface area of 100 cm^2 of sample. Depending on the weight loss or the content of components in the extract, glass is then classified into one of three resistance classes.

3.10.3 Alkali resistance of glass

Corrosion of glasses by alkaline solutions differs significantly compared to corrosion by water and acids, both in the amount of dissolved glass and in the chemical effect. Alkalis disrupt Si-O-Si bonds without the formation of silica gel, dissolve all glass components and therefore their effect is many times more intense than for water and acids.

3.10.3.1   Determination of alkali resistance

The measure of alkali resistance is the weight loss of the sample after boiling for three hours in a mixture of equal volumes of sodium hydroxide solution with a concentration $c(NaOH) = 1$ *mol.dm^{-3}* and sodium carbonate solution with a concentration $c(0.5\ Na_2CO_3) = 1$ *mol.dm^{-3}* converted to 100 cm^2 of glass surface. According to the weight loss, glass is then classified into one of three resistance classes.

4 Glass raw materials

Glass raw materials are the basis for glass melting and their ratio affects the resulting properties of glass, the economic complexity of glass melting, affects forming temperatures, affects processing and finishing, thus the composition of glass affects the life of machinery and equipment, the environment and more. The purity of glass raw materials and the homogeneity of their composition affect the resulting quality of glass.

Over the years, the view of the impact of raw materials for individual areas has evolved. The purity of artificial raw materials has increased, other natural raw materials have been gradually introduced into production, and the use of waste and recycled raw materials (especially cullet) is expanding. In the industrial production of glass, 50 to 100 glass raw materials are used, which bring about 40 elements into various glasses.

There is a significant quantitative difference between the individual raw materials. 90 to 95% of the consumption of all glass raw materials together are sand, soda, limestone, dolomite, feldspar (possibly phonolite), and cullet. The rest are boron raw materials, potash, sulphate, aluminium hydrate, and lead, barium, zinc raw materials. Consumption of other raw materials does not exceed 1 to 2% of total consumption. Therefore, raw materials are sometimes divided into large-tonnage and small-tonnage, which, however, does not say anything about their relevance.

A more practical classification of glass raw materials can be performed either according to the chemical elements introduced by them or with regard to their function in charge during glass melting process. The second option better describes the relevance of raw materials for glass technology and can be classified into four groups:

- **Glass network formers:**
  - *Oxides: SiO_2, B_2O_3, GeO_2, P_2O_5, As_2O_3, Sb_2O_3,*
  - *chalcogenides,*
  - *halides, etc.,*
- **Conditional glass formers (intermediates):**
  - *Intermediates require charge stabilization by network modifiers in order to form a stable glassy network: TeO_2, SeO_2, MoO_3, WO_3, B_2O_5, Al_2O_3, Ga_2O_3, V_2O_5, etc.*
- **Modificators (network modifiers):**
  - *Stabilizers, melting accelerators and property modifiers: Li_2O, Na_2O, K_2O, CaO, MgO, BaO, ZnO, CdO, PbO, TiO_2, SnO_2, etc.,*
  - *Colouring raw materials: ionic, molecular, colloidal colorants,*
  - *Fining raw materials: As_2O_3, Sb_2O_3, sulphates, nitrates,*
- **Glass cullet.**

4.1 Briefly about the history of glass raw materials

No product can be produced without suitable raw materials, therefore suitable raw materials were one of the conditions for success already for ancient glassmakers. The selection of the best quartz, the processing of wood ash and, above all, other additives for glass were important know-how of medieval glass masters. Raw materials from the immediate vicinity of glassworks were mainly used, but already in the 14th and 15th centuries it is possible to assume trade in raw materials transported from a greater distance (manganese minerals, arsenic, colouring

components). In the 19th century, modified raw materials began to be used gradually. First, the wood ash was refined to obtain K_2CO_3, then it was replaced by synthetic soda or sodium sulphate, other raw materials were still taken from the immediate vicinity. It was not until the end of the 19th century that the number of glass raw materials increased and that their mining and production were specialised. Deposits of pure sand are open, the growing chemical industry supplies soda, nitrates, lead and zinc compounds and more at affordable prices. The world transport network allows the import of boron raw materials, sodium nitrate and other, formerly exotic raw materials.

At the beginning of the 20th century, the ancient glassmaking custom culminated - adding any newly discovered element or any newly produced compound into glass. The roots of Faraday, Harcourt and especially Schott can be traced along the scientific line, with a series of patents and old recipes for removing the colour and staining glass with selenium and rare earth elements along the practical line, up to the patent for staining glass with indium. And so at that time, "didymoxide"[2] and selenium compounds were produced for glassmakers, glassmakers support the production of uranium salts, and glassmakers import cryolite from Greenland.

The interwar period also began to focus on basic raw materials and their purity, the use of local raw materials (sands) slowly ended, specialised sand pits opened up and the first simple treatment of sand by floating began. The first standards appeared and the control of raw materials deepened.

The shortage as a result of war then renewed interest in alternative raw materials and domestic raw materials in Europe. Feldspars were studied, and the use of phonolites and other rock raw materials was developed. The large quantitative development of the glass industry required large amounts of basic raw materials, pure deposits were not enough, and the treatment industry was developed, in particular for sand. From new raw materials, melting accelerators were introduced – fluorspar (CaF_2) and blast furnace slag.

Recent years have been marked by ecology and economics. It is mainly the massive use of recycled cullet in container glass, which is ecologically and economically advantageous, which has resulted in a significant decrease in the consumption of some raw materials. Economic requirements prefer local raw materials (sands, rock raw materials, etc.), because transport costs keep growing. Natural soda displaces Solvay soda, natural boron minerals (colemanite) are often used instead of borax. The use of waste raw materials and cheaper by-products of industry is growing. The scope of treatment of raw materials and their purity are increasing. Efforts to increase the melting rates of furnaces press on refinement of raw materials, with the transition to the use of non-dried raw materials. Ecological and hygienic requirements are becoming stricter.

4.2 Requirements for glass raw materials

Requirements for glass raw materials can be divided into several groups:

- economic and business-strategic requirements,
- ecological and hygienic requirements,
- chemical composition,

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[2] A mixture of praseodymium oxide and neodymium oxide

- foreign matters in raw materials,
- grain size of glass raw materials,
- handling properties of glass raw materials.

Economic and business-strategic requirements include the price itself, transport costs, strategic security of supplies and the assumption of price stability and supplier reliability. The savings or additional costs of raw materials are clear, while the savings in melting costs when using different raw materials may be influenced by other factors and may not ultimately lead to savings. In the case of large-scale production, such as flat and container glass, the price of raw materials is fundamentally monitored. In the case of special production, such as crystals or technical glasses, higher prices of raw materials can be afforded due to the higher price per kilogram of products. Transport costs are very important, which can, for example, exceed the price of the raw material itself for sand, dolomite and feldspar. Stocks mainly form a reserve in case of unexpected supply outages and for main raw materials it is for 5 to 15 days, for minority raw materials it is 3 or more weeks. Stocks should be at the level of a reserve and should not be unnecessarily higher, as they tie up the company's funds and increase costs (e.g. storage costs).

Ecological and hygienic requirements must be observed as most glass raw materials can damage human health under certain circumstances and some are toxic. Particularly dangerous poisons include:

- arsenic and its compounds,
- metal cyanides,
- selenium dioxide,
- sodium selenate,
- thallium and its compounds,
- antimony potassium tartrate.

Other poisons include:

- antimony compounds,
- barium compounds (barium sulphate is not a poison),
- silver nitrate,
- nitrites,
- fluorides (aluminium fluoride, cryolite and fluorspar are not poisons),
- fluorosilicates,
- lead compounds (lead sulphide is not a poison),
- selenites,
- copper sulphate,
- tellurium compounds,
- uranium compounds,
- cadmium compounds.

Other raw materials are not poisons, but they are often hazardous to health. Therefore, when working in batch houses, it is necessary to follow the work rules, work in frequently washed work clothes, and, if necessary, use a respirator, gloves and goggles.

The ecological problem that glassworks have to deal with is the fumes of raw materials during melting, packaging and their disposal, raw material waste, their spraying, scrap, defective doses of batch and contaminated raw materials.

The **chemical composition** of glass raw materials is given as a percentage by weight and it is necessary to know it for each raw material. The components of each raw material can be roughly divided into three groups:

- the active ingredients form the required part of raw materials (e.g. Na_2O for soda, SiO_2 for sand, Se in selenite, SO_3 in fining agents,…),
- ballast components do not pass into glass or do not play a significant role in glass (e.g. moisture, CO_2,…),
- harmful components degrade the properties of glass, which are usually colouring oxides (e.g. FeO, Fe_2O_3, …) and environmentally undesirable elements (e.g. F, Cl, …).

It is logical to require a raw material with the highest possible active ingredient, but the price and requirements for the final quality of glass are also critical. It is not economical to buy more expensive raw materials with a higher active ingredient for the production of container glass, where customer requirements are not high compared to other glass products.

Foreign matters in raw materials are small, different inclusions, usually not affected by routine analysis, but capable of causing serious defects in production. They come from the deposit of raw materials (e.g. mined minerals in sand), but more often they get into raw materials during their treatment, transport, storage (e.g. abrasion of iron). According to the action, they can be divided into:

- hard-to-melt minerals, causing stones and striae,
- colouring elements, forming coloured striae and colouring of glass (typically iron inclusions in cullet),
- redox-active materials, forming bubbles in glass (e.g. carbides, metals, aluminium, organic materials).

Foreign matters are mostly accidental and can be attributed mainly to the human factor (poorly separated raw materials, poorly cleaned wagons, discarded garbage in raw materials, unprofessional handling, non-compliance with technological procedures in the treatment of raw materials,…).

The **grain size of glass raw materials** is usually ensured by screening. The standards prescribe the contents of individual agreed fractions and it is appropriate to use cumulative curves to characterize the grain size of raw materials. The grain size of raw materials directly affects the preparation of glass batch, its properties (e.g. tendency to segregation) and also the melting process itself (raw materials with finer grain size are better fusible, but high fineness causes dustiness of raw materials and more difficult fining).

Handling properties of glass raw materials include packaging, transport connections, bulk capacity of raw materials, the possibility of pneumatic transport, abrasiveness. Raw materials used in large quantities (sand, dolomite, limestone, feldspar, phonolite, …) are supplied in bulk, usually in shuffling wagons, trucks or ships. Closed transport compartments are used, such as closed

wagons with a load capacity of up to 100 t with bottom emptying or tank wagons (cars) adapted for pneumatic transport. Raw materials used in smaller quantities are supplied in giant bags, sacks, barrels, plastic and tin containers, often on pallets for easier handling in the glassworks.

4.3 Raw materials of glass network formers

Glass-forming oxides appear in glass in the form of complex units (e.g. tetrahedrons SiO_4^{4-}) and with their ability to bind through "bridging" oxygen form the basis of the internal irregular structure of glass.

4.3.1 Silicon dioxide (also silica), SiO_2

The earth's crust contains 59% of SiO_2, of which about 12% is quartz, but quartz deposits with a content above 98% SiO_2 are rare. Such siliceous raw materials are needed in glassmaking. Commonly produced glasses (based on SiO_2) contain 60 to 80% of SiO_2 and this raw material is the largest component of batch.

Silica in glass has a positive effect on chemical resistance, mechanical properties and thermal expansion. At the same time, it increases melting temperatures, increases viscosity, increases the tendency to devitrify, and reduces electrical conductance.

In the past, rock crystal and lump quartz were used as raw materials. Rock crystal and quartz are still the main raw material for the production of quartz glass or high-quality optical glass. For the production of ordinary silicate glasses, glass melting sand is almost exclusively used, a certain part of SiO_2 is introduced by other raw materials (feldspar, etc.). Quartz sands were formed by weathering of rocks, subsequent transport, distribution of weathered material and its deposition. Extraction is often carried out above the groundwater level by blasting, below the groundwater level by means of amphibious excavators. This is followed by floating and washing, abrasion of grains, counterflow sorting, magnetic separation, and flotation and dry cleaning may follow. Then dewatering and drying operations are performed. The treatment is aimed at reducing the content, or removing undesired admixtures, obtaining the given granulometry and moisture.

The medium sand grain size is crucial for melting time and theoretical melting time decreases with reducing size. In practice, however, the total melting time is determined primarily by fining of glass.

Glass melting sands are obtained by extraction and treatment of raw sands. Střeleč u Jičína is the largest deposit of quality glass sands in the Czech Republic. Lower quality kinds of glass sand with a higher content of iron come also from the Provodín and Srní u České Lípy deposits. In the case of chemical composition, there are standards that regulate the composition of glass sands. The standards state the **content of SiO_2**, which has a rather indirect relevance - the higher the lower the possibility of fluctuations in the content of other oxides. Sands for crystal glass usually contain above 99% SiO_2, sands for white container and flat glass above 98% SiO_2, sands for coloured container glass from 93 to 95% SiO_2. The **content of Al_2O_3** in sand does not matter in principle, but should not fluctuate too much so that the homogeneity of the glass does not fluctuate (stated up to ± 0.1%). The most important characteristic of glass sands is the total content of iron expressed as **Fe_2O_3**. Its permissible value depends on the permissible colour of glass melt. For example, 0.001 to 0.012% Fe_2O_3 is stated for optical glass, 0.008 to 0.015% Fe_2O_3 is stated for high-quality crystal glass, 0.020 to 0.050% Fe_2O_3 is stated for white container glass and flat glass,

0.010 to 1,000% Fe_2O_3 is stated for amber and green container glass. Iron can be present in sand in several forms, e.g. as a structural component of quartz grains, as part of sand accompanying minerals, as part of surface layers on sand grains or as a component of clay minerals that occur in sand deposits. The **content of TiO_2** in ordinary glass is harmless up to 0.10% because it dissolves well in glass. However, it is a problem in high-quality or optical glasses, because it highlights the colour caused by iron (the combination of Fe + Ti creates a brown colour).

To declare the required composition, the standard ČSN 72 1202 is often mentioned in technical literature (it is often replaced by a corporate standard, such as PN-01-2014 used by Sklopísek Střeleč). According to ČSN 72 1202, individual kinds are identified by TS, followed by a number indicating a thousand times the permitted maximum content of Fe_2O_3 (in %) and the size of maximum grain in tenths of mm after the breaking line. The chemical composition and grain size of glass melting sands are given in tables (Table 4.1, Table 4.2). The properties of sands are given in Table 4.3.

Table 4.1 Chemical composition of standardized qualities of sands according to ČSN 72 1202 (in % by weight)

Kind	SiO_2 min.	Fe_2O_3 max.	TiO_2 max.	Al_2O_3 max.
TS 15/08	99.3	0.015	0.05	0.2
TS 21/10	99.0	0.021	0.10	0.2
TS 23/10	99.0	0.023	0.13	0.3
TS 25/06	99.0	0.025	0.15	0.3
TS 40/10	98.5	0.040	0.15	0.4
TS 40/13	98.5	0.040	0.15	0.4
TS 70/10	97.0	0.070	not defined	1.5
TS 100/13	97.0	0.100	not defined	1.5
KS 20/13	99.2	0.020	0.10	0.2

Table 4.2 Grain size of standardized qualities of sands according to ČSN 72 1202 (in %)

Grain size (mm)	Kind of sand								
	TS 15/08	TS 21/10	TS 23/10	TS 25/06	TS 40/10	TS 40/13	TS 70/10	TS 100/13	KS 20/13
below 0.1	max. 1.0	max. 1.0	max. 1.0	max. 2.0	max. 3.0	max. 1.5	max. 5.0	max. 5.0	max. 5.0
0.1 - 0.315	min. 84.0	min. 94.0	minimum 94.0	min. 89.0	min. 92.0	min. 90.0	min. 89.5	min. 84.5	
0.315 - 0.5				max. 8.0					min. 85.0
0.5 - 0.63	max. 14.0			max. 1.0					
0.63 - 0.8	max. 1.0	max. 5.0	max. 5.0	0.0	max. 5.0	max. 8.0	max. 5.5	max. 10.0	
0.8 - 1.0	0.0			0.00					max. 10.0
1.0 - 1.25	0.00	0.0	0.0		0.0	max. 0.2	0.0	max. 0.5	max. 0.2
1.25 - 1.60		0.00	0.00		0.00	0.0	0.00	0.0	0.0
1.60 - 1.80						0.00		0.00	0.00
over 1.80	no grain	no grain	no grain		no grain	no grain	no grain	no grain	no grain

Note to Table 4.1 and Table 4.2: Glass sand marked in ČSN as KS 20/13 is used for the production of opaque quartz glass.

Table 4.3 Properties of sands

Density	2,600 to 2,650 kg/m^3
Bulk density (in shaken state):	1,570 ± 50 kg/m^3
Specific surface area	from 8 to 20 m^2/kg, average around 14 m^2/kg
Hardness	7 according to the Mohs scale
Refractive index	1.54 to 1.55
Bulk angle in dry condition	30 to 35°
Melting point	1,710°C
Sintering	1,550 to 1,600°C

4.3.2   Boron trioxide, B_2O_3

The average content of boron in the earth's crust corresponds to about 10 ppm of B_2O_3. Among other things, boron is used in glassmaking and boron trioxide is a glass-forming oxide.

Boron trioxide increases the tensile strength of glass, reduces density, improves chemical resistance and significantly reduces thermal expansion, which improves thermal resistance. It volatilizes with water vapour during melting, resulting in its losses. From technological point of view, it facilitates melting and is used as a melting material, which alone does not impair any other property of glass. It is used mainly in the production of glasses with increased thermal and chemical resistance and glass fibres. Glasses also have improved scratch resistance. Boron improves the transmittance of glass in the UV region.

Currently, boron is used in four groups of glass products: borosilicate glasses (containing 1 to 20% B_2O_3, such as Simax, Pyrex), insulating fibres (containing up to 6% B_2O_3), E-glass (containing 7 to 14% B_2O_3 used for the production of textile fibres) and also for glass frits and glazes.

The most important raw materials include disodium tetraborate - borax ($Na_2B_4O_7.10H_2O$), sodium tetraborate pentahydrate ($Na_2B_4O_7.5H_2O$), anhydrous borax ($Na_2B_4O_7$), boric acid (H_3BO_3 - sassolin) and colemanite ($Ca_2B_6O_{11}.5H_2O$). The world's main borate deposits are in the USA and Turkey, and significantly less borates are mined in Kazakhstan, Chile, Peru, and increasingly in China. In Russia, borosilicates (datolite, danburite) are processed into borax and boric acid. Apart from colemanite, the raw materials used are produced synthetically. In our country, deposits of boron minerals do not occur.

4.3.3   Phosphorus pentoxide, P_2O_5

Another glass-forming oxide is phosphorus pentoxide. In silicate glasses, it dissolves only up to 1.5 to 3% P_2O_5, but above about 0.5% forms opacity during cooling or subsequent heating. This is used for droplet opacity, the so-called opaline. Phosphates are also added to striking glasses, such as ruby, because they facilitate striking. Phosphates are used together with fluorides as a opacifier in jewellery or lighting glasses.

Phosphorus dioxide based glasses (without silica) are generally very transparent in the UV region, while in the IR region they are non-transparent. They are interesting for their resistance to HF and are also used as special optical and sealing glasses.

Under certain conditions, phosphorus itself can form glass, it is a glass-forming element. It can also form glass in conjunction with selenium.

Natural apatite $Ca_5(PO_4)F$, synthetic calcium phosphate, bone ash and possibly other synthetic raw materials (phosphoric acid, etc.) are used as raw materials. The largest reserves of phosphate minerals are in Morocco, the USA, Australia, and in Russia (Kola Peninsula).

4.4 Raw materials of intermediates

4.4.1 Aluminium oxide

The earth's crust contains 16% Al_2O_3, which is an intermediate oxide. Al^{3+} ions can isomorphically replace Si^{4+} ions in tetrahedrons. The tetrahedrons AlO_4 and SiO_4 are close in size, so that the tetrahedrons of aluminium may isomorphically partially represent silicon tetrahedrons in silica network. Therefore, aluminium is introduced into conventional industrially produced glasses as a substitute for silicon.

Additions of aluminium increase the resistance of glass to devitrification, improve mechanical properties (increase the modulus of elasticity of glass, scratch hardness) and chemical resistance (up to 0.8 to 2% Al_2O_3 for flat and partly also domestic glass, even more in the case of container glass). Glass is also "longer". Additions of Al_2O_3 strongly increase the surface tension of glass, therefore the aluminium striae are difficult to homogenize.

Feldspars are the most used raw material (for the glass industry, alkali-containing feldspars are of practical importance, i.e. potassium feldspar, orthoclase or microcline, $K_2O.Al_2O_3.6SiO_2$ and sodium feldspar, $Na_2O.Al_2O_3.6SiO_2$ albite, which forms an isomorphic series with calcium feldspar, anorthite $CaO.Al_2O_3.2SiO_2$ collectively called plagioclase), nepheline syenite, phonolite, pegmatite and, to a lesser extent, a whole range of rocks, including kaolin. Feldspar deposits in Halámky (microcline, orthoclase) and between Krásno and Slavkov (Vysoký Kámen, albite and orthoclase) are of the greatest importance for the glass industry in the Czech Republic. Aluminium hydrate $Al(OH)_3$ is most often used of the artificially prepared materials. Aluminium waste raw materials are also used, most often blast furnace slags. Aluminium is also present in other raw materials, so glass melts without independent aluminium raw materials still contain 0.15 to 0.30% Al_2O_3.

4.5 Raw materials of modificators

4.5.1 Stabilizers, melting accelerators and property modifiers

Melting accelerators (fluxes) include substances whose action reduces melting time. Their action can be of three types:

- acceleration of chemical reactions by creating an aggressive melt, etching the surface of sand grains,
- creation of a well-flowing melt even at a low temperature, causing dissolution reactions run faster,
- better connection of reacting raw materials to each other, before the start of melting process.

Soda (sodium carbonate) and potash (potassium carbonate), both alkalis/alkali metal oxides, are common melting accelerators. Fluorides, chlorides, sulphates, sulphides are most often used as melting accelerators, but they also include water, the content of which in the charge is optimally between 2% and 4%.

Stabilizers make the glass strong and increase chemical resistance. Calcium carbonate (calcined limestone), ZnO, ZrO_2 or TiO_2 are stabilizers. Without a stabilizer, water and humidity attack and dissolve glass. The term stabilizer may also represent an agent serving for charge stabilization of intermediates as with alkali aluminosilicate glasses, where it is more energetically favorable for the initial alkali ions to act as charge stabilizers for Al_2O_3.

4.5.1.1 Sodium oxide

Sodium is present in the earth's crust at about 2.4 wt.%, which corresponds to approximately 3.2% Na_2O. Sodium is the main component of a number of minerals, including rock-forming minerals, but as with other raw materials, there is a great demand for their purity, so there are many fewer natural usable raw materials and synthetic raw materials (mainly soda) predominate in higher quality glass melts.

In ordinary glasses, sodium (and potassium) have the greatest influence on the properties and price of glass. With ordinary glasses, the costs of soda are about 70 to 80% of the costs of raw materials, so when choosing the composition, the content of Na_2O is chosen as low as possible. It is commonly found as a component of glass. Its presence facilitates melting, lowers melting temperatures, increases the coefficient of thermal expansion and reduces the chemical resistance of glass. Additions of Na_2O reduce the viscosity over the entire temperature range. Its presence greatly increases the electrical conductance of glass melt, which is used in practice when melting glass by direct passage of electric current. Na_2O further reduces the density, refractive index, modulus of elasticity, hardness as well as material strength of glass (regardless of the surface quality).

Industrially produced anhydrous soda (Na_2CO_3) obtained by the solvay process is used as a raw material for ordinary and higher quality glasses. According to the final form (bulk density and dustiness), a distinction is made between light and heavy soda, produced from light soda in the monohydrate method. The difference between heavy and light soda is in its price, when heavy soda is more expensive, but on the other hand it is better handled, has less dustiness, with less tendency to sinter and absorb moisture. In the USA, natural trona ($Na_2CO_3.NaHCO_3.2H_2O$) is also used, which is economically, energetically and usually ecologically more advantageous than production by the Solvay process. Other synthetic raw materials used are Na_2SO_4 and $NaNO_3$.

For cheap glass melts (coloured container glasses, etc.), complex natural raw materials are commonly used, simultaneously introducing, in addition to Al_2O_3 and SiO_2, a certain part of Na_2O (sodium feldspar, $Na_2O.Al_2O_3.6SiO_2$, albite, which forms an isomorphic series with calcium feldspar, anorthite, $CaO.Al_2O_3.2SiO_2$, collectively called plagioclase, nepheline syenite, phonolite, pegmatite, etc.).

The raw materials are transported in road tankers, emptying and transport to the tanks are performed with the use of compressed air. The problem with soda is its wetting and higher price.

4.5.1.2   Potassium oxide

Potassium is present in the earth's crust at about 1.8 wt.%, which corresponds to approximately 2.2% K_2O. Potassium is the main component of a number of minerals, but only potassium feldspar, $K_2O.Al_2O_3.6SiO_2$, orthoclase, is directly usable for cheaper types of glass. Potash (K_2CO_3) as the main glass raw material of potassium is made from potassium salts, which occur together with sodium salts.

K_2O is the basic alkaline raw material of lead crystals. It was also an important component of historical Czech crystal. Potassium glasses give clearer shades in colour and glass is well discoloured.

Potassium glasses are "short", easy to grind, potassium oxide reduces density, modulus of elasticity and strength. Sodium-potassium glasses have a lower tendency to devitrify and better water resistance. Due to its high price, K_2O is used only where its addition is justified (3 to 4 times higher price for potash than soda is stated).

Small amounts of K_2O are introduced into cheaper glasses with raw materials such as feldspar (orthoclase from the Halámky deposit) or phonolite. The raw material for the introduction of larger quantities is mainly potash, K_2CO_3, sometimes also potassium nitrate, KNO_3. The disadvantage of potash is its hygroscopicity (tendency to absorb moisture).

In earlier times, an alkaline raw material called "salajka" containing 10 to 25% K_2O, the main component of which was potash, was produced for the production of "Czech crystal", historical potassium lime-silicate glass from the Czech lands. Salajka was obtained by extracting the ash of wood, which was burned in bulk for this purpose. The activity of historical glassworks was therefore also the reason for the high rate of deforestation of the Czech lands in the Middle Ages, and glassworks were often moved when they depleted trees for the production of charcoal and salajka in their vicinity.

4.5.1.3   Lithium oxide

The average content of lithium as oxide in the earth's crust is 0.014% Li_2O. Lithium occurs in the form of silicates, aluminosilicates or phosphates.

Lithium oxide is the most effective melting material, even in small quantities, it accelerates and facilitates glass-forming reactions, reduces high-temperature viscosity and surface tension, and elongates glass. Li_2O reduces density and thermal expansion. Lithium glasses have a lower refractive index and dispersion than sodium or potassium glasses and transmit more short-wave rays. Li_2O already in minimal amounts (from 0.05%) favourably affects some properties of glass, but it is expensive and the resulting effect is uneconomical. Significant content of Li_2O is in some special glasses and also in glass crystalline materials of the $Li_2O-Al_2O_3-SiO_2$ system characterized by extremely low thermal expansion (hobs, heat exchangers, telescope components, rocket warheads, etc.).

The main mined mineral is spodumene, from which lithium carbonate (Li_2CO_3) is obtained, which is the main pure raw material.

4.5.1.4   Calcium oxide

Calcium of 3.4 wt.% is in the earth's crust, which corresponds to approximately 4.7 wt.% CaO. Calcium is the main component of a number of minerals, but as with other raw materials, there is a great demand for their purity, so the usable raw materials have a significantly lower proportion.

Calcium oxide strengthens the structure of glass, and is therefore used as a stabilizer. It significantly increases the chemical resistance of sodium-potassium silicate glass to water, alkalis and acids. For theses glasses (as substitute for SiO_2), it increases the density, thermal expansion and refractive index, but reduces the dispersion of light. Its effect on viscosity is more complex - at higher temperatures the viscosity is reduced, on the contrary, at lower temperatures the viscosity increases, glass becomes "short". It increases the modulus of elasticity as well as the hardness of glass and, when substituting Na_2O, increases the mechanical strength and scratch hardness.

Dolomite and limestone are mainly used as raw materials for introduction of CaO, and natural gypsum or anhydrite ($CaSO_4$) from power plant desulphurisation are also used in small quantities. CaO is also contained in some other raw materials, such as apatite (source of P_2O_5) or fluorite (source of fluorine).

Limestone, chemically $CaCO_3$, is a common mineral whose deposits are widespread. The critical indicator of the suitability of its use in the production of glass is the iron content, which is different for the glass produced, the limits for different glass compositions are given in Chapter 0. Transportation to the glassworks is either by rail or road tankers.

Dolomite is a mineral of the chemical formula $CaMg(CO_3)_2$. With this raw material, calcium oxide CaO and magnesium oxide MgO are introduced into glass at the same time. The weight ratio of these two oxides is maintained even after melting the glass, and if this ratio needs to be changed, other raw materials must be used, such as limestone, $CaCO_3$ or magnesite, $MgCO_3$. Dolomite deposits in the quality usable for glass production are found on almost all continents. The most important characteristic of chemical composition is again the iron content, the limits for different glass compositions are given in Chapter 0. After extraction, dolomite is transported to the glassworks in bulk by rail. Most of the highest quality dolomite for glassmaking purposes is imported to the Czech Republic from Slovakia (Malé Kršteňany deposit).

4.5.1.5   Magnesium oxide

Magnesium of 2.4 wt.% is in the earth's crust, which corresponds to approximately 3.9 wt.% MgO. Magnesium is the main component of a number of minerals, but as with other raw materials, there is a great demand for their purity, so there are many fewer usable raw materials.

Increasing the content of MgO reduces the density of glasses as well as the thermal expansion. MgO "elongates" the glass melt and improves its workability. It also increases the surface tension, increases the scratch hardness, reduces the refractive index and, in the case of glass melt, its workability. It probably has a positive effect on chemical resistance.

Dolomite is most often used as a raw material, where it is present simultaneously with CaO, Chapter 4.5.1.4. Magnesite ($MgCO_3$), magnesium oxide and talc are also used to a limited extent.

4.5.1.6   Lead monoxide

The average content of lead in the earth's crust is only 0.0013%, but it is concentrated in deposits with other metals (Zn, Cu, etc.). Lead compounds have been added to glass since the 17th century (England) and are mainly used for 24% and 30% lead crystal, optical and technical glasses. It is also possible to come across glasses with 80% PbO, which are used due to the absorption of ionising radiation (Chapter 3.9.3). Lead and its compounds are toxic. Lead in glass is currently being replaced by other elements for environmental and health reasons. However, the amount of lead released from the glass structure of the finished product to food is very low and according to research is not harmful to health.

Lead ions are easily "deformable" and easily adapt to the structure of glass. Lead glasses have a lower viscosity curve (they are "soft"), so they are easier to melt. During melting, however, lead oxides can be reduced to metallic lead, which sinks to the bottom and strongly corrodes the lining of the melting unit. An oxidizing environment is a prerequisite for successful melting of lead glasses. Under reducing conditions, reduced metallic lead may appear on the surface of products. PbO strongly reduces surface tension. Lead glasses have a high refractive index, dispersion, glitter and sparkle, which stands out especially for rugged surfaces obtained most often by grinding. These glasses also have a relatively low grinding hardness, so they are easy to grind. Thanks to the reduced modulus of elasticity, lead glasses have a nice sound. Due to the density of lead itself, PbO increases the density of glass.

For the introduction of lead into glass, only industrially produced compounds of sufficient purity are used. The most common raw material is red lead (minium) Pb_3O_4 (heavy red powder). Another raw material is lead monoxide, PbO, which is often supplied in the form of granules.

4.5.1.7   Barium oxide

About 0.04% of barium is present in the earth's crust. Barium together with strontium can be used, to some extent, as a substitute for lead. In the case of BaO, glass is called crystalline, its refractive index is around 1.52.

Barium significantly increases the density of glass and slightly increases the thermal expansion. The chemical resistance of barium glasses is higher than that of lead glasses, but lower than that of calcium glasses. Additions of BaO increase the modulus of elasticity, which is why barium glasses ring on impact, which is appreciated with tableware. Barium glasses are distinctly "soft" and "long". The tendency to devitrify is lower for barium glasses than for calcium glasses. Unlike PbO, BaO does not increase the dispersion, therefore barium glasses do not show the valued "play of colours" that is typical of lead glasses; on the contrary, they are ideal optical glasses without chromatic aberration.

Barium carbonate ($BaCO_3$) is mainly used for introducing BaO into glass, which is supplied exclusively artificially prepared and is supplied in the form of a fine powder or granules. Another limited raw material is barium sulphate ($BaSO_4$), which is supplied in natural form from the best deposits with a low content of Fe_2O_3.

4.5.1.8 Zinc oxide

ZnO reduces the coefficient of thermal expansion of glass, improves the meltability of glass batch and its fining. It is important especially for the production of technical and special optical glasses. It is supplied to glass melt exclusively as synthetic ZnO.

4.5.1.9 Strontium oxide

Other raw materials include synthetic strontium carbonate, which is used for introducing strontium oxide, SrO, into special glasses, for example for the production of television screens for colour televisions.

4.5.1.10 Titanium dioxide

Its presence in glass reduces viscosity, and improves meltability and chemical resistance. Its use is negligible.

4.5.1.11 Zirconium dioxide

It significantly reduces the coefficient of thermal expansion and increases the chemical resistance of glass, especially to alkalis. It is used rarely, the most commonly used raw material is zirconium $ZrSiO_4$. It is mainly important as a nucleator in the production of glassy crystalline materials. A certain low content of ZrO_2 in glasses is usually present from the corrosion of zirconium refractory materials.

4.5.1.12 Tin(IV) oxide

It does not bring any significant properties to glass, its price is high, and is expensive as opacifier raw material. It is important as a material for the production of electrodes, metal elementary tin is also encountered in the production of float glass. Tin(IV) oxide is also used as an additive in staining of glass with colloidal pigments.

4.5.2 Colouring raw materials

These are raw materials that give the glass the desired colour. Colouring particles may be present in glass in the form of ions or molecules (size < 1 nm), as colloids (size 1 to 500 nm) or as larger clumps causing opacity. The resulting colour depends on several factors, in particular:

- concentration of colouring matters,
- chemical composition of basic glass,
- redox state of glass, which depends on the presence of oxidizing and reducing agents and on the melting conditions,
- method of heat treatment (for striking colours).

Ionic colourants are divided by their effects

a) ions that occur in glass in one oxidation state (Ni, Co),
b) ions that occur in glass in two or more oxidation states (Cr, Fe, Mn, V, U, …).

4.5.2.1   Ionic colourants in one oxidation state

Nickel compounds

Nickel occurs in glass only in one degree of oxidation and thus, the colour does not depend on oxidation-reduction conditions (redox condition). Ni^{2+} ions colour glass according to its basic composition. They colour sodium glasses according to the concentration from light grey (0.5% NiO), through dark red-grey (3%) to dark brown-red (8%). For potassium glasses from purple to blue (0.5%), through bright purple (1%) and dark purple (2%) to black (8%). The raw material is mainly nickel oxide, NiO.

Cobalt compounds

Co^{2+} ions colour glasses blue-violet glasses, potassium glasses with a shade of blue, sodium and borosilicate glasses with a shade of red. Cobalt is one of the most intensely colouring elements used in glassmaking, a rich colour is achieved even at a concentration of 0.02% CoO and glass is opaque at a concentration above 1%. The raw material is most often cobalt oxide, CoO.

4.5.2.2   Ionic colourants in two or more oxidation states

Chromium compounds

Chromium is usually present in glass in two degrees of oxidation, in the form of Cr^{3+} and Cr^{6+}. The colouration depends mainly on the presence of other ions and at least on the melting conditions. The trivalent ion usually predominates and colours glasses mostly blue-green. Cr^{6+} stained glasses are coloured yellow-green to yellow, in lead glasses orange to red and significantly absorb ultraviolet radiation. Chrome colours glass quite intensely. Sodium glasses are coloured from 0.005% Cr_2O_3, a strong colour (May green) is obtained at a concentration of 0.2% Cr_2O_3. For the colouring of green container glass, natural modified chromite or secondary raw materials are used as the raw material.

Manganese compounds

Manganese is usually present in glass in two degrees of oxidation, in the form of Mn^{2+} and Mn^{3+}. Glasses containing only Mn^{2+} are colourless, but oxidise on cooling, so the final colour is usually yellow to brownish. Mn^{3+} colours glass intensely purple. Due to the sensitivity to oxidizing conditions, the reproducibility of colouration is difficult. Clear colouration is from about 1%, colouration is strong at 5%; the use is mainly in combination with other colourants. Burel (MnO_2) is used as the raw material.

Vanadium compounds

Vanadium occurs in glass as V^{3+}, which causes green colouration, VO^{2+}, which is low colouring in the visible region but strongly absorbing in the UV region, and V^{5+}, which colours yellow to brown. Usually, all three valences are present in glass in different proportions. Colouration is not very intense (300 times less than with CoO), additions between 2 and 5% are used. Above 5%, colouration is olive brown. Vanadium glasses absorb UV radiation well with considerable transmittance of visible radiation. It is thus used in the production of glasses of green shade with increased absorption of ultraviolet radiation and for welding glasses. The raw material is vanadium pentoxide, V_2O_5 and ammonium vanadate, NH_4VO_3.

Uranium compounds

Uranium stained glass is attractive because uranium glasses have significant fluorescence induced by ultraviolet radiation (Chapter 3.9.5). These glasses are light yellow at transmitting light and light green at reflected light. Uranium occurs in glass as tetravalent and especially as hexavalent (uranyl cation, UO_2^{2+}). Concentrations up to 4% U_3O_8 are used for the required colouration. Sodium diuranate (uranium yellow, $Na_2U_2O_7$), triuranium octoxide (U_3O_8) and uranyl-sodium carbonate ($UO_2Na_4(CO_3)_3$) are used as raw materials. In the past, it was the exclusive supplier of uranium dyes for the Jáchymov glassworks in the Krušné hory, where uranium ores were mined and also processed.

Iron compounds

Iron occurs in glass in the form of Fe^{2+} (FeO) and Fe^{3+} (Fe_2O_3) ions. Both ions are always present in glass, their mutual ratio is determined by the melting conditions as well as, if applicable, the presence of oxidizing agents, or reducing agents. The Fe^{2+} ion colours glass blue-green (under reducing conditions) and is 10 to 15 times more intense than Fe^{3+}. The Fe^{3+} ion colours glass yellow-green to yellow (under oxidizing conditions). The first observable colouration is at a content of 0.01% Fe_2O_3 and with a content of about 0.05% Fe_2O_3 (total iron), the greenish shade is quite apparent.

Iron compounds are used minimally for staining glass. Virtually only in flat glass, where increased absorption of thermal radiation in glass due to action of divalent iron is used (production of heat-absorbing glasses) and in fibres, where the addition of about 0.4% helps to draw the fibres.

For most glasses, iron staining is rather a defect. The requirements for the content of iron, which comes mainly from raw materials, vary considerably for different types of glass, Table 4.4. The aim is therefore to minimize the amount of iron by using quality raw materials with low iron content, appropriate storage, minimizing contact with iron surfaces, effective separation of pieces of iron by magnets. Complete removal of iron is virtually impossible, and therefore its colouration is removed by discolouration.

Table 4.4 Requirements for iron content for different types of glasses

Glass	% of Fe_2O_3
Optical glass	0.001 to 0.012
Crystal glass	0.008 to 0.015
Quality white container glass	0.020 to 0.050
Flat glass	0.020 to 0.100
Green container glass	0.1 to 1.0

4.5.2.3 Discolouration of glass

In addition to iron, other elements introduced mainly by raw materials and dissolving refractory materials can colour.

Discolouration of glass can be based on two different principles, which can be combined in practice.

Chemical discolouration represents the use of oxidizing agents, or an oxidizing environment during melting, when the balance between Fe^{2+} and Fe^{3+} ions is shifted to the side of iron ion, i.e. ion that causes colouration of lower intensity. Sodium sulphate (Na_2SO_4), arsenic trioxide (As_2O_3) and antimony trioxide (Sb_2O_3) together with sodium nitrate ($NaNO_3$) are used as chemical discolourants. The above mentioned discolourants are also used for fining in glass melt, Chapter 4.6. Cerium(IV) oxide (CeO_2) is also used as a discolourant.

Chemical discolouration can reduce the intensity of colouration of glass, but cannot remove it, because the formed Fe^{3+} ions cause yellow-green colouration. Faint yellow-green colouration, which has chemically discoloured glass, is not desirable, and it is therefore further discoloured physically.

Physical discolouration uses the principle of adding the wavelengths of light belonging to a certain colour, while choosing to colour glass to a complementary colour, which gives a neutral grey with an undesirable shade, Fig. 4.1. Additional colouration to the yellow-green shade is the purple-pink colour - this shade has historically been obtained using manganese compounds (MnO_2 or $KMnO_4$), nickel oxide (NiO) is currently used, possibly compounds of selenium and rare-earth elements.

The lowest possible iron content in glass is necessary to minimize dosed colourants, so that the resulting proportion of grey is as low as possible and the products are of the highest possible quality.

4.5.2.4   Molecular colourants

In these colourants, the resulting colouration of glass is caused by the presence of their molecules. The main difference between these colourants and colloidal colourants is the size of the colouring particles. The group of molecular colourants includes mainly sulphur, selenium and their compounds.

Sulphur and carbon compounds

The most famous compound is carbon yellow - amber. According to current knowledge, this colouration is caused by Fe^{3+} ion in tetrahedral coordination with three oxygen anions, O^{2-} and one sulphide ion, S^{2-}. Colouration is greatly affected by redox state, excessive oxidation and reduction will cause discolouration. In this case, carbon has the function of redox-equilibrium regulator, amber colouration is most stable in a slightly oxidation mode of combustion in the furnace. Brown container glass is coloured with the addition of carbon and sulphur. Sodium sulphate (Na_2SO_4), pyrite (FeS_2) and graphite, coke dust, etc., are used as raw materials. You can also encounter the use of flour (rye, wheat), millet, starch and sugar.
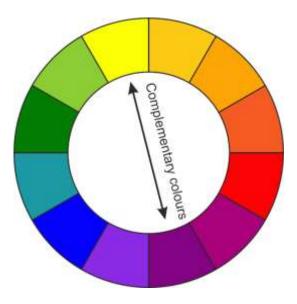
Fig. 4.1 Graphic presentation of the physical method of discolouration, coloured circle with the indication of the example of complementary colours

Staining with selenium and its compounds

The essence of pink colouration of selenium-stained glass (selenium rosaline) is elemental selenium. However, in the presence of heavy metals, dark-coloured selenides are formed, which can be prevented by adding ZnO to glass. However, selenium discolouration is much more significant because pink colouration is complementary to yellow-green colouration caused by a small amount of iron.

Metallic selenium or selenites (barium, zinc or sodium) are used as selenium raw materials.

4.5.2.5   Colloidal colourants

Supersaturated solutions of some metals in glass melt behave in such a way that, on cooling, they separate metal particles in the form of crystallites formed by a large number of atoms. With the size of these particles below 5 nm, glasses remain colourless. Further heat treatment, so-called striking, increases the clusters, accompanied by the formation of colouration, until opacity can be observed in glass when it reaches a size of 70 to 100 nm.

Gold colouring

An example is the colouring of glass with gold. Gold colouration is one of the most beautiful colours. The resulting shade is influenced by the chemical composition of basic glass, melting, annealing, but especially striking process. The essence of colouration is gold crystals of size from 5 to 60 nm. Larger particles are already causing opacity. Colour is affected, among other things, by the amount and size of gold particles. Crystals below 5 nm give colourless to light yellow glasses, particles with a size of around 10 nm give pink glasses, particles with a size of 10 to 20 nm give purple-red glasses, and particles with a size of 20 to 50 nm give a beautiful purple ruby. With the size above 70 nm, glass is opacified to opaque. Colouration is supported by additions of nucleating agents such as selenium as well as SnO_2, PbO, CaF_2. Only gold(III) chloride ($AuCl_3.H_2O$) is used as the raw material. The required doses of gold are 1 to 20 g per 100 kg of glass, because the amount is small, it is often applied as an aqueous solution.

Other colloidal colourants

Another example of a colloidal colourant is cadmium sulfoselenide Cd(S,Se), which colours glasses yellow to red according to the sulphur and selenium ratio. Cadmium sulfoselenide is used directly as the raw material and it is necessary to melt glass under slightly reducing conditions, but due to the ecological harmfulness of raw materials and melting, the use is suppressed. Nevertheless, it is still used both in jewellery and mainly for signalling glassware.

4.5.2.6   Opacifiers

Opacified glass is a designation for opaque glass. According to the nature of the opacifiers, we divide opacity into crystalline, droplet and gaseous opacities.

Crystalline opacity is caused mainly by fluorine compounds, which dissolve well in glass melt, but when cooled, fluorides crystallize from it, mainly CaF_2 (opal glass for lighting technology); arsenic oxide is used for lead glasses and lead arsenate crystallizes.

Droplet opacity is formed on a similar principle. The opacifier agent dissolves well in glass melt at high temperatures, but separates from it in the form of an emulsion on cooling. Upon further cooling, these droplets crystallize. This includes phosphate (Chapter 4.3.3), fluorine-phosphorus and sulphate opacifiers.

Gaseous opacity is not common in glassmaking. An example is opaque quartz glass, the opacity of which is caused by finely dispersed air bubbles, which did not reach the surface of glass during melting due to the high viscosity of melt and could not escape into the atmosphere.

Fluorides

Fluorides significantly reduce viscosity over the entire temperature range, lowering the liquidus temperature as well as the density. In opal glasses, the fluoride content is 2 to 6% F. With the contents lower than 2% F, fluorides can be also used as a fining agent and a melting accelerator. The disadvantage of fluorides is the higher corrosion of refractory materials and metal moulds. In an effort to reduce the content of harmful fluorides, fluorine-phosphorus opacifying is preferred.

Fluorspar (fluorite, CaF_2 content above 95%) and sodium fluorosilicate (Na_2SiF_6) are used for the production of opal glass. Fluorides are currently no longer widely used as an accelerator and fining agent due to their defective rate and environmentally problematic melting (in particular, exhalation).

4.6 Fining raw materials

The purpose of fining is to remove bubbles from glass melt and mix it at the same time. From this point of view, fining agent is a substance that releases a considerable amount of gas bubbles at a high temperature, which combine and enlarge when rising. The fining agent does not start to work earlier than at an increased temperature, often above 1200°C. The gas released by the fining agent must be soluble in glass melt so that the remaining smallest bubbles (tiny bubbles, dust) dissolve after fining. Different glasses need different fining agents, there is no universal fining agent. According to the mechanism of action, the fining agents can be divided into several groups of similar action.

Sulphate fining

The essence of this fining method is the decomposition of sodium sulphate according to the equation

$$2Na_2SO_4 = 2Na_2O + 2SO_2 + O_2 . \quad (4.1)$$

Decomposition occurs in the range of temperatures of 1200 to 1400°C. Other (calcium, barium, magnesium, ammonium) sulphates behave similarly. Sulphate fining is the main method of fining glass. It is used, among other things, in the production of flat and container glass. The use of sulphates is limited for lead glasses. During sulphate fining, it is necessary to ensure the reduction of sulphates, which colour glass by adding carbon, graphite,… The amount of SO_3 in glass is recommended at the level of 0.4%, but can be 1.4%.

Oxide fining

It is similar to the previous method with the difference that fining oxygen is released from oxides. Oxide fining agents include arsenic trioxide (As_2O_3), antimony trioxide (Sb_2O_3) and cerium dioxide (CeO_2). Oxide fining is evident from the following equations

$$As_2O_5 = As_2O_3 + O_2 , \quad (4.2)$$

$$Sb_2O_5 = Sb_2O_3 + O_2, \quad (4.3)$$

$$4CeO_2 = 2Ce_2O_3 + O_2 , \quad (4.4)$$

If arsenates or antimonates are not used, sodium nitrate must be added to the charge, which oxidises trivalent arsenic (or antimony) to pentavalent arsenic (or antimony) at lower temperatures. Then chemistry looks as follows

$$As_2O_3 + 4NaNO_3 = As_2O_5 + 2Na_2O + 4NO_2 . (4.5)$$

In this case, Sb_2O_5 decomposes at the lowest temperature and CeO_2 decomposes at the highest temperature.

The traditional raw material for fining is antimony with a dosage of 0.05 to 0.5% per glass melt. Antimony trioxide and antimony nitrates represent more modern fining agents and the dosage is reported to be between 0.3 and 0.5%. Cerium dioxide is used infrequently, as the oxidizing effect predominates over the fining effect.

In addition to the above fining agents, halides or nitrates themselves are sometimes used.

4.7 Cullet

The use of cullet in melting brings a number of advantages, such as acceleration of the melting process, raw materials saving, energy saving, ecology, saving of costs of import and waste disposal. Part of the energy necessary for the course of chemical reactions and processes between the components of the batch is already contained in the cullet. On the other hand, the costs of collecting and recycling cullet increase. For conventional melting units, the saving when using 1 ton of cullet is stated to be 2 GJ of energy. The purity of both own and foreign cullet is important, which is mainly influenced by cullet management, which ensures collection and treatment before loading into the furnace. For more information see Chapter 5.6.

4.8 Examples of glass composition

As can be seen from the above, the chemical composition of glass can be very diverse, however, large volumes of some types of glass products are made of glass of similar chemical composition. The following table (Table 4.5) shows (with some simplification and rounding) examples of the chemical composition of selected glasses.

Table 4.5 Chemical composition of glasses (in % by weight)

Component	Flat glass	Container glass green	Lead crystal	SIMAX glass
SiO_2	72.2	71.8	57.5	80.6
Al_2O_3	0.9	2.0	–	2.1
Fe_2O_3	0.1	0.4	–	–
CaO	8.7	10.1	3.2	–
MgO	4.0	1.9	–	–
Na_2O	13.6	12.7	10.4	3.7
K_2O	0.3	0.8	3.9	1.1
SO_3	0.2	0.1	–	–
Cr_2O_3	–	0.2	–	–
PbO	–	–	25.0	–
B_2O_3	–	–	–	12.5

5 Preparation of glass batch and charge

Glass raw materials of the required purity and their correct ratio are the basis of glass production. Before loading into glass furnace, raw materials are mixed into a so-called batch or charge.[3] The homogeneity of the batch to a large extent also affects the homogeneity of glass melt, therefore the basic requirements for glass batch are as follows: homogeneity, low dustiness, minimal tendency to separate.[4]

The raw materials are first transported to the glassworks, then moved to a warehouse by handling, stored or treated, weighed, then mixed and finally can be further treated. A large part of these operations is carried out in batch houses, which have the necessary equipment. The basic equipment of batch houses includes raw material containers, weighing equipment, mixers and systems ensuring the transport of both individual raw materials and finished batch.

Mechanization in batch houses has been appearing since the second half of the 19th century and it is thus today possible to encounter exceptionally a batch house without machinery. Today, the process is largely automated in medium- and large-size batch houses. This means that the mutual ratio of raw materials or the weight of these raw materials is entered directly from the computer.

5.1 Inspection and acceptance of raw materials

Large glassworks consume hundreds of tons of few raw materials a day and detailed inspection of each wagon is neither possible nor effective. It is more advantageous to choose a reliable supplier with constant and long-term quality.

The *acceptance of raw materials* is carried out for each wagon, car, pallet, packaging. Its aim is to avoid the use of supplies that could cause production losses. It basically consists of visual inspection (whether it is the specified raw material, inspection of coarse contamination, mixing with another material, grain size, colour, …) and simple tests (screening,…).

The *inspection of raw materials* is performed according to the specified inspection plan on samples from part of the deliveries; the chemical composition and granulometry are determined. A full inspection is also performed on consignments suspended at acceptance.

For low-tonnage raw materials for the production of quality glass (e.g. crystal and technical glass), acceptance is performed together with inspection for each delivery.

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[3] The glass batch is a homogenized mixture of glass raw materials without cullet . The glass batch with cullet ready for loading into furnaces is called a charge.

[4] Separation is a violation of homogeneity (uniform distribution of raw materials) in the batch and the possibility of subsequent formation of inhomogeneous regions in glass melt due to different density and granulometry of raw materials, in particular due to shocks.

5.2 Storage and handling of glass raw materials

The individual raw materials are delivered to the glassworks in standard ways. Some in bulk (sand), others in containers. The method of transporting raw materials to the glassworks is given by their nature. Transport is most often carried out by rail using wagons adapted to the possibilities of mechanical unloading (e.g. sand, dolomite, and others), also using road tankers with the subsequent possibility of pneumatic transport, e.g. soda, possibly in smaller containers in case of minor components.

The area of handling glass raw materials includes their transport, acceptance, storage and cullet management.

The transport of raw materials in the glassworks is carried out using:

- belt conveyors,
- pneumatic transport,
- containers,
- pallets,
- vibrating conveyors,
- screw conveyors,
- other usable mechanization.

At present, raw materials are most often transported on belt conveyors and by means of pneumatic transport. The belt conveyor is a well-known and means often used in practice for transporting bulk materials. Pneumatic transport is a closed transport system that is used for transporting bulk materials at distances from tens to hundreds of meters. In general, pneumatic transport can be divided into overpressure or underpressure (vacuum) transport. The advantage of pneumatic transport as compared to mechanical transport is, among other things, the minimum number of moving parts and thus low maintenance costs. Pneumatic transport is easy to operate and easy to install. Since this is a closed transport system, pneumatic transport is dust-free. On the contrary, the disadvantage is the high energy consumption as well as abrasion of pipes and the used air must be dust-free.

Raw materials are stored according to the volume of their delivery and the required pre-supply. Warehouses can be of granary type, representing loose storage in separate covered boxes (e.g. for sand, cullet), as well as silo-type warehouses, minor components of the batch can be stored in smaller containers in lockable facilities. The easiest way is to store raw materials in silos above the weighers, which significantly reduces the handling of raw materials, but requires a completely accurate supply of raw materials, usually dry raw materials. If the silos above the weighers are small, special storage containers and warehouses must be used. All raw materials are basically stored under the roof, an exception is possible only for untreated cullet.

During storage and subsequent weighing, cylindrical silos are preferred - containers with a conical constriction in the lower part (dead corners always occur in the case of square profiles of silos). In feeding into the weighing device, the raw materials fall under their own weight, the fall is supported, for example, by attached vibrators. The material for the production of containers is a steel sheet provided with a resistant layer on the inside. Containers can be equipped with level indicators to check the content of the raw material, more recently, installation of the containers on strain-gauge scales and continuous monitoring of the weight of the content are used.

For economic reasons, it is necessary to store as few raw materials as possible, but on the other hand, it is necessary to ensure production even in the case of expected and unexpected situations. The total stocks of raw materials are the sum of current and safety stocks, for which storage containers and warehouses must also be dimensioned. The size of current stock is determined by agreement with the supplier on the size and frequency of deliveries and corresponds to the size of one delivery. The safety stock must be able to cover supply disruptions due to weather, public holidays and holidays, as well as political and industrial difficulties. In countries where it is possible to supply raw materials normally, the stock of raw materials is chosen for 5 to 15 days, for minorities for 3 weeks or more.

5.3   Treatment of raw materials

The treatment of raw materials has often been carried out in the past, but nowadays treated raw materials are primarily supplied to glassworks. Raw material treatment operations can be divided into:

- drying - rotary drying drums, fluidized bed dryers, etc.,
- sieving - ensuring the necessary granulometry using a system of sieves,
- crushing and grinding - in the case of deliveries of lump raw materials (limestone, dolomite, etc.),
- magnetic sorting focused on the separation of mainly steel particles.

The drying drum is a continuous device that ensures the drying of raw materials by means of supplied flue gases. During drying, the drum rotates around its axis and thus mixes the raw materials, which are poured into it at one end and emptied at the other. The drum can be inclined from the raw material inlet to the outlet, it can have built-ins that increase the contact surface of the dried raw material. They are usually designed as counter-flow, i.e. flue gases flow against the raw material. The drying drum rolls along steel circular tracks. The transmission of torque is effected via driven rollers or via a link chain encircling the segment sprocket wheel screwed to the drying drum housing or via a pinion driven gear. Heat losses are reduced by thermal insulation of the cylindrical part of the drying drum. The rotating part of the drying drum is mounted in a base structure, to which stationary parts of the material inlet and outlet sections are further attached.

 Representatives of machines used for crushing raw materials include a double-toggle jaw crusher and a pin disintegrator for grinding. As already mentioned, treated raw materials are supplied to the glassworks, and crushing and grinding processes are used rather exceptionally.

Magnetic sorting and separation of steel parts and particles take place during the preparation of batch and charge in several places, at least at the end of the batch house line. Both permanent magnets and electromagnets are used.

5.4   Weighing and feeding of raw materials

Treatment of raw materials is followed by their weighing and mixing. For the smallest glassworks with pot furnaces, the gradual weighing of individual raw materials is carried out manually into a movable container. Today, however, feeding and weighing of raw materials in most batch houses are mechanized and automated.

In modern batch houses, each container is equipped with weighers under the outlet, which enable the program-determined weighing of the required dose. In the past, mechanical scales were used, today strain-gauge scales[5] are used almost exclusively, where the weighing container is usually placed on three strain gauges. They work without movement and, compared to mechanical scales, they are more reliable and cheaper.

An example of scale design is shown in Fig. 5.1. In this case, the conical weighing container is suspended on three strain gauges. The strain gauges are mounted on a steel supporting frame made of rolled steel profiles. On the underside of the scales there is a tilting pneumatically operated flap. The scales are made of sheets and profiles from normal structural steel.
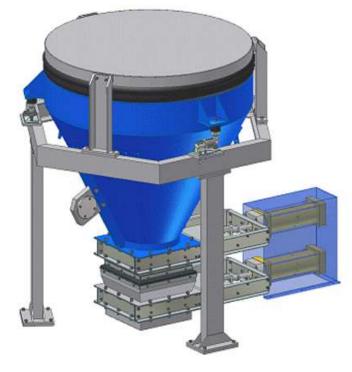

Fig. 5.1 3D model of a limestone scale (source: Dites spol. s r.o.)

Turnstile, vibrating or screw feeders with continuously variable feeding speed are built into the outlet for fast and accurate weighing, Fig. 5.2. Feeding of raw materials can then be:

- single-speed feeding, used mainly for minor raw materials,
- double-speed feeding, applied to large-volume raw materials; it doses the greater part of the charge at high speed (90-95%) and the rest is dosed at about a tenth of the speed up to the accurate balance (± 0.1% to ± 0.5%).

The view of the actual part of the batch house is shown in Fig. 5.3.

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[5] Strain-gauge scales are based on the deformation caused by the weight of the object being weighed. Deformation is usually measured using a piezoelectric effect, which is the ability of a crystal to generate an electrical voltage during its deformation (the best known piezoelectric substance is monocrystalline quartz). A significant advantage of strain-gauge scales is the fact that they can be connected to a computer, which ensures the registration and further processing of measured values.
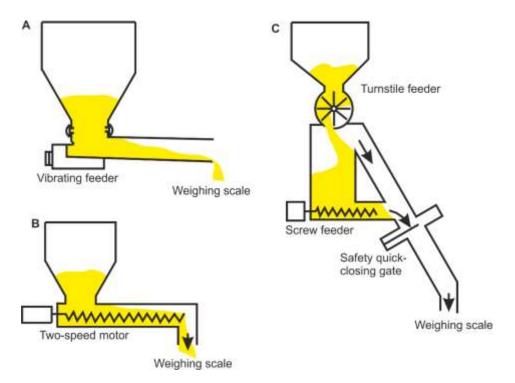
Fig. 5.2 Raw material feeders from silo to weigher: A - single-speed vibrating feeder, B - double-speed screw feeder, C - double-speed combined feeder with turnstile for fast feeding and screw for accurate weighing

Fig. 5.3 View of the actual part of machinery of the batch house, the lower part of containers, raw material feeders, weigher, container (source: Dites spol. s r.o.)

5.5   Batch mixing

Weighing and feeding are followed by mixing of the batch. The aim is to perfectly mix the raw materials of the glass batch and adjust its moisture. The design of the mixer can be according to the construction:

- auger,
- gravity,
- disk.

Auger mixers use an auger or similarly arranged blades as a homogenization tool. This type of mixer is no longer used because it is energy intensive and does not give a good homogeneity of the batch.

Gravity mixers work on a similar principle as concrete mixers. These are most often vessels that rotate around a horizontal axis, with inserted partitions helping to mix the batch. The historical model today is the Saxonia mixer (Fig. 5.4), which consists of a mobile container into which the batch is weighed, the cradle cover, and the mixer drive. The indicated mixing time is 5 minutes. Today, so-called container mixers (Fig. 5.5) are a frequent mixer in small- and medium-sized glassworks. It again uses a container into which raw materials are weighed. The container is conical in shape, narrows downwards and is also used for transporting and storing the batch. An example of a container is shown in Fig. 5.5. The container is loaded into the mixer, covered and closed by a lever and rotated together with the closure around a horizontal axis for 15 minutes.
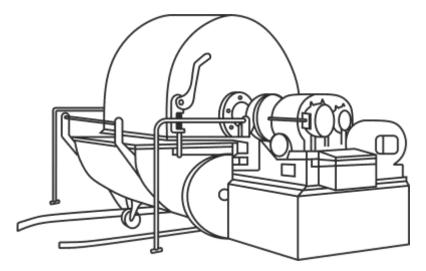
Fig. 5.4 Diagram of the historic Saxonia mixer

The most commonly used are the pan mixers (Fig. 5.6). The mixer is characterized by horizontally placed disk and mixing tools, which are a star and a swirler. The disk rotates clockwise and the swirler counter-clockwise. There may be several mixing tools and they can rotate at different speeds and at different radii. Thanks to a suitably selected ratio of speeds of the disk and the mixing tool, fast homogenization is achieved. A fixed squeegee acts as a static element, which cleans the walls and bottom of the disk during operation and directs the material to the area of the swirler. Mixing has no dead corners and is fast. The mixer is filled from above and emptied through an outlet in the middle of the bottom, both of which take place while the mixer is running. Pan

mixers are manufactured with a useful capacity of 500 to 3,000 litres with a capacity of 7.5 to 45 t/hour. It takes about 1 minute to fill and empty the mixer and the mixing time is chosen 2 to 3 minutes, depending on the requirement for homogeneity and quality of the batch. For dust-free operation, the mixer is equipped with an expansion tube.
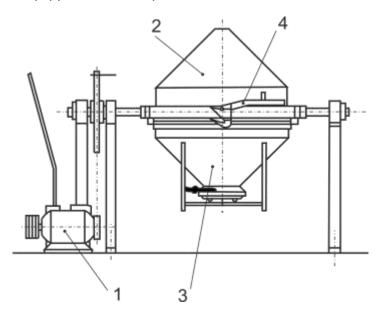

Fig. 5.5 Diagram of the container/cone mixer: 1 - electric motor, 2 - mixer lid, 3 - container, 4 - lever for closing the mixer
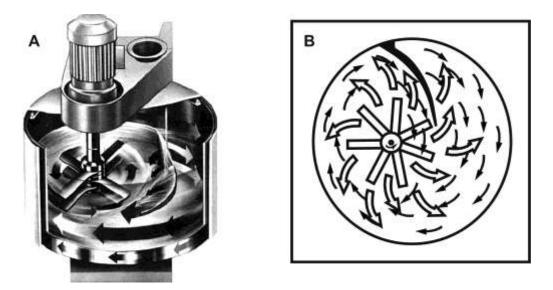

Fig. 5.6 Diagram of the pan mixer: A - 3D display, B - indication of the mixer function (movement of the batch inside the mixer)

When mixing the batch, it is often moistened to a moisture content of 2 to 4%. It is moistened with water or steam.

5.6 Cullet management, recycling

The use of cullet is an economic necessity in most productions. It is mostly the use of own cullet, Chapter 4.7. The sources of this raw material are:

- process waste,
- defective products,
- cullet obtained by collection.

The first two sources of cullet are referred to as own cullet. They are usually created directly in the glassworks or at processors. For most technologies, only own cullet can be used and are used virtually by all glassworks with any production range. Own cullet is always a material that has already been melted once, but was not sold in the form of a product and is therefore a loss. However, if this material was not used, the loss would be logically greater. For container glass, 10 to 20% of own cullet is used, which corresponds to losses. In domestic glass, 40 to 50% of total cullet of the total volume is stated during manual production. Up to 60% of own cullet (blown products with moil) is created during the automatic production of domestic glass.

Cullet obtained by collection is referred to as foreign cullet and cannot be used for all types of glass products. Foreign cullet is used in the production of container glass, fibres and other types of products, where slight changes in the composition of cullet do not matter. In the case of foreign cullet, we can clearly talk about savings in melting. Foreign cullet (obtained by collection or purchased) is mainly used in the production of container glass. The proportion of cullet can then be 70% in the charge and in the case of green container glass over 80%, in the short term even 100%.

Modern lines includes a system for obtaining and transporting process waste. This cullet is first cooled (if necessary) and usually transported under the production line by belt conveyors to the batch house, where they can be crushed (for example with a hammer crusher), sieved to a given size and impurities are separated. The separation, processing and storage of cullet during the production of glass coloured throughout the mass must be strictly monitored.

In crushing of glass, the so-called hammer crushers are mainly used, which selectively crush only brittle material. Fast-rotating hammers in the crusher throw cullet on the impact plates, where they are crushed. Hammers and impact plates are mostly made of hard nitrided steel.

Single-sieve or double-sieve devices are used for sieving, which always remove the coarse fraction above 25 mm and sometimes even the fine fraction below about 5 mm, because impurities are concentrated in these fractions. The sieves are vibrating and have a surface area of 2 to 3 m^2. Suction is also applied during sieving, which removes dust from cullet and, in the case of recycled glass, also paper, loose aluminium foils and other impurities.

Magnetic and non-magnetic separation is performed very often in order to remove impurities that could be a source of defects during melting. These operations are performed mainly on foreign cullet, but they can also be found on own cullet (especially with magnetic separation). Permanent magnets and electromagnets are used for magnetic separation. The efficiency of separators is determined by the thickness of the layer of cullet. The separation process is performed twice to ensure that cullet is mixed, the magnetic parts are released and reach the surface. Inductive metal detectors, eddy current detectors, optical sensors and cameras in general are used for separating

non-magnetic components such as aluminium, lead, ceramics and others. An example of using a metal indicator is shown in Fig. 5.7. The vibrating feeder brings cullet onto a wide oblique belt divided into strips, where an electromagnetic metal indicator detects metal parts. The signal from indicators is evaluated by computer, which controls the electromagnetic nozzle with a given delay. The efficiency of this separator is stated at the level of 90%.
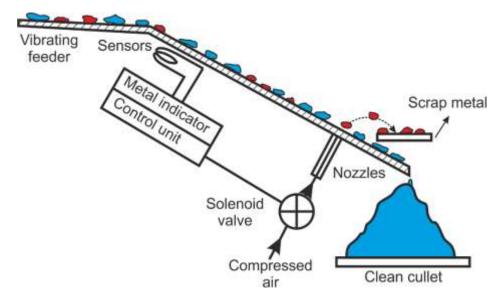

Fig. 5.7 Scheme of non-ferrous metal separator

The arrangement of lines for the treatment of foreign cullet is very often similar. An example is shown in Fig. 5.8. The line starts with a hopper, from which cullet is dosed to the conveyor belt by a vibrating feeder, while moistening cullet to prevent dusting. This is followed by the first magnetic separation, manual sorting, crushing, sieving and suction, the second magnetic separation, and finally treated cullet.
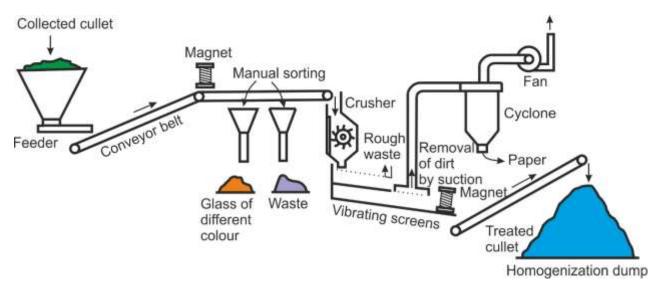

Fig. 5.8 Scheme of standard line for cullet treatment

There are also automatic systems for sorting cullet. An example of an optical-electric sorting line is shown in Fig. 5.9. Cullet treated in a standard way and crushed to a size of 8 to 40 mm are divided into several tens of sorting channels. Each channel contains several inductive and optical sensors that give an impulse to blow away the impurities. Lines also allow to sort by colour. The separation efficiency of metals and ceramics is reported to be at least 99.5% and the colour separation efficiency is reported to be 99.7%.
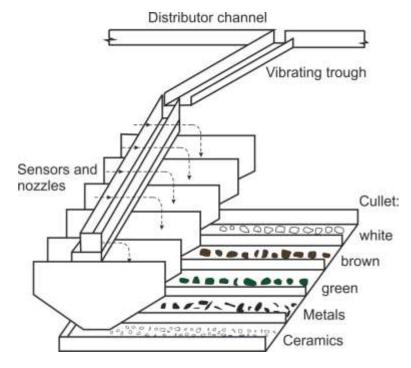

Fig. 5.9 Scheme of automatic sorting line for cullet

For example, the line shown in Fig. 5.10 is used for processing laminated glass and wire glass. The glass sheet is crushed first in a primary crusher, which consists of several pairs of breaking rollers provided with mandrels with an independent drive. After magnetic separation, the crushed material comes to the main crusher, which is a hammer crusher that separates foil or wire from glass. Foil or wire is separated from glass on a vibrating sieve. This is followed by a second magnetic separator and, if necessary, a non-ferrous metal separator. Foil and wire are also subsequently recycled.
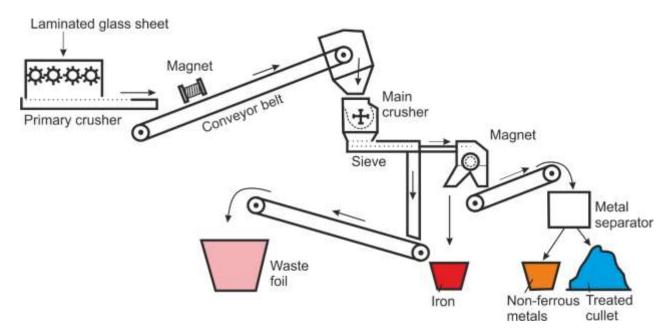
Fig. 5.10 Scheme of line for processing cullet of laminated glass and wire glass

The cullet is usually added at the end of charge preparation, often directly on the belt, which transports the charge to the loaders or at the end of mixing. The main reason is the highly abrasive effect of cullet on the equipment of batch houses. Commonly produced glasses have a hardness in the range of 5 to 7 degrees of the Mohs hardness scale and their hardness is comparable to hardened steel (Chapter 3.6.4). These properties of cullet cause rapid wear of the parts that come into contact with them. The proportion of metals released by cullet abrasion also increases.

5.7 Batch adjustment

At present, it is possible to come across some ways of additional adjustment of the glass batch. We can divide them into two groups. These are both agglomeration and preheating methods.

The agglomeration of the glass batch represents a process where agglomerates such as granules, tablets or briquettes are formed from a powder mixture. The importance of these procedures is the reduction of dustiness and the risk of separation during transport over longer distances, as well as energy savings during the actual melting, as a more intensive course of reactions and processes taking place in the melting furnace is expected.

Preheating is another variant of utilizing the heat of the exhaust gases. According to the methods used, the following classification of preheating systems can be performed:
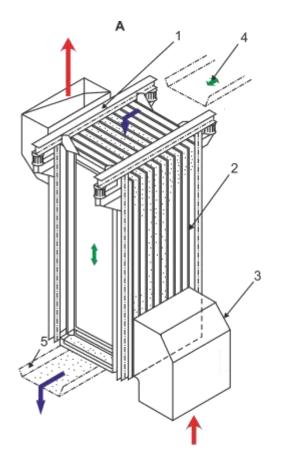
- by the nature of contact between the flue gases and the charge:
    - direct contact,
    - charge and flue gases are separated from each other,
- by preheated material (example is shown in Fig. 5.11):
    - charge preheating,
    - preheating of batch or cullet.

5.8 Batch houses

The actual preparation of the batch takes place usually in separate buildings - batch houses. The technology, machinery and equipment of batch houses must meet:

- quantitative aspect, i.e. to produce the necessary quantity of batch with a reasonable reserve,
- qualitative aspect, i.e. to produce a batch of the required composition with the highest possible homogeneity,
- economic aspect, i.e. to prepare the batch while minimizing the costs of its production: minimization of investment costs (price of all equipment and buildings) and operating costs (e.g. operation of the batch house),
- ecological and hygienic aspect, i.e. minimization of dustiness, waste and other effects on working environment and the environment.

The batch houses differ in their size and complexity, in particular with regard to the number of prepared recipes (composition of the batch), the volume of the prepared batch, the properties of the raw materials used and the local conditions. The aim is to minimize the handling of raw materials and the finished batch. In the case of preparation of large volumes of the batch, tower batch houses are chosen with the arrangement *in line, Fig. 5.12. The individual raw materials are first weighed on a belt, the minor components are mixed as a master batch.* The summation weigher is placed in front of the mixer and the cullet is added on the belt leading to the furnaces. A 3D model of the batch house is shown in Fig. 5.13.
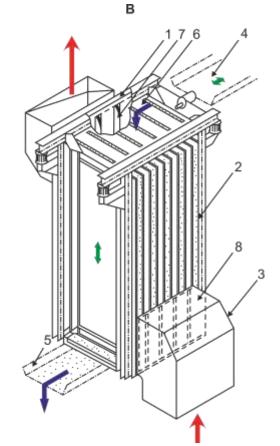
Fig. 5.11 Plate type preheater for: A - cullet with direct contact of flue gases with cullet, B - batch with heating through the wall, 1 - preheater frame, 2 - plates between which the heated material falls (the space is closed from the outside by sheet metal), 3 - flue gas inlet, 4 - preheated material inlet, 5 - preheated material outlet, 6 - separating sheet metal for the supply of batch between selected plates, 7, 8 - separation of plates for removal or supply of flue gases

Medium- and small-sized glassworks usually have a wider range of recipes. Central batch houses for multiple furnaces are often chosen, where the batch is transported in containers after agglomeration to avoid separation. The preparation of the batch into a container can be divided into

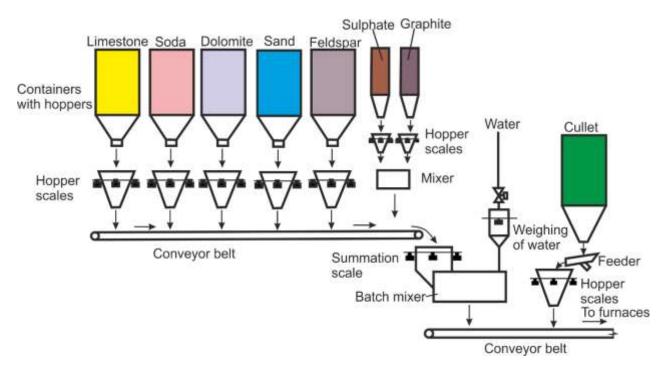- single-container method,
- multi-container method.

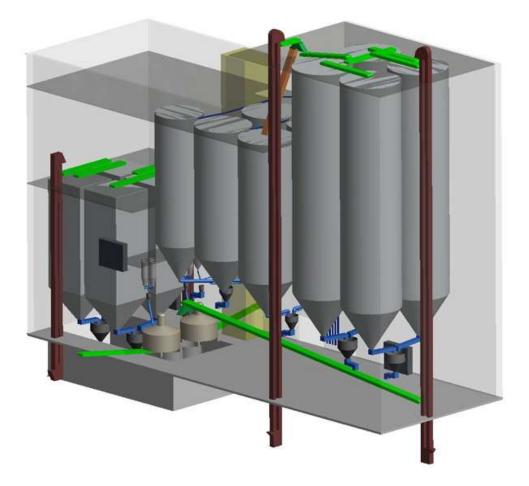*Fig. 5.12 Diagram of an in-line batch house with one-component weighers*

Fig. 5.13 3D model of the batch house (source: Dites spol. s r.o.)

Drawing assemblies of the plan view of the design of these batch houses are shown in Fig. 5.14 and in Fig. 5.15. In the case of single-container method, the raw materials are gradually weighed in several positions into one container (see also Fig. 5.3). In the case of multi-container method, several containers can be weighed at once. This method is designed for larger volumes and a wide range of batch recipes. In both cases, the handling of container during weighing and feeding is mechanized, the loading of container in the first position and the subsequent handling are often performed by the operator using a pallet truck or a forklift truck.

For the smallest glassworks, there is currently a trend of buying a finished batch or charge in the form of pellets, briquettes, etc. The actual batch houses for small volumes are not economical.

The development trends in the field of batch houses are quite clear. It is a full automation of batch preparation, batch houses are getting bigger, more accurate, more universal and more efficient. Despite all the progress, intermittent preparation of batch (described herein) is likely to continue to be used.
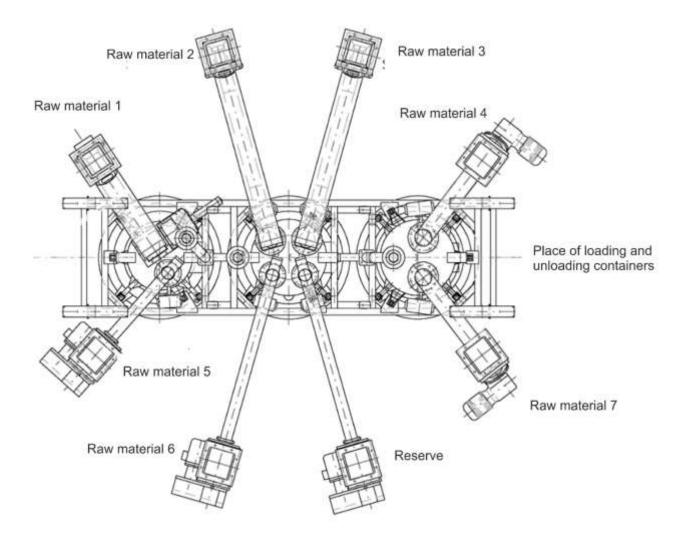
Fig. 5.14 Single-container method of batch preparation (source: Dites spol. s r.o.)
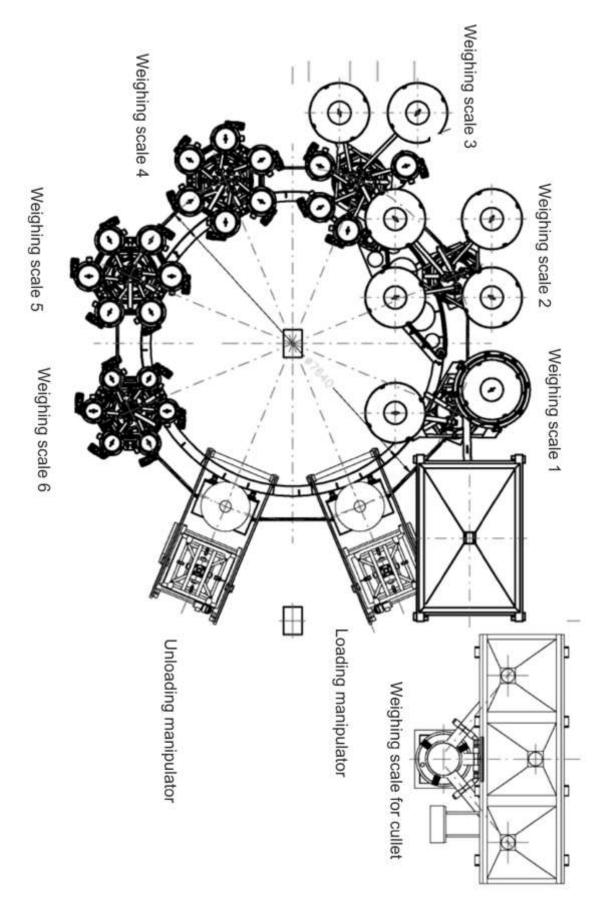
Fig. 5.15 Multi-container method of batch preparation (source: Dites spol. s r.o.)

6   Charge loading

Loading of glass charge into melting units, like other operations, has undergone a long-term development. Since manual loading into pot melting furnaces, continuous GMUs (glass melting unit) have introduced mechanical or automatic principles of loading by machine, so-called batch charger (also doghouse, day-hopper). Batch chargers are GMU machinery, which are used for loading the charge transported from the batch house.

The methods of loading the glass charge are different depending on the type of melting furnaces. Mechanical pots are used for pot furnaces; for continuous GMU, loading differs according to the method of furnace heating (Chapter 7.4).

For flame furnaces, ***batch charger loading the charge covering the entire width*** of the melting section are most often used:

- piston systems, an example of piston batch charger is shown in Fig. 6.1,
- vibrating chute systems with adjustable chute angle,
- a special case of construction is a roller batch charger (Fig. 6.2), which loads the glass batch and cullet separately in two layers.

It is also possible to find systems for loading in large doses and more numerous small doses.
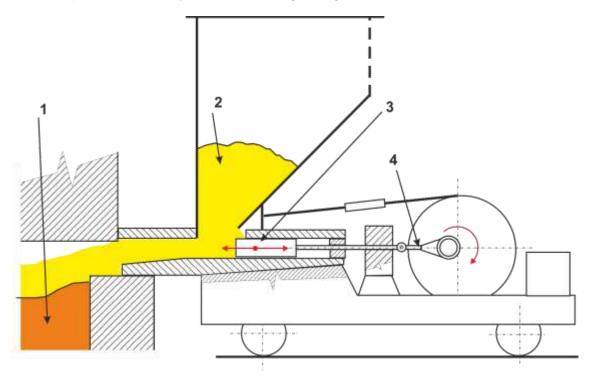
Fig. 6.1 Piston batch charger: 1 - glass melt, 2 - charge, 3 - piston with indication of movement, 4 - mechanism of piston movement
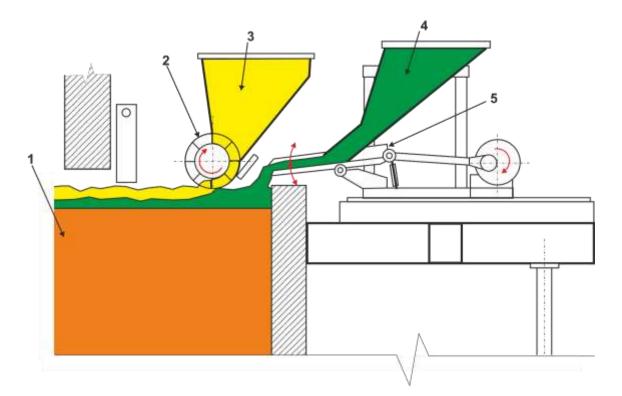
Fig. 6.2 Roller batch charger: 1 - glass melt, 2 - feed roller, 3 - batch, 4 - cullet, 5 - shaking mechanism

For all-electric melting furnaces, where the heating elements are located below the surface of the glass melt, **batch chargers are used, which evenly cover the surface of the glass melt**:

- belt batch chargers (Fig. 6.3),
- louvre batch chargers used for smaller furnaces (Fig. 6.4).
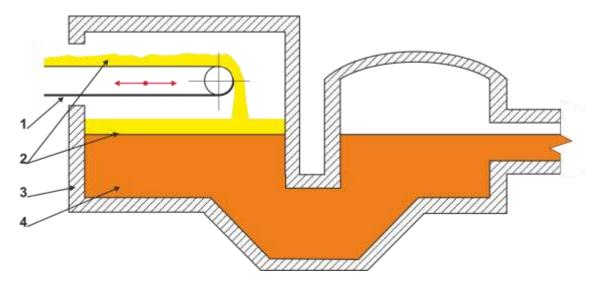
Fig. 6.3 Belt batch charger: 1 - belt, 2 - charge, 3 - tank, 4 - glass melt
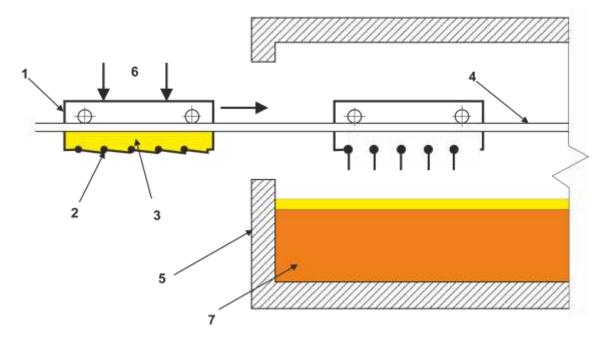
Fig. 6.4 Louvre batch charger: 1 - trolley, 2 - louvre, 3 - charge, 4 - rail, 5 - tank, 6 - charge loaded on the trolley, 7 - glass melt

The batch chargers meet the requirements of ensuring the required performance, control of the loading and the required volume of glass melt at the working end of the tank. The dimensioning of the batch charger is based on the requirements for the amount of glass melt, but also on the "loss" that occur during melting. These are "melting loss" caused by chemical reactions during melting, which are about 20% in melting only from the batch. Further losses can be caused by the volatilization of some components at high temperature and the mechanical escape of fine dust fractions of some of the raw materials forming the charge as a result of flowing of furnace atmosphere.

An example of a top batch charger for large volumes of charge (e.g. for the production of flat glass by floating) is the batch charger from Zimmermann-Jansen GmbH. This batch charger ensures a smooth loading of the glass charge by means of two loading tables from above virtually over the entire width of the melting section of the tank furnace. The supply of charge to the batch charger is realized by means of transport belt conveyors, which supply the charge from the batch house. The performance of the batch charger is controlled by a computer according to the immediate consumption of glass melt, if necessary, the batch charger can be operated manually. Due to the high temperatures that prevail in the loading area, some structural elements of the batch charger are intensively cooled. The main parts of the batch charger are as follows:

- frame, the structure of which carries the charge containers, loading tables, drives and other operating elements,
- travels that allow the batch charger to be set in the correct position,
- charge container divided into 8 sections,
- flaps, by means of which the thickness of the layer of the loaded charge is adjusted,
- two loading tables made of refractory material, the front part of which is protected by a welded-on heat shield, which is intensively cooled during operation. The inclination of tables is adjusted by support levers and swinging supports,

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- air cooling, which consists of two radial fans and cooling air distribution,
- drive, which is provided by two electric motors, which are connected to the tables by a handle with a rod.

Fig. 6.5 Batch charger for large volumes of charge (source: Zimmermann-Jansen GmbH)

The basic technical data of the batch charger described above are as follows:

- maximum capacity   620 t/24hour
- volume capacity of containers 13.5 m^3
- height of containers   1650 mm
- batch charger width   12000 mm
- number of tables   2
- number of drives   2
- width of tables   5675 mm
- gap between tables   150 mm
- number of strokes   from 0.456 min^{-1} to 4.56 min^{-1}
- stroke length   adjustable 175 mm, 210 mm, 250 mm

7 Glass melting

Glass melting is performed in glass melting furnaces, technically speaking in glass melting units (GMU). GMUs include a whole range of glass melting equipment and are chemical reactors in which both the temperature rises and the chemical reactions take place, which are the prerequisite for producing the glass melt.

First of all, it is appropriate to mention the historical development of GMU, which explains the current complexity of these facilities and their production capacities.

7.1 Development of GMU in historical context

Glass furnaces were initially a very simple device for melting glass, but with a rather complex production technology. This included a multi-phase process for the preparation of low-melting glass and a rather complicated method of its application to clay cores. Glass furnaces have become quite complicated and expensive devices over time. The furnaces had a combined melting and cooling part. Before the industrial revolution, it is possible to encounter an improved wood-fired melting furnace, which was called the Czech furnace. Thanks to the improved wood burning system, it was possible to reach temperatures of 1,300 to 1,400°C, compared to older furnaces, which allowed to reach temperatures of 1,100 to 1,320°C. In the Czech furnace, it was no longer necessary to perform multiphase melting. Nevertheless, the melting process at that time usually lasted 24 to 26 hours, the work of glassmakers usually took about 12 hours to prepare all pots, but with breaks up to 18 hours. It is stated that the type of Czech glass furnace became the basic and technically most perfect type of furnace for direct wood heating in Central Europe during the 17th to 19th centuries.

The new conditions made possible by the Industrial Revolution[6] in the second half of the 19th century, i.e. the transition to coal heating, the new transport network, mining and production of higher quality and cheaper raw materials including refractory materials, etc., combined with the boom in the 1970s manifested themselves in the revival of the glass industry and a new wave of founding of glassworks.

Heating of glass furnaces with wood was first replaced by coal. The main reason was restrictions and bans on logging. Direct coal heating was not very efficient at first, produced low quality glass and the life of furnaces was short. Over time, black and brown coal heating furnaces have been improved. In addition to brown and black coal, wood, peat and lignite were also used as fuel. However, the operating conditions significantly improved only with the introduction of so-called half-gas heating, which was the transition to the development of generators for gasification of solid fuels.

In all of the above heat sources, the flue gases were removed without further utilization of the heat they contain. A major turning point in the design of furnaces was the invention using the heat

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[6] The Industrial Revolution is the period from the end of the 18th to the end of the 19th century, when agriculture, production, mining, transport and other economic sectors changed fundamentally. The beginning of the Industrial Revolution is closely connected with the transition from manufacturing production with a dominant share of manual labour, to factory machine mass production, which has managed to multiply the current production several times. There was an increasing division of labour and specialization. The Industrial Revolution has been made possible by the growing pace of industrial, commercial and technological activity since about the 11th century.

of exhaust flue gases, the so-called regenerative system, which was patented by Friedrich Siemens in England and Austria-Hungary in 1856. This system is based on heating the lining of regenerators with heat from flue gases and subsequent change-over (change of combustion direction) transfers this heat to preheated air and gas (see more in Chapter 7.3.2). The regenerative system meant fuel savings of 30 to 50%. In addition to the regenerative system, a recuperation system was developed by G. Nehse in 1874, which works without changing the direction of combustion, the flue gases are separated from the heated air and gas by a wall (Chapter 7.3.2).

The first truly continuous GMU was put into operation again by Friedrich Siemens in Dresden in 1867. The introduction of continuous melting tank furnaces has led to significantly higher production volumes, higher production efficiency and a reduction in the price per unit of glass produced. It can be said that these GMUs were the basis for the industrial production of glass.

With the new furnaces, the cooling furnaces are also separated from the melting furnaces. Cooling furnaces are no longer tied to the waste heat from melting furnaces. They are still designed as separate furnaces, first chamber (Chapter 10.2.1) and subsequently tunnel (belt, Chapter 10.2.2) furnaces. Heating was first realized with solid fuels and then with the help of generator gas.

At the turn of the 19th and 20th centuries, the so-called Siemens-Siebert low-flame furnace (improved Siemens furnace) became the most efficient and economical pot furnace, and during the First World War there was a gradual unification of this type in the Czech lands, several of which even persist until the beginning of the 21st century.

After 1946, new materials were used in the construction of furnaces, such as basic refractory materials (MgO from 45% to 95% and Cr_2O_3 from 0 to 35%) or electro-melted refractory materials (characterized by melt casting technology). The outputs of continuous GMUs are still growing and in 2013 they were at a maximum of 1000 t/day (production of flat glass by floating technology - FLOAT, Chapter 9.6.3). Melting is increasingly being used in the combustion of gaseous fuels with oxygen.

7.2   Introduction to the theory of glass melting

During melting, processes occur that can be defined as physical, chemical and physical-chemical processes:

a) Transformations in the components of glass batch (polymorphic transformations, thermal decompositions, melt transition).

b) Reactions between the components of glass batch:

- solid-state reactions to form solid products,
- solid-state reactions to form a melt, solid-melt reactions to form a liquid product, e.g. dissolution of residual solids (SiO_2) in the melt,
- mutual reactions of some components in the melt, e.g. oxidation-reduction processes,
- reactions of the melt components with gases or to form gases, e.g. reactions during fining.

c) Compensation of concentration differences by diffusion. These differences can be caused by heterogeneity of the glass charge and other influences (separation, corrosion of the lining, volatilization of components, etc.).

  d) Flowing of glass melt caused by charge feeding and glass melt consumption, temperature gradients in glass melt, fining, etc.

  e) The rise of gas bubbles usually accompanied by diffusion processes (dissolution of gases in the melt or, conversely, release of gases from the melt).

All these processes usually take place in parallel, so it is not possible to observe them separately. Furthermore, it should be noted that most chemical reactions take place under conditions where the direction of their course is determined by the values of thermodynamic quantities, but the control process is the kinematics of the accompanying physical processes. Therefore, it is necessary to pay attention to the geometry of the distribution of individual reactants, diffusion coefficients, viscosities of the resulting liquid phases and wettability of solid reagents by these melts.

The melting process consists of three immediately consecutive phases:

- melting, i.e. conversion of a mixture of raw materials into a melt,
- fining and homogenization, which represent degassing of the glass melt and its homogenization in terms of chemical composition and temperature,
- cooling-down, in other words temperature reduction of the glass melt to be appropriate for feeding and subsequent forming.

These three stages take place during continuous melting simultaneously, but in different parts of the melting unit. When melting intermittently (in pots), they take place in the same place, but in a certain time sequence.

7.2.1 Melting process

Due to the chemical heterogeneity of charge (batch), it is very complicated to describe its behaviour during heating to the melting temperature and melting itself. The research of the melting process was therefore focused on the study of the kinetics of individual melting stages regardless of the chemical composition. As for chemical reactions, for various alkali silicate glass systems, the basic chemical processes are described in general terms, especially within the temperature ranges.

The first consequences of raising the temperature are dehydration of the batch and decomposition of any volatile organic additives. The release of adsorbed water proceed above 100 °C and organics volatiles burn off even up to 450 °C. The evaporation of water, which is also a phase transformation, requires a considerable amount of energy and represents an important part of the total energy consumption. In addition, a low-temperature quartz is converted to high-temperature quartz at 573°C. This process has no direct technological relevance, but during this conversion the lattice is loosened, so that the quartz is more accessible for solid-state reactions. The grains also crack, which can increase reactivity.

This is followed by thermal decompositions and phase transformations. In other words, solid-state reactions between individual raw materials forming binaries and ternaries are in procedure. A significant phase transition is the thermal decomposition of dolomite and limestone (alkali rich carbonates). Formation of this primary melt phase (also called the "carbonate route" of solid-state reactions) takes place already from 600 °C up to 900°C and is typically accompanied by the evolution of gases such as CO_2 produced by decomposition of carbonates.

$$CaMg(CO_3)_2 = CaCO_3 + MgO + CO_2, \quad (7.1)$$

$$CaCO_3 = CaO + CO_2, \qquad\qquad (7.2)$$

$$Na_2CO_3 + CaCO_3 = Na_2Ca(CO_3)_2 . \qquad (7.3)$$

As the melting process continues, sand reacts between about 750-1000°C with sodium silicates or soda to form liquid sodium silicates (so-called "silicate route" of solid-state reactions). Dissolving of the SiO_2 in the alkali rich carbonate melt phases, takes place typically above 1000°C and is again typically associated with release of gases (CO_2, volatile alkali oxides etc.) when limestone, soda or dolomite is reacting with sand. Examples of such solid-state reactions are:

$$SiO_2 + Na_2CO_3 = Na_2SiO_3 + CO_2, \qquad (7.4)$$

$$Na_2SiO_3 + SiO_2 = Na_2Si_2O_5. \qquad\qquad (7.5)$$

Those reactions proceed at the beginning on the surface of grains of the individual components to form a liquid phase (e.g. product of the reaction 7.3 - a double carbonate which lately forms with silica a viscous $Na_2O \cdot CaO \cdot SiO_2$ melt accompanied by release of CO_2 gas.). Among other things, crystalline sodium metasilicate (Na_2SiO_3, product of the reaction 7.4) is also formed, which further reacts to form a melt. Solid-state reactions and melt formation are then followed by mutual reactions in the melt; continuing sublimation of volatiles; gradual removal of bubbles from the molten mass by rising to the surface or by dissolution back into the glass and homogenization of the melt.

It is important to realize that pure silica melts at very high temperature (> 1700°C). In standard glasses (except e.g. pure silica glass) sand is incorporated in the glass melt by dissolution within the alkali rich carbonate melt, and not by melting. If we focus on general alkali silicate glass, the so-called "rough melt" appears at around 1200 °C followed by sand grain dissolution forming "seedy melt" at 1400 °C. Because of various techniques of fining, the "clear melt" is obtained at around 1500 °C, which is followed by another fining and conditioning, leading to the so-called "conditioned melt" at around 1250 °C.

It is reported that the melt is formed from 80 to 90% of the batch within 15 to 20 minutes and the remaining 10 to 20% are isolated undissolved grains. They dissolve in the last phase of the melting process within 1 to 2 hours, followed by fining. In general, glass melt is maintained at a high temperature for several hours, but during the first 45 to 60 minutes, 75 to 90% of total thermal energy is supplied to the glass melt. Melting as a whole is an endothermic reaction, which does not exclude the possibility of partial exothermic reactions

The melting process continues by sintering, during which the dispersion system coalesces and solidifies. For silicates, the relationship between melting point and sintering temperature is as follows

$$T_{slin} = 0,8 - 0,9 \, T_{tání} , \qquad\qquad (7.6)$$

where T_{slin} [K] is the sintering temperature and

$T_{tání}$ [K] is the melting point.

At the beginning of melting process, solid-state reactions also take place, where solid phase diffusion is a decisive factor. The reaction rate thus depends on the number of contact points between the grains of the respective components.

The above examples of reactions take place in most common glass melts, since they are melted (among other things) from soda (Na_2CO_3, Chapter 4.5.1.14.5), limestone ($CaCO_3$, Chapter 1) and sand (SiO_2, Chapter 4.3.1). Soda-lime-silica glass is used for the production of flat and container glass. The relationship between the individual oxides in this system in terms of liquidus temperature (maximum temperature at which a stable crystalline phase can exist with the given chemical composition) can be expressed using the so-called ternary diagram, Fig. 7.1. Other oxide systems are also important for glass production, such as K$_2$O – CaO - SiO$_2$, K$_2$O – PbO – SiO$_2$, Na$_2$O – B$_2$O$_3$ – SiO$_2$, and others.
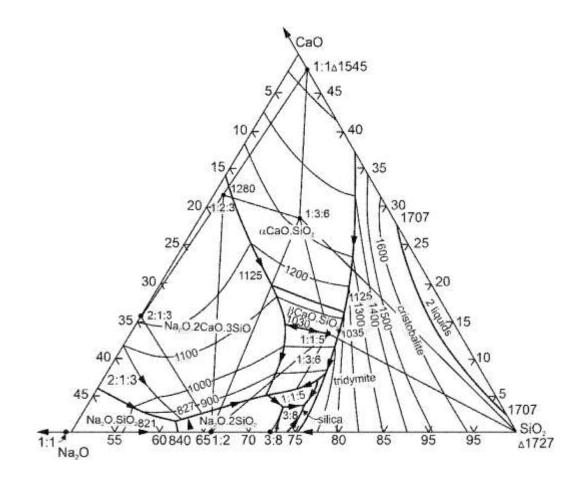

Fig. 7.1 Ternary diagram of the SiO$_2$ – Na$_2$O - CaO system

7.2.2   Fining of glass melt

During the whole melting process, there is also the release of gases as products of chemical reactions, the release of gases that have been introduced by charge, and other processes. Gases, such as carbon dioxide, carbon monoxide, nitrogen, water vapour, oxygen, sulphur dioxide and argon, form bubbles in the glass melt which, if not removed, will remain in the final products. Bubbles present in glass are a significant and most common defect. This is followed by fining of the glass melt, which is the common name for removing bubbles from the glass melt.

In terms of the mechanisms of bubble formation during melting, it is possible to divide them into five classes, Fig. 7.2. All bubbles above a certain minimum size and number per unit volume

must be removed, regardless of the mechanism of formation. The mechanism of their formation determines the ease/complexity of their removal.

Fining is performed:

- by increasing the temperature (decreasing the viscosity of glass melt),
- by changing the chemistry of the melt (e.g. adding fining agents to the glass batch),
- by agitating the melt mechanically (e.g. by introducing gases into the glass melt-bubbling).
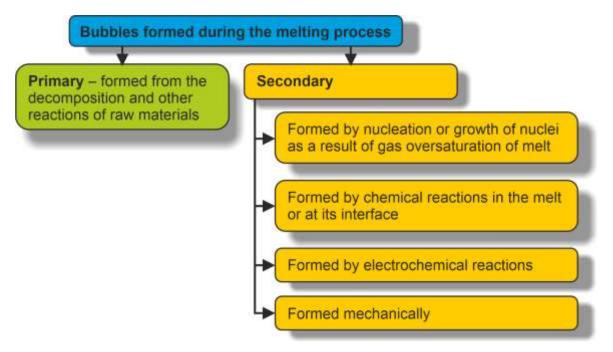

Fig. 7.2 Distribution of bubbles according to the mechanism of their formation during melting of glass melt

The individual effects are combined very often. The mechanisms which allow fining are as follows:

- supporting the rise of bubbles to the surface level of glass melt,
- binding together small bubbles and large bubbles,
- supporting the upward flow,
- diffusion processes (dissolution of bubbles in the glass melt).

An ***increase in temperature of the glass melt*** can be described as a physical principle, where a decrease in viscosity will allow the bubbles to rise faster to the surface level of glass melt. The viscosity is decreased to about 10 Pa·s, which corresponds to an increase in the temperature of common glasses for the production of container and flat glass to values in the range of 1,400 to 1,500°C. The lower viscosity reduces the resistance of glass melt to rising bubbles. The rate of rise of bubbles v [m·s^{-1}] is determined by the relation

$$v = \frac{1}{3} \cdot r^2 \cdot g \cdot \frac{\Delta \rho}{\eta} \qquad (7.6)$$

where r is the radius of bubbles [m],

g – is the gravitational acceleration [m·s^{-2}],

$\Delta\rho$ – is the difference in density of glass melt and gas [kg·m^{-3}],

η – is the viscosity of glass melt [Pa·s].

It follows from the relation that, in addition to viscosity, the size of bubbles is also important: larger bubbles are removed faster because their rate of rise in glass melt is higher, Table 7.1. Other factors include an increase in the volume of gases as the temperature of glass melt increases (bubbles increase their volume with temperature) and a decrease in the solubility of gases in glass melt (bubbles grow with additional proportions of undissolved gases).

Table 7.1 Calculated rate of rise of bubble in glass melt with a viscosity of 10 Pa·s

Diameter [mm]	Rate [mm·s^{-1}]	Rise time along 1,000 mm track [h:min:s]
4	3.270	0:05:06
2	0.817	0:20:24
1	0.204	1:21:42
0.5	0.051	5:26:48
0.2	0.008	34:43:20

As can be seen, tiny bubbles are much harder to remove and the mere decrease in viscosity (temperature increase) to normal fining values is usually insufficient, therefore **fining agents are added** to the charge. The fining agents themselves do not participate in the reaction itself at the beginning or only to a minimal extent. The fining process itself is triggered by exceeding the fining temperature, when fining gases are released from fining agents dissolved in the glass melt (such as sodium sulphate, Chapter 0, arsenic oxide, Chapter 0, …), which then diffuse into existing bubbles and increase their volume, thus also diameter. The process can be described as physical-chemical process. The bubbles gradually grow, thus accelerating their movement towards the surface level. This phase is sometimes called primary fining. For primary fining, the release of a sufficient amount of fining gas and the low viscosity of glass melt are essential. Strong flow is not advantageous for primary fining, as there is a risk of recirculation of bubbles into the lower layers before reaching the surface level.

Tiny bubbles, formed from fining agents, should dissolve in the glass melt during the subsequent cooling-down process (decrease to temperatures of 1,200 - 1,300°C for container and flat glass), because higher solubility of gases occurs in glass melt at lower temperature. This process is referred to as secondary fining. The rate of secondary fining depends on the quality of primary fining, the cooling rate and the diffusion of gas in the melt.

The fining process can be accelerated by increasing the dose of fining agents, the accompanying effect is a decrease in the initial fining temperature. On the other hand, the negative effect is the risk of foaming initiated by an excessive volume of gas in the glass melt.

In practice, there is also a mechanical principle of fining, which is called ***bubbling,*** Fig. 7.3. This involves the introduction of nitrogen, air, oxygen, helium or other gases through nozzles located at the bottom of the melting section of the furnace and the creation of an upward flow which supports the fining process. At the bottom of the basin, the design of bubbling nozzles is often complemented by a cross fire sill that promotes vertical flow. This facilitates the removal of bubbles to the surface level and also contributes to the homogenization of glass melt.
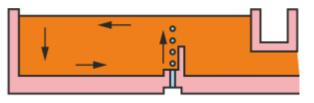

Fig. 7.3 Example of introducing bubbling

The degree of fining of the glass melt is expressed in two ways:

a) total number (volume) of bubbles in glass melt (by comparing the density of such glass with the density of glass not containing inclusions),
b) number of bubbles per unit volume (performed by microscopic observation).

7.2.3   Homogenization and flow of glass melt

As already stated, the goal of melting is a homogeneous glass melt both in terms of its composition and its temperature. The fining process itself should free the glass melt from visible bubbles, but it will not remove inhomogeneous regions. Differences in the composition of glass are manifested by different properties, in particular optical properties. This creates optical interfaces in glass, which manifest themselves as defects in finished products. Inhomogeneities in the composition of glass melt can be divided into:

- local inhomogeneities - isolated regions of glass melt of different composition,
- continuously coming striae - these extend for a long time in a certain profile of the outlet flow,
- volume inhomogeneities - they fill the entire volume of the glass melt flowing out and the differences in concentration are often small and difficult to detect.

Thermal inhomogeneities can mainly affect forming and again manifest themselves as defects in finished products.

A significant source of inhomogeneities in the composition of glass melt is the glass batch. Its composition should be ideally homogeneous up to the grain size of individual raw materials (Chapter 5.5). However, reality is far from ideal. Inhomogeneities are caused by poor mixing of the batch, separation and loss of part of the batch due to its dustiness. Furthermore, when the composition of batch fluctuates, glass melts of different compositions are mixed in the melting process, which results in inhomogeneous glass. Similar results are given by the change in composition caused by the outflow of glass melt components, the dissolution of refractory materials, the release of glass melt from dead corners and other mechanisms. Because it is very difficult to eliminate the above-mentioned effects and because inhomogeneous regions enriched in

SiO_2, CaO with a size of a few millimetres also occur in the fined glass, it is necessary to homogenize the glass melt.

Two main processes are involved in homogenization, which combine with each other:

- diffusion,
- flow of glass melt.

Although both processes take place simultaneously, the homogenization process can be seen as a gradual process. Macroscopic inhomogeneities are first attenuated by glass flow and then dissolved by diffusion.

Diffusion is a spontaneous process in which particles of matter (atoms, ions, molecules) are transported by a disordered thermal motion. The diffusion flux is directly proportional to the driving force, which is the concentration gradient. The constant of proportionality is the diffusion coefficient (Fick's law). The diffusion coefficient in glass melt must be high enough for the diffusion to take place. On the contrary, the refractory material has a low value of this coefficient, which on the one hand increases the resistance of the furnace lining to the corrosive action of glass melt, but on the other hand leads to the formation of hardly soluble striae in glass melt.

The ***flow*** is closely related to the type and design of a particular melting unit. The flow of glass melt then not only affects the homogenization of glass melt, but is also important for other melting processes. Flow is especially important for continuous melting units, where it is one of the basic prerequisites for successful melting. In glass furnaces, flow is created on the basis of several mechanisms:

- consumption flow (primary),
- free convection (secondary),
- rising bubbles,
- mechanical effect of stirrers (if installed in the furnace),
- in the initial stages, the Marangoni flow[7] is also applied on a scale of individual grains, caused by inhomogeneity of the composition.

The driving force of primary flow is the pressure difference caused by the loading of charge and removal of glass melt, Fig. 7.4 A. For flame GMUs, the secondary flow initiated by inhomogeneous distribution of the temperature fields and subsequently by change in density in glass melt stabilizes in both longitudinal and cross fire directions. Due to heating of the surface level from heated atmosphere and cooling of the regions along the side walls of the GMU, a temperature maximum is created at the intersection of the vertical plane passing through the longitudinal axis of the furnace and the surface level, Fig. 7.4 B. In this place, the glass melt has the lowest density, which is manifested by "swelling" of the surface level upwards, from where it

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[7] Movement of a liquid along a liquid/gas or liquid/liquid phase interface from places with a lower interfacial tension to places with a higher interfacial tension. The surface tension gradient can be created due to local temperature differences in the system - in places with lower temperature there is a higher surface tension (surface tension of liquids decreases with temperature), which causes the surface layers of liquid to flow to these places. In multicomponent systems, the surface tension gradient can be induced by the concentration gradient caused by different evaporation rates of the individual components of the mixture or by adsorption phenomena (Gibbs-Marangoni effect).

spills out to the sides. The place with the maximum temperature acts as a source of flowing glass melt.

The nature of the flow of glass melt in the basin is determined by interaction of secondary and primary flows, therefore the nature of the flow in GMU is also diametrically different in flame and electrically heated GMUs.
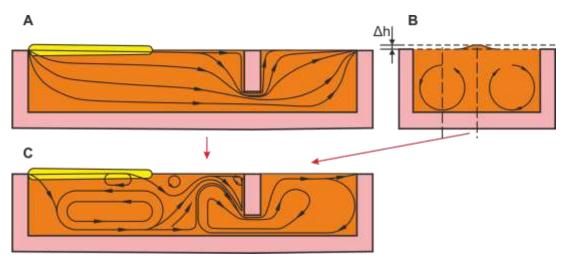

Fig. 7.4 Flow of glass melt in continuous GMUs: A - primary flow (longitudinal section of GMU), B - secondary flow (cross fire section of GMU), C - main flow scheme (longitudinal section)

The rate of homogenization depends on the velocity gradient of glass melt, therefore mixing and bubbling are used in practice to increase the homogenization process. However, stirrers must be placed at a sufficient distance from the walls of the melting unit.

7.2.4   Cooling-down of glass melt

Chemical reactions and homogenization no longer occur during the ***cooling-down process of glass melt*** It is assumed that the tiny bubbles in glass melt will completely dissolve and the temperature will reduce to a level suitable for forming. Cooling-down occurs in continuous GMUs in the so-called working end, which is usually separated from the melting section.

7.2.5   Other important processes during melting

Significant processes in glass technology include **oxidation-reduction (redox) processes**, which take place in the temperature range starting around the glass transition temperature of glass and ending at maximum melting temperatures. This wide temperature range covers all basic processes of glass production - melting, homogenization, processing and cooling. In the field of melting, the redox processes have a fundamental effect on the course of the fining of glass melt (gas release behaviour) and the heat transfer from the combustion chamber. A particularly important aspect of the course of redox processes is their influence on the properties of the final product, in particular its colour, Chapter 4.5.1.

Another important process is the **loss of volatile components**. During melting, the glass melt is always depleted of some components relative to the original composition of the glass charge. This results in the creation of inhomogeneous regions in glass melt and the released components are the main source of dust emissions of the GMU. These emissions clog the exhaust

routes, deposit in regenerators and recuperators, and cause corrosion of the GMU crown and other parts. Melting losses can be of two types. On the one hand, they are formed by the drift of fine fractions of raw materials due to the flow of atmosphere in the GMU (losses due to dusting), especially by evaporation of volatile components of the melt. This volatility of some components depends on the melt temperature, but also on other conditions, in particular on the overall composition of glass melt. For example, the largest losses were noted for lead and borosilicate glasses.

There are other processes during melting such as the already mentioned corrosion of the lining, thermal-insulation properties of the lining, flow of the furnace atmosphere, and more.

7.2.6 Factors influencing melting time

Knowledge of melting conditions allows to influence in practice the melting time and thus the economic complexity of melting processes; these are mainly the following factors:

- melting temperature,
- chemical composition,
- particle size,
- water content,
- cullet additive,
- melting accelerators,
- batch adjustment,
- electric boosting.

The effect of ***melting temperature*** consists mainly in reducing the viscosity of glass melt, which results in an acceleration of the diffusion processes, an increase in the solubility of the components and an increase in the flow intensity. This shortens the melting time, but increases the melting costs (increase in temperature losses) and also increases the corrosion of the refractory materials used for building the GMU.

The ***chemical composition*** of the charge has a fundamental impact on the melting time and economy. As follows from the chapter on glass raw materials (Chapter 4), increasing the content of some oxides will reduce melting temperatures (e.g. Na_2O, K_2O, B_2O_3,…), other oxides (e.g. SiO_2, Al_2O_3) have the opposite effect, and others have different effects for different temperatures (e.g. CaO). Important in the calculation procedure for a batch composition and the determination of glass melting process is the batch redox number characterizing the balance between reducing (oxygen consumers) and oxidizing (oxygen suppliers) species in the batch.

Most of the work dealing with the influence of ***particle size*** on the melting of the glass leads to the same conclusions, i.e. the contact surface of reactants increases with decreasing grain size, which leads to faster melting. On the other hand, too fine grain size of the glass batch increases its dustiness and part of the batch leaves together with the flue gases, Chapter 7.2.5. Using too fine raw materials also worsens and prolongs the fining process due to the formation of very tiny bubbles.

The ***water content*** in the glass charge has a positive effect on the melting rate. This is either free moisture, which prevents dusting and improves contact between the reactants, or chemically bound moisture. For free moisture, the water content is usually in the range of 2 to 4%.

The **cullet additive** forms an integral part of the glass charge of all common industrial productions. In addition to shortening the time, their use also affects the price of the final production. This issue is described in details in Chapters 4.7 and 5.6.

Melting accelerators have a positive effect on the melting rate and economy. Their effects on melting have already been discussed in Chapter 4.5.1.

The **adjustment of batch** is based on its agglomeration and its preheating. For more information see Chapter 5.7.

Electric boosting is used in flame furnaces and its principle and influence are described in the following Chapter 7.6.3.

7.3 Energy intensity of the production of glass products

Glass production is a relatively energy-intensive technology. On the other hand, it is necessary to mention that glass products, thanks to their long life and their properties (e.g. insulating properties - glazing of buildings) will save many times more energy than is consumed during production.

The total energy consumption and thus the ecological burden from the production of glass products is affected by:

    a) Batch preparation (the whole process from storage, through handling of raw materials and their weighing, mixing up to transport to the GMU).
    b) Glass melting (especially the melting and fining of glass melt).
    c) Glass forming (especially heat exchange between glass, tools and coolant).
    d) Product cooling (often associated with reheating of the product and its controlled cooling).
    e) Processing and finishing (thermal, mechanical, chemical).

The melting process is the most energy-intensive phase of glass production. For some products with a given glass composition, more than 60% of the total energy demand is spent on melting. Conventional glasses are melted in the temperature range of 1,350 to 1,600°C (quartz glass even around 2,000°C) and even in subsequent technological operations (forming, annealing, processing and finishing) the energy consumption is significantly lower, Table 7.2.

7.3.1 Heat balance of GMU

Glass production is one of the technologies that makes significant use of heat, and thermal energy is the most important for melting. The simplest and clearest form of describing GMU from this point of view is its heat balance, which maps the areas of heat fluxes and their mutual ratio for a given unit, which, among other things, allows comparing different types of GMU.

As an example, the heat balance of a continuous flame melting furnace heated by gaseous fuel is given; the balance period is one hour. Under certain conditions, the heat balance model can also be applied to furnaces using liquid fuels or to electric furnaces. It clearly describes the heat fluxes in the GMU, the so-called Sankey diagram (Fig. 7.5).

Table 7.2 Energy intensity of individual operations in the production of glass products for different types of glass composition, data on the required energy are in kJ per 1 kg of glass produced and as a percentage of the total energy intensity

| Technological operations	Flat glass		Container glass		Glass fibres		Pressed and blown products	
	kJ/kg	%	kJ/kg	%	kJ/kg	%	kJ/kg	%
Batch preparation	717	5.2	717	8.1	717	3.4	717	4.2
Melting and fining	9,070	66.3	5,800	65.2	8,859	41.6	7,699	44.8
Forming	1,582	11.6	422	4.8	7,593	35.7	5,589	32.6
Annealing of products, processing and finishing	2,320	16.9	1962	21.9	4,113	19.3	3,164	18.4
Total	13,689	100	12,698	100	21,282	100	17,169	100
Share of glass melt preparation in the total energy intensity	9,787	**71.5**	6,518	**73.3**	9,576	**45**	8,416	**49**
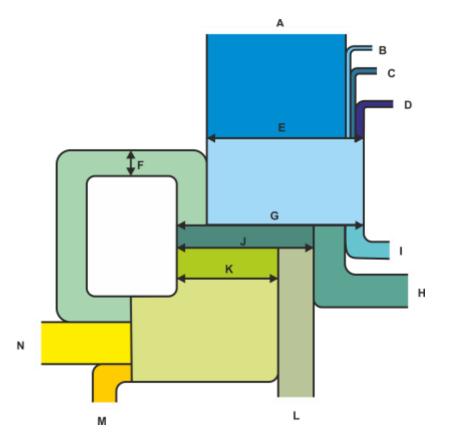
Fig. 7.5 Sankey diagram of heat fluxes in glass melting unit: A - chemical heat of fuel, B - physical heat of fuel, C - physical heat of oxidizer (most often combustion air, possibly oxygen), D - heat supplied by charge, E - primary heat supplied, F - heat recovery, G - total heat supplied to melting unit, H - heat losses to the surroundings, I - heat used for loading glass melt, J - heat removed by flue gases, K - heat of flue gases at the recovery inlet, L - heat losses at the section of flue gas outlet from the furnace - flue gas inlet to the recovery plant, M - heat losses through the surface of the recovery plant, N - stack loss

A. The chemical heat supplied by fuel is the product of the consumption and the calorific value of fuel (the calorific value is given by the amount of heat released by combustion of the fuel, while water remains in flue gases in the form of steam).

$$Q_A = H_U . V_P \ [MJ·h^{-1}] \qquad\qquad (7.7)$$

where H_U - is the calorific value of fuel [MJ·m^{-3}],

V_P - is the fuel consumption [m^3·h^{-1}].

B. The physical heat supplied by fuel can be calculated as follows

$$Q_B = c_{pp} . T_p . V_p \ [MJ·h^{-1}] \qquad\qquad (7.8)$$

where c_{pp} – is the specific heat capacity of fuel at constant pressure [MJ·m^{-3}·°C^{-1}]

T_p - is the fuel temperature [°C],

V_p - is the fuel consumption [m^3·h^{-1}].

C. Physical heat supplied by oxidizer (combustion air, oxygen), so-called sensible heat

$$Q_C = c_{pox} . T_{ox} . V_{ox} \ [MJ·h^{-1}] \qquad\qquad (7.9)$$

where c_{pox} - is the specific heat capacity of oxidizer at constant pressure [MJ·m^{-3}·°C^{-1}]

T_{ox} - is the oxidizer temperature [°C],

V_{ox} - is the oxidizer consumption [m^3·h^{-1}].

D. The heat supplied by charge can be calculated as follows

$$Q_D = c_{pb} . T_b . M_b \ [MJ·h^{-1}] \qquad\qquad (7.10)$$

where c_{pb} - is the specific heat capacity of charge [MJ·kg^{-1}·°C^{-1}],

T_b - is the charge temperature [°C],

M_b - is the mass of charge [kg·h^{-1}].

E. The primary heat supplied to the furnace is given by the sum of the items A+B+C+D, i.e.

$$Q_E = Q_A + Q_B + Q_C + Q_D \ [MJ·h^{-1}] \quad (7.11)$$

F. Heat recovery is the last input item of the heat balance (it does not have to be considered for furnaces heated by fuel-oxygen combination and for all-electric furnaces). Heat recovery is currently used in the form of preheating of combustion air, rarely natural gas in recuperators or regenerators. It is also possible to use the heat of flue gases to preheat the charge or only the cullet. The item can be expressed as follows (when some terms can be zero)

$$Q_F = Q_{pp} + Q_{op} + Q_{bp} \quad [\text{MJ·h}^{-1}] \qquad (7.12)$$

where Q_{pp} - is the heat energy in preheated fuel [MJ·h⁻¹]

Q_{op} - is the heat energy in preheated oxidizer [MJ·h⁻¹]

Q_{bp} - is the heat energy in preheated charge, cullet [MJ·h⁻¹]

$$Q_{pp} = c_{ppp} . T_{pp} . V_{pp} - c_{pp} . T_p . V_{pp} \quad [\text{MJ·h}^{-1}] \qquad (7.13)$$

where c_{ppp}, c_{pp} - is the specific heat capacity of preheated or non-preheated fuel at

constant pressure [MJ·m⁻³·°C⁻¹],

T_{pp}, T_p - is the temperature of preheated or non-preheated fuel [°C],

V_{pp} - is the amount of fuel that is preheated over the balance period [m³·h⁻¹].

$$Q_{op} = c_{poxp} . T_{oxp} . V_{oxp} - c_{pox} . T_{ox} . V_{oxp} \quad [\text{MJ·h}^{-1}] \qquad (7.14)$$

where c_{poxp}, c_{pox} - is the specific heat capacity of preheated or non-preheated oxidizer at

constant pressure [MJ·m⁻³·°C⁻¹],

T_{oxp}, T_{ox} - is the temperature of preheated or non-preheated oxidizer [°C],

V_{oxp} - is the amount of oxidizer that was preheated over the balance period [m³·h⁻¹].

$$Q_{bp} = c_{pbp} . T_{bp} . M_b - c_{pb} . T_b . M_b \quad [\text{MJ·h}^{-1}] \qquad (7.15)$$

where c_{pbp}, c_{pb} - is the specific heat capacity of preheated or non-preheated charge [MJ·kg⁻¹·°C⁻¹],

T_{bp}, T_b - is the temperature of preheated or non-preheated charge [°C],

M_b - is the mass of charge over the balance period that is preheated [kg·h⁻¹].

G. The total heat flux entering the furnace is the sum of the primary heat supplied and the heat obtained by flue gas recovery

$$Q_G = Q_E + Q_F \quad [\text{MJ·h}^{-1}] \qquad\qquad (7.16)$$

The following items relate to heat expenditure and may not be equal to income, which in practice is often used for quantifying items that are otherwise difficult to determine.

H. The surface losses of the melting unit can be easily calculated by subtracting the heat in glass melt and the heat removed by flue gases from the heat fed to the furnace in total

$$Q_H = Q_G - Q_J - Q_I \quad [\text{MJ·h}^{-1}] \qquad (7.17)$$

I. The heat removed by glass melt can be expressed as follows

$$Q_I = (q_r + q_v + q_o) . G_g \quad [\text{MJ·h}^{-1}] \qquad (7.18)$$

where $\quad q_r$ - is the heat of reaction of glass melt [MJ·kg^{-1}],

$\qquad q_v$ - is the heat of vaporization of water [MJ·kg^{-1}],

$\qquad q_o$ - is the heat required to heat up the glass melt [MJ·kg^{-1}],

$\qquad G_g$ - is the melting rate for the balance period [kg·h^{-1}].

J. Flue gases leaving the furnace have a certain temperature, composition and volume, therefore

$$Q_J = c_{psp} . T_{sp} . V_{sp} \quad [\text{MJ·h}^{-1}] \qquad\qquad (7.19)$$

where $\quad c_{psp}$ - is the specific heat capacity of flue gases at constant pressure [MJ·m^{-3}·°C^{-1}],

T_{sp} - is the temperature of flue gases at outlet of the melting area of the furnace [°C],

V_{sp} - is the volume of flue gases [m^3·h^{-1}].

It should be noted that the volume of flue gases may not only correspond to the combustion of fuel, but gaseous products may also enter that are released from the charge (especially water and CO_2).

K. Flue gases entering recovery process

$$Q_K = c_{psr} \cdot T_{sr} \cdot V_{sr} \quad [\text{MJ·h}^{-1}] \qquad (7.20)$$

where c_{psr} - is the specific heat capacity of flue gases at the recovery inlet at constant pressure [MJ·m^{-3}·°C^{-1}],

T_{sr} - is the temperature of flue gases at the recovery inlet [°C],

V_{sr} - is the volume of flue gases entering the recovery process [m^3·h^{-1}].

L. Heat losses through the surface on the way from the melting space to the recovery plant can most easily be determined as the difference between the heat of flue gases at the furnace outlet (Q$_J$) and at the recovery inlet (Q$_K$)

$$Q_L = Q_J - Q_K \quad [\text{MJ·h}^{-1}] \qquad (7.21)$$

M. Heat losses through the surface of the recovery plant can most easily be determined as the difference between the heat of flue gases at the recovery inlet (Q$_K$) and at the recovery outlet (Q$_N$) minus the heat obtained by recovery (Q$_R$).

$$Q_M = Q_K - Q_N - Q_F \quad [\text{MJ·h}^{-1}] \qquad (7.22)$$

N. Stack loss determines how much heat the flue gases carry to the stack with no use.

$$Q_N = c_{psk} \cdot T_{sk} \cdot V_{sk} \quad [\text{MJ·h}^{-1}] \qquad (7.23)$$

where c_{psk} - is the specific heat capacity of flue gases at constant pressure [MJ·m^{-3}·°C^{-1}],

T_{sk} - is the temperature of flue gases at the recovery outlet [°C],

V_{sk} - is the volume of flue gases [m^3·h^{-1}].

Indicators allowing the comparison of different types of GMU are based on the heat balance. With long-term monitoring of a specific melting unit, their development over time can be monitored. In general, these indicators can be used for describing any thermal installation in which fuel, whether solid, liquid or gaseous, is burned.

7.3.2 Regenerators, recuperators and other devices to reduce energy consumption

Due to energy intensity of glass melting, there is an effort to use waste heat. In gas-air flame furnaces, the use of waste heat is an economic necessity. In this case, heat that leaves together with flue gases is reused for melting the glass melt. The basic devices for recovering heat back into the melting process are:

- regenerators are used for preheating the combustion air by heat accumulated by lining of the regenerator with a periodic change in the direction of burning - they are based on heat accumulation,
- recuperators are based on smooth transfer of heat through the partition wall; they serve for continuous preheating of combustion air (sometimes gas) at a constant direction of flue gas flow.

Regenerators are only a few years older than recuperators. The original purpose of both was not to save energy, but to achieve higher melting temperatures.

Regenerators are filled with a through lining, or a checker with a large heat capacity, which is used for accumulating heat. There are several design options for the checker (often made of fireclay), Fig. 7.6. The regenerators are made of refractory material and are always in pairs, each of the pair for one side of the GMU.

In one cycle, the checker is heated on one side by heat of flue gases and then the heat is transferred to the combustion air. The optimal cycle time for air combustion is in the range of 40 - 60 minutes, depending on the heat capacity of the filling of the regeneration chamber. In heating with burners from the right side of the tank furnace, combustion air from the right chamber of the regenerator flows into the combustion space and waste heat of flue gases accumulates in the checker space of the left chamber, which come to the regenerator via burners on the left side. After 20-30 minutes, the process is reversed and the burners on the left side of the tank furnace are ignited. During the change-over, which lasts about 30-60 seconds, there are no flames in the tank furnace. About 15 seconds after reversing the direction of combustion air, the fuel can be fed back into the space of burner chamber. The chamber is composed of several types of refractory materials, Fig. 7.7. During recovery, air preheating up to a temperature of 1,350°C can be achieved.
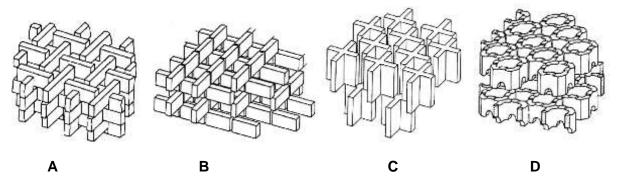

A   **B**   **C**   **D**

Fig. 7.6 Shape of regenerator checkers: A - open basket weave, B - pigeon hole, C - cruciform, D - chimney block
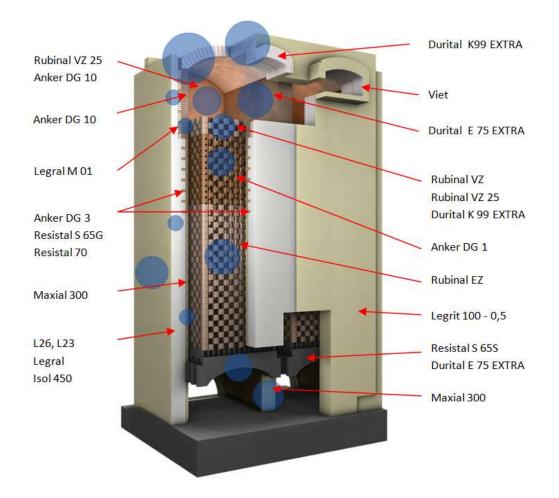
Fig. 7.7 Modern GMU regenerator chamber with commercial names of refractory materials (source: RHI AG)

Recuperation is based on obtaining heat from flue gases by a continuous transfer of heat through the partition wall. The two media (flue gases and combustion air) are spatially separated from each other. According to the used material and design, recuperators are divided into ceramic and metal recuperators. Recuperators are smaller, have lower space requirements and lower construction costs. They work without change-over and all burners thus work simultaneously. Therefore, recuperative furnaces have a constant temperature of preheated combustion air, but a considerably lower average temperature than regenerative furnaces. The specific heat consumption per unit of glass melt is thus higher in recuperative furnaces. The advantage is more stable temperature in the furnace space, without fluctuations during change-over. Preheated air can be heated to about 500°C, with two-stage recuperators up to 800°C can be achieved (Unit Melter).

When comparing the use of systems, it is possible to use data from the beginning of the new millennium, when 75% of all GMUs worldwide used a regenerative system.

Another possibility of using flue gases is preheating of cullet, charge and batch, Chapter 5.7. Another option is the production of hot water, compressed air or electricity.

7.4 Classification of melting units

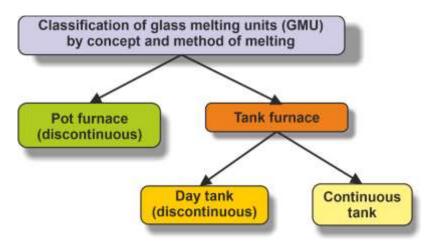The basic classification of GMU is into pot and tank furnaces (continuous, day), Fig. 7.8.

Fig. 7.8 Classification of GMU by concept and method of melting

Pot melting furnaces are used for small production volumes, in which melting takes place periodically.

The transition to tank furnaces with continuous operation are the so-called **day tanks**, in which the melting cycle takes place in the same way as in pot furnaces.

Continuous tanks operating continuously are designed for high melting rates. These melting units can be designed for melting rate of up to several hundred tons of glass melt in 24 hours.

Another option is to classify the melting units by the **energy used for melting** - there are the following types (Fig. 7.9):

- flame furnaces (burning gaseous or liquid fuels),
- electric furnaces using a direct passage of electric current for melting, and
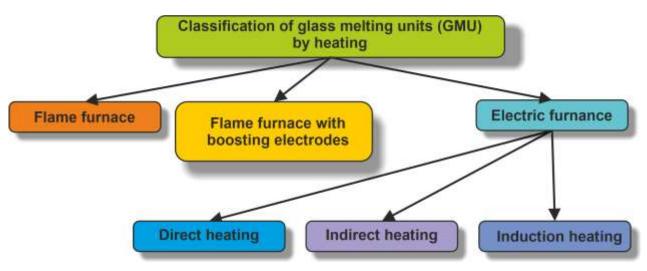- flame furnaces with electric boosting.

Fig. 7.9 Classification of GMU by primary energy used for melting

The use of electricity in melting glass is given by the following possibilities:

a) direct heating, using the passage of electric current through glass melt, which is used in all-electric continuous tank GMUs, Chapter 7.6.2,
b) indirect heating, using heating coils located outside the glass melt, an example of the application of indirect heating can be the electric pot furnace, Chapter 7.5,
c) induction heating, e.g. for melting quartz glass in graphite crucibles, Chapter 7.11.3.

7.5 Melting in pot furnaces

Pot melting furnaces work on a periodic basis and the individual phases of the melting process alternate gradually. The main advantage is their variability and operational capacity in changes in the types of glass melt, their colour and physical-chemical properties of glass melt, as well as the possibility of melting a small amount of glass. Furnaces can have different sizes, which are determined by the number of pots placed therein. There are single- or double-pot furnaces, but the number of pots is often in the range of 8 to 12. Melting in pot furnaces is mainly used in manual production.

Pot furnaces can be divided using several criteria. One of them can be the division by energy for heating into:
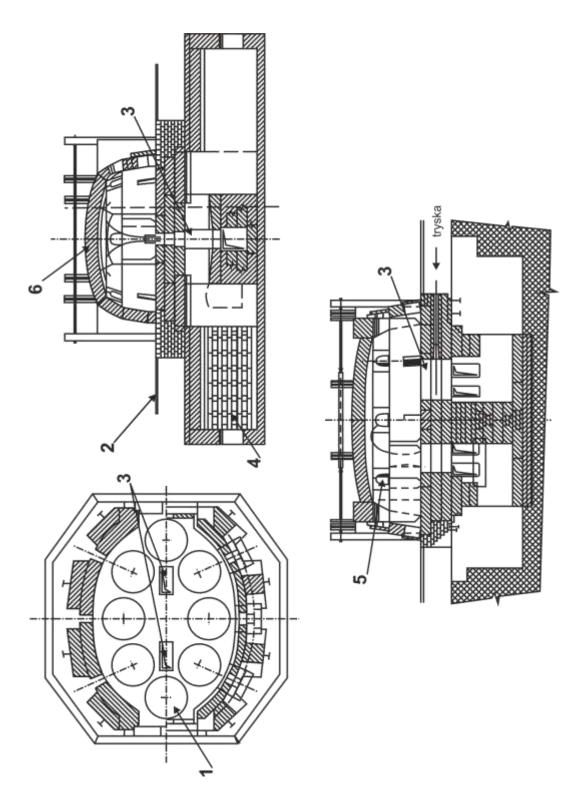
- flame furnaces (burning gaseous fuels with air or oxygen), and
- electric furnaces (with indirect heating by means of kanthal coils).

Flame furnaces are equipped with preheating of combustion air, either regenerative with change-over of the direction of burning or recuperative with a constant direction of flame, Chapter 7.3.2. They are also equipped with a so-called glass pocket, which can be either hot (Siemens-Siebert furnace) or cold. In practice, glass flows into the pocket from possibly cracked or otherwise damaged pots, during collection and the like.

The oldest concept of a flame furnace that is still in use is the Siemens-Siebert low-flame furnace. The furnace can hold 8 to 12 pots, depending on the design size. Its development began in the second half of the 19th century, when it was most widespread for the production of sheet and container glass. The scheme of this furnace in the modern concept is shown in Fig. 7.10.

Newer are top-flame furnaces, where the burners are located above the edge of the pot. Furnaces with direct flame spread and furnaces with a double end-port are distinguished. Furnaces are used for 3 to 8 pots.

Tangential pot furnaces are the latest type. They were developed and industrially applied at the end of the 20th century. The pots have a balanced temperature field in this furnace, which leads to a higher quality of the glass melt. The furnace contains one to three pots with a diameter of 1,100 mm and a height of 700 mm, which are used either separately or as building modules for four to nine pot furnaces, Fig. 7.11. Heating is provided by two short-flame low-pressure burners located one above the other in the area of the bottom and the upper edge of the pot. The flue gas exhaust is on the other side in the floor of the furnace. Flue gases are ducted through a metal recuperator into the stack.

Recently, flame pot furnaces using oxygen for combustion have also begun to appear, see more in Chapter 7.7.

Fig. 7.10 Sections of low-flame regenerative furnace of the Siemens-Siebert type: 1 - pot, 2 - working platform, 3 - burner ports, 4 - regenerator, 5 - working hole for collecting glass melt from the pot, 6 - furnace crown
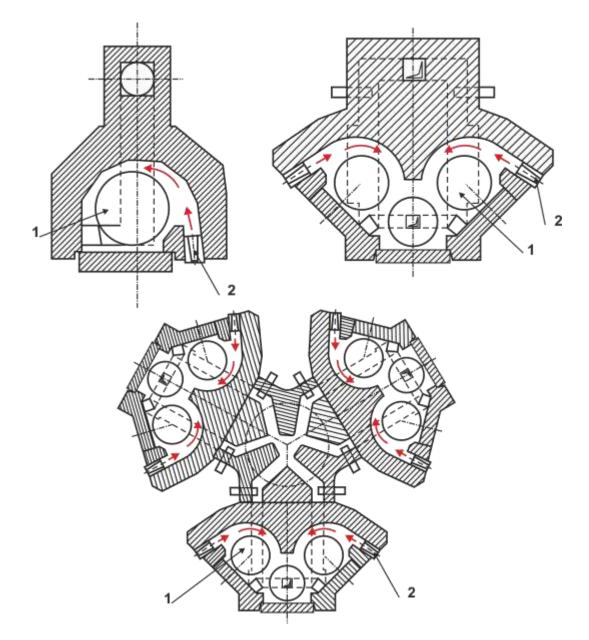
Fig. 7.11 Floor plans of some shape alternatives of tangential pot furnaces: 1 - pot, 2 - burner, red arrows indicate the direction of flame

Electric pot furnaces are heated indirectly, resistively, by means of heating coils made of KANTHAL SUPER alloy[8], which are high-performance electric heating elements with a long service life for very high temperatures. They are manufactured as finished elements of many shapes and sizes, straight or bent in a wide range of standard and special designs. The construction of a pot furnace with these heating elements is shown in Fig. 7.12. There are more heating elements in the furnace, they are suspended vertically and are often arranged around the pot except for the front part. The glass melt is heated through the furnace atmosphere together with the radiant component of heat transfer.

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[8] KANTHAL SUPER is a compact ceramic material composed of $MoSi_2$ and a component of oxides, mainly of glass base, which resists oxidation at high temperatures.
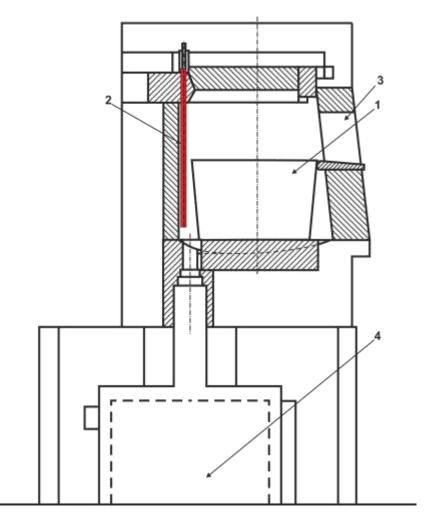
Fig. 7.12 Electric resistance pot furnace: 1 - pot, 2 - heating coil made of KANTHAL SUPER material, 3 - working hole for collecting glass melt from the pot, 4 - glass pocket

Electric pot furnaces are well controlled and the melting process can also be automated to some extent. On the other hand, compared to flame furnaces, their operation is more expensive. They are designed in such a way that one pot is always placed in one separately heated space. Each pot is therefore autonomous and allows the melting mode to be carried out completely independently of the adjacent pot.

7.6   Melting in tank furnaces

Tank furnaces resulted from the development and demands of new mass production technologies. Day tanks were used first, which operate on a periodic principle of melting just like pot furnaces. However, the volumes of glass melt are larger. Today, this type of furnace is used only exceptionally for glass volumes above the production capacity of pot furnaces and below the production capacity of continuous tanks.

In continuous tank furnaces, the individual phases of the melting process take place simultaneously, but at different places of the melting unit. The main advantages are low production costs, lower emissions and lower energy consumption per unit of glass melt and the possibility of mass production. Their construction, operation and control require a high level of expertise.

Continuous GMUs include a wide range of glass melting equipment; their sizes are often given in the amount of glass produced per day, i.e. in tonnes per 24 hours. It is possible to encounter units with production from several tons per day (for example for glass jewellery components) up to 1,000 tons/day (production of flat glass by means of technology of floating in melted tin bath - FLOAT). Furnaces can be very roughly divided by volumes as follows:

- cross fire regenerative melting units are large-capacity plants, with outputs over 300 tons/day,
- end-port regenerative melting units usually have medium outputs, 100 to 300 tons/day,
- recuperative UM (unit melters), End-port regenerative and all-electric melting units (low-capacity plants also at the level of 3 tons/day, more often 25 to 100 tons/day).

The design of glass melting units with continuous operation shows a number of specific elements according to which GMUs can be distinguished. According to the construction, the continuous tank GMUs can be divided into single-chamber, two-chamber and special furnaces. Single-chamber furnaces are rather a history. The current GMUs are built mostly as two-chamber with a clear separation of the melting section and the working end.

One of the basic classifications is by the energy used for melting (Chapter 7.4) into continuous flame, electric with direct heating (all-electric) and flame with electric boosting GMUs. This classification is used in the following text.

7.6.1   Continuous flame GMUs

Continuous tank flame furnaces vary greatly in design. It depends on many factors according to which the optimal GMU variant is designed. Accordingly, it is also possible to divide the continuous flame GMUs, Fig. 7.13.

Heating of flame furnaces can be designed with gaseous or liquid fuels, or a combination thereof. In the Czech Republic, flame furnaces for gaseous fuels, virtually exclusively for natural gas[9], are the most widespread. Liquid fuels are used in France, the Benelux countries and others. Light fuel oils are mainly used, which have a slightly higher calorific value than natural gas, but the melting process with them is more expensive due to the unit price.

In flame furnaces, different directions of flame spread can be encountered relative to the flowing glass melt:

- cross fire (side fire),
- longitudinal fire, or
- an end-port (U-flame).

Some types of melting furnaces are schematically shown in Fig. 7.14.

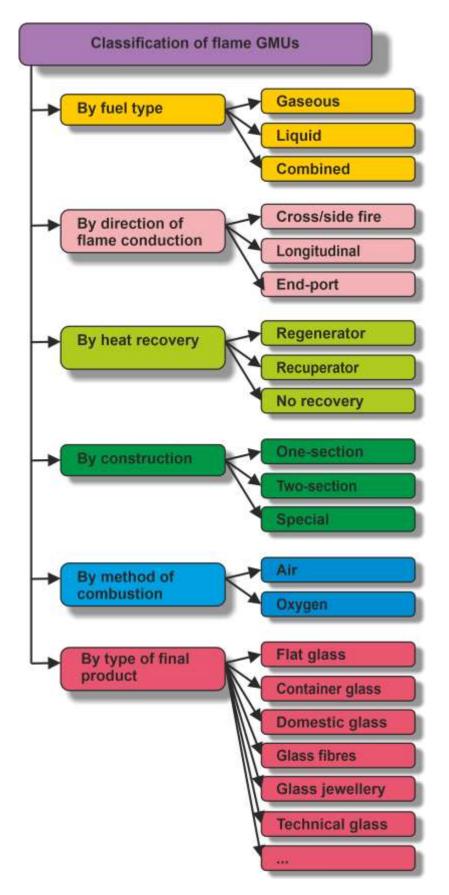[9] The main component of natural gas is methane, CH_4.

Fig. 7.13 Classification of flame GMUs

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The utilization of waste heat of flue gases relates to flame furnaces using air for combustion. They are usually equipped with a regenerative or recuperative system for the reuse of heat from exhaust flue gases, Chapter 7.3.2.

Flame furnaces use air or oxygen to burn fuel. Oxygen combustion brings some advantages, Chapter 7.7.
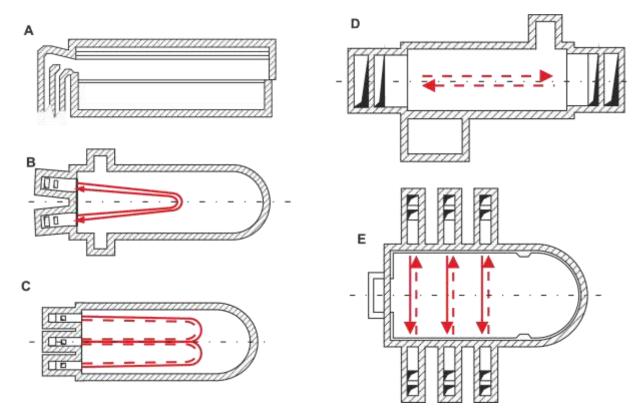

Fig. 7.14 Selected types of continuous GMUs (red arrows indicate the direction of flame): A - longitudinal section of the regenerative end-port furnace with horizontal U-flame, B - floor plan of the furnace from Fig. A, C - floor plan of the regenerative end-port furnace with double U-flame, D - floor plan of the regenerative furnace with longitudinal spread of flame, E - floor plan of the regenerative furnace with cross (cross fire, side-port) spread of flame

Flame GMUs are most often regenerative and with cross (cross fire) spread of flame or with End-port. A view of the cross fire regenerative furnace is shown in Fig. 7.15. Flame GMUs also include the aforementioned recuperative UM.

Cross fire furnaces (Fig. 7.16) are used mainly in the production of flat and container glass and have large regenerative chambers (mostly vertical) on both sides of the melting section, Chapter 7.3.2. There are inlets to the exhaust ducts at the bottom of the chambers, which meet and lead to the stack. Combustion air is supplied through the lining in chambers to the ports, at the outlet of which it is mixed with fuel in a predetermined ratio. Cross fire furnaces therefore have the same air inlet for fuel combustion as the outlet for gases released by combustion. The combustion thus takes place in one direction and the ports on the opposite side serve as gas exhaust, which brings flue gases into the regenerative chambers. After a certain time (20 to 30 minutes), the so-called change-over takes place, Chapter 7.3.2. On each side, there can be one common

regenerative chamber for all ports or split into individual regenerative chambers for each port separately.
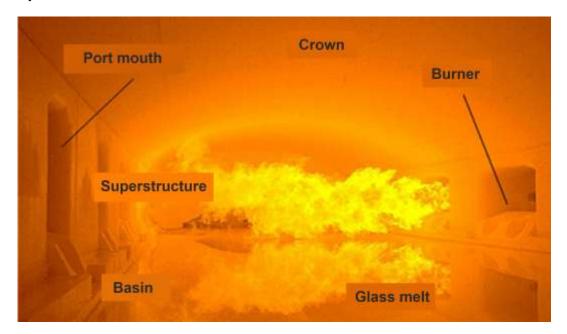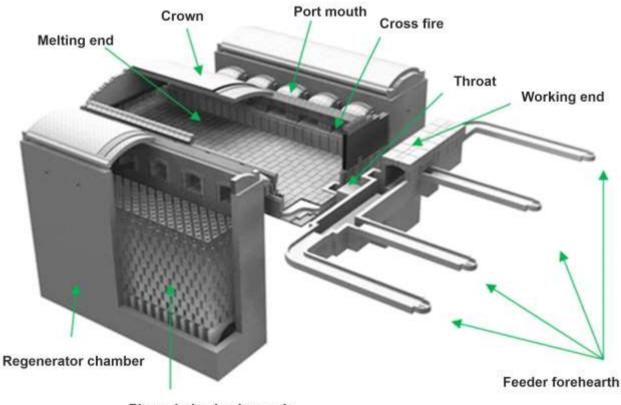

Fig. 7.15 View into the cross fire regenerative furnace

Fig. 7.16 Diagram of the construction of regenerative GMU with cross fire and common regenerative chamber for all ports (source: Toledo Engineering Co., Inc., TECO)

The melting of glass raw materials itself takes place by the effect of radiant heat of flames and radiant heat from the crown and side walls. Depending on the size of the furnace, there are 2 to 8 ports on each side. The ports have one or more burners and can use gas or fuel oil. Metal burners can be placed either in the sides of the ports, below the connection of ports to the furnace, above the port or inserted in the middle of the ports through their bottom or crown, Chapter 7.10.

The furnace basin is rectangular with a size depending on the required melting rate. The length to width ratio usually ranges from 1.5 to 2.3, the depth of the furnace depends on the type of furnace and its intended use. There is a tendency to build deeper basins to increase melting rate, but for dark colours of glass, for example, the depths are lower. In the case of flat glass production, the depth of the basin is around 1,500 mm, the surface area of the basin is over 500 m^2.

The design of the cross fire furnace allows easier temperature setting compared to the End-port furnace in the longitudinal axis. On the other hand, these furnaces have a higher specific heat consumption due to the relatively larger surface area. For example, for conventional soda-lime flat glass, a specific consumption of 4,800 kJ/kg is achieved to melt 1 kg of glass.

End-port regenerative furnaces (Fig. 7.17) operate with a flame that turns into a U letter in the furnace. The furnaces are usually smaller, have two large ports located in the front wall, and the batch chargers are on one or both sides of the furnace near the burners. Regenerators can be horizontal (usually located under the tank) or vertical (located behind the tank), or a combination of both, and they can also be of multi-pass type.
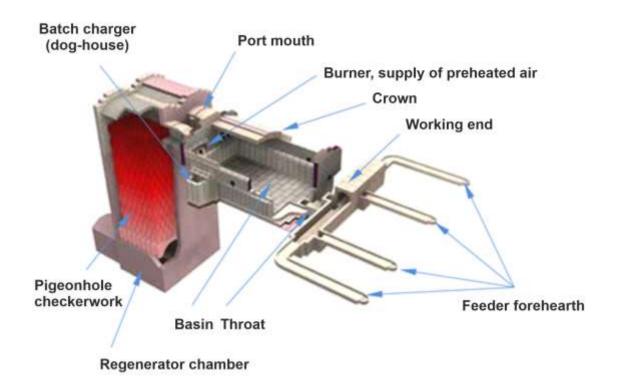

Fig. 7.17 Schematic section of an end-port furnace for the production of container glass (source: Toledo Engineering Co., Inc., TECO)

The main application of these furnaces is in the production of container glass. This type of furnace is sensitive to the correct setting of tensile and compressive conditions in the furnace space so as to achieve the correct shape of flame. Incorrect proportions of these conditions lead to rapid wear of the furnace or even to its destruction. The inlet of fuel into the furnace space is provided by metal burners, which can be situated, as in the case of a cross fire furnace, below or above the connection of the port, in its side, or through an intermediate burner to the centre of the port. There can be multiple burners in each port.

End-port furnaces are usually less slim than cross fire furnaces and their length to width ratio ranges from 1.2 to 2.0. The depth of the basin ranges from 600 to 1,600 mm, depending on the colour, the composition of glass and the dependence on melting surface area. The size of melting surface area ranges from 25 to 125 m^2 with a daily melting capacity higher than 400 tons/day. The fuel is natural gas or fuel oil.

The construction costs of the End-port furnace are lower than of a comparable cross fire furnace due to the reduction in the volume of masonry and lining of regenerative chambers. These furnaces have a smaller external surface area and therefore lower heat losses to the surroundings. Relatively longer path of flame brings very good heat transfer and, therefore, these furnaces have a lower specific energy consumption for melting compared to cross fire furnaces. Up to 3,600 kJ/kg can be achieved for conventional soda-lime-silica bottle glass.

Recuperative furnaces are equipped with recuperators (Chapter 7.3.2) for the use of waste heat. Continuous preheating of combustion air (sometimes gas) by recuperators at a constant flow direction of flue gases and preheated medium ensures more stable conditions in the furnace space without fluctuations during change-over. On the other hand, the average temperature of preheated medium is lower than in regenerative furnaces, therefore the specific gas consumption of recuperative furnaces is higher. In some cases, the residual heat after passing through the recuperator is further used (production of hot water, compressed air or electricity). An example of a recuperative furnace is, for example, Unit Melter, Fig. 7.18.

These furnaces are heated by a set of burners which are distributed along each side wall. The heating system is divided into several zones over the length of the furnace to allow better control of the temperature profile in the longitudinal axis. Flue gases are discharged through one or two exhaust ducts in the front part of the furnace and are guided to one or two metal recuperators and from there to the stack.

Unit Melters are designed for a wide range of capacity from 3 to 350 tons/day with a melting surface area of up to 160 m^2. They are suitable for all common types of glass and the fuel used is natural gas or fuel oil. The specific heat consumption for standard soda-lime-silica glass is above 5,000 kJ/kg.

Recently, continuous tanks have also been used, which are partially or completely heated by the combustion of gas by oxygen. It is stated that furnaces are more economical, faster, more environmentally friendly, etc., but it is necessary to take into account additional costs of supply or production of oxygen; see more in Chapter 7.7.
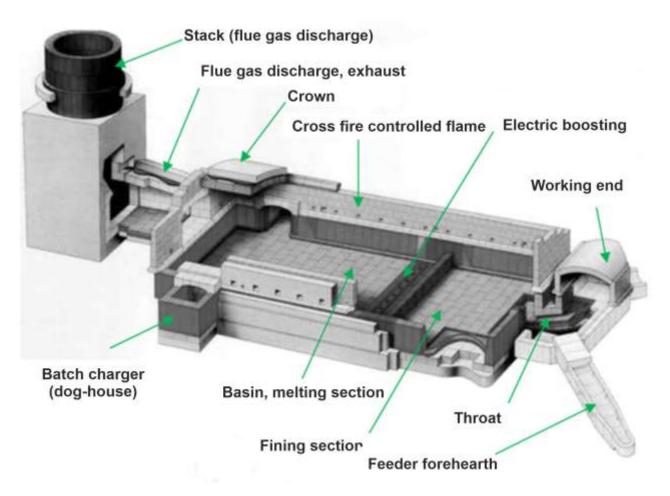
Stack (flue gas discharge)
Flue gas discharge, exhaust
Crown
Cross fire controlled flame — Electric boosting
Working end
Batch charger (dog-house)
Basin, melting section
Throat
Fining section
Feeder forehearth

Fig. 7.18 Diagram of the Unit Melter recuperative furnace

7.6.2   Continuous all-electric GMUs

The continuous melting of glass by direct passage of electric current through glass melt allows the presence of alkali metal ions, in particular Na^+ and K^+. As mentioned in Chapter 3.8.1, this concerns ionic conductivity, which increases with increasing temperature.

Advantages of all-electrically heated furnaces:

- very efficient use of supplied electricity,
- heat generation directly in glass melt,
- very good control and regulation of the melting process,
- glass melt is well isolated by a "batch blanket",
- energy consumption in an all-electric melting furnace is about half that of a furnace heated by standard fuel (gas-air); the consumption for melting standard soda-lime boron glass is 2.8 to 2.9 MJ/kg (on average 80 to 85% of energy),
- thanks to the covering of glass melt with the so-called batch blanket, emissions, in particular nitrogen oxides (NO_X), are minimized,
- the issue of regeneration and recuperation is not addressed, so in that aspect, all-electric furnaces are simpler.

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The main disadvantage of all-electric melting is the price of electricity and, therefore, melting of glass in all-electric GMUs is generally more expensive.

7.6.2.1 Basic principles

All-electric melting takes advantage of the fact that after melting, the glass melt becomes a good conductor of electric current. When electric current passes through a circuit in which the glass melt represents a resistive element, heat is generated in accordance with Joule's law:

$$P = R.I^2 = U.I = U^2/R, \qquad (7.24)$$

where P is the heat output [W],

R - is the electric resistance of a conductor [Ω],

I - is the intensity of electric current [A],

U - is the electric voltage [V].

Melting of glass in all-electric glass melting furnaces is a complex technological process, the successful completion of which requires knowledge of not only the electrical properties of glass (glass melt) of a given chemical composition, but also thermal-mechanical properties and viscosity, including their temperature dependences.

Tanks are usually designed as deep, so compared to flame tanks, the melting process takes place vertically, for example see Fig. 7.19.
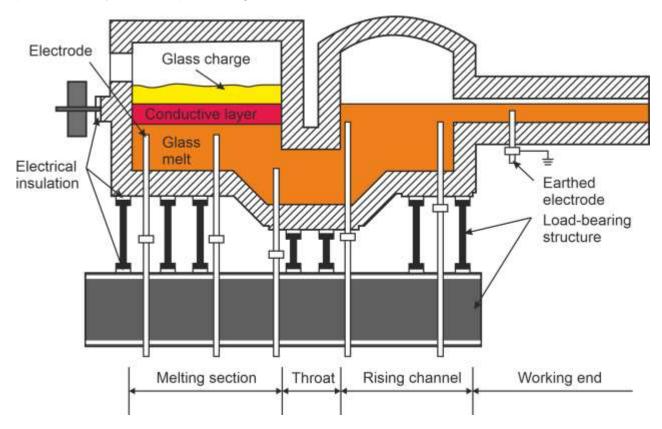

Fig. 7.19 Diagram of continuous GMU with all-electric melting

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In contrast to the melting of glass in flame furnaces, when applying the Joule principle, the glass charge is heated from below, and therefore the melting conditions also differ. The warmest glass melt is not located on the surface of the bath, but inside the so-called convective layer. In the region with the glass surface covered with a layer of glass batch (so-called "batch blanket"), the structure shown in Fig. 7.20 is created. Under the layer of loose glass charge 50 - 300 mm thick, there is the so-called crust, which is a layer of freshly glass melt with a high content of bubbles and residuals of sand grains. This layer forms not only a physical but also a thermal interface between the glass melt and the glass batch, as the high density of scattering particles contained therein creates an opaque screen preventing heat leakage by radiation into the glass charge and subsequently above the charge.

Layer	Thickness	Temperature
Glass charge	50-300 mm	100-150 °C
Crust Layer of freshly melted glass melt with a high content of bubbles and residuals of sand grains	5 (3) mm	
Conductive layer Layer of vertically non-flowing melt, worst optical purity	100-150 mm	1000-1100°C"
Convective layer Different melting conditions compared to flame furnaces: - glass charge is heated from below, - the warmest glass melt is inside the convective layer, not on the surface		

Fig. 7.20 Vertical structure in an all-electric furnace with the glass surface covered with a layer of glass charge

A layer of vertically non-flowing melt with a relatively high viscosity, referred to as "conductive layer", is formed under the crust. Because convection heat transfer does not apply in this layer and the intensity of radiation heat transfer is moreover limited by poorer optical purity, the average thermal relative conductivity in this layer is very low, ranging, depending on the thickness of layer (50-150 mm), between 2.5 and 15 $W \cdot m^{-1}$.

In the convective layer, where the temperature of glass melt is highest, the glass melt flows. With a relatively homogeneous supply of energy in the tank, the flow has the character of cylinders.

The thickness of conductive layer is not constant over the entire surface area. As a result, a local thinning of the conductive layer to about 50 mm occurs in the area of upward flow and, on the contrary, the thickness of conductive layer increases by 50 - 100 mm in the areas of downward flow. Disruption of the homogeneity of the thickness of conductive layer leads to the formation of so-called drips - release of part of the conductive layer, its fall to the bottom, resulting in a local drop in temperature in the convective layer.

Bubbles are generated in glass melt and accumulate in the warm region above the upward flow. With a weak and discontinuous layer, gases leave through the entire surface of the charge.

In the case of a thicker crust, or conductive layer, there is a more significant concentration of gases under the crust, formation of large bubbles, lifting of the crust and the formation of the so-called "boiling-off". In the extreme case of an impermeable crust, a continuous gas layer may form under the insulating charge, the formation of which is accompanied by the development of foam on the surface.

7.6.2.2   Electrodes

Only alternating voltage is used for melting, due to the suppression of electrolysis. Alternating current is introduced into the glass melt by means of electrodes. The requirement for the material and design of the electrodes is corrosion resistance to glass melt and high heat resistance.

The most common electrode material is molybdenum[10]. The electrodes are made as rod electrodes (diameter 31.7 mm, 50.8 mm, 101.6 mm and others) or less often as plate electrodes. The electrodes dissolve in glass melt, which is compensated by moving the rods into the furnace a few millimetres per month, depending on the melting conditions and the chemical composition of glass melt. The electrodes are used up to temperatures of 1,600°C, the surface current density is reported to be $2 - 3$ A·cm^{-2}. Their reducing effect on glass melt (e.g. lead crystal) has a negative effect. Anodic or frequency protection is used for suppressing this effect.

Another material for the production of electrodes is sintered SnO_2 (the highest degree of oxidation of Sn^{4+}, it has no reducing effects) and is used up to temperatures of 1,450°C. In contrast to molybdenum electrodes, only a tenth of the surface current density can be virtually used, around 0.2 A·cm^{-2}. The electrodes are thus larger in diameter than molybdenum electrodes. They are also more prone to cracking in thermal shock.

Platinum and its alloys (especially PtRh with the amount of Rh up to 40%) are used in controlled discharge feeders, so-called homogenizers (Chapter 8.3.2). One of the alternatives of using these homogenizers is to heat the glass melt by passing low-voltage electric current directly through the platinum shell of the homogenizer.

Graphite electrodes have historically been used, but these have had a strong reducing effect on the glass melt, poor wettability of the surface of glass melt, high temporary resistances in the transfer of electric current from the electrodes to the glass melt, and low current density.

In all-electric GMUs, electrodes are arranged horizontally from the side (even several rows), from the bottom or at an angle, which is rarely used. Electrodes can be so-called level electrodes, where the electrodes are inserted into the glass melt through the surface level from above. A very important device is the electrode holders, which are usually cooled and allow the electrodes to move during melting process as the electrodes corrode.

Electrodes can be supplied in one, two or most often three phases. Due to the fact that glass melt shows a negative characteristic of its temperature on specific electric resistance, the resistance of glass melt decreases with increasing temperature (thermal instability or also deregulation effect, Chapter 3.8.1). To suppress this effect, the power supply must be regulated to constant current or impedance. Tapped transformers (step change) and induction regulators

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[10] The melting point of Mo is 2,623°C, it has high electrical and thermal strength, low specific heat and coefficient of thermal expansion

(referred to as Varivolt with continuous regulation in load) are most often used as power supplies for electric GMUs.

The power input is regulated according to the resistance between the electrodes, according to the temperature (in glass melt or on the crown), according to the thickness of the charge layer or constant power input is maintained at constant consumption.

Corrosion occurs in electrodes, which should be minimized. Several factors contribute to corrosion. The most important factor is the oxidation of electrode material caused by the components of glass melt, which increases with temperature. Oxidation is also affected by current density, AC frequency and electrode composition. In order to protect the electrodes, it is thus necessary to limit the action of the mentioned factors, such as the composition of glass melt, to set an appropriate current density and current frequency. In the case of molybdenum electrodes, the melting of lead glass requires electrochemical protection, which is provided by changing the potential or frequency of heating current. It is also possible to perform anodic passivation with direct current, cathodic protection, their combinations and low-frequency protection.

7.6.2.3   All-electric GMUs

Despite the existence of a number of design alternatives occurring in operational practice, most all-electric GMUs can be classified into two groups: uniform and intensive, Fig. 7.21.
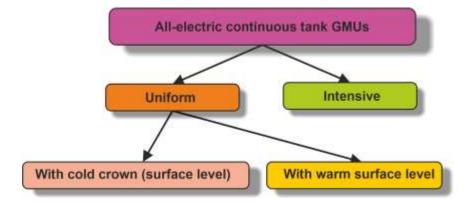

Fig. 7.21 Classification of all-electric continuous GMUs

In the glassworks, with a few exceptions in the field of glass fibre production, there are so-called uniform GMUs ("Uniform Melters"), which have the electrodes placed and dimensioned to ensure symmetrical supply of energy supply in glass melt. In these furnaces, the occurrence of hot spots and convective flows, which would be caused by uneven heating of glass melt, is systematically minimized. Energy consumption for these types of GMU can be below 3,000 kJ/kg.

Cold-crown tanks are most often used, in which the melting section is fully covered by a batch blanket (layer of charge), which ensures good thermal insulation of the surface level of glass melt (Fig. 7.22). The glass charge, or especially the glass batch and cullet, are evenly loaded over the entire surface area of the melting space, usually by means of a louvre or belt batch charger (Chapter 6). The second alternative is ***hot-surface tanks***, which use the original method of loading from one place, which allows the movement of the layer of loaded charge from the wall.
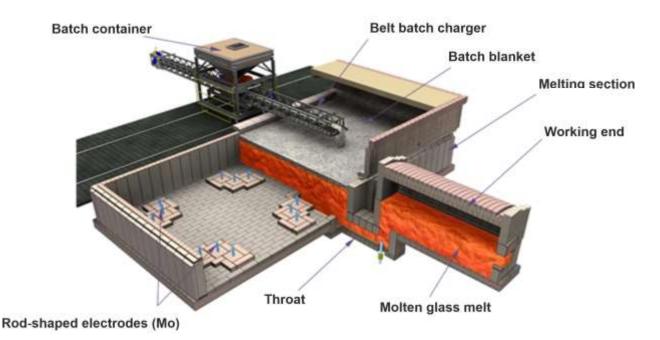
Fig. 7.22 Model of all-electric furnace with covered surface level, vertical electrodes (source: Toledo Engineering Co., Inc., TECO)

In the case of intensive all-electric GMU, the so-called Pouchet type, the energy is purposefully supplied, which leads to locally high temperatures, strong convective flows. The advantages are small size, low initial costs and short conversion time, while the disadvantages are high energy costs per tonne of glass and low service life. These furnaces are used for the production of textile and insulating glass fibres.

In order for the glass to be efficiently heated by conducting an electric current, glass melt must have a sufficient temperature. For this reason, it is necessary to convert glass into glass melt at the beginning of the melting, which is done either permanently or temporarily by installed gas burners.

7.6.3 Continuous GMUs with electric boosting

The use of electric boosting often consists in the additional installation of heating electrodes in the basin of the melting furnace. It follows that the introduction of an additional energy source does not necessarily require special interventions in the GMU structure, only the choice of location and intensity of boosting. The importance of installing an electric boosting, for example in container tanks, is due to a certain increase in output, but especially to the influence of the glass flow system in the furnace. An example of a barrier arrangement (molybdenum electrodes placed vertically in glass melt) is given in Fig. 7.23, showing the most frequently used variant of the implementation of electric boosting. It is the placement of electrodes both in the area of charge loading, where the additional energy supply is most efficient, and in the area of temperature maximum, where the thermal barrier is strengthened and although the return flow is intensified, it has a positive effect on glass homogeneity. Similarly, electric boosting can be used in the production of flat glass by the Float method, where the electrodes are most often placed in the area of significant cooling of the

melt by the charge to be loaded. It can be noted that the introduction of additional power directly into glass melt can positively affect the size of heat losses through the crown.
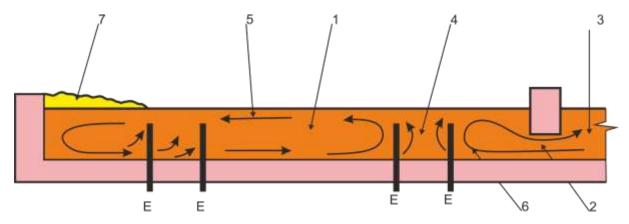

Fig. 7.23 Barrier arrangement of vertical electrodes to strengthen the thermal barrier: 1 - melting section, 2 - flow, 3 - working end, 4 - thermal barrier, 5 - convection, 6 - return current, 7 - charge, E - electrode

In general, the use of boosting electrodes can be divided by their location and function as follows:

- location in the space for loading the charge, which prevents the "freezing" of glass melt when increasing the amount of charge,
- location in the melting section, which supplies the necessary energy under the floating charge and accelerates its melting by heating from below,
- location in the fining zone (primary), which causes an upward flow of glass melt and an increase in temperature accelerates the fining,
- location in the working end of the tank, which helps to maintain a constant temperature.

7.7   Oxygen-enhanced combustion in glass melting

In recent years, the use of oxygen has become increasingly common in glass melting. Its main advantage is the complete or partial absence of nitrogen during combustion. It burns with oxygen alone. During air combustion, it is also heated to high temperatures and nitrogen, which is almost 80% in the air, reacts partially. Only 20%, which is the oxygen, is used for combustion. Heat from heated nitrogen is then obtained through regenerators and recuperators. The product of nitrogen reactions at high temperatures are nitrogen oxides (NO_x - noxy), which are harmful to health. Oxygen combustion can reduce operating costs, but also the costs of building GMU, thanks to the elimination of regenerators and recuperators. It also has an effect on radiation losses, when the exhaust in the oxygen furnace has smaller dimensions than in conventional air combustion furnaces. In general, burner ports have smaller dimensions and thus reduce radiation losses, savings are reported at the level of 4.2%. The flame is also more luminous, and therefore there is an improved heat transfer.

The disadvantage, or rather ancillary costs, is the oxygen itself, its transport or production. Oxygen is transported in liquid form for lower consumption, stored in tanks and gradually gasified

in evaporators. For larger volumes, it is produced directly at the place of consumption. Various methods are used for producing oxygen by selectively separating it from the air through molecular sieves.

Oxygen is used in practice for partial replacement of combustion air, so-called oxygen enrichment, or oxygen boosting or for complete replacement of air, which is called oxy-fuel heating.

Oxygen enrichment is based on the supply of oxygen to the burner ports and its injection by nozzles into the flame at higher oxygen velocities than the flame (3 to 6 times). Oxygen enrichment is performed for the following reasons:

- improvement of combustion and improvement of furnace operating conditions,
- increase of melting rate,
- reduction of the performance of electric boosting or its replacement.

Oxygen boosting also supplies fuel to the furnace space along with oxygen, and these are separate oxygen burners located in a suitable place in the furnace. The burners are often placed in the front of the furnace near the batch loading, where they supply energy locally. The heat transfer to the charge is very intense and brings its earlier sintering and "glazing", which reduces the rate of batch outlet and accelerates key reactions in the batch, melt formation and gas leakage from the charge. Another place is the location of the expected temperature maximum in the GMU to achieve the required flow of glass melt in the basin.

Oxygen boosting can be applied to common types of GMU. Recuperative furnaces are very suitable (mainly due to space) and also GMU for the production of FLOAT flat glass (to the places of loading the charge, then they accelerate the melting process, improve the quality or volumes of production). In regenerative End-port furnaces, oxygen burners are placed in places of maximum temperature, because they do not have this region clearly defined.

Oxygen-fuel melting completely replaces the combustion of fuel by air. The design of all-oxygen furnace, the so-called oxy-melter, is relatively simple, without regenerative chambers or recuperators. Due to the higher specific melting rates achieved, the oxygen furnace may be smaller than a conventional furnace for the same amount of glass melt. For this reason, it also has a smaller surface area and therefore less heat losses. The oxygen-fuel furnace works similarly to the Unit-Melter (Chapter 7.6.1). The burners are usually located in the side walls close above the glass surface and are offset relative to the burners on the opposite side. Savings by reducing fuel consumption range from 20 to 35% depending on the type of furnace. However, the increased costs are with the production of oxygen from the air. Some specific problems are also mentioned, such as foaming of glass melt in the fining area.

7.8   Structural elements of GMU

The main components of the tank furnace are:

- load-bearing structure and grate,
- melting basin and working ends,
- loading extensions,
- throat,

- peripheral masonry of the furnace superstructure,
- crown of the furnace or the working end,
- burner ports (for flame GMUs),
- steel tightening and binding structure,
- heat exchanger (for flame GMUs: regenerators and recuperators, Chapter 7.3.2),
- flue-gas ducts (for flame GMUs).

The **furnace basin** consists of a bottom and external walls. The inner walls of the basin are exposed to corrosive effects and permanent wear by constant contact with glass melt. The degree of wear of the individual blocks in the basin must be similar throughout the life of the basin. Replacement of individual blocks in the basin during operation is virtually excluded. The greatest wear occurs at the interface of the glass melt, the furnace atmosphere and the lining, i.e. at the surface level. Higher quality materials are used here. The requirements for the design of GMU are as follows:

- higher specific melting rates,
- increasing melting temperatures,
- improving the quality of produced glass,
- extending the service life of furnaces,
- ensuring maximum energy savings (using insulations).

The overall requirements lead to a "sandwich" arrangement of materials, as materials with high resistance to elevated temperature and glass melt do not have good thermal-insulation properties. On the contrary, materials with good thermal-insulation properties are not well resistant to higher temperatures. The construction of basins is thus composed of several layers, where the first layer - in contact with glass melt - is highly resistant, followed by a safety layer, then a sealing layer, then tank blocks and another is insulation.

In the case of two-compartment tanks for container and special glass, the melting and working ends are completely separated and for the supply of glass melt they are connected by a so-called **throat**, which is relatively narrow and is below the surface level of glass melt. Its purpose is to transport the glass melt from the melting to the working end, a large temperature difference between the melting and working ends is overcome on a relatively short path, the throat also prevents non-fined glass melt from flowing into the working end and also retains surface impurities from the glass surface.

In tanks for the production of flat glass, **floats** or **gates** may be placed on the surface. The purpose is to retain surface impurities from the surface of glass melt.

In the case of flame furnaces, the **superstructure of the furnace** creates a combustion space above the surface level of glass melt, which is closed by a crown, side and front walls, and allows access of fuel, combustion air and discharge of flue gases. The design of the shape, geometry and dimensions of this space is therefore crucial for the efficiency of the furnace combustion system. The **side walls of the superstructure** are built on so-called load-bearing blocks, which are placed on horizontal steel benches along the entire perimeter of the furnace. These fittings are characterized by their "nose", which aims to protect their load-bearing, steel profile. The basis for binding the superstructure of the furnace is primarily a **steel load-bearing structure** for load-bearing blocks, which is fixed to the furnace webs. The walls themselves are

then tied through their insulation by means of horizontal profiles, which are also screwed to the webs.

The **crowns** are used for closing the upper part of the melting or working end of the glass furnace and are also used on regenerative chambers. Arched crowns are used, which are constructed as a sector of a hollow cylinder. At both ends, they are supported on bases and are built as gravity, i.e. they hold their own weight.

The **burner ports** of regenerative furnaces (also called burner jets) connect the furnace space with the regenerative chamber and serve to supply preheated combustion air and in the opposite period to remove flue gases from the furnace. The burner ports are made of brick and they include burner fittings through which fuel is supplied.

7.9   GMU lining

Due to the high temperatures achieved during melting, it is necessary to use suitable refractory materials for the construction of GMU, which not only withstand these temperatures, but at the same time must withstand corrosion by glass melt. During the life of the melters, energy consumption increases by 2 - 4% per year due to their wear.

The range of refractory materials used for the construction of GMU is wide, the main materials used are only briefly mentioned below.

Dinas is a highly silica refractory material with a minimum content of SiO_2 of 93%. Accompanying additives are mainly oxides CaO and Al_2O_3. The highest temperature of the use of dinas is 1550°C to 1590°C.

Aluminosilicate refractory materials contain two basic oxides, Al_2O_3 and SiO_2, in different ratios. According to the content of Al_2O_3, we can divide them into two basic groups:

a) *Fireclay materials* with the content of Al_2O_3 from 10% to 45% (these are further divided into acidic materials with the content of Al_2O_3 below 30% and normal materials with the content of 30% to 45% Al_2O_3). They have good all important properties in terms of heat resistance, but none of them is excellent. It is a basic, mass-produced refractory material with the largest range of standardized shaped elements with a usability up to a maximum temperature of 1370°C.

b) *High-aluminium materials* with the content of Al_2O_3 above 45%. These include corundum materials with the content of Al_2O_3 above 90%.

Basic refractory materials are characterized by the presence of MgO in the range from 45% to 95% and Cr_2O_3, the content of which ranges from 0 to 35%. They are characterized by considerable resistance to the effects of alkali, high heat capacity and high heat resistance (1600°C to 1640**°**C).

Electro-melted refractory materials are characterized by the technology of production by melt casting, which is prepared in electric arc furnaces, the chemical composition is similar to ceramic materials, i.e. from pure silicate, through aluminosilicate with the addition of zirconium or chromium oxide, to pure aluminium materials. The most used is the group of so-called *corundum-baddeleyite materials* with the content of ZrO_2 from 30% to 40%. Materials with the content of

about 30% ZrO_2 and 30% Cr_2O_3 resist the corrosive effects of glass melt even better. They are used on heavily exposed areas of container tanks melting coloured glass melt (they are not suitable for crystal - they stain glass melt).

The possibilities of using some refractory materials in the construction of glass melting units are given on several typical examples.

Superstructure brickwork

In pot furnaces, it is the brickwork above the hearth level. In the past, dinas material was almost exclusively used; today it is replaced by highly aluminium materials, in particular in furnaces with a low number of pots.

The glass tanks have brickwork above the level of the upper edge of the basin. The most common is still the use of dinas material. For heavily loaded tanks and where oxygen-enhanced combustion is used, transition is made to corundum-baddeleyite materials.

Lining of regenerators, fittings for ceramic recuperators

Pot furnaces use almost exclusively fireclay materials. For tanks, fireclay, high-aluminium or even magnesite masonry is used for the side brickwork and crown. The crowns can also be made of dinas. The lining is usually made of fireclay, high-aluminium, magnesite or corundum-baddeleyite material.

Brick backings

In modern designs of glass furnaces, the so-called sandwich, i.e. multilayer, brickwork is used. The inner walls are made of durable, compact material, to which a multi-layer brick backing is attached. Multiple layers are chosen primarily to optimize the use of insulation materials, as thermal conductivity and temperature of use are usually conflicting variables. It is necessary to take into account the price of individual materials.

Direct contact with glass melt

The direct contact of the refractory material with the glass melt takes place in glass tank furnaces in melting and working basins and feeding forehearths. The most commonly used materials for these parts are electro-melted blocks, cast AZS materials on corundum-deldeliteite basis for melting basins, and corundum materials are also used for working basins and feeding forehearths. Chrome ceramic blocks are used in the melting of glass for the production of glass fibre. Glass melting pots are made of fireclay.

Substructure brickwork

The brickwork of the substructure means linings to the level of the hearth of pot furnaces and brickwork under the basins of glass tanks. These linings are characterized mainly by fireclay material, which is usually supplemented with highly aluminium materials in exposed places.

Refractory materials are still being used in larger dimensions, they are more compact, more durable and more expensive. The world's glass industry consumes about 400,000 tons of refractory materials a year, of which about one third is in Europe. The largest manufacturer is the French company SEPFRO with its main plant in Le Pontet, France, and nine other plants around the world.

Cast palisade blocks up to 2.5 meters high are produced, new ones are cast blocks based on 94% ZrO_2. Today, electro-fused refractory materials predominate slightly over ceramic materials. A novelty here is a ceramic bonded block with 95% ZrO_2 for the bottoms of tanks for lead glass and isostatically pressed materials with 96% Cr_2O_3. Thanks to better refractory materials, their specific consumption has fallen about four times since 1960, and it was 3 to 5 kg per tonne of glass melt in 2000.

7.10 Control systems, burners

From the point of view of modern operation of GMU, these devices are necessary. These include

- burners in which flame furnaces mix fuel with air (or oxygen) and burn the mixture,
- fittings; a system of beams and rods reinforcing the furnace structure,
- GMU control systems (fuel supply, composition of the furnace atmosphere, level indicators with a link to the control of the function of batch chargers, other necessary sensors enabling feedback to the relevant regulation systems),
- regenerators,
- recuperators.

The dominant fuel for the combustion systems of current furnaces is natural gas. The gas supply for a typical natural gas heating system is through a gas line that includes the following equipment:

- precise flow measurement,
- pressure regulator for regulating the gas pressure to the required value,
- flow valve for regulating the gas supply to the burners,
- reversing valves for combustion control of individual sides,
- safety shut-off valve for emergency gas shut-off.

The location of burners in the furnace depends mainly on the type and design of the furnace. Theoretically, the burners can be connected in different parts of the furnace structure, but most often they are connected directly to the port (to its sides, bottoms, crowns), often also below the port plate (called under-port arrangement), less often they are connected above the port (above-port arrangement), Fig. 7.24. The burners are made of metal and are structurally diverse with regard to the type of fuel, the type and design of the furnace, and the use of waste heat (regenerative, recuperative furnaces).
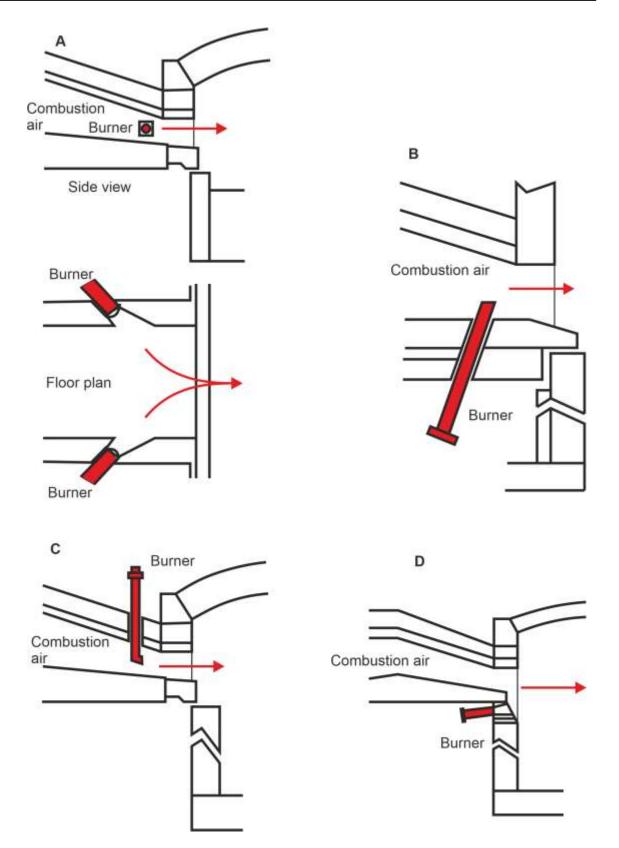
Fig. 7.24 Burner placement options: A - in the side walls of the ports, B - in the bottom of the port, C - in the crown of the port, D - under the port

7.11 Special melting equipment

The design of furnaces intended for melting special glasses differs fundamentally from the design of pot and tank furnaces, which were discussed in the previous paragraphs. The main causes are in particular the following aspects:

- special chemical composition of glass melt,
- significant corrosion of equipment,
- often very high melting temperatures,
- sometimes the need for melting under special conditions (vacuum, special materials of melting equipment, etc.).

These glasses include, for example, special optical glasses (with a high content of PbO), quartz glasses, highly corrosive glasses and others. Melting processes of such glasses are often discontinuous and the capacity of melting equipment is often relatively low. Selected examples of these systems will be given below.

7.11.1 Crucible medium- and high-frequency furnaces

In these furnaces, optical glass or special glasses for electronics and microelectronics are particularly melted under special conditions. The crucibles used are platinum, platinum-rhodium, ceramic, quartz crucibles or are melted in a so-called cold crucible. A special example is the microwave glass furnace, which has been under development since the end of the 20th century. The principle consists in generating energy using magnetrons and in absorbing the generated energy directly by the charge. The current conditions represent a dimension of the studio furnace type with the possibility of using 10 kg of charge at a melting time of 2 to 3 hours.

7.11.2 Melting of quartz glass with graphite electrodes

In this way, opaque quartz glass is produced from specifically treated quartz sand (KS 20/13, Chapter 4.3.1). The melting process takes place in metal moulds, the working procedure consists in assembling a furnace with one or more graphite electrodes, filling the mould with sand, melting, ejecting the electrodes from the viscous melt and pressing the desired shape. In the case of blocks, the cavities after the electrodes are also closed during moulding. After annealing (which does not require a annealing furnace, because the material, glass SiO_2, has a very low coefficient of linear thermal expansion), the semi-finished products are machined (cutting, grinding) and in the case of blocks, they can be used as lining of melting furnaces for melting borosilicate glasses.

7.11.3 High- and medium-frequency melting of clear quartz glass

The melting process takes place under vacuum in a graphite crucible with a content of about 10 kg of charge, the raw material being crushed rock crystal or modified vein quartz. The device is shown in Fig. 7.25. The graphite crucible is placed in a cylindrical furnace, which consists of a large-diameter tube made of opaque quartz, the space between the crucible and the inner wall of the furnace is filled with insulating magnesite chips. After closing the lid, air is sucked out of the furnace space and melting takes place under vacuum, electric energy is supplied by a water-cooled inductor located outside the furnace (induction takes place in the wall of a conductive graphite crucible, which heats up and transfers heat to the charge). The melting process takes place at a temperature of about 2000°C, at which the melt remains highly viscous. After 2 to 3 hours, it is

possible to pull tubes or rods through the hole in the bottom of the crucible, possibly to let the block to cool down and then to process it mechanically.
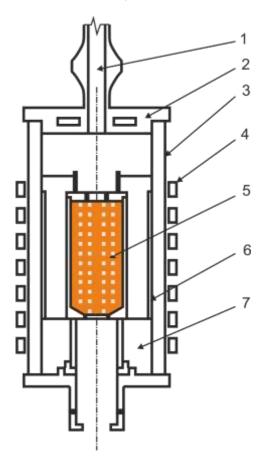

Fig. 7.25 Melting of quartz glass in a graphite crucible: 1 - exhaustion, 2 - top cover, 3 - furnace shell made of opaque quartz, 4 - inductor, 5 - melt, 6 - thermal insulation, 7 - magnesite chips

8   Feeding of glass melt

The transition between the melting furnace and the forming operation is the feeding of glass melt. In manual production, the gob (glass charge) is usually taken on a glass-blowing pipe. Machine production requires a higher feeding frequency and accuracy, which can only be ensured by machine feeding systems. According to the production technology, we distinguish between spout feeders, which are usually part of the forming technology (the glass melt is fed continuously) and gob feeders, which form a drop (in glass terminology called "gob" or "bit") from the collected glass, Fig. 8.1.
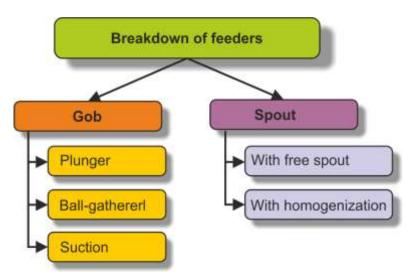
Fig. 8.1 Breakdown of feeders

The gob/spout requirements are as follows:

- same weight (for gob feeder)/same volume of outflowing glass melt (for spout feeders),
- appropriate shape/appropriate cross-section of the glass strip,
- appropriate viscosity (temperature) for the given forming,
- temperature homogeneity.

In the case of two-chamber furnaces, it follows the working end, in which the temperature of glass melt is reduced and the glass melt is thermally stabilized (cooled down) and the glass melt is prepared for feeding and subsequent forming. Stirrers, burners and a cooling system can be placed in the working end. From the working end of the furnace, the glass melt is often distributed through feeder forehearths to the individual places where the forming machines are located. The feeders themselves then follow.

Feeder have different principles and designs. They often consist of a forehearth and a feeder head.

8.1 Feeder forehearths

The purpose of forehearths is to distribute the glass melt to the individual forming machines and to carry out the final treatment of glass melt (ensuring thermal and chemical homogeneity, purity, suitable feeding temperatures). The forehearths themselves can replace the working ends of melting furnaces and are then connected directly to the melting section of the GMU. They can be of different numbers on the tank and design, Fig. 8.2.
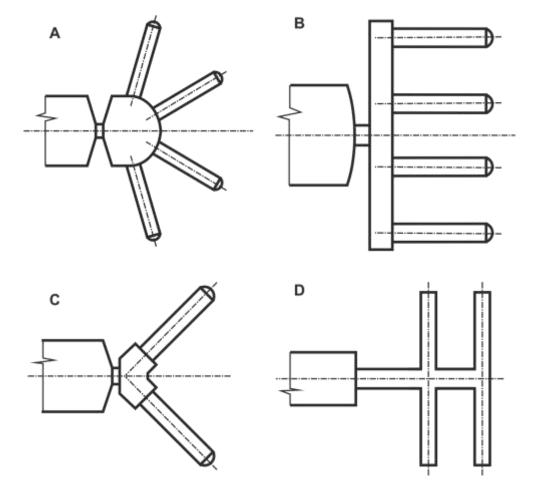

Fig. 8.2 Diagram of the working end of GMU for machine production: A - classic design, B - with minimized working end, C - in the form of a distribution forehearth, D - in the form of an H-shaped forehearth for single-stage drawing of fibres

The feeder forehearth usually consists of cooling and conditioning zones, Fig. 8.3. The difference in the cross-section of the two parts is shown in Fig. 8.4 and Fig. 8.5. The heating of the forehearth can be realized by natural gas burners, electric resistance coils (indirect electric heating), by means of electrodes (passage of electric current through the glass melt) or in combination. An important element of the forehearths is also the cooling system, which is usually designed as a system of ventilation chambers (air cooling). The temperature homogeneity of glass melt is highly dependent on the method of boosting and the method of cooling.
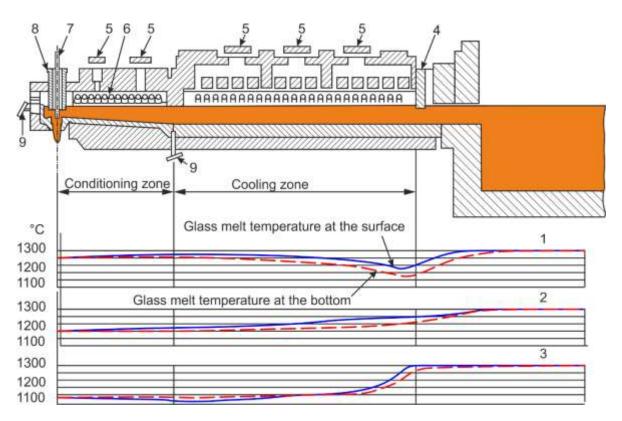
Fig. 8.3 Schematic longitudinal section of a conventional Hartford forehearth with a plot of temperatures along the forehearth: 1 - temperature distribution at light gob, 2 - at medium-heavy gob, 3 - at heavy gob, 4 - barrier block, 5 - ventilation blocks, 6 - gas burners, 7 - feeder plunger, 8 - tube, 9 - immersion thermocouples
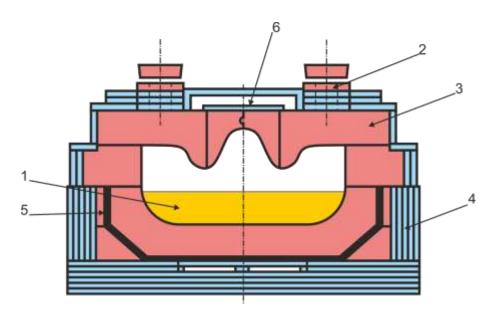

Fig. 8.4 Cooling zone of the Emhart forehearth: 1 - glass melt, 2 - vent holes, 3 - lining, 4 - fibrous insulation, 5 - expansion gap, 6 - upper cooling profile
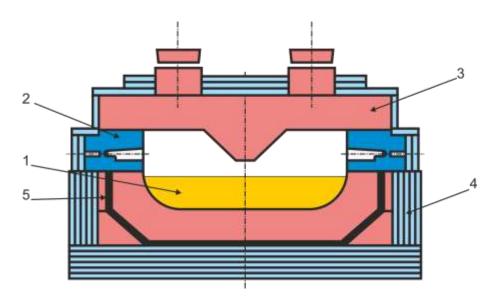
Fig. 8.5 Conditioning zone of the Emhart forehearth: 1 - glass melt, 2 - burner, 3 - lining, 4 - fibrous insulation, 5 - expansion gap

Fig. 8.3 shows the forehearth with boosting of the glass level by gas burners and cooling by air flowing across the longitudinal axis of the forehearth. The forehearth connects to the working end of the GMU, passes behind the barrier block into the cooling zone and further into the conditioning zone. The cross-section and the height of the glass level do not change substantially in the cooling zone, but in the conditioning zone the forehearth narrows as required and the depth of glass melt in the forehearth decreases or increases depending on the circumstances. In the conditioning zone, the glass melt is always boosted. In the cooling zone, it cools down when feeding large gobs and heats up when feeding smaller gobs.

In order to obtain a high homogeneity of glass melt, stirrers are introduced into the forehearths, Fig. 8.6. They are usually located in the cooling zone of the forehearth, but sometimes also in the conditioning zone as needed. These are usually propeller or screw stirrers.
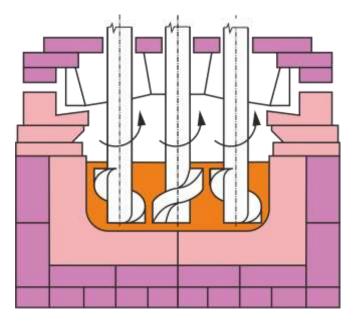

Fig. 8.6 Stirrer in the cooling zone of the forehearth

8.2   Gob feeders

These feeders are used for feeding individual doses into forming machines. Gob feeders create a gob of the required parameters such as weight, shape, viscosity, quality and number. By setting the feeders, these parameters can be changed to a certain extent. The basic types of gob feeders are: plunger feeder, ball-gatherer feeder and suction feeder.

8.2.1   Plunger feeder

The plunger feeder (also called mechanical) consists of a forehearth (Chapter 8.1) and a feeder head (Fig. 8.7). Shears are also an integral part. In most cases, the gob is discharged by means of deflection forehearths (or a system of forehearths) into moulds where it is formed.

The process of gob formation takes place in the feeder head, in which a plunger moves vertically, which pushes the glass melt through the opening of the orifice ring. The gob, which is extruded through the opening, is separated by shears and transported to the forming device. The plunger is located centrally inside the continuously rotating tube, which performs the final homogenization of glass melt. The weight of the gob is in the range of 14 to 1420 g at a frequency of 1 to 220 (up to 300 as reported in the technical literature) gobs per minute. In case of a multi-gob, the number of gobs increases and for a four-gob you can reach up to 900 gobs per minute. The shape of the gob and its weight is determined primarily by the shape, movement and position of the plunger in the initial and final phases, the position of the rotating tube, the diameter of the orifice ring and of course the viscosity of glass melt, the glass level and other parameters. The shape and weight of the gob is important for the correct shape and quality of the subsequently formed glass product. It is stated that the shape of the gob should be close to the shape of the product, i.e. narrow and tall products, such as bottles, which require a longer and slimmer gob. Smaller and wider products require a shorter and wider gob.
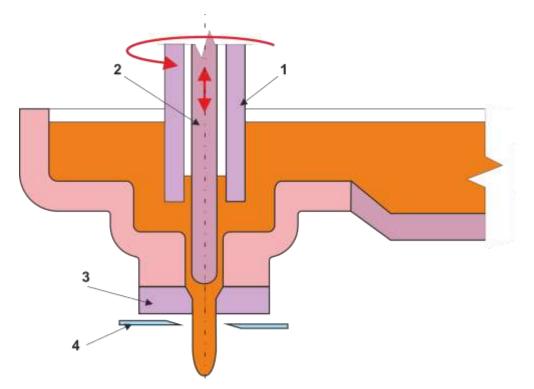

Fig. 8.7 Plunger feeder diagram: 1 - rotating tube, 2 - plunger, 3 - orifice ring, 4 - shears

The mechanism for driving the plunger through the cam is shown in Fig. 8.8. As the cam rotates, the rotary motion is converted into a sliding motion via a lever and the plunger thus performs the prescribed movement in the vertical direction. The movement of the plunger can be changed by means of adjusting screws, or by replacing the cam.

In addition to the drive of the plunger via the cam, the drive from the pneumatic cylinder is used. Currently, the trend is to use servomechanisms or a combination of a servomechanism with a mechanical cam. The use of servomechanisms allows to change the gob parameters during production. For example, in the production of container glass, several sizes of bottles can be produced on one line.
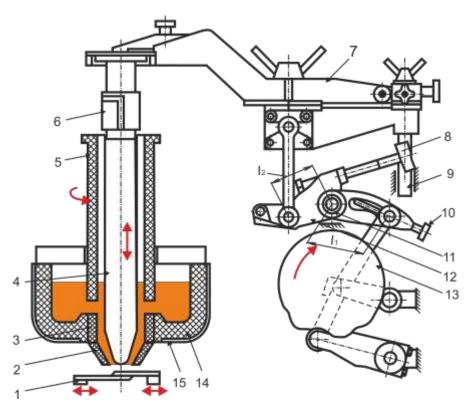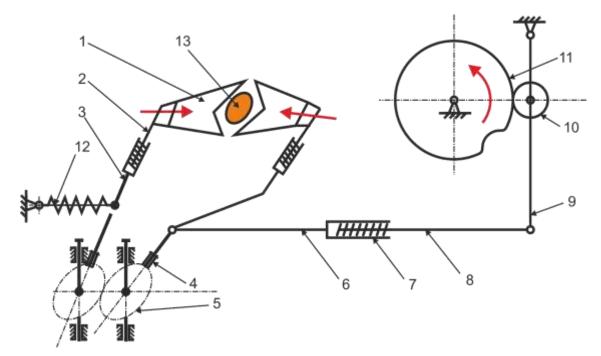

Fig. 8.8 Plunger feeder mechanism, plunger drive via cam: 1 - shears, 2 - orifice ring, 3 - cup, 4 - plunger, 5 - rotating tube, 6 - clutch, 7 - arm, 8, 10 - adjusting screw, 9 - guide, 11 - bearing, 12 - lever, 13 - cam, 14 - feeder head, 15 - steel casing

An important part of this type of feeder are shears, which separate the gob of glass melt. The basic division is into lever and linear shears. The number of cut gobs can be from one to four, and the arrangement of the shears, which must cut the given number under the same conditions for each of the gobs, corresponds accordingly.

The diagram of operation of machine lever shears with cam drive is shown in Fig. 8.9. The cams on the scissor drive are interchangeable, their shape depends on the number of cuts per minute and the weight of the gob being cut. The cam drive is synchronized with the drive for feeder and forming machine. More modern shears are equipped with a servo drive, which allows operational interventions in production and a very fast change of the cutting cycle; an example of shears is shown in Fig. 8.10. The advantage of lever shears is their simplicity and therefore the

price. On the contrary, the disadvantage is the different cutting conditions when cutting the multi-gob.

Fig. 8.9 Simplified kinematic diagram of lever shears with cam drive: 1 - knife 2 - arm, 3 - lever, 4 - arm holder, 5 - gearing, 6 - rod, 7 - adjusting clutch, 8 - rod, 9 - lever, 10 - roller, 11 - cam, 12 - spring, 13 - a gob of glass melt

Fig. 8.10 Lever shears with servo drive (source: Walter)

Linear shears are mainly used for multi-gobs, as they maintain the same geometric and dynamic conditions of the cut of the gob for all simultaneously cut gobs. The model of linear shears is shown in Fig. 8.11. This type of shears is significantly more expensive compared to lever shears.
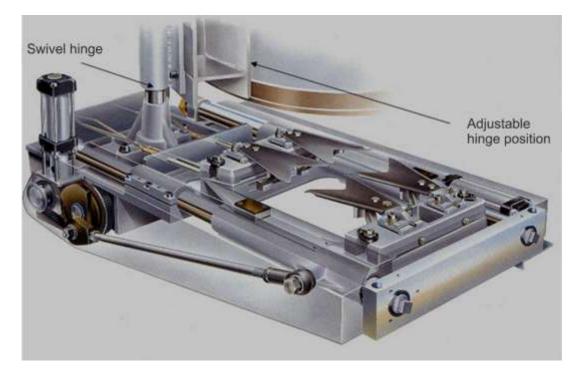

Fig. 8.11 View of linear shears with servo drive (source: BH-F Ltd)

The knives of shearing machine are significantly thermally stressed, as the gob of glass melt has a temperature of 1,000°C to 1,250°C at the cutting point, depending on the type of glass melt and the size of gob. During the cutting of the gob, the knife edge is intensively heated and then intensively cooled with water mist or oil emulsion.

8.2.2 Ball-gatherer feeder

The ball-gatherer (hammer) feeder is most often used for feeding glass melt into multi-position presses. The diagram is shown in Fig. 8.12 and shows that this type of feeder very clearly simulates the activity of a glassmaker during manual feeding using a glass-blowing pipe. The function is that the feeding rod with the gathering feeder ball enters the furnace, is partially immersed and collects the glass melt by rotation. Then it rises above the surface level, the gob is separated by rotation and moved above the mould, where it falls down after separation by shears. The shears are synchronized with the feeder, are often lever-operated and have a similar design to the plunger feeder. The function of the feeder is also synchronized with another follow-up device (forming machine). The weight of the gob ranges from 100 to 6,000 g, the frequency even more than 12 gobs per minute. The size of the gob is mainly affected by the replacement of the ball head. The gob has a higher temperature compared to a mechanical feeder, as it is not cooled by the orifice ring and the deflection forehearth.
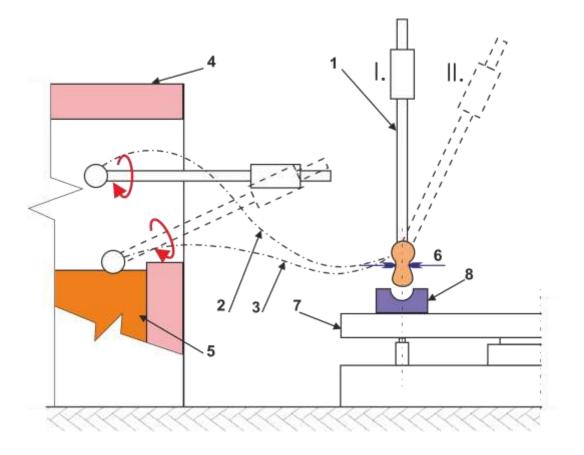
Fig. 8.12 Ball-gatherer feeder diagram: 1 - feeding rod with head, 2 and 3 - trajectory of the feeding head, 4 - working end of the furnace, 5 - glass melt, 6 - shears, 7 - press table with mould, 8 – mould

The ball-gatherer feeder is preferably used where part of the production is automated and part remains manual. The construction of a ball-gatherer feeder is often designed by means of a four- or six-axis robot, which can be attached to the floor (column design, Fig. 8.13) or can be suspended on the ceiling (suspended design).

8.2.3 Suction feeder

This type of feeder (Fig. 8.14) is used for larger gobs. The principle of operation is that the rotating arm carrying the suction head enters the working end of the furnace, lowers and the glass melt is sucked in under vacuum. Then the suction head is lifted, the knife forming the lid at the same time separates the glass melt, the suction head comes out of the furnace, turns upwards through the opening and the gob of glass melt is removed by means of a hand tool. All thermally stressed parts of the feeder are water cooled. The weight of the gob can be affected by replacement of the suction head, it ranges from 1,000 to 9,000 g, the frequency is 4 - 6 doses per minute. It is used in manual production, where the gob is taken over by a glassmaker, who continues to work with it. The gob can also be taken over by the robot arm on the automatic line and transferred, for example, to the press.

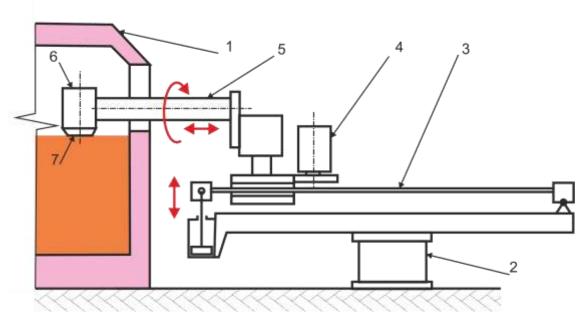Fig. 8.13 Example of a ball-gatherer feeder (source: NOVAXION)

Fig. 8.14 Suction feeder diagram: 1 - melting section of the furnace, 2 - frame, 3 - guide rods, 4 - electric motor, 5 - rotating arm, 6 - suction head, 7 - hinged lid

8.3   Spout feeders

Spout feeders can be divided into continuous spouts and platinum homogenizers.

8.3.1   Continuous spouts

These are spouts of strips of circular, annular or rectangular cross-section, which are used in the continuous production of rods, tubes, fibres, pressing of jewellery components and more. It is also possible to include the discharge of glass melt in the form of a strip on a tin bath in the production of flat glass using the FLOAT technology, which connects to the discharge channel. The regulation of the amount of glass melt at the inlet to the tin bath is performed by the front gate (Chapter 9.6.3). In the case of continuous discharge, e.g. in the production of jewellery components, the discharge of glass melt takes place from an opening of circular diameter and the amount of glass melt is regulated by a stopper (Chapter 9.3.3). In the case of the production of tubes by the VELLO system, the cross-section of glass melt has the shape of a ring. The inner cavity is formed by a hollow mandrel with a fitting at the end (hollow plunger), through which air is supplied under a slight pressure. The glass melt is homogenized similarly to the plunger feeder by means of a rotating tube (Chapter 9.7.3). Similarly, the feeding of glass melt is solved in the production of seed beads (rocaille) (Chapter 9.7.5).

8.3.2   Platinum homogenizers

Platinum homogenizers are connected to the end part of the forehearth and solve, in addition to the stirrers in a separate forehearth of the feeder, the final chemical and thermal homogeneity of glass melt for its subsequent forming; the diagram is shown in Fig. 8.15. Platinum homogenizers give a glass melt of excellent quality, which has a appropriate temperature gradient for forming, i.e. the higher temperature is on the surface of the outflowing strip and the lower temperature is in its centre. Homogenizers are commonly used in the production of glass jewellery components, optical and domestic glass. The casing of the platinum homogenizer is usually a sheet made of a platinum alloy and an additive of 20% rhodium. The glass melt can be boosted either by heating resistance coils built into electric heaters or by KANTHAL-SUPER heating loops, or by direct passage of a low-voltage electric current through the platinum casing of the homogenizer.
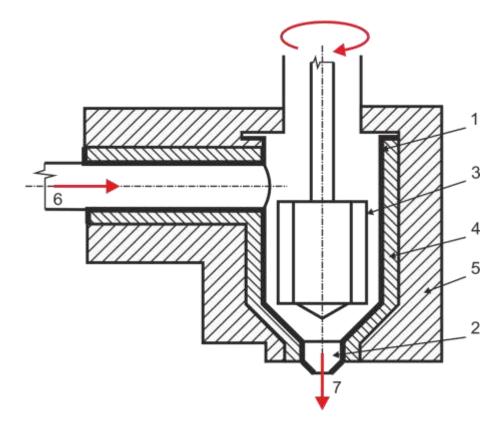
Fig. 8.15 Diagram of platinum homogenizer (platinum tube): 1 - platinum homogenizer casing, 2 - discharge attachment, 3 - rotating blade stirrer, 4 - electric resistance heating element, 5 - lining, 6 - glass inflow from the forehearth, 7 - glass strip discharge from the homogenizer

9 Forming of glass melt

The first mechanization of glass production occurred at the very beginning of the industrial revolution, but the main development of glass machines did not occur until after 1850. The aim of mechanization was initially to increase the volume of production. With the development of the industrial revolution, the aspect of reducing the unit price of a product also became important. Over time, whole lines with high acquisition costs have been developed, which are able to produce a large number of products. However, the acquisition price is budgeted for a large number of products and the unit price for the product is therefore relatively low.

The chapter is structured to include processes and machinery for forming all major commodities of glass products. The introduction presents the historical connections in the development of glass forming technologies. Finally, a subchapter is attached dealing with materials and principles of construction of glass moulds, which can be encountered in individual forming machines, with a few exceptions.

9.1 Development of forming technologies in historical context

The basic production tool was a glass-blowing pipe, which was used for the production of luxury, domestic and container glass, as well as for the production of flat glass. It is assumed that the glass-blowing pipe was invented in the 1st century BC. The basic production processes with simple auxiliary glass tool were mastered around the year 50 AD. Pontil rods and feeders have been known since the 12th century, including basic tools, i.e. mainly various types of tweezers, shears, pliers, blocks, taglias and press forming elements.

Czech glassmaking has been associated with the term Czech crystal since the last decade of the 17th century and during the 18th century, from which *luxury goods* were made. The production was manual using various tools. This situation lasted for a relatively long time. In the case of cheaper pressed glass, semi-automatic presses of a completely simple construction with a manually rotated carousel-type table with 6 to 9 moulds (positions) were introduced after 1900. Pressing was performed with a pneumatic cylinder, but the glass feeding was manual. Later, gradually introduced automatic presses used the newly developed automatic glass feeders and the rotation of the table was also automatic.

The complex automation of the production of *domestic glass* can be encountered in the 1970s. Following the foreign model, the first automatic line (LINKUŽ) in Czechoslovakia for the automatic production of domestic glass (stemware and tumblers) was put into operation in Nový Bor in 1972. More automatic lines were gradually added to the plant; since 1978, one line has also been in operation in Světlá nad Sázavou (later another for lead crystal, such as the LAURA assembly). A novelty was the injection pressing machines installed for the first time in 1975. The hand-made production of drinking glasses persisted until the end of socialism, but its volume decreased.

In the 1970s and 1980s, new technologies were also applied in the production of pressed glass, such as ringless pressing, centrifugal casting, finishing of preformed objects by free fall or hanging, and press-blowing again gained in importance. Unlike other types of Czech domestic and decorative glass, pressed glass was more significantly used on the domestic market.

The dominance of Czech crystal pushed the production of **container glass** (ordinary bottles) into the background, because it was more advantageous for glassworks to produce luxury hollow glass. The production of container glass thus faded in our country. It was not until the turn of the 18th and 19th centuries when the situation in the field of container glass began to change. Interest in container glass increased gradually, intended in particular for artificial and natural mineral waters and probably also for wine. In the first half of the 19th century, technical innovations appeared in the world in the production of container glass, which simplified and streamlined the work of glassmakers. These were various presses, step-on glass moulds - so-called dummies, when the glassmaker controls the mould by stepping-on, thus speeding up work and reducing the number of helpers, as well as bottle pliers for handling of a semi-finished product in bottle production, roller neck pliers for forming the bottle neck, and three- and four-part metal moulds (cast iron) and more began to be used more. This made it possible to rationalize and reduce the costs of production. Nevertheless, one glassmaker and one carrier then produced 400 to 500 bottles in 8 hours. In 1886, the first semi-automatic device, the so-called Ashley's machine, was put into operation in England. Ashley discovered the forming principle, which is still used by the most modern bottling machines. Instead of one mould used in hand production, this machine had three moulds: blank (which forms the blank), neck (which forms the neck of the container) and finish (in which the blank is formed into the final form of glass container) moulds, Chapter 9.4. Perhaps the most significant invention was the feeding of a gob into the blank mould (Chapter 8.2) and the inversion of the front shape. Again, these inventions are used in modern sectional (in-line) machines to this day, Chapter 9.4.3.

The real revolution in container glass came with the introduction of production on Owens suction-and-blow machines. This machine began to be manufactured for the first time in 1905 after several years of intensive and demanding development in the USA. The capacity of one machine was between 1000 and 1500 bottles per hour between the wars, and even large producers of container glass had a problem selling such volumes on the market at that time. This machine was the beginning of the end of small glassworks focused on container glass and significantly contributed to the full automation of glass production. The service life of Owens machines and their timeless design are also remarkable. In Czechoslovakia, the last of the machines was put out of service in 1982. The success of the Owens machine was followed by other types of machines, such as Roirant, Lagena, AMCO, Pöting. These machines usually had less capacity than the Owens machine, which was often taken as an advantage.

An important act of the post-war period in Czechoslovakia in the field of container glass was the introduction of Hartford IS sectional machines (IS - individual section). It was developed in the USA around 1925. The decision to develop and manufacture its own individual section AL machine led to a decisive step in the development of Czechoslovak production of container glass. A design office was established in Sklostroj Turnov and the company was appropriately expanded. Knowledge of imported Hartford IS machines helped to develop the world-class machine. The Sklostroj company performed overhauls and replacements of spare parts on these machines for many years. The prototype of the six-section AL machine was tested in 1961 and put into operation in Czechoslovak glassworks in 1962.

The Heye company has developed a narrow-neck press-blowing technology for container glass. This made it possible to reduce the weight of the bottles by more than 40%. The technology was also adapted to individual section machines and used under license for machines manufactured in Sklostroj Turnov.

In the case of *flat glass*, the so-called spun glass (target glass) was first produced, which were wheels with a diameter of 100 to 150 mm glazed in lead bars. Until the 17th century, it belonged to the common assortment of products of forest smelters in the territory of today's Czech Republic. Since the 14th century, flat glass has been produced with an improved technology, the so-called crown glass (or also moon glass). At the turn of the 14th and 15th centuries, the technology of producing flat glass from cylinders was also developed - broad sheet glass – flattening of blown cylinders. All the aforementioned technologies were based on the use of a glass-blowing pipe and can be referred to as hand production.

During the industrial revolution, technologies from the previous period were preserved, especially production from rolls. Although the production was rationalized, it was mainly the organization of work, the change of furnace heating and partial changes enabling the production of larger rolls and thus larger dimensions of glass sheets.

After 1900, the development first focused on mechanization of the production of flat glass from rolls. At the beginning of the 20th century, the English company, Pilkington Brothers, solved the forming of sheets from rolls up to 4 m long and 0.6 m in diameter blown with compressed air and American Window Glass Co., known in our country as Oppermann - Lubbers, solved a similar technology with rolls up to 13.4 m long and 0.6 - 1 m in diameter blown by compressed air in 1903. Despite the incomparably higher production of glass compared to hand technology, this technology finally failed to compete with technology based on drawing glass from the surface of glass melt. In the territory of today's Czech Republic, the Fourcault technology[11] was used, which is based on the vertical drawing of flat glass (endless band) from the surface of glass melt through the debiteuse, Chapter 9.6.1.1. The first industrial production with the use of this technology was started in the Dampremy glassworks in 1916, and commercial production was started in Hostomice near Bílina in Czechoslovakia in 1919. In addition to the Fourcault technology, other similar technologies have been used around the world, such as the American Colburn system (also called Libbey-Owens) or the Pittsburgh technology.

Although the technology of drawing flat glass from the surface of glass melt gradually replaced hand production, this technology was gradually replaced by a more progressive technology in the second half of the 20th century, which enabled the production of flat glass in higher quality. The new technology was the floating of glass on a tin bath, the so-called FLOAT technology, Chapter 9.6.3. The first mention of the use of the principle of glass floating technology on the surface of melted metal dates back to the mid-19th century (Henry Bessemer, British patent from 1848). However, key problems of the technology, such as its limitation to a thickness of about 6 mm or an inert atmosphere above the tin bath and the reliable operation of the technology, were resolved not earlier than by Pilkington Brothers company between 1953 and 1957. Subsequently, the technology was profitable not earlier than after 1960. Although Czech glassmakers did not contribute to the development of FLOAT technology, they were the first in the so-called Soviet bloc to acquire revolutionary technology and began to produce high-quality flat glass in 1969. At that time, the capacity of this line was 280 tons per day (t/24 hours). In 1988, the second Float II line was put into operation with a capacity of 700 t/24 hours.

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[11] The author of the principle is Emil Gobbe, but history called the technology after Fourcault, who improved and brought the technology to industrial use.

Development in the ***components of glass jewellery*** first began with imitations of real stones and pearls. Already in the Middle Ages, in addition to the demand for real stones, there was also a demand for cheaper imitation stones, and the Venetians came up with these imitations at the beginning of the 16th century. The glass stones were first ground from pieces created by breaking high-gloss melted high-lead glass, the so-called composition. An innovation that can be referred to as the beginning of the rationalization of jewellery production was the casting of semi-finished products for imitations in clay moulds. The shape of the resulting semi-finished product could thus be adapted to the customer's requirements and subsequent finishing operations. In the case of bead production, manual wire winding was also widely used in addition to blowing technology. In the second half of the 18th century, the production process was simplified. A short rod was drawn from the composite glass and cooled as a semi-finished product (the first form of a later widely used pressing rod). The glassmaker held the rod by one end and heated the other end in the furnace. The heated end was formed with pliers. This creates pressing technology. The resulting semi-finished product was then finally ground to the desired shape and did not have to undergo a complicated grinding, which not only accelerated production, but also reduced price due to excessive production.

A pressed button was invented by an unknown manufacturer in 1829. It was a very important technological innovation, leading to a reduction in price. Innovation has spread rapidly. In the 1960s, buttons were the main export item of the jewellery industry in the Jablonec region.

There was an effort to mechanize the production between 1900 and 1945. The oldest automatic machine for pressing non-tapped goods is a rotary presser (Chapter 9.3.3), which has been known since the 1920s. To this day, chaton raw material[12] is produced in this highly productive way. However, despite several patents, the fundamental problem of reliable mechanized production of beads (perforated products) has not been solved. The mechanization of the production of this assortment appeared abroad only sporadically.

After 1946, the production of beads was successfully gradually mechanized and subsequently automated. The first machine was the Kopal's presser (Chapter 9.3.3), where, unlike manual pressing, lever gears are replaced by cam gears and are driven by an electric motor via belt gears. Automatic pressing was made possible by the commissioning of the Matur's presser (Chapter 9.3.3), which is still one of the most commonly used devices today, mainly due to its flexibility, relatively high performance, low production costs and productivity.

In the 1970s, excess glass-free technologies were developed for the automated production of jewellery, where the semi-finished products are not coupled by glass melt, so-called excess glass, after forming. This saves the costs of glass melting and the costs associated with the subsequent removal of the excess glasss.

9.2   Basic principles of glass forming

In general, the basic rule applies to all forming technologies. When forming the glass, the gob/spout (glass charge) must be given the desired shape in a suitable manner, i.e. the gob/spout must have a sufficiently low viscosity to be well formed. The viscosity of conventional technologies

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[12] Raw material for the production of chatons, which are the most produced jewellery stones.

is in the range of 10^2 to 10^7 Pa·s (forming area, Chapter 3.1). After obtaining the required shape, on the other hand, the requirement is the opposite, i.e. to increase the viscosity so that the shape is fixed and allows the product to be removed without deformation, i.e. below the deformation temperature of 10^{10} Pa·s, M_g (dilatometric softening point). However, only the surface layers of the product have an increased viscosity after forming, and it is necessary to take into account the heating of these layers from the inside. The viscosity of the surface layer could decrease due to heating, resulting in deformation of the product during handling, so the product must be cooled down more. The deformation area is approximately in the range of 10^9 to $10^{11.5}$ Pa·s.

As follows from the above, the basic property that must be respected is the viscosity of glass melt and its temperature dependence (Chapter 3.1). The viscosity of glass melt increases continuously during most forming technologies (the temperature of glass melt decreases). Another important property acting during forming is the surface tension (Chapter 3.2), which can directly form, have a positive effect on the surface quality or, conversely, round the edges in an undesirable manner. Other thermal properties of glass as well as forming tools are important, which affect the removal of heat from the surface layers of formed products (Chapter 3.4).

It is appropriate to mention the thermal conditions during glass forming at this point. The heat passes through both conduction and radiation.

The amount of heat Q [J, Wh], that passes through the wall of the product can be derived from formula 3.28 (Chapter 3.4.3)

$$Q = Q_T \cdot \tau = \frac{k\, A\, \Delta T}{d}\, \tau\,, \quad (9.1)$$

where Q_T is the heat flux [W],

τ - is the heat transfer time [h],

k - is the coefficient of thermal conductivity [W·m^{-1}·K^{-1}] (depends on the chemical composition of glass and on the temperature),

A - is the surface area of the wall through which the heat passes perpendicularly [m^2],

ΔT - is the temperature difference of opposite surfaces [K],

d - is the wall thickness [m].

The heat transfer from the glass melt to the glass mould is more complicated and involves the storage capacity of glass melt E_s (for non-lead glasses, at a temperature of 400 to 700°C E_s = 2130 J·m^2· K^{-1}·s$^{-1/2}$) and the mould material E_f. The heat passed through the wall is given by the relation

$$Q = \Delta T\, \frac{2/\sqrt{\pi}}{\frac{1}{E_s} + \frac{1}{E_f}}\, \sqrt{\tau}\, A\,. \quad (9.2)$$

Relation 9.1 also applies to the amount of heat passed through the mould wall when the coefficient of thermal conductivity of the mould is substituted.

The heat transfer from the glass mould to the surroundings is given by the relation

$$Q = \Delta T \propto_e \tau A , \qquad (9.3)$$

where $\propto_e$ is the coefficient of heat transfer from the outer surface of the glass mould to the surroundings.

The above formulas apply to surface areas and to ideal conditions. In real conditions, the issue is much more complicated and a simplified approach must be clarified. In addition to this approach, computer-aided calculation using the finite element method is preferably applied in practice. However, the numerical model requires input data from practice and its accuracy increases or decreases with the experience of the person executing the calculations.

In addition to thermal processes, the mechanical action of forces is mainly applied during forming. The principles of technologies used in glass forming can be divided into:

a) **_Forming by the action of an external force_**, in particular by the proof of a forming tool (mould) - for example pressing, injection pressing, pressing.
b) **_Forming by the effect of internal forces_**, especially surface tension forces at a sufficiently low viscosity - for example, flat glass float technology, drawing tubes, capillaries, generally also free blowing.
c) **_Mutual combination_** - for example casting of pressing rods (lower part is formed by chain conveyor and upper part is formed by surface tension), blowing into moulds - in forming by blowing into mould without rotation the outer part of semi-finished product is formed by mould proof and the inner surface is formed by surface tension, - in forming by blowing into mould with rotation of the product or mould, the basic shape is given by the shape of the mould and the surface of the outer and inner parts is clearly affected by surface tension, as a "steam cushion" is formed between the glass and the mould.

It is also worth mentioning the basic concepts of glass machines. Single-position machines were at the beginning of mechanization and automation of glass forming. All technological forming operations were performed in single position. Due to the effort to increase production and shorten production times per product, multi-position machines began to be used, which can be designed in the form of a carousel, such as so-called individual section machines or conveyor machine. Carousel machines have several positions around the circumference, which rotate either continuously or more often intermittently. Individual section machines are mainly widespread in the production of container glass.

9.3 Forming of glass melt by pressing and squeezing

During moulding and pressing, the resulting shape is obtained mainly by external forces, which act on the gob with a relatively low viscosity, so the glass melt is sufficiently mouldable and must perfectly fill the mould by the effect of the pressing force. The actual flow of glass melt takes place very quickly and depends on the magnitude of the pressing force, on the viscosity of glass melt at the time of pressing, on the shape of the mould and on the size of the gob.

The mould in which the forming process takes place has two functions:

- form the product,

- remove the required amount of heat from the product, thus increasing the viscosity and thus fixing the shape.

The speed of the forming process is mainly given by the time required to remove heat from the surface of the product in machine production so that the product retains its shape during handling. The speed is thus not limited by the time required to fill the mould, because this occurs almost immediately after closing the mould. The mould temperature is always lower than the temperature of moulded glass. Immediately after the first contact of the glass melt with the mould, the surface temperature of the pressing decreases and the surface temperature of the mould increases. The heat is transferred to the mould by glass melt and from there it passes into the surrounding environment. Heat removal from the mould is almost always supported by various cooling methods.

With regard to the requirement of perfect filling of the mould with glass melt, it is necessary that its transport be as short as possible. The gob should thus be as close as possible to the shape of the finished pressed object before pressing and placement in the mould.

Defects in moulded or pressed products can be caused, for example, by too low mould surface temperature (high mechanical load) or, conversely, by too high mould temperature, where the glass can "stick" to the mould. The bonding temperature is in the range of approximately 550 to 630°C and depends on the contact time, the pressing pressure and the use of mould lubricants. The chemical composition of glass melt and its surface tension, the influence of the mould material and its surface is negligible. Another defect can be gobs on larger surface areas, which are caused by heating of these surface areas from the inner layers of the product and shrinkage, which is thus compensated.

Pressing machines (presses) are used for the production of domestic, technical and optical glass, but also for the production of semi-finished products in the field of glass jewellery. The pressing process is relatively simple in comparison with other production methods and takes place practically in single mould and one working operation. The following principles should be respected in the construction of pressing machines:

- the shape of moulded products must be designed so as to allow them to be removed from the mould after pressing (the mould can also be split),
- the cavity of the product must have smooth walls and a shape allowing the press forming element to extend,
- thin-walled products cannot be moulded, because glass melt quickly loses its formability and becomes brittle due to heat dissipation through the mould wall,
- the surface quality of moulded products due to contact with the mould wall is not ideal and in some cases it is necessary to apply another (finishing) operation. The problem is sometimes solved by choosing a surface embossment that masks the defects (e.g. lamp shades).

The applied pressing force can be developed:

- mechanically,
- pneumatically, or
- hydraulically.

According to the level of construction, the following presses are recognized:

- manual,
- semi-automatic, or
- automatic.

Another criterion for distinguishing presses may be the production technology. It is either a classic arrangement with a press forming element and a pressing ring (Chapter 9.3.1) or presses with an injection chamber (Chapter 9.3.2) and finally special presses used in the production of glass jewellery (Chapter 9.3.3).

9.3.1 Pressing of glass melt

The pressing procedure is schematically shown in Fig. 9.1: feeding of glass melt by one of the gob feeders, pressing itself (plunger ring forms the upper edge of the pressed object), cooling of the product (increasing the viscosity of surface layers), removal of the finished product, heat treatment of mould and press forming element (heating or cooling), mould cleaning and lubrication. The mould assembly is shown in Fig. 9.2.
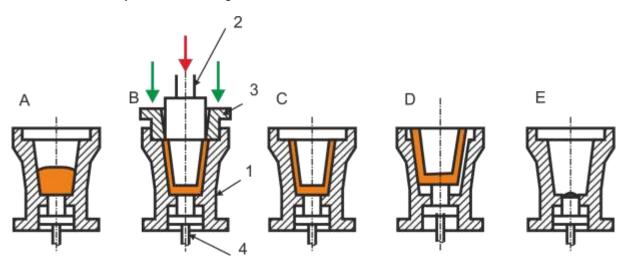
Fig. 9.1 Pressing with press forming element and plunger ring: 1 - mould, 2 - press forming element (plunger), 3 - plunger (pressing) ring, 4 – ejector (plug), A - feeding, B - pressing, C - cooling, D – pressed object removal, E - press forming element annealing, mould cleaning and lubrication

Hand presses are mainly used in small series production of smaller pressings. The pressing force is generated manually by means of a lever mechanism, which allows its multiple increase.
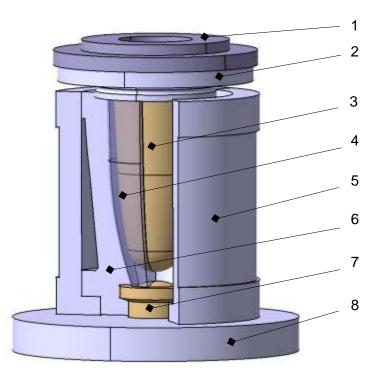
Fig. 9.2 Pressing mould: 1 - clamping plate, 2 - plunger ring, 3 - plunger (press forming element), 4 - product, 5 - holder, 6 - glass mould insert, 7 - plug, 8 - table board

In the production of large glass pressings (e.g. glass blocks/bricks), the pneumatic press LTB-1 is used, the scheme of which is shown in Fig. 9.3. The press is designed as a carousel press; the meaning of individual positions results from Fig. 9.4.
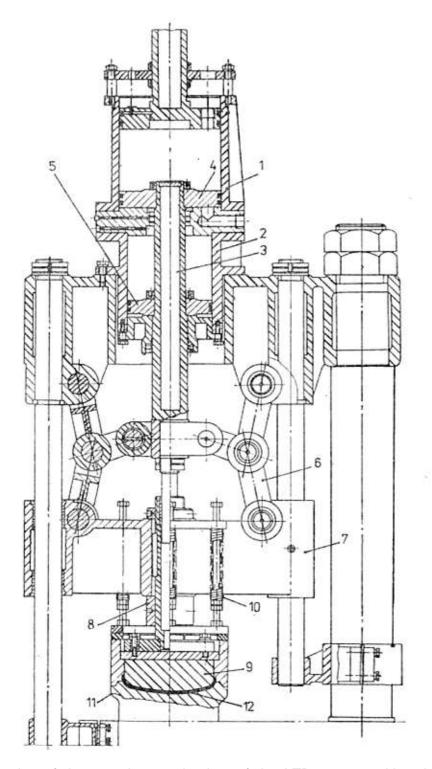
Fig. 9.3 Construction of the pressing mechanism of the LTB-1 press with a lever amplifying mechanism: 1,2 - coaxial pneumatic cylinders, 3 - piston rod, 4,5 - pistons mounted on common piston rod, 6 - lever amplifying mechanism, 7 - bottom movable cross member, 8 - housing, 9 - press forming element, 10 - guide pins with springs for fastening the pressing ring, 11 - mould, 12 – pressed object
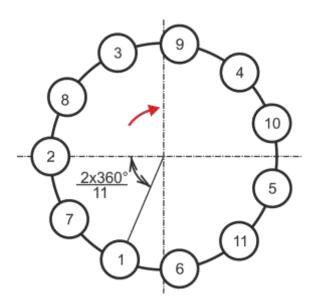
Fig. 9.4 Working position of the LTB-1 press: 1 - feeding, 2 - pressing, 3, 4 - cooling of the pressed object via the so-called last, 5, 6, 7 - cooling of the pressing from above, 8, 9 - free cooling, 10 - removal, 11 - cleaning by blowing and boosting of moulds

The next figure (Fig. 9.5) schematically shows the process of pressing a glass block. Positions 1 to 3 show the placement of the gob of glass melt in the mould, positions 4 and 5 show the pressing process, position 6 shows the transport of pressed objects, positions 7 and 8 show the connection of two opposite-oriented pressed objects by heating their edges, approaching and pressing, position 9 shows product transport to the annealing furnace.

In addition to the above examples, presses of various designs and purposes can be found, for example the automatic carousel press (Fig. 9.6) and the single-position pressing module (Fig. 9.7).

The diagram of the production line for domestic glass is shown in Fig. 9.8, in which a carousel press is included as a forming machine.
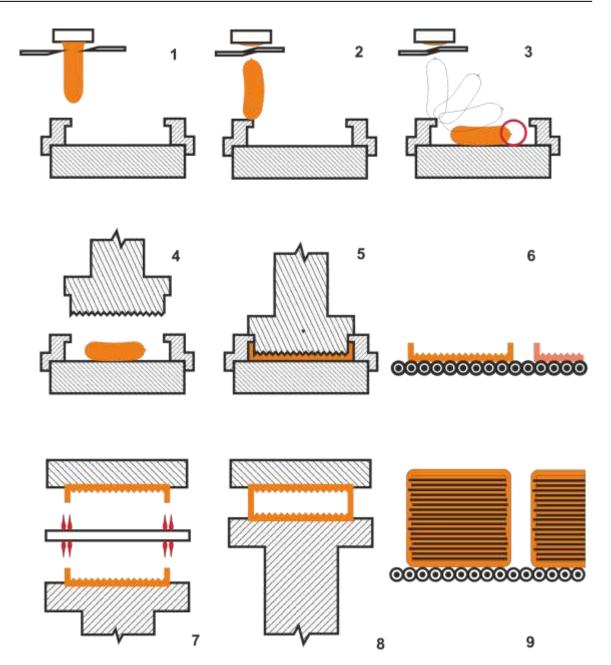
Fig. 9.5 Glass block pressing procedure: 1 to 3 - feeding, 4 and 5 - forming, 6 - transport of semi-finished products, 7 - heating of the edges of two opposite-oriented pressed products, 8 - approach and pressing, 9 - transport of finished products

Fig. 9.6 Automatic carousel press

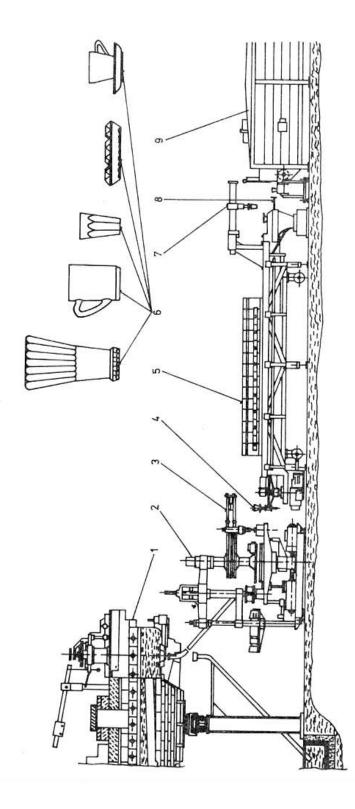*Fig. 9.7 Single-position pressing module*

Fig. 9.8 Diagram of the production line for domestic glass of the Eurovetromechanica company: 1 - feeder forehearth and mechanical gob feeder, 2 - carousel press, 3 - pneumatic product take-out, 4 - pressing, 5 - burning-off machine, 6 - assortment of pressed objects, 7 - take-out, 8 - feed-in device, 9 – annealing furnace

9.3.2 Injection pressing machine

An example of a device with an injection chamber can be the so-called injection pressing machine used for smaller products without a cavity, such as smaller chandelier trimmings, foot of goblet, etc. In very small products it is possible to mould several pieces at the same time, which is used in automatic carousel machines of the Persiano company. The principle of production (Fig. 9.9) consists in feeding a gob of glass melt onto the table of pressing station (press forming element), which closes the assembly of moulds by moving upwards. Then the needles are inserted (in the case of hole punching) and the glass melt is injected under pressure into an enclosed space, where a semi-finished product is formed. Metal moulds remove heat and the glass melt solidifies. Immediately after the pressing is completed, the needles are moved out to prevent them from overheating, the pressing station with the table moves down and is ready for the next gob of glass melt. Pressed objects are then released (knocked out) and placed in the cooling furnace.
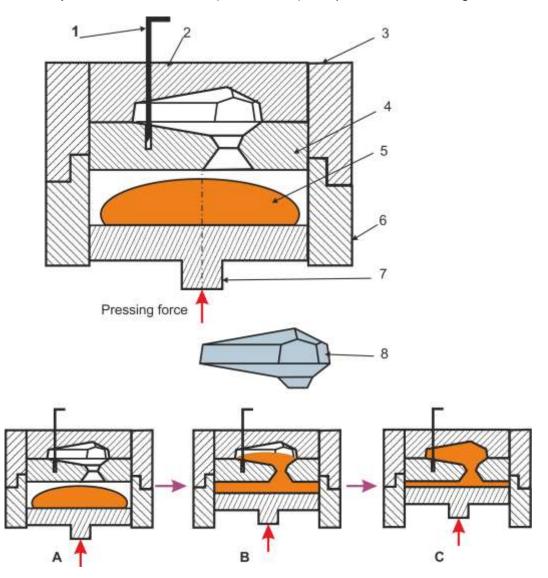

Fig. 9.9 Injection pressing technology on the G 12 machine: 1 - punching needle, 2 - upper mould, 3 - frame of the mould assembly, 4 - lower mould, 5 - gob of glass melt, 6 - feeding mould, 7 - pressing station table (pressing piston), 8 - finished pressed object, A - closed mould , B - pressing process (filling in the mould), C - end of pressing

9.3.3 Squeezing of glass melt

Squeezing technology is essentially the pressing of smaller or minor products, where the technology allows quick adaptation to the requirements of production of a wide range of sizes, colours and shapes.

The development of squeezer presses went from manual squeezing with the use of squeezing pliers to today's automatic machines and stabilized on two basic principles. It is squeezing on rotary squeezer press and on squeezer press, which can be called linear squeezer press. Another division is by the source of glass melt Fig.9.10.
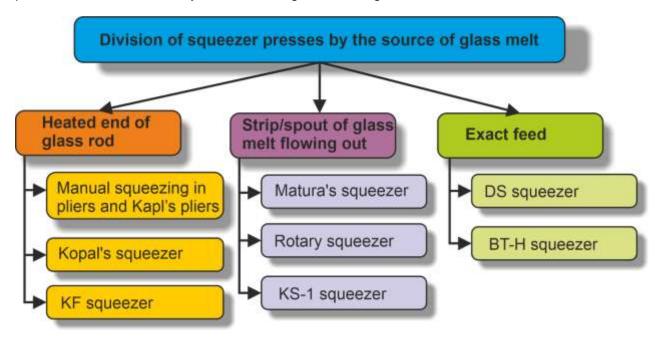
Fig.9.10 Division of squeezer presses by the source of glass melt

The heated ends of glass rods were used and are still used for squeezing, the production of which is described in Chapter 9.7.1. The end of the glass rod heated in the squeezing furnace has a favourable temperature gradient. The heated surface of rod end has a higher temperature than the core of rod end. This has a favourable effect on the forming, since the temperature is removed from the surface faster than from the deeper layers, the surface of the blank is not reheated from the core of the resulting blank after forming and the core did not significantly increase in volume due to lower temperature. In general, the effect of dips on the surface areas of products is thus minimized. However, it is more modern and productive today to press directly from the spout or from the exact gob.

During forming from the spout, a strip of glass melt flows either from the remelting furnace (two-stage production) or from the pot spout of the melting unit (single-stage production). The glass melt flowing in the strip has the opposite temperature gradient under normal conditions (the temperature in the centre of the spout is higher than that on the surface). This can reduce the quality of the semi-finished products produced. A better temperature profile can be achieved with a heated platinum spout, which ensures a higher temperature on the outer surface than inside, Chapter 8.3.2.

As a first example of a device for forming glass jewellery components, a rotary squeezer press is mentioned, which is a representative of an automatic squeezer press. In squeezing on rotary squeezer press (Fig. 9.11), a strip of glass melt is fed between two rotating moulds (also called rollers) provided with cups on the circumference. By turning the moulds, the glass melt fills the individual cups, the squeezed objects remain connected by the excess glass melt, the strip of squeezed objects is carried by the conveyor belt and broken off at its end. Irregularly large parts fall into the so-called thermal box, where they gradually cool down spontaneously.
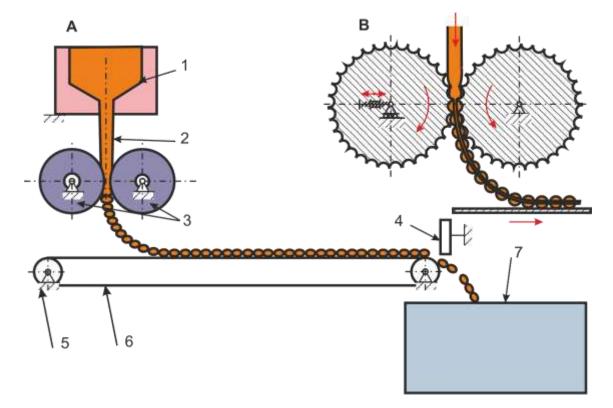
Fig. 9.11 Function of the rotary squeezer press: A - scheme and principle, B - section through rotary moulds, 1 - source of glass melt, 2 - stream of glass melt, 3 - rotary moulds, 4 - breaker, 5 - machine frame, 6 - transport belt of the presser, 7 - thermal box

This is followed by removal of excess glass and further treatment. The main characteristic of the process is the high output, which for a bead diameter of 2 mm reaches up to 1,300,000 pieces per hour and for a diameter of 6 mm more than 100,000 pieces per hour. The products usually do not have a hole and the raw material produced in this way is used for the production of chatons.

Devices that are derived from the primary manual pressing with pliers work differently from the principle of rotary pressing. They can be called linear according to the direction of movement of the moulds (cups).

An example of a mechanized (machine-hand) squeezer press with a source of glass melt in the form of a pressing rod with a linear movement of moulds is the Kopal's squeezer press, Fig. 9.12. The glassmaker has two guide paths along which the slid of the upper mould and the punching mechanism moves. The drive is provided by an electric motor via transmission belts and a cam on the slide. The presser operator gradually inserts the melted end of the pressing rod between the moulds and after a few squeezing operations separates the rod from the product by

means of shears and the squeezed semi-finished products fall into the thermal box. The movement of the upper mould, the upper edge of the shears and the needles is ensured by the machine. Moulds are often cooled and can be simple (for larger semi-finished products) or multiple moulds. The advantage of the Kopal's squeezer press is that it can be easily used for implementing a wide range of small jewellery semi-finished products. For each type of glass product, almost optimal conditions for pressing and punching of holes can be ensured by changing the cams. The main disadvantage is the need to operate the device by an experienced glassmaker.
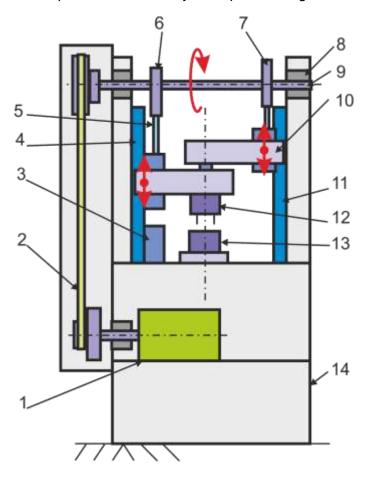

Fig. 9.12 Kopal's squeezer press: 1 - electric motor, 2 - belt drive, 3 - shear blade, 4 - slide, 5 - adjustable rod, 6 - cam for moving the upper part of the mould, 7 - cam for the punching mechanism, 8 - shaft bearing, 9 - drive shaft, 10 - punching mechanism, 11 - needle bar slide, 12 - upper part of the mould, 13 - lower part of the mould, 14 - machine frame

An example of an automatic device with linear movement of moulds is the Matura's squeezer press, Fig. 9.13. The presser consists of the frame of the stand, one part of which contains a pressing mechanism and the other part contains a cabinet with a drive including control elements. A strip of glass melt flows vertically between a pair of water-cooled moulds - cups. The fixed cup is clamped in the frame of the presser, the second, movable, is on a sliding carriage. The movement of the carriage is derived from the cam controlling the closing of the moulds. The vertical movement of both cups provides the oscillating movement of the entire squeezing (pressing) mechanism derived from the respective cam. The presser is equipped with a punching mechanism, which can be used for punching holes in the direction of the axis of the cups (so-called punching from the top) or perpendicularly to the axis of the cups (punching from the side), the needles are lubricated with

oil or oil mist. All movements are controlled by cams on the central shaft, the machine is driven by an electric motor via a continuously variable transmission (CVT) enabling continuous regulation. The described Matura's squeezer press is one of the most frequently used pressers due to its flexibility, relatively high performance and relatively low production costs.
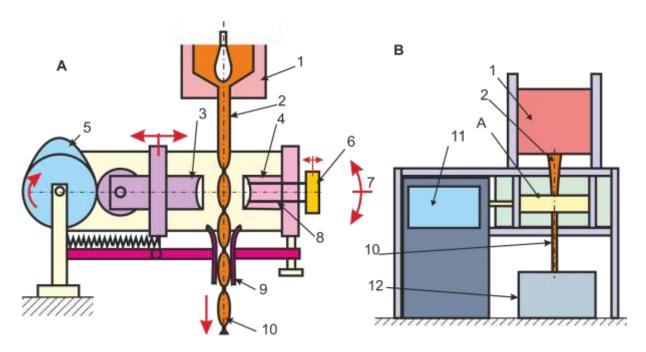

Fig. 9.13 Diagram of the Matura's squeezer press: A - squeezing mechanism, B - diagram of the machine, 1 - source of glass melt, 2 - strip of hot glass, 3 - squeezing cup, movable, 4 - squeezing cup, fixed (upper), 5 - cam, 6 - punching mechanism, 7 - indicated movement of the whole mechanism by means of another cam (not illustrated), 8 - needles, 9 - jaws of holders, 10 - strip of squeezed objects with a excess glass, 11 - cabinet with mechanism drive and control, 12 - thermal box

The above-mentioned squeezer press form small mouldings from a strip of glass melt, while the mouldings remain connected by an excess glass. The technologically youngest are excess glass-free squeezer presses, which form the moulding without external glass. This method of pressing presupposes an exact gob of glass melt with its volume corresponding to the volume of the future squeezed object and a specially adapted mould which, when pressed, does not allow the glass melt to flow out of the mould and at the same time makes it possible to compensate for small differences in gob and squeezed object volume. A typical representative of these devices is a DS squeezer press operating in a two-stage mode, the first stage being the forming of a gob (ball) on a rotary squeezer press. The exact volume of the balls is achieved by tumbling and sieving after previous volume measurement. The diagram of the DS squeezer press is illustrated in Fig. 9.14, showing the technology used by the squeezer press. The vibrating feeder feeds balls onto a heating path formed by a smooth roll and a roll provided with a helix (screw). By rotating the rollers, the balls roll and at the same time move to the forming unit. They are heated by gas burners. Preheated balls then fall into the forming unit, where squeezing takes place between two cups, and after squeezing process the finished squeezed object falls into the heating-up container (Fig. 9.15). The movement of the cups is controlled by cam mechanisms, the whole machine is driven by an electric motor with a continuously variable transmission (CVT) regulating speed. The squeezer press can

be equipped with a pneumatic punching mechanism, which creates holes in the direction of the axis of the cups. The described type of squeezer press most often produces chaton raw material and its main advantage is the high dimensional accuracy of the squeezed objects. On the contrary, the disadvantage is the limited assortment and demanding preparation of the raw material.
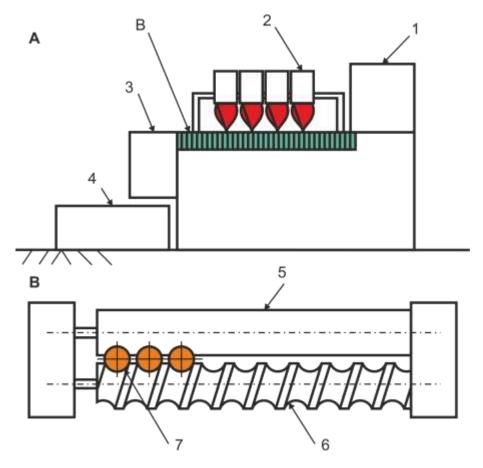

Fig. 9.14 Diagram of the DS squeezer press: A - squeezer press diagram, B - heating path, 1 - vibrating feeder of balls, 2 - burners, 3 - squeezing mechanism, 4 - bin for finished products, 5 - roll, 6 - screw, 7 - heated glass ball
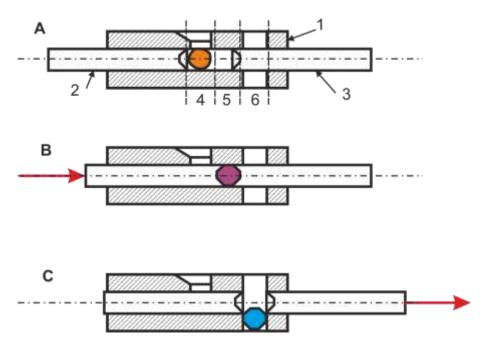
Fig. 9.15 The principle of pressing on the DS squeezer press, A - feeding, B - pressing, C - removing the squeezed object from the mould, 1 - body of the mould, 2 - left cup, 3 - right cup, 4 - feeding section, 5 - pressing section, 6 - removing the semi-finished product

In addition to DS squeezer presses, there are also squeezer presses for excess glass-free forming of chandelier heads and chandelier trimmings. One of them is the BTH squeezer press, into which the glass melt is fed directly from the spout and it is therefore a single-stage production.

9.4   Forming of container glass

Container production includes beverage bottles and glass jars produced for the food industry (beer, wine, liqueurs, soft drinks, mineral waters, fruit, etc.) as well as glass containers for products of the chemical, pharmaceutical and cosmetic industries.

With a few exceptions, the forming cycle of container production technology is two-stage, i.e. creating the basic shape (blown post, blank) in the first phase and final forming in the final form. For a general overview, technologies that are obsolete will also be briefly listed here. At present, container glass is produced on efficient automatic individual section machine or carousel machines. Individual section machines are assembled from individual sections, in each of which the whole forming cycle takes place independently with a certain time shift. Carousel machines have the moulds placed on one or two rotary tables. The following moulds are used in forming:

- neck mould (NM), forming the neck of the container,
- blank mould (BM), where the blown post (blank) is formed,
- finish mould (FM), where the product is finally formed,
- intermediate mould (IM), used exceptionally.

Cast iron or steel (Chapter 9.11) is used as a material for the production of moulds. Depending on the method of placing the gob of glass melt in the blank mould, a distinction is made

between feeding machines and suction machines. The forming of the container, as already mentioned, takes place in two phases and we distinguish four basic technologies accordingly:

- suck-and-blow method (SB),
- suck-and-suck method (SS),
- blow-and-blow method (BB),
- press-and-blow method (PB) and the newer narrow-neck press-and-blow method (NNPB) derived from it.

9.4.1 Suck-and-blow technology

In this forming method, the glass melt was sucked into the cavity of the blank mould by creating a vacuum. Two pulses of compressed air (pre-blows) followed, then the finish mould was closed around the blank and the final shape of the container was created by the action of compressed air. This device was the first automatic machine used in the production of container glass since 1905. This forming method belongs to history, the last carousel machines of the Owens type were put out of operation in 1982 (the Lesní Brána plant). The main disadvantages of this method were the strong cooling of glass melt at the point of suction of the gob, the uneven wall thickness of the container and the trace of cutting the glass melt after suction into the blank mould.

9.4.2 Suck-and-suck technology

A typical representative is the Roirant BB machine, which produces large-capacity glass containers (up to 60 litres in volume). The machine has two blank moulds suspended on a support arm, which rotate intermittently by 60 degrees, one intermediate mould and one finish mould. The whole production process is shown in Fig. 9.16. During forming, the glass melt is sucked into the blank mould by the action of a vacuum (position 1). Two pre-blows follow in positions 2 and 3, in position 4 the blank is moved to the intermediate mould (position 5), where an intermediate shape is formed by sucking air from the space between the blank and the inner wall of the intermediate mould. The blank is then transferred to the finish mould, position 6, where the final shape of the product is formed again by sucking air out of the space between the blank and the inner wall of the mould. From the finish mould, the finished container is transferred to a dead plate, where it is finally formed and the bottom solidifies.
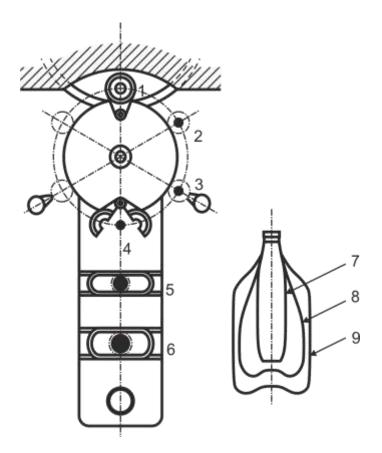
Fig. 9.16 Flow sheet of the production process on the Roirant BB machine: 1 - suction of glass melt into the blank mould, 2 and 3 - pre-blow, 4 - transfer into the intermediate mould, 5 - intermediate mould, 6 - finish mould, 7 - blank, 8 - intermediate shape, 9 - final shape

9.4.3   Charging technology

Modern glass technologies are based on the feeding mode of BB, PB and NNPB and are manufactured as individual section machines. An individual section machine consists of individual sections, machines often bear the designation "IS" (Individual Section). The sections are arranged side by side and each represents a machine-technological unit that can independently perform the entire forming cycle, working with one-, two-, three- to four-gob. On individual section machines, narrow-neck containers are produced in the BB or NNPB method, or wide-neck in the PB method. Blow-and-blow machines are designed to allow relatively easy conversion to the press-and-blow method.

9.4.3.1   Blow-and-blow forming

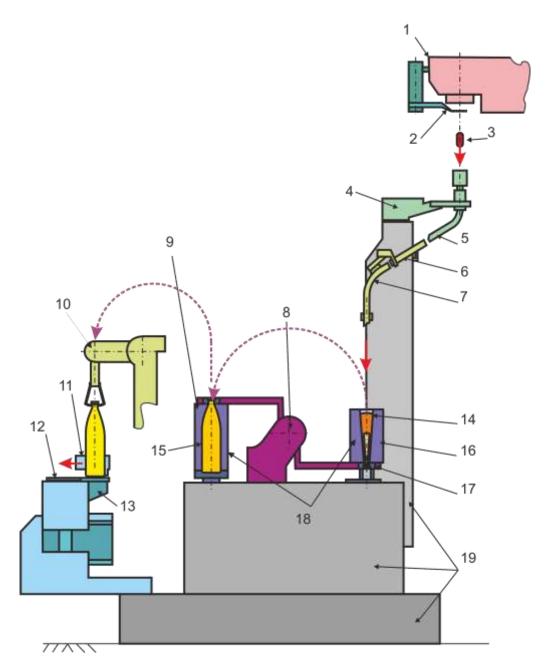The principle of blow-and-blow forming is shown in a schematic side view of one section (Fig. 9.17).

Fig. 9.17 Schematic side view of one section of an individual section machine: 1 - feeder, 2 - mechanism of shearing machine, 3 - gob of glass melt, 4 - gob distributor, 5 - trough, 6 - chute, 7 - gob deflector, 8 - invert, 9 - finish mould, 10 - bottle take-out, 11 - pusher, 12 - conveyor belt, 13 - dead plate, 14 - blown post, 15 - bottle, 16 - blank mould, 17 - neck mould, 18 - mould cooling system, 19 - frame of individual section machine

The gob of glass melt is fed through the gob distributor into the blank mould and, by means of a blowing head, is pressed by compressed air into the cavity of the neck mould, in which the neck of the container is formed. After the neck-piece is moved out, the parison is formed by blowing with compressed air (the blank is still in the neck-down position). Then the blank held in the neck mould is transferred (flipped) by means of an invert in a semicircular movement into the finish mould, where it remains suspended for a certain time. The surface layers, which have been cooled in contact with the blank mould, are heated by the glass melt inside the walls of the blank. The

blank is stretched under its own weight, and at the moment of contact with the bottom of the finish mould, compressed air is introduced into the cavity of the blank, which forms the final shape of the product. The take-out transfers the product to the dead plate, where the bottom cools down, and the bottle is transferred by a pusher onto a belt conveyor, which moves it in front of the annealing furnace. The scheme of forming in the BB method is shown in Fig. 9.18, the arrangement of sections in the six-section machine is shown in Fig. 9.19. Modern machines of the AL type are manufactured by Sklostroj Turnov in 4-, 6-, 8-, 10- and 12-section versions, they are equipped with servo or hydraulic control and enable the production in the BB, PB, NNPB or LPBB (light production blow&blow) method. The view of the ten-section AL machine is shown in Fig. 9.20.
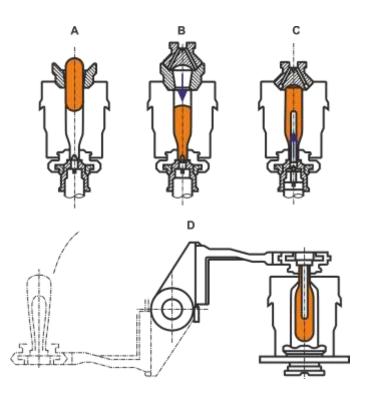
Fig. 9.18 BB forming procedure: A - feeding of glass melt into the blank mould, B - "blowing" of the gob and creation of the neck of the bottle, C - creation of the blown post in the blank mould with compressed air (the bottle is formed upside down), D - transfer of the blank into the finish mould by turning by 180° using an invert and blowing of the final shape
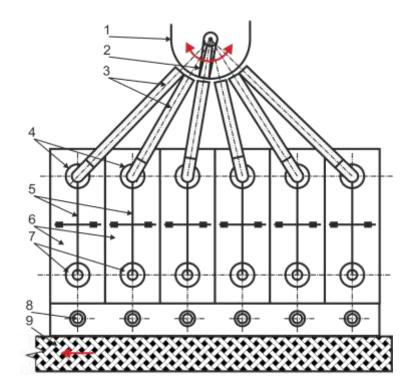
Fig. 9.19 Floor plan of the six-section machine layout: 1 - feeder, 2 - gob distributor, 3 - chutes, 4 - blank mould, 5 - invert, 6 - individual sections, 7 - finish mould, 8 - dead plate, 9 - conveyor

Fig. 9.20 View of the ten-section AL machine (source: Sklostroj Turnov CZ, s.r.o.)

9.4.3.2   Forming by press-and-blow method

The principle of forming by press-and-blow method is characterized by two successive operations, namely pressing into the blank mould and blowing into the finish mould. Diagram of the production of a wide-neck container with a description of the production cycle is given in Fig. 9.21.
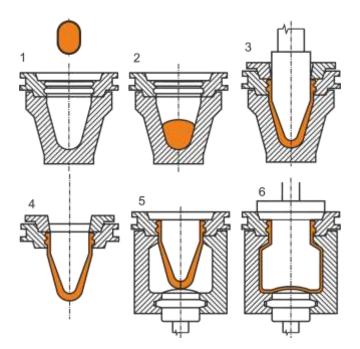
Fig. 9.21 Diagram of forming by press-and-blow method: 1,2 - feeding of the gob into the blank mould, 3 - pressing (creation of the blank and the upper edge of the container), 4 - transfer of the blank into the finish mould, 5 - heating of the blank, 6 - blowing of the final shape

9.4.3.3   NNPB forming machines

The narrow-neck press-and-blow method (NNPB) developed by the German company Heye makes it possible to form even narrow-neck containers using the press-and-blow method. The main characteristics of this technology are as follows:

- precise distribution of the glass melt enabling the production of thin-walled narrow-neck containers with a weight about 30 percent lower,
- more productive production (the blank mould is assigned two finish moulds, sometimes placed on independent carousels, so that there is no delay in the finish mould necessary to reheat the blank),
- the gob is fed into the blank mould in the rest position without the need for transport by chute, which brings improved thermal homogeneity,
- the position of the blank in the blank and finish moulds is consistent with the neck upwards (invert is omitted).

Schematically, the forming process on the Heye 1-2 machine is shown in **Chyba! Nenalezen zdroj odkazů.**. The NNPB technology was subsequently transferred to individual section machines, which enables the production of bottles with a more even and thinner wall thickness and thus lighter wall. These lightweight bottles made by NNPB method can have a weight up to 50% lower compared to BB method. By lightening the containers, several goals can be achieved, in particular:

- reduced requirements for energy and raw materials for the production of one bottle,
- reduced fixed costs per bottle,

- reduced transport costs of raw materials, filled containers and cullet for recycling (weight affects 50 to 60% of production costs).
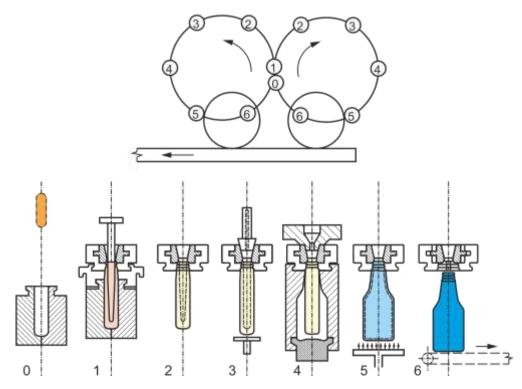
Fig. 9.22 Forming procedure on the Heye 1-2 machine for narrow-neck bottles: 0 - feeding of the gob into the blank mould, 1 - pressing of the blank, 2 - heating of the blank, 3 - heating and blowing of the blank, 4 - blowing of the product in the finish mould, 5 - cooling of the finished product, 6 - removal and transport to the annealing furnace

9.4.3.4   RIS forming machine

The Emhart company brought another method of modern design. It is an individual section machine, in which each section contains two finish moulds and two blowing heads placed on a rotary table for one blank mould. The system is called RIS (rotary IS) and its benefit is that it theoretically allows to double the forming speed, because the necessary time delay in the final form is eliminated. The diagram of one section for a two-gob is shown in Fig. 9.23. A certain size limitation is the need to place a rotary table.
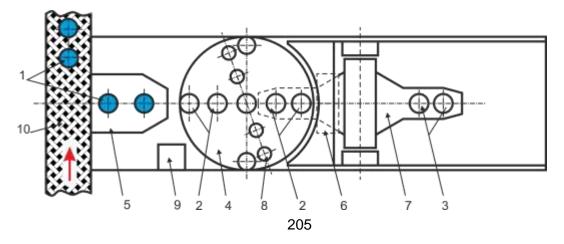
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Fig. 9.23 RIS machine section diagram: 1 - finished bottles, 2 - finish moulds, 3 - blank moulds, 4 - rotary table, 5 - dead plate, 6 - insert, 7 - invert, 8 - blowing heads, 9 - take-out, 10 - belt conveyor

9.4.3.5   ISS forming machines

The most modern ISS machine for the production of container glass was developed by Sklostroj Turnov (Fig. 9.24). It is characterized as universal, compact and durable machine, equipped with the latest servotechnology and eliminates complicated mechanisms, which makes the new machine more compact and durable. It can work from one- to four-gob method, it is available in 4-, 6-, 8-, 10- and 12-section versions as well as in tandem. It enables the BB, PB and NNPB forming in a way that existing moulds can be used on the machine. The design of the new machine meets both ergonomic and safety aspects, as well as the requirements for quick replacement of accessories and drives. The new machine is designed for high speeds, which is achieved primarily through the use of servo-drives and efficient cooling. Energy savings of up to 40% are reported for this machine.

Fig. 9.24 Container glass forming machine type ISS (source: Sklostroj Turnov CZ, s.r.o.)

9.4.3.6   Example of container glass production line

The above example of a container glass production line is prepared for feeding machines for the production of container glass in a blow-and-blow method using a two-gob. In addition to the principles described in the previous paragraphs, the description of the line is supplemented by the characteristics of additional systems, without which the operation of the line would be excluded (shears, distributor, chutes, take-outs, dead plate, pushers and inspection section). These devices will be characterized only briefly.

Shears - have the function of separating the gob of glass from the feeder spout. Their design is mentioned in Chapter 8.2.1. The cutting edges are protected, for example, by an oil-in-water emulsion. Separated gobs fall into the distributor.

Distributor - feeds the gobs of glass melt into individual chutes, which transport them into the blank mould of forming machines.

Chutes – are steel troughs Fig. 9.25, which alternately, in a predetermined order, supply the blank moulds of forming machines with glass melt. Upon completion of the forming cycle, the finished products are moved onto a dead plate.
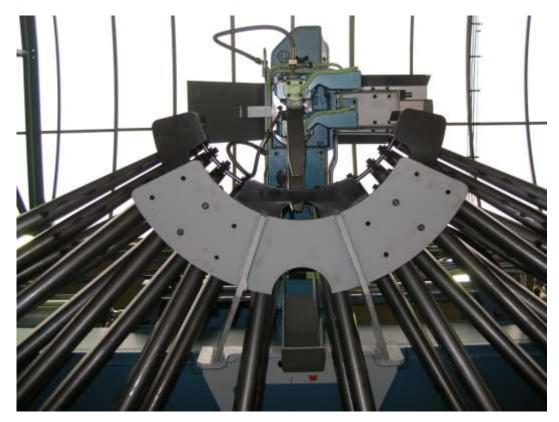

Fig. 9.25 View of the chute system (source: Sklostroj Turnov CZ, s.r.o.)

Take-out – is a system working separately for each section of the individual section machine and its task is to take out the formed product and move it onto a dead plate.

Dead plate – is an independent position where the products are cooled down before further transport. After-cooling by air exhaust is directed mainly to the area of the bottom of the container, where a larger amount of glass mass is concentrated. When after-cooling is finished, the containers are transferred by a pusher onto a belt conveyor. The view of the pusher is shown in Fig. 9.26.
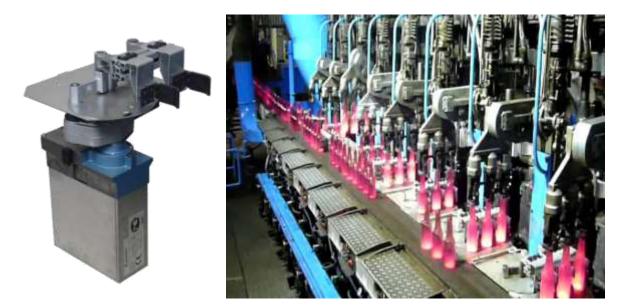
Fig. 9.26 View of the pusher and its location in the individual section machine (source: Sklostroj Turnov CZ, s.r.o.)

The bottles are then transported to a annealing furnace. Before being placed in a annealing furnace, they pass through a zone where they are shortly in contact with tin tetrachloride vapours and pyrolysis of this compound forms a protective layer of SnO_2 on the hot surface of the glass. It is the first phase of chemical surface finishing, which takes place at the so-called "hot" end of the production line (for more details, see the chapter on finishing). As soon as a row of bottles is arranged in front of the annealing furnace, it is automatically inserted into the space of the annealing furnace by means of a mechanical rake.

The belt conveyor brings the finished containers to the inspection device, where the final quality control is performed automatically, based on optical or mechanical impulses (e.g. outer diameter of the neck, inner diameter of the neck, height, presence of inhomogeneities, etc.). Non-conforming products are dropped by a mechanical impulse onto a collection conveyor, which transports them to the batch house as a secondary raw material.

9.5   Forming of thin-walled glass

The group of thin-walled glass products can include tumblers, mugs/cups, beakers, lamp bulbs, etc. The common characteristic is that thin-walled products are seamless (without mold joint) and have a very high quality surface. This is achieved by blowing the preformed blank into the mould with a slight rotation (either a shaped blank or mould rotates) and the mould wall is covered with a wet porous sawdust-, cork- or graphite-based layer. The contact of the hot glass melt with this wet porous layer leads to intense steam generation and the resulting steam cushion reduces friction, thus allowing easier rotation of the formed blank in a closed mould and surface tension is simultaneously applied which ensures a smooth surface. At the same time, no trace is created at the point of contact of the two parts of the closed mould, and thus thin-walled products differ, for example, from container glass, on the wall of which traces remain after contact of both parts of the closed finish mould.

In the production of thin-walled products, technological waste, the so-called moil/cap, is usually generated, which is a consequence of the technology used, both in manual and automatic production. In the next phase, the moil is removed, for example, by remelting, Chapter 11.2.3.

Machines for the production of thin-walled glass are divided by production technology into suck-and-blow and press-and-blow machines, and by design into carousel and continuous machines. Some types will be characterized hereinafter.

9.5.1   Production technology on M-type machines

The technology is currently quite widespread. This is a press-and-blow technology, i.e. similarly to the container glass, a preform is first formed by pressing, which, however, does not have the shape of a blown post, but a flat plate. The final shape of the product is subsequently formed by blowing during rotation (of the mould or product). The M-type machines are designed with 12, 16, 18, 20, 24 to 28 forming stations as required. These are carousel machines with continuous rotation. Fig. 9.27 shows the schematic diagram of the forming cycle of the M-type machine in the upper five figures and its design in the lower figures.
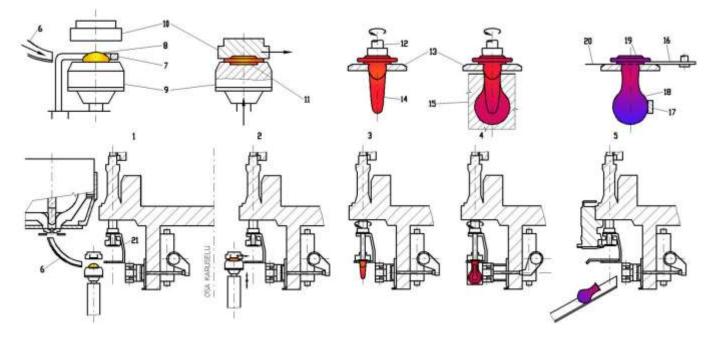

Fig. 9.27 Diagram of the forming cycle of M-type machine: 1 - feeding of a gob onto the pressing head, 2 - pressing of the preform (flat plate) and its transfer by the suction and transfer head to the blowing station, which does not rotate during transfer, 3 - gradual blowing of the blown post while rotating, 4 - forming of the blown post (blank) in the finish mould while rotating, 5 - separation of the finished blank with a circular knife, 6 - gob guide trough, 7 - gob holder, 8 - gob of glass melt, 9 - pressing head, 10 - vacuum transfer head, 11 - preform, 12 - glass-blowing pipe, 13 - neck mould, 14 - successive shapes of the blank, 15 - finish mould, 16 - circular knife, 17 - ejector stop, 18 - finished lamp bulb, 19 - moil, 20 - parting plane

A gob of glass melt slides into the pressing station, where it is pressed onto a flat plate. The pressed object is transferred onto the rotary table of the forming station, it is somewhat deepened by pressing the glass-blowing pipe and the glass melt is pressed into the neck mould at the same time. Now the air pressure from the glass-blowing pipe, which rotates at the same time, begins to act on the pressed object. After free forming by blowing while rotating, final forming by blowing

while rotating is performed in a closed mould. The blank is then broken off with a circular knife and transported for further processing.

These machines are part of the technological units. An example of the inclusion of a machine in a technological unit can be an automatic line for the production of cups (*domestic glass* **line**). The line consists of a foot (a stem) pressing machine and a carousel press-and-blow machine, which also ensures the connection of the blank with the preformed stem. A variant of the arrangement of individual machines is shown in Fig. 9.28, which is further followed by a annealing furnace, equipment for separation of moils, working of edges after separating the moil, output control and packaging. The products can be further finished. The view of the Olivotto production line is shown in Fig. 9.29, giving the schematic view of the production of thin-walled domestic glass with the use of the M 16 machine.
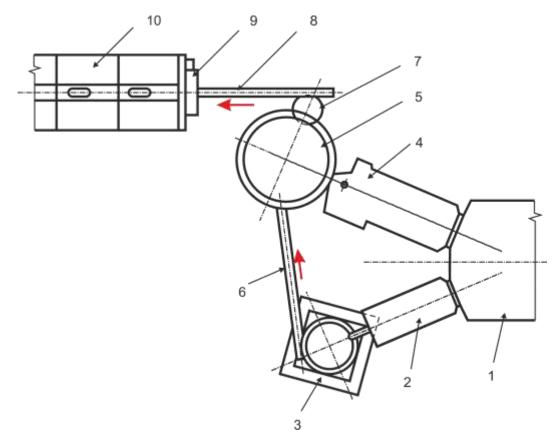

Fig. 9.28 Diagram of cup production line: 1 - melting unit, 2 - automatic press feeder, 3 - press, 4 - blowing machine feeder, 5 - automatic blowing machine, 6 - pressed stem conveyor, 7 - cup and stem take-out, 8 - conveyor for products to the annealing furnace, 9 - loader of products to the annealing furnace, 10 - annealing furnace
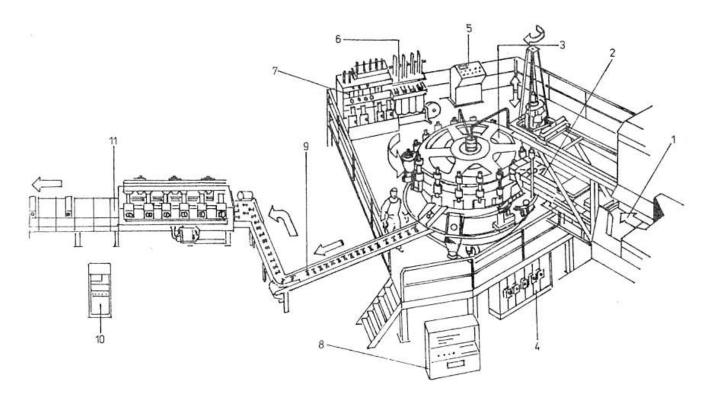
Fig. 9.29 Olivotto production line: 1 - melting unit, 2 - trough with gob feeder, 3 - M 16 machine, 4 - gas-air mixing station, 5 - regulation of cooling air distribution, 6 - regulation and distribution of blowing air, 7 - compressed air station, 8 - control panel, 9 - belt conveyor, 10 - control panel, 11 - annealing furnace

9.5.2   Technology of H-28 type machines

This is again a press-and-blow technology, where the preform is often formed into a blank. The H-28 type machines are carousel machines with continuous rotation. A gob of glass melt is fed into the blank mould. It is raised to the neck mould, on which the pressing ring is placed, and a press forming element is inserted into the blank mould, which presses the blank. After pressing, the press forming element with the pressing ring is raised, the blank mould is lowered and the blown post with the neck mould starts to rotate while heating up. The blowing head rests on the neck mould and the blown post is blown out with low air pressure, about 2.5 kPa. The bottom is subsequently pushed in, the two-part finish mould is closed and the blown post is further blown. After closing the compressed air, the finish mould opens, the bottom moves away and the neck mould stops rotating. The take-out subsequently grabs the product and, after opening the neck mould, moves it to a conveyor, which transports it to the remelting machine. The forming cycle of the machine is shown in Fig. 9.30.
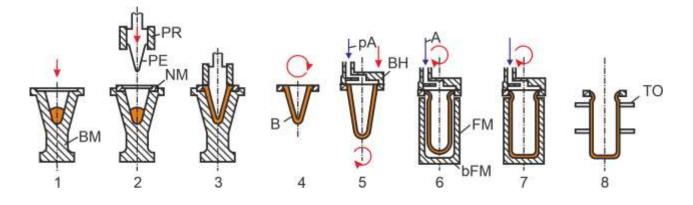
Fig. 9.30 Forming cycle of the H-28 machine: 1 - feeding of glass melt, 2 - preparation of pressing, 3 - pressing, 4 - rotation and heating, 5 - blowing, 6 - closing of the finish mould around the blown post (blank), 7 - blowing of the final shape, 8 - removal of the finished product, BM - blank mould, NM- neck mould, PE - press forming element, PR - pressing ring, B - blown post, BH - blowing head, pA - pulses of low pressure air, A - low pressure air, FM - finish mould, bFM - bottom of the finish mould, TO - take-out pliers

9.5.3   Continuous glass ribbon machine

The machines for the production of thin-walled glass also include a large-capacity automatic machine for the production of lamp bulbs, the so-called ribbon machine (Fig. 9.31).
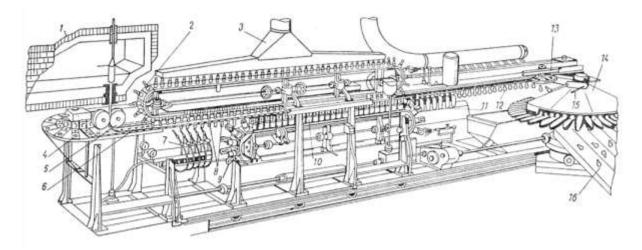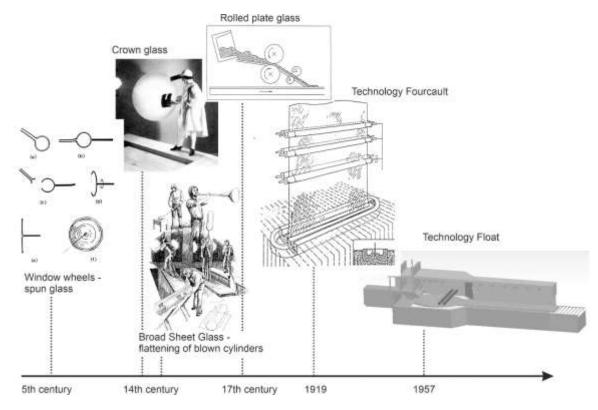

Fig. 9.31 Automatic machine for the production of lamp bulbs: 1 - working end of the tank, 2 - glass-blowing pipes, 3 - cooler, 4 - supporting plate belt, 5 - roll, 6 - glass strip, 7 - device for cooling blown post with water mist, 8 - blown posts, 9 and 10 - open and closed split finish moulds, 11 - cooling zone, 12 - final shapes of blanks, 13 - separating device, 14 - rotary table, 15 - separation of blanks, 16 - belt conveyor

The forming takes place in such a way that the strip-shaped glass melt flows continuously between the rolls, which rotate to preform the thicker lenticular areas. Glass-blowing pipes located on the chain conveyor move to these thicker areas from above, pressing through and slightly blowing the thicker lenticular areas, which are cooled by water mist. Then the finish moulds, also placed on the belt conveyor, move on them from below, the split moulds are closed and rotated,

while blowing the blank into the final shape. After final forming, the moulds are opened, the blanks are cooled with a blast of air and pass through a separating device. The output of this machine reaches up to 2,000,000 pieces in 24 hours.

9.6 Flat glass production technology

Historically, flat glass was made by hand, for example in the second half of the 20th century, it was the production of signalling glassware, where the sheets were obtained by broad sheet glass – flattening of blown cylinders. The quality and productivity of hand production did not meet the demand, so machine production technologies were developed. Flat glass production technologies can be divided into drawing, rolling (casting) and floating.

9.6.1   Glass drawing technology

The technology of machine drawing of flat glass is performed upwards (a number of methods, some of which will be described below) or downwards. Drawing upwards can be further distinguished between methods using a debiteuse and methods without a debiteuse.

9.6.1.1   Upward drawing

The Fourcault method (Fig. 9.32) of vertical drawing of an endless bolster (strip) is based on the use of a fireclay debiteuse, which forms the nucleus of a shaped sheet and at the same time makes it possible to keep the constriction of the drawn bolster within acceptable limits. The mechanism of this effect is that the fireclay prevents the edges of the drawn bolster from converging due to the good wettability of its surface by glass. The glass melt used for the Fourcault drawing process is melted in continuous melting units and is fed through canals to the drawing chamber, in

which the actual drawing begins. The drawing takes place by means of a fireclay debiteuse, holders for the edges of the drawn bolster and coolers. The formed bolster is continuously drawn upwards by the drawing machine through a vertical pit, which at the same time performs the function of a annealing furnace. On the upper working platform, the basic formats of the glass sheet are cut and broken off. This method was most widespread in Europe.

This technology is characterized by the fact that after a certain time the quality of the drawn glass deteriorates, the temperature of the lower layers of glass melt in the drawing chamber decreases, so it is necessary to interrupt the drawing process, heat the glass melt perfectly and resume the drawing process. These drawing cycles have different durations, from about 200 operating hours they have been extended to almost two months. The resumption of drawing process takes place after the glass melt has been heated by means of a bait, which is lowered from above and immersed in the glass melt. After about three minutes, the glass melt adheres to the bait and a slow drawing begins, while gradually pushing away the pressure rollers. When the required speed is reached, the drawing process takes place continuously.

The thickness of the glass produced by drawing according to the Fourcault method is between 1.2 mm and 9 mm, with the upper limit being 14 mm, larger thickness cannot be drawn because the frictional force between the sheet and the drawing rollers cannot hold the glass. The width of the drawn bolster is determined by the length of the slot and ranges most often from 1600 mm to 2500 mm, the maximum reached was over 3000 mm. However, machines were also built to draw bolsters up to 1000 mm wide.

The surface quality of drawn glass is influenced mainly by the fireclay debiteuse, which causes the formation of fine stripes. This defect is called "optic" caused by debiteuse.
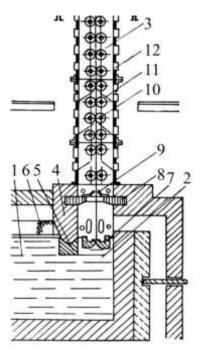

Fig. 9.32 Section of the drawing chamber of the Fourcault drawing method: 1 - glass melt in front of the curtain, 2 - glass melt in the drawing chamber, 3 - drawing machine, 4 - curtain, 5 - skim bar, 6 - handling opening, 7 - fireclay debiteuse, 8 - upper closure of the drawing chamber, 9 - bell cranks, 10 - drawing rolls, 11 - trays used for collecting cullet, 12 - working openings

A certain variant of the Fourcault method can be considered the Japanese Asahi method, where the fireclay debiteuse was replaced by two cylindrical blocks made of refractory material. The rollers were rotatable, but did not move in drawing. It was possible to rotate them if necessary and thus improve the "optic".

The American Libbey-Owens technology (also called Colburn, Fig. 9.33) was developed several years later than the Fourcault technology. The technology is characterized by drawing a bolster from the free glass surface level across the entire width of the drawing chamber (i.e. without the use of a debiteuse), while at about 400 to 600 mm above the glass surface level the drawn bolster is bent horizontally over a hollow steel roll (cavity is used for cooling by flowing air). Further drawing takes place in the horizontal direction, in which the bolster passes through the annealing furnace.

Another drawing technology without the debiteuse is the Pittsburgh method, which is younger than the above technologies and is a combination thereof. In particular, the drawing of the bolster from the free surface level and the vertical drawing pit having the function of a annealing furnace were preserved.

At present, it is possible to encounter the Fourcault technology for the production of special glasses such as welding glass (e.g. Severosklo Kamenický Šenov s.r.o.).
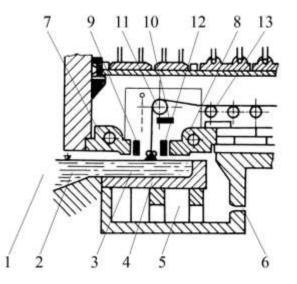
Fig. 9.33 *Section of the working chamber of the Libbey-Owens furnace: 1 - furnace basin, 2 - drawing pot, 3 - drawing chamber, 4 - bottom of the drawing chamber, 5 - heating chamber, 6 - burners, 7 and 8 - special closing blocks, 9, 10, 12 - water coolers, 11 - bending roll, 13 - transport rollers*

9.6.1.2   Downward drawing

The production of flat glass sheets of smaller dimensions was solved in an original way, with the possibility of more frequent change in the assortment, in particular with regard to the colour of melted glass.

The method of downward drawing of flat glass is schematically shown in Fig. 9.34. The glass melt is fed from the working end of the melting furnace through a short trough, in the lower part of which there is an outlet opening, from which the glass melt flows onto a dissolving wedge located in the dissolving chamber, see Fig. 9.35. The space of the dissolving chamber is well insulated and there are built-in heating resistance elements enabling precise temperature control. The dissolving wedge is made of heat-resistant steel and has the shape of an inverted letter A in the cross-section. The upper part of the wedge is constructed as a tray, the space of which is delimited by raised edges. Glass melt flows into this section, fills it and overflows over the raised edges and flows down the two sloping walls of the wedge to the lower edge, where the two flowing layers join. The uniformity of the thickness of the resulting bolster is affected by the decreasing depth of the glass melt in the "tray" section at the opposite end of the dissolving wedge (caused by increased viscosity of glass melt and hydrodynamic losses during glass melt flow), which is therefore provided with the regulation of longitudinal axis inclination. The surface of the formed bolster is of very high quality (it is not in contact with any forming element), its narrowing is eliminated by metal roller holders of edges. These roller holders are not driven, they are freely rotatable and have a ribbed surface. There is another space for precise temperature control between the dissolving chamber and the vertical pit of the annealing furnace (the walls are formed by fittings provided with heating coils, air can be extracted from this space through the gaps between the fittings). The bolster is cooled in a four-compartment vertical annealing furnace, the three upper compartments are electrically heated. There are two pairs of drawing or holding asbestos-cement rollers in each compartment. Below the annealing furnace, there is a separating device for making basic formats.
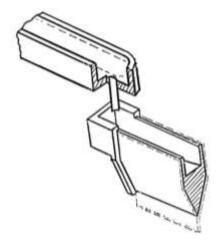

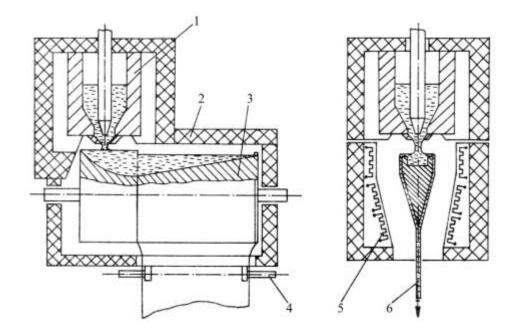*Fig. 9.34 View of the dissolving wedge with feeder forehearth section*

Fig. 9.35 Structural arrangement of the spout of glass melt onto the dissolving wedge: 1 - feeder forehearth, 2 - dissolving chamber, 3 - dissolving wedge, 4 - bolster edge holders, 5 - heating elements, 6 - drawn bolster

In the conditions of Czechoslovak glassmaking, it was a replacement for the manual production of signalling glass, which was still in operation in the 1990s. A similar device was earlier in operation at Corning and PPG companies with the ability to produce flat glass in the thickness range of 0.3 to 12 mm with a width of the drawn bolster of 1,000 mm. The technology also appears in modern lines for the production of special glass-ceramic materials.

9.6.2 Rolling technology

The rolling (casting) technology is based on forming the glass melt between at least two casting rolls. This leads to direct contact with the forming device, which results in a low surface quality. At present, the technology is used for the production of ornamental glass (patterned glass with decoration), wire glass and also for the production of cover glass solar cells provided with a structure that is to reduce the reflection of light from the glass surface and thus increase the efficiency of the cells.

Machine rolling of flat glass takes place intermittently or continuously. The most perfect method of intermittent rolling between a system of casting rolls was still in operation in our glassworks (Chudeřice) in the 1960s. This is the Bicheroux method, the scheme of which is shown in Fig. 9.36. The glass melt is melted in pots with a volume of about 1,500 kg. After melting, the pot *1* is transported by a crane to the casting machine, the glass melt flows into the trough *2* and is formed by two metal water-cooled rollers *3*. The formed bolster arrives on a water-cooled shoot *4*, on which a smaller roller *5* is placed, allowing easier separation of the bolster *6* from the shoot plate, and continues to the metal table *7*. The transport of the formed bolster is provided either by several casting tables or by a roller conveyor to the annealing furnace. The Bicheroux line enables the forming of bolster up to 4,000 mm wide and up to 30 mm thick. Three sheets of glass with the size of 4,000 x 6,500 mm can be produced from one pot.
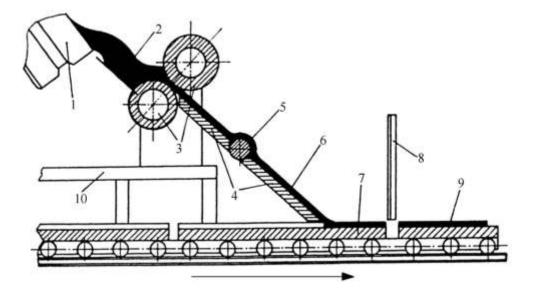
Fig. 9.36 Continuous glass casting using the Bicheroux method: 1 - pot (with a volume of about 1,500 kg of glass melt), 2 - glass melt, 3 - forming rollers, 4 - water-cooled shoot, 5 - auxiliary roller, 6 - formed bolster, 7 - transport table, 8 - shears, 9 - cut sheet, 10 - work platform

At present, flat glass is cast with the use of the continuous method. The glass melt is fed from the melting furnace between the rolls of the rolling machine (Fig. 9.37 A), where it is formed and then cooled in a roller annealing furnace, followed by separation into output formats. Contact with casting rolls results in the creation of a low-quality surface, which is why rolls provided with a surface embossment are often chosen, which creates a single-sided or double-sided decoration on the bolster.

The material and surface treatment of water-cooled metal rolls significantly affects the surface quality of the cast bolster. Two groups of materials are most often used for the production of casting rolls. On the one hand, it is chromium steel with a chromium content of 12 to 15% used for smooth rolls or carbon, well-machinable steel of which patterned rolls are made. The method of creating a pattern on the surface of the casting roll is called "transfer roll process". The pattern is engraved on a steel roller with a small diameter and after tempering it is transferred to the smooth surface of the casting roll by the action of high pressure.

The variant used is the introduction of a wire mesh (Fig. 9.37 B) during casting. This mesh ensures the cohesion of the sheet even in the event of mechanical damage, e.g. by impact, and represents a variant of safety glass.
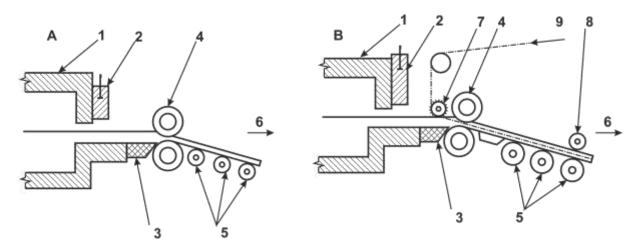
Fig. 9.37 Diagram of continuous rolling (casting) of flat glass: A - rolling machine with the same size of forming rolls, B - rolling machine with adjustment for introduction of wire insert, 1 - working end of melting unit, 2 - shutter, 3 - seal block, 4 - casting rolls (hollow, water cooled), 5 - rollers of the shoot path, 6 - annealing furnace, 7 - wire insert loading element (grooved roll), 8 - polishing roll, 9 - wire mesh

9.6.3 Floating technology (FLOAT)

This is the most modern method of flat glass production, which is characterized by high surface quality of the produced bolster and high production productivity. The principle of the technology (Fig. 9.38) consists in feeding the glass melt to a bath of melted tin and drawing the formed bolster horizontally through a annealing furnace. During drawing, some properties of the final product may be target-affected (e.g. passivation of the surface, formation of functional layers on the surface of the bolster, washing, etc.). At the exit from the annealing furnace, defects are detected, the edges are cut off and the product is separated output formats.
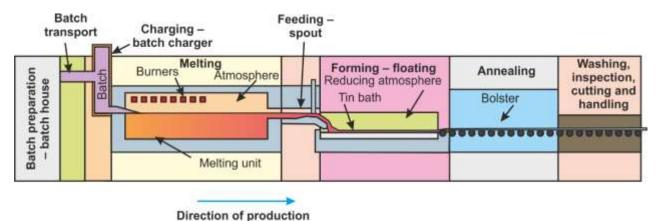

Fig. 9.38 Diagram of the whole production technology by floating glass on a tin bath (FLOAT)

The view of the forming section of the FLOAT line is shown in Fig. 9.39. The glass melt from the working end of the GMU flows through the trough lip through onto the tin bath.
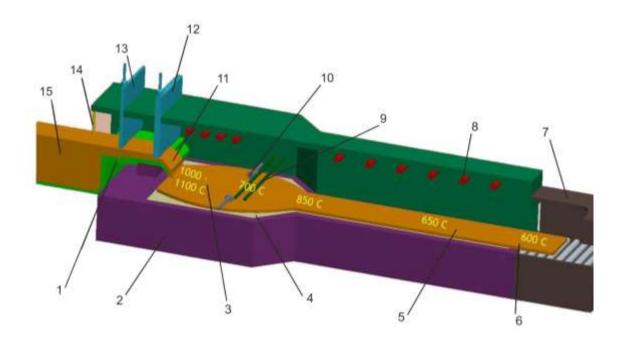
Fig. 9.39 View of the forming section of the FLOAT line: 1 - trough of melting unit, 2 - tank with tin bath, 3 - glass melt, 4 - melted tin, 5 - strip of formed flat glass, 6 - exit from the forming bath (lifting rolls), 7 - annealing furnace, 8 - heating elements, 9 - through-flow water cooler, 10 - metal grooved rollers, 11 - glass melt spout, 12 - regulating gate, 13 - gate, 14 - pyrometer, 15 - glass melt

The glass melt brought to the surface of the tin bath is poured so that its upper and lower surfaces are plane-parallel, which is caused by the effect of gravity and surface tension forces. These quantities are actually responsible for forming of the glass melt. The glass melt forms a "puddle" on the surface of the tin, of the shape shown in Fig. 9.40. The central thickness of the "puddle" is the result of an equilibrium that stabilizes between the force of gravity and the force of surface tension causing an inward draught. This equilibrium thickness t_L [m] is determined by the relation

$$t_L = \sqrt{(S_s + S_t + S_{st}) \cdot \frac{2\rho_t}{g \cdot \rho_s \cdot (\rho_t - \rho_s)}} \qquad (9.4)$$

where S_s is the surface tension at the glass melt-atmosphere interface [N·m⁻¹],

S_t - is the surface tension at the tin melt-atmosphere interface [N·m⁻¹],

S_{st} - is the surface tension at the glass melt-tin melt interface [N·m⁻¹],

ρ_t - is the density of tin melt [kg·m⁻³],

ρ_s - is the density of glass melt [kg·m⁻³],

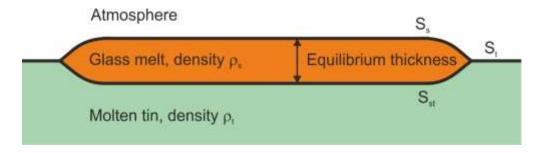g - is the gravitational acceleration [9.81 m·s⁻²].

Fig. 9.40 Vertical cross-section of the "puddle" of glass melt on the surface of the tin bath

The glass melt is fed continuously to the tin bath and has a temperature of approximately 1,050°C. The movement on the surface of the bath is influenced by the traction force caused by the friction of the bolster and the support rollers conveying the bolster through the annealing furnace. The viscosity of glass melt is initially low enough (around the processing point, 10^3 Pa·s, see note[13]), to be able to spill on the surface of the tin melt and compensate for surface irregularities. However, the glass melt must not reach the edges of the bath to prevent it from "sticking". As the thickness gradually decreases towards the equilibrium thickness value under normal conditions, the viscosity gradually increases up to 10^{10} Pa·s (see note[14]). This viscosity already allows the bolster to be lifted out of the tin bath without the risk of deforming the lower surface of the bolster in contact with the lifting rolls.

The equilibrium thickness is about 6 mm for a normal composition of flat glass. If the rate of glass melt removal from the tin bath were to increase, the result would be a reduction in the width of the bolster but not the thickness of the glass. In the production of a thickness other than the equilibrium thickness, water-cooled rotating metal rollers with grooved edges are used, which stretch or narrow the bolster on the tin bath. The function of metal rollers in influencing the thickness of the bolster is shown in Fig. 9.41 and Fig. 9.42. In addition to this mechanical intervention, it is necessary to boost the space of the tin bath by means of resistance heating elements when drawing smaller thickness of glass. In the production of larger thickness of glass, this boosting is eliminated, because the formed glass melt brings an increased heat content already at the spout to the bath.

The tin bath is protected against oxidation by a reducing atmosphere consisting of a mixture of nitrogen and hydrogen (hydrogen content ranges from 5 to 12 %), its parameters depend mainly on the melting rate of the furnace (at 700 tons of glass in 24 hours and a bolster width of 3.5 m is the width of the bath 6 m, length 45 to 70 m, the amount of melted tin 170 to 200 t, the depth ranges from approximately 52 to 105 mm).

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[13] The viscosity of 10^3 Pa·s corresponds to temperatures of around 1050°C in conventional glass melts for the production of float glass.

[14] The viscosity of 10^{10} Pa·s corresponds to temperatures of around 600°C in conventional glass melts for the production of float glass.
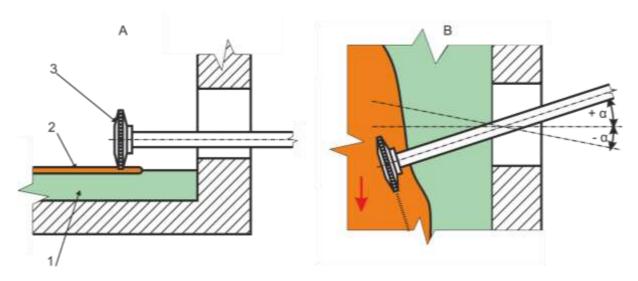
Fig. 9.41 Influencing the width of the bolster using metal grooved rollers: A - location of the roller (side view), B - positions and setting of the roller (floor plan), 1 - tin melt, 2 - glass melt, 3 - water-cooled roller, +α - smaller thickness of bolster (stretching), -α - larger thickness of bolster (skimming)
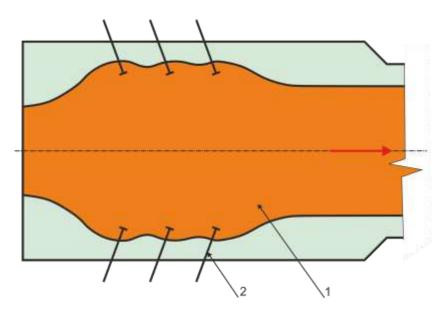
Fig. 9.42 Use of three pairs of rollers to reduce the thickness of the bolster (top view): 1 - bolster, 2 - metal rollers

In addition to tin melt, it would be practically possible to use other materials that meet certain conditions:

- form a melt in the range from 520 to 1,080°C,
- their melt has a density higher than glass melt,
- have a low vapour pressure,
- do not chemically react (too much) with the glass melt.

These requirements are met by melts of three metals: tin, gallium and indium. The choice of tin was a matter of availability and price. Tin has a melting point of 232°C, boiling point 2,362°C, and volatiles from 1,200°C.

It is known that the properties of the *"tin"* and *"non-tin"* sides of the bolster differ somewhat, rather than the chemical reaction it is the diffusion of tin into the surface layers of glass and the locally mechanically trapped tin oxides on the glass surface. Some optical properties, both mechanical and chemical, are usually worse on the tin side. It is therefore necessary for a number of subsequent processing and finishing operations to take these characteristics into account by the appropriate orientation of the sides.

Due to the completeness of the production line, the following text describes the subsequent technological operations that follow the forming process.

After exiting the metal bath, the bolster enters the tunnel annealing furnace, which is a continuous device with a roller conveyor, which is usually designed as a multi-section device. Annealing is performed to reduce the permanent internal stress (Chapter 3.7.2) to the allowable limit using the annealing procedure (Chapter 10.1). The basic division of the annealing furnace can be done into six zones. The first, pre-annealing zone, includes temperatures from about 600 to 540°C and is intended primarily to equilibrate temperatures across the bolster and to warm it to the annealing point (10^{12} Pa·s). The second, annealing zone, includes a temperature range of approximately 540 to 470 up to 500°C, there is a gradual decrease in temperature to the strain point temperature ($10^{13.5}$ Pa·s). The rate must be low enough so that the residual permanent internal stress is lower than permissible. The third, after-annealing zone, includes a decrease from 470 to 500°C to 380 to 400°C. Only a temporary stress (Chapter 3.7.1) is created in this zone, so the annealing rate can be higher. In other zones, annealing takes place by forced convection, i.e. by supplying air. In the fourth zone, both surfaces of the bolster are cooled with warm air. In the fifth zone, it is cooled with cold air. In the last sixth zone (below 220°C), the bolster is already exposed and is after-cooled with cold air on both sides. The outlet temperature of glass is about 60°C.

This is followed by an emergency cut, which is used for separating and discarding the glass. It cuts the bolster cross fire ly (Chapter 11.1.1.1) and directs the cullet to the crusher and to the conveyor belt below the line. It is used, for example, in cases of transition to another thickness (transitional thickness is not usable), deterioration of quality (until the defect is removed), technical problems at the cold end of the line, ...

A washing device can be installed after the annealing furnace. Washing is performed with hot demineralized water, which is supplied to the upper and lower surfaces of the bolster by cylindrical rotating brushes which do not touch the glass surfaces, but only spray them, followed by hot air drying. This may be followed by passivation of the surface with a passivation agent[15], which is applied by a passivation roll.

This is followed by laser defect detection and defects are marked in colour on the bolster, which are classified into several groups by their size. The number, size and distribution of defects are stored in the optimization system, which classifies individual sheets into certain groups in

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[15] The passivation solution is prepared by dissolving citric acid, chelatone, zinc sulphate and slimcide.

connection with quality requirements. Defects even with a size below 0.5 mm are detected. When defects incompatible with the given quality requirements are detected, a part of the glass is cut out and the defective glass is discarded. A conveyor belt runs under the entire production line, which returns the cullet to the batch house.

The separation of an endless float bolster is performed by breaking (Chapter 11.1.1.1), which takes place in two operations. The first is the "longitudinal cut", which separates the edges from the sheet, where there is marking of the rollers and does not ensure the requirement of constant thickness, the so-called edge. This is process waste. The second operation is a "transversal cut" which separates a sheet of the required dimensions from the bolster. The device is equipped with at least one cross fire curtain, which is placed not cross fire ly to the bolster, but obliquely, in order to compensate for the movement of the bolster in marking by scratching. The speed of movement of the cutting head is derived from the movement of the bolster, which ensures a perpendicular cut even when changing the assortment, i.e. changing the speed of the bolster.

This is followed by powdering with anti set-off powder, which prevents the glass sheets from sticking. The sheets are then stacked in attached racks by means of reloaders. The racks are transported to the warehouse and then shipped.

9.7   Technology of production of tubes and rods

Glass tubes are produced by continuous drawing from the spout of glass melt. Technologies are distinguished by direction of drawing between horizontal and vertical. A common element of all the methods used is the hollow plunger, through which the glass melt flows and which forms the nucleus of the cavity, otherwise rod would be drawn. Air is supplied to the plunger (mandrel) under slight pressure.

Glass rods can be produced using the same drawing technology without the use of a mandrel or the so-called casting technology.

9.7.1   Casting of pressing rods

The casting technology on an endless chain conveyor is applied in the production of semi-finished product for further processing in two-stage production. It is mainly used in the production of pressing rods produced in larger series.

The glass melt is either melted in a pot (capacity about 400 kg) with an annular opening, which is closed during melting by means of a metal, water-cooled plug (for smaller series) or in a day or continuous tank (for larger series). The glass melt flows through the orifice ring onto a metal chain conveyor ("chain mould"), the links of which form an endless through, which is filled with glass melt (Fig. 9.43). The chain mould forms the sides and bottom of the glass rod and removes most of the heat. The top of the rod is formed by surface tension and the upper surface also removes part of the heat to the surroundings.

The parameters that are set in casting of rods are the speed of the conveyor and the temperature of the outflowing glass melt (viscosity). The chain mould must remove enough heat to prevent the rod from spontaneously deforming subsequently. After the cracking-off and breaking-off of the rod to the required length (usually 1,200 mm), the rods are placed in a annealing furnace.

This technology also produces blocks for the production of larger pieces of glass products (e.g. 60 x 58 mm and 90 x 30 mm). The movement of the chain conveyor is much slower compared to the production of pressing rods.

Cross-section of produced rod and conveyor link
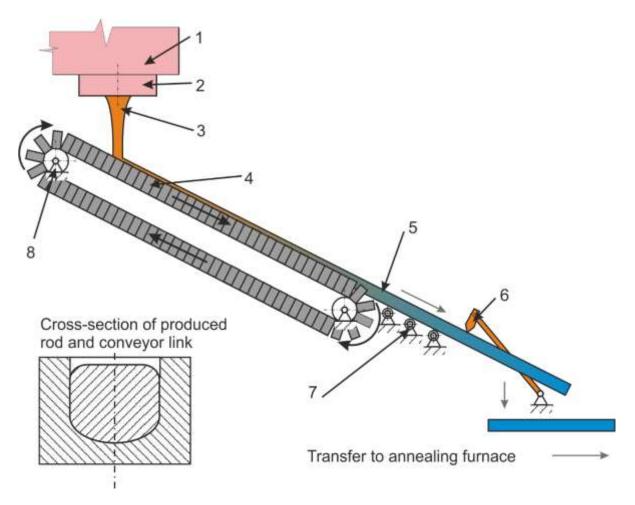
Transfer to annealing furnace

Fig. 9.43 Diagram of machine production of pressing rods: 1 - pot furnace, forehearth of day or continuous tank, 2 - orifice ring with annular spout, 3 - spout of glass melt (around 1000°C), 4 - chain conveyor forming an "endless" mould, 5 - rod, 6 - cracking-off and breaking-off mechanism, 7 - curve rocket, 8 - machine frame

9.7.2   Horizontal drawing (Danner method)

This technology is obsolete, but forms an integral part of the development of tube forming technologies. In this method of drawing, the glass melt flows onto the inclined rotating fireclay nose, forms a lap on it, runs down slowly and is drawn as a tube by a drawing machine initially on a curve rocket with a removable cover (slow uniform annealing), then on a curve rocket without covering. After the drawing machine it is cut into the required lengths. The machinery of the Danner method is shown in Fig. 9.44. The outer diameter of the drawn tubes ranges from 8 to 50 mm, the pressure of the air supplied to the pipe is about 6 kPa, the drawing rate is 4 to 80 m·min⁻¹.
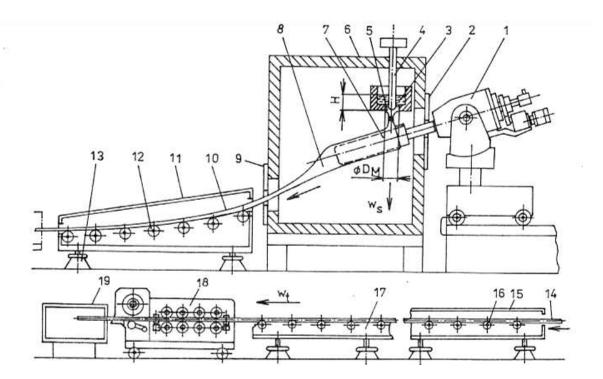
Fig. 9.44 Machinery for horizontal tube drawing: 1 - forming machine, 2 - insulating barrier, 3 - forehearth with spout, 4 - stop, 5 - strip of outflowing glass melt, 6 - chamber, 7 - nose with glass-blowing pipe, 8 - tube nucleus, 9 - insulating barrier, 10 - tube, 11 - covered part of the runway, 12 - roller, 13 - height locking washer, 14 - tube, 15 and 17 - covered and open carrying roll, 16 - roller, 18 - drawing machine, 19 - pallet

9.7.3   Vertical drawing of rods and tubes downward

This technology occurs in two versions - drawing tubes of large diameters over 80 mm (Verta method) and drawing tubes up to a diameter of about 50 mm (Vello system). The only difference is that the originally vertical direction of drawing the tube in the Vello method changes to horizontal and then takes place in the same way as with the Danner system. A diagram of the Vello device is shown in Fig. 9.45. The glass melt flows out through the bottom of the feeding head, flows around the forming mandrel, through the cavity of which air is blown. This creates a tube, the dimensions of which are given by the level of glass melt, the viscosity of glass melt, the diameter of orifice ring, the drawing speed, the position and diameter of the plunger, the air pressure in the hollow mandrel - glass-blowing pipe.

The diameter of the tubes produced by the Vello method ranges from about 5 to 55 mm. Compared to the Danner method, the drawing takes place at approximately twice the speed, about 10 to 160 m·min^{-1}. This drawing method is used in the glass jewellery industry for the production of thick-walled capillaries with a precise hole and a high-quality inner surface. The drawn capillaries are further processed by wet and dry cutting. Glass rods can also be drawn on the line.

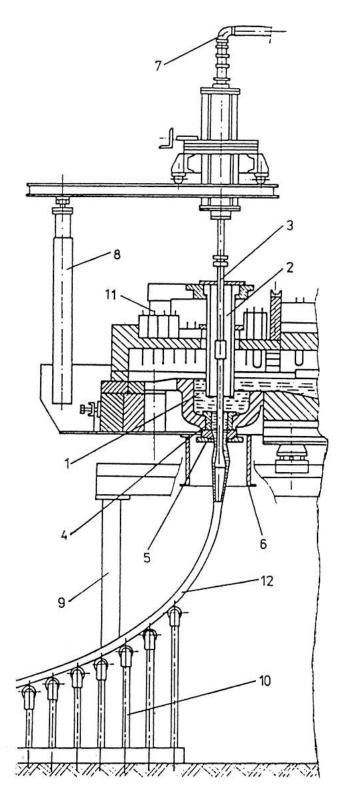Fig. 9.45 Diagram of the Vello line for vertical drawing of tubes downward: 1 - glass melt in the forehearth, 2 - tube, 3 - glass-blowing pipe with forming end, 4 - spout insert, 5 - ring holder, 6 - stabilizing roll, 7 - compressed air supply, 8 - supporting structure of the glass-blowing pipe control device, 9 - supporting structure of the feeder, 10 - roller conveyor, 11 - electric heating system, 12 - drawn tube

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9.7.4   Vertical drawing of tubes upward

In this way, tubes of larger diameters were drawn (this is an older method), from about 50 to 200 mm. The diagram of the device is shown in Fig. 9.46, the drawing speed ranges from 2 to 25 m·min^{-1}. Glass melt with a viscosity of $10^{2.4}$ Pa·s to $10^{2.9}$ Pa·s is fed through a canal into a circular forehearth. In the centre of the forehearth (diameter 1.8 to 2.3 m) there is a fireclay nozzle with an extension, into which air with an overpressure of 900 Pa is supplied. A water-cooled cooler is placed above the surface level, which removes heat from the tube and nozzle.
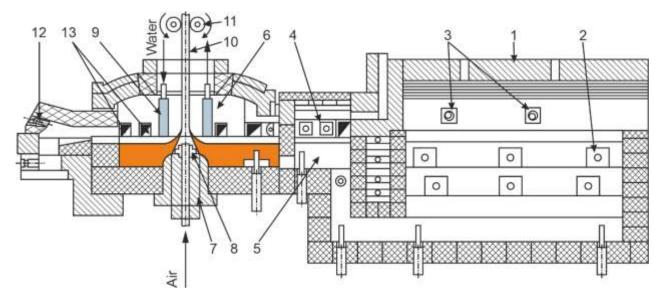
Fig. 9.46 Device for drawing of tubes upward: 1 - melting unit, 2 - electrodes, 3, 4 - burners, 5 - canal, 6 - working chamber, 7 - forming body, 8 - forming nozzle, 9 - cooler, 10 - drawn tube, 11 - drawn rollers, 12 - burners, 13 – flues

9.7.5   Drawing of seed beads tubes

This device is used in the glass jewellery industry for the production of the basic raw material for glass beads, so-called seed beads. The system is either two-stage or single-stage system. In the two-stage process, drawing is performed using a pre-prepared bar (Fig. 9.47), in the one-stage process, the drawing principle is similar to the Vello technology and is shown in Fig. 9.48. The glass melt flows onto a hollow mandrel, into the cavity of which air is supplied under a slight pressure. Drawing is initially vertical, then passes to a horizontal direction, with separation taking place after the drawing device.

Fig. 9.47 Diagram of two-stage drawing of seed beads: A - bar, B - production, 1 - mandrel (it is removed before inserting into the furnace), 2 - metal ring, 3 - toothed guide shaft, 4 - drawing furnace, 5 - heating coils, 6 - guide shaft drive, 7 - wooden board, 8 - drawn tube, 9 - drawing device, 10 - separator, 11 - bin
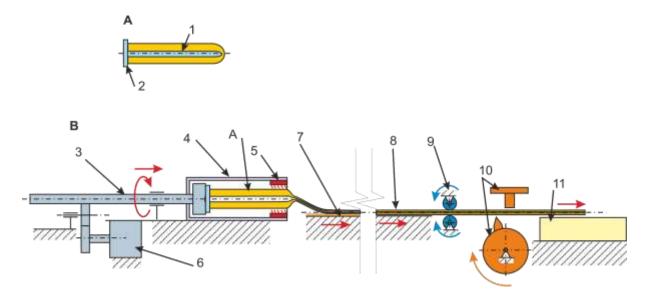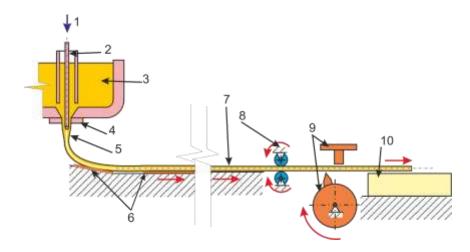

Fig. 9.48 Diagram of single-stage drawing of seed beads: 1 - compressed air, 2 - plunger, 3 - glass melt, 4 - orifice ring, 5 - glass melt spout, 6 - wooden board, 7 - drawn tube, 8 - drawing device, 9 - separator, 10 - bin

9.8 Glass fibre production technology

Glass fibres represent a separate group of products. They are divided into two basic groups, on the one hand there are fibres of infinite length (continuous filament), on the other hand there are fibres of finite lengths (short fibre, staple). The characteristics of production technologies and associated machinery also correspond to this division. Glass fibres of infinite length are of uniform quality and are most often produced in thickness from 5 to 12 μm. They are processed by technologies used in the textile industry, their use is possible for the production of glass fabrics or laminates, other uses are in the optoelectronic area (waveguides). Fibres of infinite length have several times higher strength than piece glass of the same chemical composition. Their usability for textile processing is determined primarily by the flexural strength, which decreases with

increasing diameter. Abrasion resistance of glass fibres and mechanical strength are increased by surface treatment, so-called lubrication, i.e. protection of the surface against damage. Glass fibres of finite lengths show a wider spread of thickness, about 0.5 to 30 μm and sometimes uneven quality (they may also contain granulated glass). Their processing is most often carried out by layering and bonding into mats and boards, special blocks, or processing by one of the technologies of production of non-woven fabrics. They are used for acoustic, thermal or electrical insulation. This group also includes fibres with increased resistance to high temperatures, glass wool, slag and rock fibres. Four basic principles are used in practice for the production of glass fibres:

- mechanical drawing,
- centrifugal method,
- drawing with gaseous medium,
- combined methods.

9.8.1 Technology of mechanical drawing of glass continuous filament

The production is based on drawing the fibres while winding them up with a rotating drum of the winder. The glass melt flows through platinum furnaces with small nozzles.

9.8.1.1 Two-stage technology

The diagram of two-stage production method is shown in Fig. 9.49. The raw material is glass marbles, which are automatically fed from the bin into the platinum furnace, in which they are melted, and the glass melt flows out through nozzles in the bottom of the furnace. The nucleus of the monofilament (separate fibre) is a gob formed on the nozzle. The gobs are connected by a hand tool into the form of a "conglomerate" and guided as a roving of all monofilaments onto a spool located on the drum of the winder. Lubrication is applied between the winder and the bottom of the furnace, either on the lubrication foot (Fig. 9.49, position 4) or through the passage of vapours. After winding up a certain amount of roving, the spool is removed and replaced by another. The diameter of the monofilament is a function of the temperature (viscosity) of glass melt, the diameter of nozzle orifice, the magnitude of hydrostatic pressure and the withdrawal rate.

9.8.1.2 Single-stage technology

The diagram of the machinery of the one-stage method of glass continuous filament production is shown in Fig. 9.50. It has been developed as a more sophisticated and significantly more productive method, based on a two-stage method, in which the individual furnaces replace platinum jigs (sheets) provided with nozzles and located as part of the bottom of the canal through which the glass melt is fed. A more detailed drawing of the bottom of "one furnace" is given in Fig. 9.51. The number of nozzles gradually changed, increasing from the original 400 to about 2,000. For modified devices (C-process), the number of nozzles increased to 4,000. The amount of fibre produced from one nozzle is 0.020 to 0.022 kg per hour, the output of one furnace is 45 kg per hour in the conventional method and 80 to 84 kg per hour in the C-process.
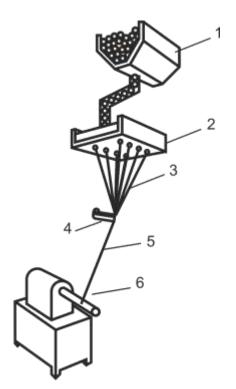
Fig. 9.49 Diagram of two-stage drawing of glass continuous filament: 1 - ball magazine with feeder, 2 - platinum furnace, 3 - single fibres, 4 - lubrication, 5 - roving, 6 - winder
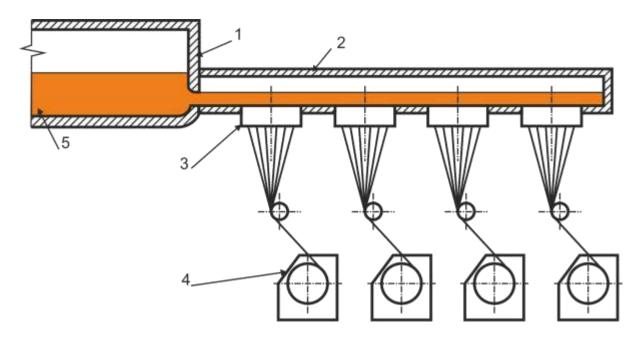
Fig. 9.50 Diagram of single-stage drawing of glass continuous filament: 1 - melting unit, 2 - canal, 3 - furnace, 4 - winder, 5 - glass melt
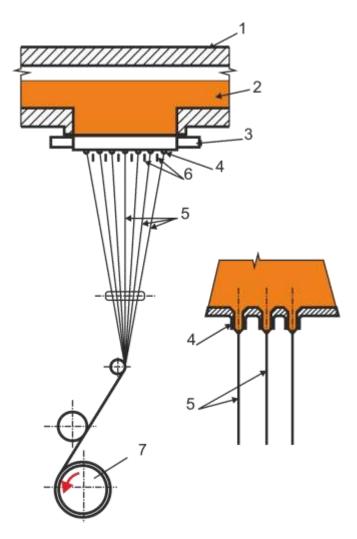
Fig. 9.51 More detailed diagram of single-stage drawing of glass continuous filament: 1 - canal, 2 - glass melt, 3 - furnace, 4 - nozzle, 5 - fibres, 6 - fixed cooler, 7 - winding

9.8.2 Centrifugal forming technology for staple

This technology (Fig. 9.52) processes crushed glass cullet as a raw material, which is melted in a shaft furnace. The melted glass drains into a homogenization pit, from which it overflows through a cooled overflow bridge and flows into the centre of a rotating drawing disc through a fireclay conical hole. The disc is ceramic, placed in a cast steel head, its diameter is approximately 200 mm and thickness is 50 mm. The surface of the disc is provided with radial grooves and rotates at a speed of 3,000 to 5,000 rpm about a vertical axis. The glass melt is sprayed and torn into fine fibres up to 30 μm in diameter on contact with the centre of the rotating disc. The fibres form a closed ring around the rotating head and are carried by flowing air into a collection basket, from where they are periodically transferred to a pneumatic conveyor and then for further processing. Basalt fibres used in the same way as glass fibres for insulation purposes are also produced in the manner described.

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Fig. 9.52 Diagram of centrifugal forming line for staple: 1 - shaft furnace, 2 - cullet loader, 3 - exhaust stack, 4 - gas burners melting glass, 5 - balancing section of the furnace, 6 - conical spout, 7 - drawing machine, 8 - collection basket, 9 - protective cover, 10 - circular saw, 11 - blower fan, 12 - combustion air fan, 13 - recirculation water tank, 14 -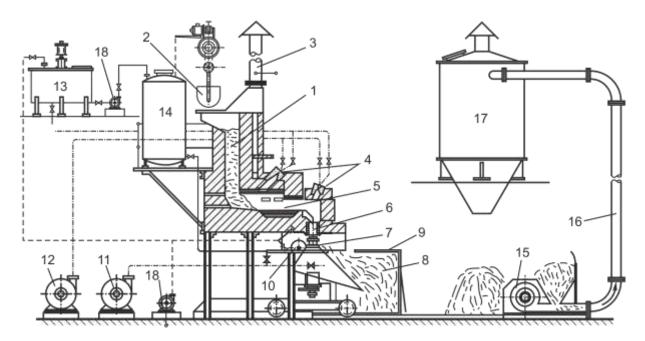 pressure water tank, 15 - transport fan, 16 - pipes for pneumatic transport, 17 - separator and tank, 18 - water pump.

9.8.3 Drawing with gaseous medium

The energy of flowing gas or water vapour is used for drawing glass fibres. As an example, the technology of flame blowing with steam flowing in the vertical direction is given here. The melted glass flows into the feeder and flows through the outlets in the feeder head into the platinum furnaces attached to the bottom of the feeder. These furnaces are similar as with the mechanical drawing of a glass continuous filament - they have spout nozzles at the bottom. A steam nozzle is placed under each platinum furnace and a mixture of steam and air flowing at a speed of 400 to 700 m·s^{-1} entrains the rovings of glass melt flowing out of the nozzles of the platinum furnace and forms irregularly long fibres. These pass through a diffuser cover and are deposited on a belt conveyor. The height of the layer of deposited fibres can be regulated by the speed of the belt. Deposition is due to the strong suction effect of the fan located under the belt conveyor. During deposition, the fibres are sprayed with a binder, usually based on an aqueous solution of synthetic resins or organic origin, the layer is compressed to a certain height by a pressure roller, dried and heat-cured. The arrangement of the platinum furnace and the steam nozzle is shown in Fig. 9.53. The product is mats or boards for insulation purposes.
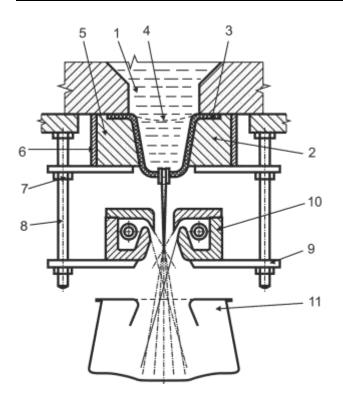
Fig. 9.53 Platinum furnace with steam nozzle: 1 - hole in the feeder, 2 - platinum furnace, 3 - furnace connection flange, 4 - perforated lid, 5 - fireclay lining of the furnace, 6 - cover, 7 - furnace attachment nut, 8 - connecting screws, 9 - steam nozzle bottom plate , 10 - steam nozzle, 11 - diffuser

9.8.4   Combined methods

These production methods are based on the mechanical drawing of primary fibres and their subsequent blowing.

9.8.4.1   Production of fibres by mechanical drawing and blowing

The two-stage process is used for producing a very fine fibre with a diameter of 1 to 3 μm by combining mechanical drawing and subsequent blowing with very hot gases flowing at high speed. The diagram of the production line is shown in Fig. 9.54. Glass made of glass marbles is melted in a platinum furnace, the fibres are drawn out of the nozzles by means of drawing rollers, which advance along the guide plate through grooves for each fibre into the blowing chamber, where a burner is placed, from which flue gases with a temperature of 1,500 to 1,800°C flow at a speed of 400 to 700 m.s^{-1} perpendicularly to the row of drawn fibres. The ends of fibres are melted and blown into very fine fibres, which pass through a diffuser and are placed on a belt conveyor by the action of vacuum. The layer of fibres is wound on a roll and after reaching a certain layer thickness, the strip is cut. Rolls or mats of insulating fibre are produced. The diagram of double drawing is shown in Fig. 9.55, the blow burner is shown in Fig. 9.56. The output of the device is 0.5 to 1.5 kg.h^{-1}.
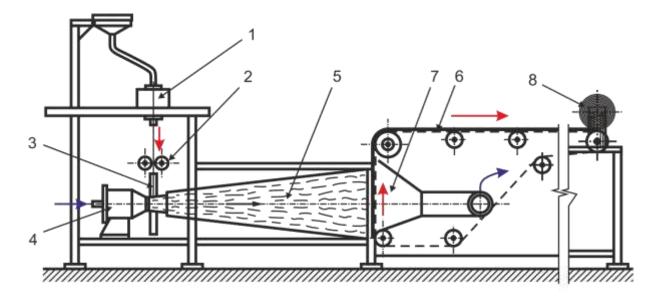
Fig. 9.54 Diagram of the line for the production of very fine fibre: 1 - platinum furnace, 2 - drawing rollers, 3 - guide plate, 4 - blow chamber, 5 - diffuser, 6 - belt mesh conveyor, 7 - suction, 8 - winding device
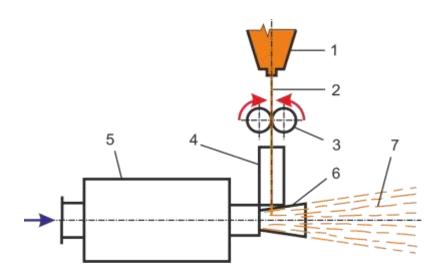
Fig. 9.55 Diagram of double drawing: 1 - platinum furnace, 2 - primary fibre, 3 - drawing rollers, 4 - guide plate, 5 - burner, 6 - blow chamber, 7 - secondary fibre

9.8.4.1   Production of fibres by blowing under rotation

This method is used for producing staple glass fibres under the technical name "Rotaflex". The melted glass flows vertically into a metal inner distributing rotating head (rotation speed is 3,000 to 5,000 rpm) provided with holes through which the melt flows by centrifugal force into the outer pre-moulding head, out of which the fibres exit in front of the mouth of the circular burner. Due to the high temperature and rate of the flue gases, the direction of formed fibres is changed to axial and secondary pulping, the fibres are entrained by oscillating diffusers and are sprayed with a resin binder on the travel. At the outlet of the diffusers, they are deposited on a belt conveyor, the layer formed passes through a drying and firing furnace and behind it the strip is wound on a winding drum, the layer being interleaved with paper. The diagram of pulping is shown in Fig. 9.57.

Staple fibres with a diameter of 7 to 10 μm are produced using the described method, the output of the pulping unit is 8.4 tons in 24 hours. Manufactured mats are used for thermal and sound insulations.
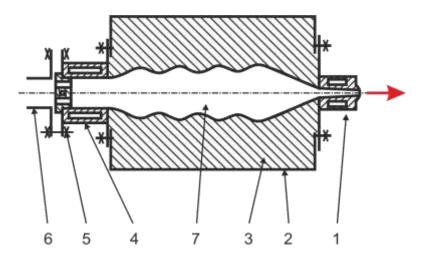
Fig. 9.56 Blow burner: 1 - metal water-cooled blow nozzle, 2 - combustion chamber casing, 3 - lining, 4 - water-cooled adapter, 5 - safety burner plate, 6 - gas and air mixture supply, 7 - burner combustion chamber
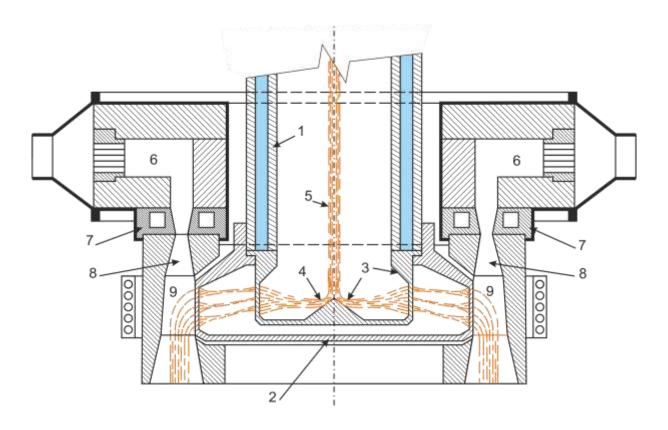
Fig. 9.57 Diagram of pulping head: 1 - water-cooled hollow shaft, 2 - outer pre-moulding head, 3 - inner (distributing) head, 4 - distributing cone, 5 - bolster, 6 - circular combustion chamber, 7 - water-cooled inter-ring nozzle, 8 - inter-ring combustion chamber, 9 - flue gas flow

9.8.5 Production technology for optical-fibre waveguides

Optical-fibre waveguides are based on the total reflection of light, 3.9.1. The basis of the fibre waveguide is a glass fibre formed by two layers. The core has a higher refractive index than the peripheral layer, on which the light ray is completely reflected and the light propagates along the path given by the shape of the fibre. Optical fibres are used in communications, where they allow transmission over longer distances and at higher transfer speeds. They are more advantageous than metal conductors because the signal is transmitted with less loss and are resistant to electromagnetic interference. Other benefits include security (optics are difficult to eavesdrop), small size and low weight, flexibility, good mechanical properties, low acquisition costs, large volume of transferred data, and more.

Optical fibres are produced in several ways. In the production of standard optical fibres, pre-moulds of larger dimensions are prepared in the first phase, from which a thin optical fibre is formed by drawing. There are two methods,

- double crucible method (the fibre is drawn from two concentric crucibles, one containing the core melt and the other, the outer crucible, containing the melt of cladding material - the advantage is the possibility of continuous replenishment of both melts), and
- "rod-in-rod" method (the fibre is drawn from a rod of core material sealed in a tube made of cladding material, from the so-called pre-mould), Fig. 9.58.
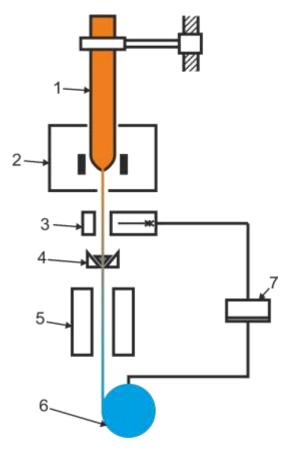
Fig. 9.58 Diagram of the principle of drawing an optical fibre from a pre-mould: 1 - pre-mould, 2 - furnace, 3 - measurement of fibre diameter, 4 - nozzle for application of protective polymer, 5 - curing of polymer, 6 - winding spool, 7 - monitoring and control system

9.9   Glass melt forming by centrifugal casting technology

Forming of thick-walled glass products of a rotary shape by centrifugal casting is more advantageous in many respects than moulding. The formed product is in contact with the mould wall only with the outer surface, the inner surface is formed only by the action of the centrifugal force and the effect of surface tension forces of the glass melt. The wall thickness of the product is also uniform and the product does not deform in the mould. According to the orientation of the axis of rotation, we divide the technologies into technology with a vertical axis of rotation and technology with a horizontal axis of rotation.

9.9.1   Centrifugal forming with vertical axis of rotation

The principle of centrifugal casting will be shown on the example of a single-station machine (Fig. 9.59). However, it is more common to encounter multi-position machines, which will be listed below.
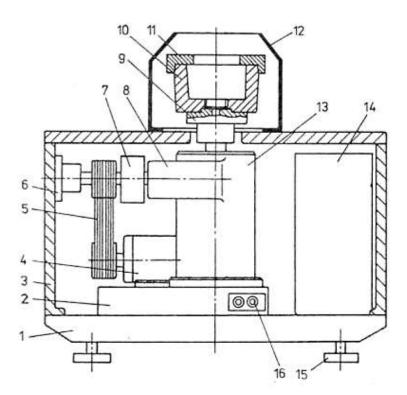
Fig. 9.59 Single-station centrifugal casting machine: 1,2,3 - machine frame components, 4 - electric motor with speed control, 5 - V-belt, 6 - foot bearing, 7 - electromagnetic clutch, 8 - bevel gear drive, 9 - flange, 10 - mould, 11 - closing ring , 12 - cover, 13 - bearing housing, 14 - control panel, 15 - levelling foot, 16 - connection of fluids

The forming procedure consists in placing a gob of glass melt in the mould (manually using a glass-blowing pipe or using, for example, a ball feeder, Chapter 8.2.2), rotating the mould with increasing speed, followed by a period of constant speed, a period of decreasing rotation speed, cooling of the product and its removal from the mould. The centrifugal casting cycle is shown in Fig. 9.60.
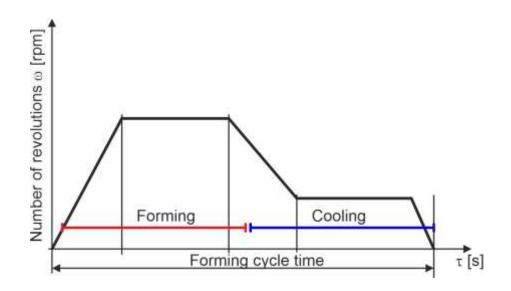
Fig. 9.60 Centrifugal casting forming cycle

High productivity of the process is achieved by multi-position machines, on which thick-walled products up to a diameter of approximately 320 mm, a height of up to 200 mm and a maximum weight of 10 kg are formed. Fig. 9.61 shows a Bowe eight-position machine. Current devices can centrifugally produce products not only circular, but also elliptical in shape.
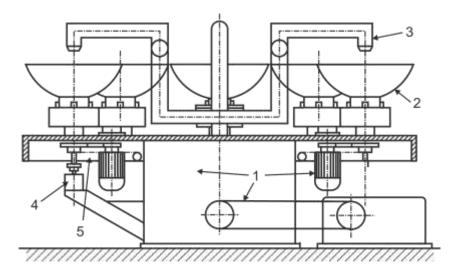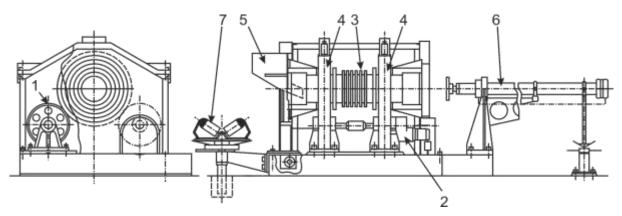
Fig. 9.61 Bowe eight-position centrifuge: 1 - machine frame with appropriate drives, 2 - mould with cover, 3 - adjustable cooling air supply, 4 - push up, 5 - source of cooling air

9.9.2 Centrifugal forming with horizontal axis of rotation

Technologies of this type are less common. As an example, the technology for producing large-size basalt tubes (Fig. 9.62) is given. Two pairs of motor-driven carrying rollers are mounted on a massive frame, on which a cast iron mould is rolled. The basalt melt is poured into the mould under full rotation and formed until solidification by cooling. The finished product is pulled out of the mould with an ejector and transferred to a annealing furnace. The cast iron mould is exchangeable

according to the type of tubes produced. Tubes up to a length of 1,000 mm with an inner diameter of 150 to 500 mm and a wall thickness of 20 mm can be formed.

Fig. 9.62 Machine for centrifugal casting of basalt tubes: 1 - two pairs of carrying rollers, 2 - drive, 3 - cast iron mould, 4 - collars, 5 - funnel, 6 - finished tube ejector, 7 - manipulator for finished products

9.10 Production technology for special products

Some machines could not be included in the previous chapters due to their specifics, so they will be discussed here.

9.10.1 Production of marbles

This machine produces glass marbles with a diameter of approximately 18 mm, which are the starting semi-finished product in the two-stage production of a glass continuous filament, Chapter 9.8.1. The principle of the machine is shown in Fig. 9.63. Its main components are four pairs of spirally grooved drums. The profile of grooves is semicircular, always two drums are pushed close to each other, so the profile of grooves is circular. The grooving of the drums has the same pitch. The drums of one pair have different diameters and the same number of revolutions (50 to 60 rpm). In the same direction of rotation, the circular profile of grooves remains constant and the gob of glass melt placed in the extreme position of the drums while rotating moves to the opposite side. Due to the different circumferential speed, it is gradually formed into a marble by friction against the walls of grooves and falls as a finished product into the container.

9.10.2 Production of ballotini

Ballotini is a technical designation for glass beads up to a diameter of 1.25 mm. Their use is common, for example, in transport (horizontal and vertical reflective marking), they are also used for blasting metal parts (removal of old paint, surface finish), cleaning and regeneration of moulds in casting industry, as a filling material for special filters, as a grinding medium, etc. The production of ballotini is in principle carried out by crushing the glass and by fluidized-bed edging, in which the crushed glass is heated to the softening temperature and the edging occurs under the effect of surface tension forces. The final operation is sorting by size. The diagram of the line for the production of ballotini is used from the Sovitec company (Fig. 9.64).
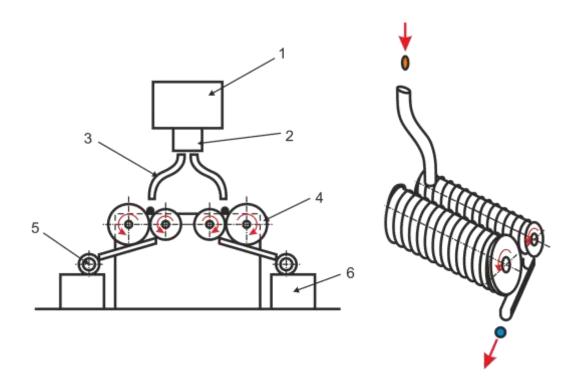
Fig. 9.63 The principle of the machine for the production of glass marbles: 1 - feeding trough, 2 - feeder, 3 - shoot, 4 - forming groove drums, 5 - feeding screw, 6 - bin for finished marbles
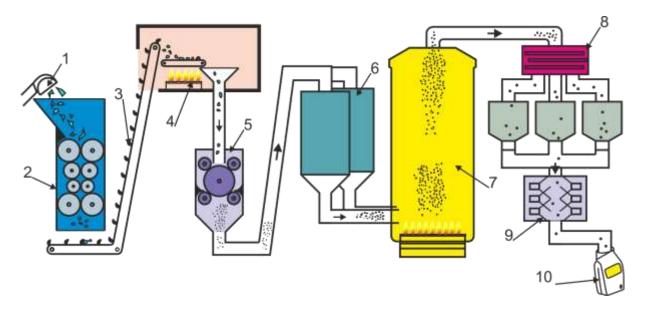
Fig. 9.64 Diagram of balottini production line: 1 - loading with glass cullet, 2 - crushing, 3 - removal of foreign bodies, 4 - drying, 5 - grinding, 6 - intermediate storage of crushed stone, 7 - edging, 8 - granulometric networking, 9 - surface finish, 10 - packaging

9.10.3 Production of foam glass

Foam glass is a porous material (closed pores), which has excellent thermal insulation properties, its specific mass is about 150 kg.m^{-3}, has zero absorption capacity, is non-flammable, resists the action of bacteria and if the product is a blocks, has a sufficient mechanical strength. Its mechanical treatment is very easy.

Foam glass is made of special aluminosilicate glass or, in a cheaper variant, of recycled glass. The glass is melted and then ground into a very fine powder. This glass powder is mixed with even finer carbon powder during grinding. The resulting mixture is spread in a thin layer into steel moulds. The moulds are then heated in a tunnel furnace to about 1,000°C. This results in remelting of the glass powder and simultaneous oxidation of the carbon particles. This gas creates tiny bubbles that increase the original volume of molten glass up to twenty times and fill the entire mould. After foaming, the resulting block of foam glass is slowly cooled from 1,000°C to 20°C. After the final annealing of the foam glass, CO_2 remains in its individual cells at a vacuum of about 1/3 of the atmospheric pressure, which occurs due to the reduction of volume of the cooled gas. After annealing, the blocks of foam glass are ground, stripped of the surface "crust". Blocks that pass all inspections are further cut into boards of, for example, 600 x 450 mm format with a constant thickness (often from 30 to 180 mm) or into sloping boards or other fittings. The whole production is fully automated for standard blocks.

9.10.4 Production of sintered glass

Sintered glass products are made by pressing glass powder (pressing materials, glass frits) into the desired shape and subsequent heat treatment (sintering) causes the grain of powder to sinter into a compact material. During sintering, the glass does not yet melt, but the particles on the surface of grains are mobile enough that they behave like a melt at the grain interface, i.e. they are able to form one phase and thus connect the individual grains.

 Due to this technology using glass powder, the products are only white or in rich colours and transparent glass cannot be obtained (due to fine - powder bubbles of air enclosed in the material).

The production process consists of melting, fritting, crushing and grinding of glass. This is followed by preparation of the pressing material, colouring and homogenization, addition of 3 to 4.5% of water, which acts as a plasticizer.

This is followed by pressing of the material from powder glasses. During pressing, the most important factor is the pressing pressure. During the forming process, compaction occurs in the arrangement of particles in the pressing and an increase in the contact surface between the particles. Both effects are the result of breaking the bridges formed between the particles, filling the space between the large particles with the particles of smaller dimensions and the mutual shape adaptation of the adjacent particles. These effects increase with increasing pressing pressure and consequently also affect the course of sintering in furnaces.

Sintering is influenced by the properties of the initial powder glass, the forming of the semi-finished product from powder glass (material) and the effect of the temperature regime during sintering. The sintering process and its processes take place, with regard to the functional relationship between viscosity and temperature in glass, from the beginning of the gradual heating to the sintering temperature. From a certain temperature, the pressings shrink (T_{Dst} – *lower sintering temperature*), which ends at certain temperatures with the formation of opaque glass and reaching

the final linear shrinkage (T_{Hst} – *upper sintering temperature*). Above this temperature, the linear shrinkage does not change measurably in a certain temperature range (so-called "sintering delay") up to the point T_{def} - *temperature of the starting deformation* of the pressed object. The sintering process of different glasses is generally identical, and therefore, based on the temperature dependence of viscosity, the sintering temperature of the initial glass used can be easily determined. Technological parameters, such as powder glass granulometry, pressing pressure, heating rate and others, must be strictly adhered to if good reproducibility of the results of the whole process is to be achieved.

Using a close glass particle size distribution, lower pressing pressures and lower sintering temperatures, glass filters for laboratory and industrial use (liquid and gas filtration) are reproducibly produced. Chemically resistant borosilicate glass (e.g. Simax) is mainly used for this purpose.

9.11 Glass moulds

The material and surface properties of the mould have a significant effect on the quality of the final product in technologies that use direct contact of the glass melt with the mould to form. The design and material are decisive. In glassmaking, metals and wood are used for making moulds, but graphite and ceramics can also be found. The surfaces of glass moulds can be treated chemically, thermally, provided with a metal or organic coating, or special plastics. The general division of glass moulds depending on the production is given in Fig. 9.65. A specific case is the use of a tin bath for the forming of flat glass using the FLOAT technology, where the level of molten tin actually replaces the mould. Other technologies use the effect of surface tension and other properties for forming.

During forming, it is necessary to remove so much heat to prevent the product from deforming during further handling. If less heat is removed, the product collapses after being removed from the mould and a defective product is formed (Chapter 9.2). With longer cooling times, on the other hand, excessive heat removal occurs, performance is reduced unnecessarily with delays, and a defective product of a different kind may result.

The requirements for glass moulds in terms of the forming process are:

- fast and precise creation of the desired shape of the glass product and achieving a good surface quality of the glass product,
- rapid cooling of the formed glass melt to prevent the glass product from deforming as a result of removal from the mould during subsequent handling,
- long service life,
- low production costs.

The glass mould is periodically heated on the inner surface (press forming element on the outer surface) with hot glass melt and cooled immediately after removing the glass product. Depending on the type of glass melt and the forming technology, its surface in contact with the hot glass melt is heated to 300 to 720°C and the temperature fluctuates by about 60 to 150°C during the forming cycle, the temperature gradient on its surface being from 1 to 10 K.mm^{-1} (°C.mm^{-1}). The life of the mould decreases with higher thermal stress.
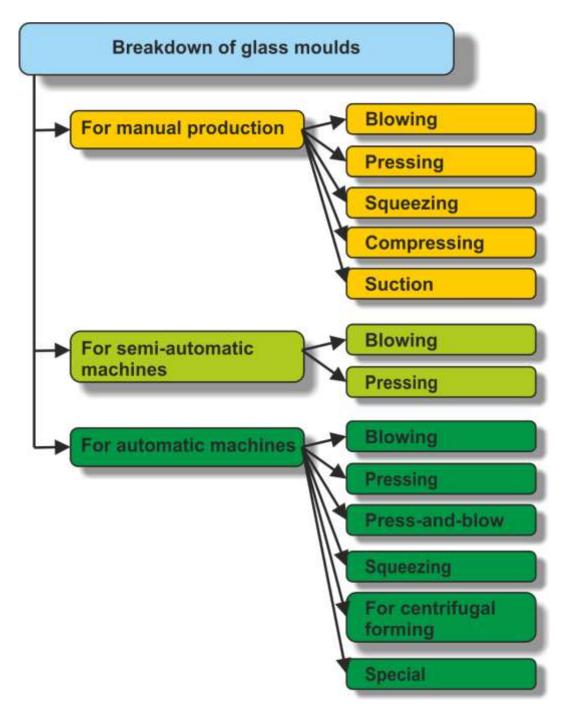
Fig. 9.65 Breakdown of glass moulds by glass production

The requirements for the material of glass mould are as follows:

- high thermal conductivity,
- high heat storage capacity,
- low thermal expansion - high volume stability,
- high resistance to the effects of molten glass and oxidation at higher temperatures,
- good resistance to thermal shocks,

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- good machinability and polishability,
- high wear resistance (in particular abrasion resistance),
- cheapness and availability.

9.11.1 Materials of moulds

In practice, the material of moulds is usually determined by the glass product, production technology and operating practices. In history, the most frequently used material was wood. Today, metals are mainly used, wood is often used for various jigs and in the hand-made production of domestic, decorative and art glassware.

The most widely used material in glassmaking is generally **graphite cast iron with graphite flakes** (grey cast iron) for its properties such as high thermal conductivity, easy machinability, operational production and the possibility of obtaining relatively simple quality castings at a relatively low cost. Resistance to surface oxidation is generally satisfactory. The disadvantages are lower structural stability, low polishability, almost zero drawability and often unsatisfactory wear resistance.

Where longer service life, higher mould surface quality (and therefore higher product quality) and better resistance to the effects of molten glass and oxidation at higher temperatures are required, cast iron alloys or alloy steels, non-ferrous metals and their alloys or sintered carbides are used. Special surface treatments of moulds that come into contact with the glass melt are often made, and so-called explosive welding can also be encountered.

Carbon steels (case-hardening steel 1.1141 - 12 020 -VAR and tool steel 19 191 - EZH are used) have good machinability using common cutting tools, but moulds made of them have a lower service life. Formability is good for tool steels only at high temperatures (steel 19 191 in the range 800 - 1000°C), their hardness decreases with temperature above 400°C.

Alloy steels - tool steel 1.2436 - 19 436 (Poldi 2002) is difficult to machine in the production of moulds, but compared to carbon steels it has a 50% longer service life. Case-hardening steel 1.7131. - 14 220 is easy to machine and form, its hardness above 400°C does not decrease so dramatically. It is used for the production of manual and machine moulds. (Case-hardening is the saturation of steel surface with carbon and subsequent hardening. Three methods of case-hardening are used: in powder, in salt baths and in gases.)

Nitriding steel - 1.8504 - 14 340 is mainly used for manufacturing rotary moulds. This steel is highly dependent on well-performed nitriding. (Nitriding is the saturation of a surface with nitrogen to form a layer of nitrides.) The advantage of the nitriding layer is its high hardness, which hardly decreases at operating temperature.

Austenitic steel - 1.4841 - 17 255 (AKC) has good corrosion resistance and durability, but is difficult to machine and has poor thermal conductivity. This steel contains 20% nickel and 22% chromium.

Nickel is a frequently used material in jewellery production, as glass pressings have a high surface quality. The main disadvantage is the price.

Aluminium bronze has 9 to 11% aluminium. Compared to other materials used for glass moulds, it has an increasing thermal conductivity and heat storage capacity with increasing temperature.

Sintered carbides - have very good abrasion resistance, which is the most important property affecting the life of moulds. Moulds made of this material are relatively expensive, but have a good service life, so they are used in moulds for large series and on high-performance machines (e.g. rotary pressers). The material used in jewellery production is sintered tungsten carbide (G3), which contains 85% tungsten carbide and 15% cobalt as binders. Glass needles are made of case-hardened carbon steel or tungsten.

In the case of glass moulds for domestic glassware (Chapter 9.5), where the products are manufactured with a slight rotation of the glass product or mould, it is necessary to ensure low friction between the mould and the formed glass melt. In this case, the moulds are provided with surface layers ensuring the above. The moulds are intensely moistened before forming, the surface layer ensures even and intensive evaporation of water, which creates a so-called steam cushion, which, due to low friction, allows surface tension to be applied to the surface. Most often it is the gluing of sawdust to the surface. It burns after contact with the glass melt, but the combustion products remain on the surface of the moulds (so-called "crust"). The surface can also be provided with a layer of graphite. It is also possible to meet special plastics that can withstand high temperatures. The result is products without a trace of the parting plane of two-part moulds.

9.11.2 Construction of moulds

Many types of moulds of various designs can be encountered in glass production. In principle, they can be divided by the number of simultaneously formed products into single and multiple moulds. Multiple moulds are often used in jewellery production (Fig. 9.66) and in the production of container glass (moulds are up to quadruple).

The moulds can be designed as one piece or more often divided into two or more parts so that the product can be removed from the mould without damage and without damage to the mould itself. The moulds can be also divided by the method of cooling, Chapter 9.11.4.
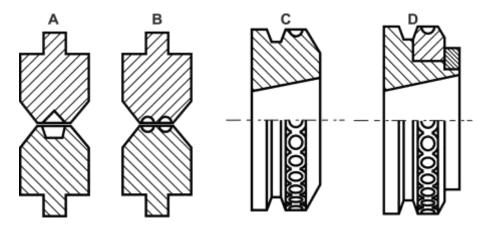

Fig. 9.66 Samples of moulds: A - single mould, B - multiple mould for the production of glass jewellery components, C - steel mould for rotary presser, D - mould with sintered carbide ring for rotary presser

9.11.3 Mould manufacturing

Today, the manufacture of moulds is mostly performed on CNC automatic machines by metal cutting. The surface of the moulds can be machined by diamond grinding and polishing. It is also possible to meet the manufacture of moulds by cold forming, where a hard metal moulding core corresponding to the future shape of the glass product (jewellery mould) is pressed into the polished surface of the prepared metal material. Another technology for the manufacture of moulds is electrical discharge machining, which is based on the generation of repeated electric discharges between the tool - electrode (often made of copper) and the workpiece connected as a second electrode. Electric discharges melt small particles out of the workpiece, washed away by the dielectric. This creates a trace that is determined by the shape of the electrode.

In the production of jewellery components made of glass, explosion welding process, is also used, which is the application of a layer of nickel on the base of the mould made of low-carbon steel. The working ends of the mould (the surface of moulds that come into contact with the glass melt) are then made of nickel and the body of the mould is made of the original cheaper low-carbon steel. Steel moulds are sometimes nickel plated. The cups themselves with the working end can be made of sintered carbide, soldered by brazing brass solder to the body of the steel mould.

Another possibility of surface treatment of moulds is galvanic chromium plating, diffusion chromium plating, boriding, and others.

Regular maintenance is performed to achieve the largest possible number of mould products and a sufficiently long service life. The cleaning of moulds during operational use is usually carried out by hand with the help of the finest abrasive only to the extent necessary, as it degrades the mould in general (surface quality and dimensions). It is possible to use only polishing agents with the lowest possible abrasive effect and care must be taken to ensure that these agents do not degrade glass fragments and dust from the environment. The service life of the mould is affected by:

- working temperature,
- frequency of temperature shocks,
- temperature gradient,
- degree of accuracy (dimensional tolerances) of the pressed object,
- requirements for surface quality,
- mould adjustment,
- cleaning and maintenance of moulds,
- storage environment,
- handling of moulds, etc.

9.11.4 Methods of cooling glass moulds

Cooling of glass moulds is performed during machine forming of glass by flowing air, water or water spray. Press forming elements, for example, are cooled by water, and the moulds themselves are cooled with air.

The moulds can furthermore be cooled radially or axially. Radial cooling is based on blowing the sides of the mould with air (perpendicularly to the mould axis), the moulds are provided with

profiling, an example is given in Fig. 9.67. Axial cooling is based on a system of axial holes (in the direction of the mould axis) in the glass mould through which the cooling air passes, Fig. 9.68.
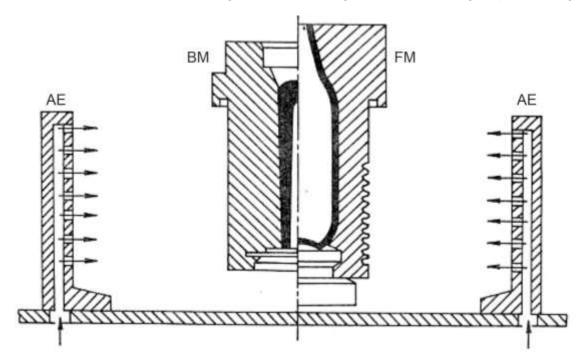

Fig. 9.67 Diagram of radial cooling of moulds with "cooling stacks": BM - blank mould, FM - finish mould, AE - air extensions
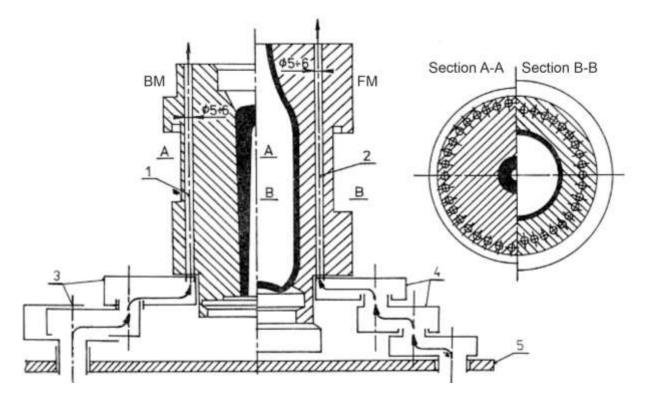

Fig. 9.68 Diagram of axial cooling with feeds of the Heye company: BM - blank mould, FM - finish mould, 1 and 2 - system of cooling holes (boreholes) in BM and FM, 3 and 4 - movable supply of cooling air in BM and FM, 5 - frame of sectioning machine

10 Glass annealing

One of the factors significantly influencing the usability of glass products is their mechanical strength. This strength is, among other things, a function of internal stress (Chapter 3.7), which can be created in the product due to imperfect annealing. During forming, the contact of the outer surface of the product with the surrounding environment (air, mould) results in a temperature gradient between the surface of the product and its inner layers due to the poor thermal conductivity of glass. This temperature gradient results in the generation of stresses between differently warm layers of glass. If the viscosity is low, this stress is equalized by viscous flow. If, due to the high viscosity, a viscous flow is not possible (at lower temperatures), this stress remains in the product even after it has cooled, the stress is called permanent. In order to minimize the amount of residual stress in glass, the glass products are subjected to controlled cooling – annealing, which is carried out in annealing furnaces. The basis is the annealing process, which is determined on the basis of the least favourable properties of the product, which is most often the widest thickness.

10.1 Annealing process

The annealing process is a technology of heat treatment of products, the purpose of which is to ensure that the permanent stress (Chapter 3.7.2) in the products does not exceed a certain prescribed level, which is no longer dangerous in terms of cracking of products. The principle of product annealing is based on heating the product to the temperature in the annealing zone (between strain and annealing point) and holding at this temperature to equalize the temperature inside the product (there is no temperature gradient in the product and viscous flow equalizes the stress occurred as a result of forming). After that, controlled, relatively slow cooling takes place in the annealing furnace to a temperature below the strain point, when the viscous flow no longer takes place. It is then possible to cool the product faster, but with regard to the tolerable degree of temporary stress (Chapter 3.7.1).

The annealing process of a glass product can in most cases be divided into four sections, Fig. 10.1:

    A. Heating to annealing temperature.
    B. Holding annealing temperature.
    C. Cooling in the cooling zone.
    D. After-cooling to a temperature of 20 to 50°C.

The basis for the calculation of the annealing rate in the individual sections of the annealing process is the cooling rate in the cooling zone denoted h_1 [K·min^{-1}] and is calculated from the relation

$$h_1 = \frac{X}{C.a^2.\xi(x)}, \qquad\qquad (10.1)$$

where X is the permissible specific path difference [nm·cm^{-1}],

a - is the standard size of the product [cm],

$\xi(x)$ - is the dimensionless function expressing the effect of the shape and size of the product and containing a conversion from the resulting speed h$_1$ in K·s^{-1} to K·min^{-1},

C - is the cooling module of glass melt [nm·s·cm^{-3}·K^{-1}].
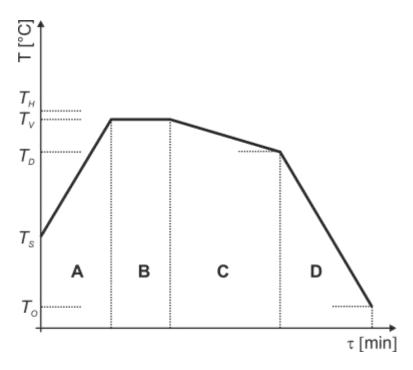
Fig. 10.1 General diagram of the annealing process: T_H - annealing point, T_V - holding temperature, T_D - strain point, T_S - product inlet temperature, T_O - product outlet temperature, A - heating to annealing temperature, B - holding at annealing temperature, C - controlled cooling (cooling zone), D - faster cooling to ambient temperature

For most products, the maximum permissible specific path difference of 100 nm.cm^{-1} is selected. The calculation is usually performed with a margin for *X=50 nm·cm^{-1}*.

The cooling module C is determined experimentally. If not known, the mean value *C=3,100 nm·s·cm^{-3}·K^{-1}* is used.

The standard dimension characterizes the shape of the product. E.g. for double-side cooled plate the thickness t_L is

$$a = \frac{1}{2}t_L, \qquad (10.2)$$

for the plate cooled on one side

$$a = t_L. \qquad (10.3)$$

The values of the shape function $\xi(x)$ are tabulated for basic geometric shapes, Table 10.1.

Because when calculating the cooling rate h_1, we always consider the maximum stress arising in the cooled objects, the values $\xi(x)$ for the surface of the objects are always substituted from Table 2.1. The values $\xi(x)$ for other shapes and for hollow objects are given in technical literature. For products with a more complex shape, this parameter must be determined experimentally.

Table 10.1 Values of shape function $\xi(x)$ for solid objects

Solid objects	Considered place in the object	Value of the function $\xi(x)$
Double-side cooled plate	surface	0.0056
	centre	0.0028
One-side cooled plate	cooler surface	0.0056
	warmer surface	0.0028
Cylinder	surface - axial stress	0.0021
	surface - tangential stress	0.0021
	surface - radial stress	0
	centre - axial stress	0.0021
	centre - tangential stress	0.0010
	centre - radial stress	0.0010
Sphere	surface - tangential stress	0.0011
	surface - radial stress	0
	centre - tangential stress	0.0011
	centre - radial stress	0.0011

The following text describes the individual sections of the annealing process.

A. Heating to annealing temperature

During forming and transfer to a annealing furnace, the product usually cools down, differently in different places. Individual products can also have different temperatures (e.g. bottles formed on multi-section individual section machines). Therefore, the product must be heated. The heating rate to the annealing temperature is denoted h_2 [K·min⁻¹]. It should be as high as possible, usually determined from the cooling rate in the cooling zone h_1 using the relation:

$$h_2 = 3h_1 \text{ to } 5h_1 , \qquad\qquad (10.4)$$

Thus, the rate h_2 can be selected between three to five times the cooling rate h_1.

B. Holding annealing temperature

This delay is necessary to equalize the temperature gradients in the product wall and to remove the internal stress by viscous flow. The level of annealing temperature is usually chosen in the range 0 to 10°C below the annealing point (corresponds to viscosity $\eta = 10^{12}$ Pa·s). If it is not known, the annealing temperature is chosen in the range 0 to 10°C below the dilatometric glass transition temperature (viscosity $\eta = 10^{12.1}$ Pa·s). For common types of glass products, the time of holding annealing temperature is selected in the range of 5 to 20 minutes.

C. Cooling in the cooling zone

During cooling in the cooling zone, a temperature gradient is created in the glass, which, after equalizing the temperatures in the cold product, causes a permanent stress. During cooling in the cooling zone, therefore, no larger temperature gradient must be created than the maximum permissible value of the permanent (residual) stress. Therefore, the rate h_1 is selected. The lower limit of the cooling zone is selected according to the type of furnace 30 to 75°C (modern furnaces

with air circulation) or 100 to 150°C (furnaces with static atmosphere) below the holding temperature.

D. After-cooling to a temperature of 20 to 50°C

The after-cooling rate is selected the same as when heating to cooling temperature (h_2).

10.2 Annealing furnaces

The annealing process takes place in annealing furnaces, which are designed as either chamber or tunnel furnaces. Further breakdown can be by heating into gas, electric and combined furnaces. The breakdown by construction into furnaces with a stationary and circulating atmosphere is also often mentioned.

10.2.1 Chamber annealing furnaces

Chamber annealing furnaces are among the oldest but, in spite of that, their use, in particular in manual production, is still quite common. They work periodically, they are thermally insulated chambers heated by gas or electric heaters. The work cycle, most often twenty-four hours, represents filling the furnace with products, running the entire annealing process and emptying the furnace. Their operation is not economical from an economic point of view, the disadvantages are eliminated by new thermal insulation materials (mineral fibres). A diagram of a gas-fired chamber annealing furnace is shown in Fig. 10.2.

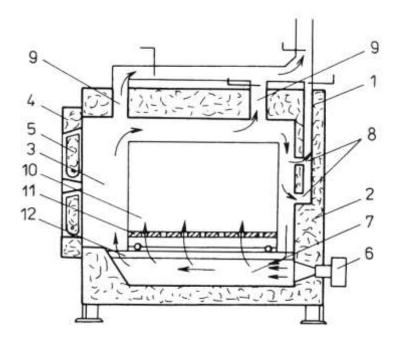*Fig. 10.2 Diagram of a gas-fired chamber annealing furnace: 1 - metal casing, 2 - thermal insulation from inorganic fibres, 3 - loading port, 4 - loading port door, 5 - hinged loading door, 6 - short-flame burner, 7 - combustion chamber; 8 - flue gas exhaust openings in the rear wall, 9 - flue gas exhaust openings in the ceiling, 10 - metal pallet, 11 - perforated pallet bottom, 12 - steel beams*

10.2.2 Tunnel annealing furnaces

These annealing furnaces operate continuously and are used mainly in large-capacity production technologies. They are designed either as roller furnaces (for annealing flat glass and tubes) or as belt furnaces for annealing piece glass (domestic and container glass), in which the transport element is a wire mesh belt. Furnaces are usually composed of a heating zone, a cooling zone, an after-cooling zone, and a drive unit. Tunnel annealing furnaces are heated either by gas or electrically. Gas furnaces have been designed either for direct contact of products with flue gases or more often as muffle furnaces, in which the muffle section is directly heated and the heat is transferred to the products indirectly via partitions separating the annealing section from the muffle section.

At present, these furnaces are gradually being replaced by tunnel annealing furnaces with forced circulation of furnace atmosphere. These furnaces with air circulation caused by fans consist of a number of mutually independent sections, which are assembled according to specific requirements. Due to the forced circulation of furnace atmosphere, they undergo more intensive heat exchange, work more economically and have a higher output. An example of such a furnace is given in Fig. 10.3 , showing the arrangement and function of the individual sections. The cross-section of the heating section of the single- and double-fan system is shown in Fig. 10.4 . The air circulation is indicated by arrows in the figure. The air is sucked out of the space of cooled products by fan, forced to the sides of the furnace, where the air is heated by electrical heaters and blown under the mesh of the belt on which the products are placed. The individual sections have a separate temperature control in order to ensure the annealing of glassware according to the theoretical annealing curve. The speed of the mesh conveyor belt is also regulated.
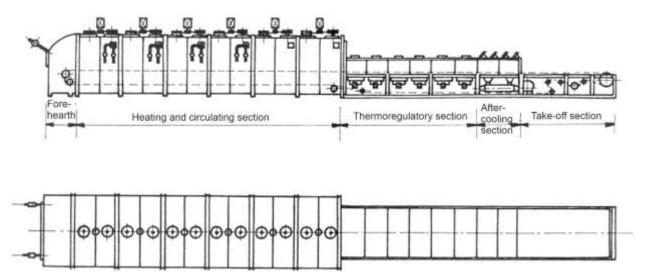
Fig. 10.3 Diagram of a tunnel annealing furnace with air circulation
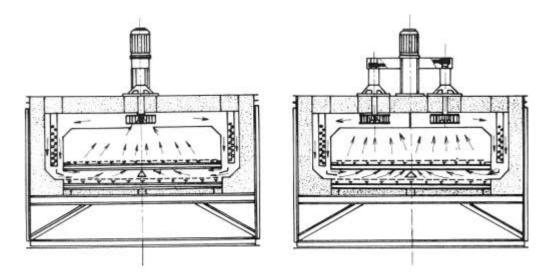
Fig. 10.4 View of the heating section of the single- and double-fan system of the annealing furnace

Tunnel annealing furnaces are often part of production technologies. This is evident in the production of flat glass using the FLOAT technology. Here, in the first phase, the bolster is not heated to the cooling temperature, but is cooled to the cooling temperature, since its temperature is too high after forming.

10.3 Other annealing procedures

It is true that glass products of small dimensions (wall thickness) are usually not cooled to minimize permanent internal stress. Products with a small wall thickness are cooled in air. Examples are glass fibres, seed beads, small jewellery products. For the latter type, the products usually fall into double-walled insulation boxes (so-called "thermoboxes"), in which the products cool spontaneously, usually until the next day.

10.4 Determination of stress in glass

Glass is an isotropic substance. However, if there is an internal stress in glass, it becomes optically anisotropic and birefringent (Chapter 3.9.7). A beam of linearly polarized light is split into ordinary and extraordinary rays, passing through the glass at different speeds. The path difference of the two rays Δ is directly proportional to the birefringence of glass and the length of the path of ray through glass d. The birefringence of glass is directly proportional to the stress σ that induced it. The combination of these dependencies created a basic relationship for the calculation of stress in glass.

$$\Delta = B.\sigma.d, \qquad (10.5)$$

where Δ is the path difference between the ordinary and extraordinary rays [nm],

B - is the photoelastic constant of glass, for conventional soda-lime silicate glasses it has a value of about 25 to 28 [nm·cm^{-1}·MPa^{-1}];

σ - is the stress in glass [MPa];

d - is the length of light path in glass [cm].

The maximum permissible values of stress in glass are specified in the standards for individual products. Because glass annealing check is performed on polarizing devices, these maximum permissible values are given directly as the maximum permissible specific path difference in nm.cm^{-l}.

A rapid qualitative method uses a polariscope, the quantitative determination is performed in a polarimeter with a Sénarmont compensator.

11 Glass processing and finishing

At the end of the 17th century and during the 18th century, finishing of artistic glassware, including Czech crystal, by painting, grinding, engraving, etc., also spread in addition to glassworks. Apart from jigs, no mechanization was virtually used for this production.

In the past, processing and finishing technologies were mostly difficult to mechanize and subsequently automate. Their mechanization began to occur as late as in the second half of the 19th century, as evidenced by efforts in the production of glass jewellery components. Historically, each individual piece of glass jewellery has been ground separately using a quadrant, or in several pieces using a jig (so-called little machine or apparatus). The first grinding machines have been introduced since the 1990s. The real advent of automation in finishing and processing can be seen in most operations as late as in the second half of the 20th century.

The boundary between processing and finishing is very thin in many technologies and cannot be clearly defined in some cases. **Processing** can be defined as obtaining the final shape, where the product significantly changes its shape and obtains a utility value. The processing technology is referred to in some publications as basic finishing. **Finishing** is a process in which the overall shape changes less, but the surface properties change in particular, i.e. appearance of the product and/or functional properties.

Processing technology and finishing techniques can be divided into:

- mechanical,
- thermal,
- chemical,
- combined methods.

The technology of mechanical processing and finishing uses materials with a hardness equal to but more often higher than that of glass and the application of their properties through suitable tools and technologies.

In the case of thermal processes, a local increase in temperature is sometimes made to such a value that the desired effect is achieved by the action of surface tension forces. It is mainly about creating a smooth surface of products, rounding of sharp edges, etc. Another common finishing is the so-called tempering and strengthening of glass, when a compressive stress is induced in the surface layer in order to increase mechanical and safety properties. Glass, especially flat glass, can be formed by gravity and under own weight. An example is automobile glazing closure. It can also be a process of striking and opacification, when the colour and transparency of the semi-finished product changes throughout the volume.

Due to the action of other substances, chemical processes change surface properties, in particular visual and functional properties, as well as mechanical and chemical resistance properties.

Combined procedures cannot be clearly assigned to previous technologies. An example is safety laminated flat glass (safety compound glass).

For most products, there are several processing and finishing operations on one product, which follow each other in a certain technological sequence, they can be repeated and combined with each other.

The main and important technologies are listed below according to the above breakdown.

11.1 Mechanical procedures

Mechanical processing and finishing technologies can be divided into the following procedures:

- glass cutting (processing),
- drilling (processing),
- milling (processing),
- grinding and polishing (finishing),
- sandblasting (finishing).

11.1.1 Separation of glass

The separation of glass can be performed with the use of several technologies. The most common include:

- breaking,
- cutting, and wet and dry cutting,
- water jet cutting,
- chipping.

Technologies, machines and equipment will be described hereinafter.

11.1.1.1 Breaking

The technology of breaking glass after marking by scratching is most often used for flat glass. Diamond cutters or, today, more often carbide wheels, are used for marking by scratching. Carbide wheels are ground at different apex angles for different glass thickness from 120° for glass up to 2 mm, up to an angle of 165° for glass 25 mm thick. A universal cutter with an angle of 135° for glasses from 2 to 6 mm is common. When cutting, kerosene is used for keeping the cut clean. Cracks are formed and stress is concentrated at the point of marking by scratching, and after bending the glass, for example over the edge of the bench, a controlled fracture occurs at this point.

Hand work can be found at a glassworker who uses simple hand cutters and benches. Glass-breaking machines are called cutting machines.

Cutting machines for flat glass cutting technology are either stand-alone machines or directly integrated on production lines. The degree of automation can be different, but CNC machines are currently used, which allow the import of the cutting plan (in standard formats of drawing programs) via the control computer. Automatic lines also include automatic transport and automatic breaking and subsequent handling. The machines are often directly integrated into the lines for the production of the flat glass semi-finished product itself, where it is used for cutting the glass into the necessary formats, cutting out defective glass, cutting process waste in the form of so-called borts (Chapter 9.6.3). Cutting machines are also at the beginning of lines for the production of

automobile glazing closures, where complicated formats are often cut out from basic formats for subsequent processing (Chapter 11.4.4). The main advantage of these lines is the accuracy of cut shapes, speed and efficiency in cutting, optimization of the cutting plan and thus minimization of waste.

The cutting head (Fig. 11.1) can be only one on the machine or there can be several cutting heads. Most often, the heads are placed on a movable bridge. The speed of the cutting head is 1.4 to 3.4 m/s. The cutting capacity can be increased by several cutting heads. The thickness of the cut glass is usually reported from 3 to 12 mm. Top machines range from less than 2 mm to 25 mm.
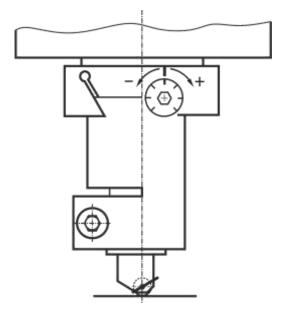
Fig. 11.1 Detail of cutting head

Transport within the line is provided by either rollers or straps, and compressed air supplied under the glass is often used for handling, creating an air cushion (the glass is buoyant). The breaking of the sheet is done either manually or more often automatically, usually by lifting the glass at the point of cut. You can also encounter heating at the point of cut. This creates a temporary stress in glass and the glass breaks (cracks) in the cut. The cracking-off technology is based on this principle, Chapter 11.2.1.

The separation of laminated glass is a more complicated task. The separated glass must be cut on both sides, then broken partially and finally heated by a resistance coil to melt the film between the glasses.

11.1.1.2   Cutting, and wet and dry cutting

The separation of glass by cutting is based on the principle of wet and dry cutting of a narrow area of a glass product, usually using narrow grinding wheels. Diamond tools (DIA tools) are mainly used today. Their expansion occurred after mastering the technology of production of synthetic diamonds. This method of separation is used when cutting by breaking or cracking-off is not possible, where high accuracy and parallelism of the cut surfaces are required, or where the cut is to be oblique, for example. A clear advantage is the higher quality of the cut surfaces compared to breaking.

Diamond wheels are used as tools, which can have two designs, either with a continuous circumference or segmented, Fig. 11.2. The size of diamond grains is from 0.15 to 0.25 mm. Water, kerosene or emulsions are used for cooling the wheels (diamond tools must always be cooled). The cutting circumferential speed of the wheel is up to 80 m/s, the feed rate is from 10 to 200 mm·min^{-1}. The wheels usually have a diameter from 60 to 700 mm.
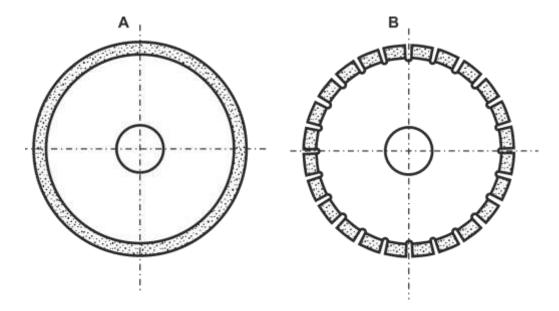
Fig. 11.2 Diamond cutting wheel, A - with continuous circumference, B - segmented

When designing wet and dry cutting machines, care must be taken to avoid vibrations that result in rapid wear of the tool and reduced accuracy of the dimensions of the cut glass. Therefore, the machine frame, the slide rest, the cut glass clamping jig and the spindle are designed to minimize vibrations of the diamond wheel.

An interesting solution at present, in particular for mechanized glass processing and for the hobby sector, are the so-called diamond ring saws (also referred to as diamond string saws). They use a diamond tool in the form of a thin ring, Fig. 11.3. The ring is fixed in nylon sleeves in the form of rolls. The drive is provided via a belt, which is immersed in a water bath and also provides a water supply for cooling the wheel. Glass is placed on the bench, from which the shape is then cut out virtually without limitation. This concept is probably not yet suitable for industrial use in series production.

11.1.1.3   Water jet cutting

This technology has undergone great development in recent years. Water jet cutting makes it possible to separate a whole range of different materials, such as plastics, paper, metals, ceramics, granite and glass. As with a diamond saw, the glass can be single-component or laminated glass. The cut is clean, without thermal effects and stress, the process is dust-free and without the development of harmful gases. The advantage is the possibility of producing virtually any shape.

There are two principles of cutting (Fig. 11.4):

- single beam cutting, used for softer materials,
- abrasive water jet cutting, used for hard materials.
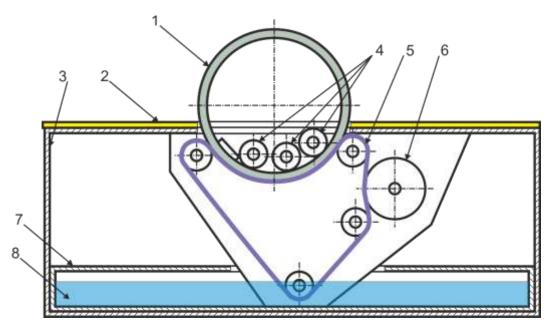
Fig. 11.3 Diagram of diamond ring saw: 1 - DIA ring (string), 2 - work bench, 3 - machine frame, 4 - pulley system for fixing the ring, 5 - drive belt of the ring, 6 - belt drive, 7 - tray with coolant, 8 - coolant
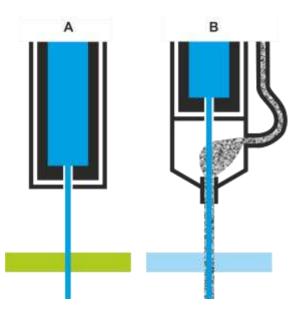
Fig. 11.4 Principle of water jet cutting: A - non-abrasive, B - abrasive

In the case of clean water jet, a supersonic jet stream mechanically disrupts the material. Clean water jet cutting is mostly used for cutting rubber, sealants, filter mats, but also, for example, disposable diapers, tissue paper and car interior equipment.

In the case of abrasive water jet, the water jet accelerates the movement of abrasive particles (e.g. garnet sand or olivine). These particles, not water, disrupt the material. Properties of abrasive water jet:

- no heat affected zones,
- no mechanical stress,
- thin stream (diameter 0.508 to 1.27 mm),
- extremely detailed geometry,
- cutting of thin material,
- cutting of material up to a thickness of 254 mm,
- low waste of material during cutting,
- low cutting forces during cutting, maximum of 4.5 N,
- one beam setting for almost all variants of abrasive cutting,
- limitation of the number of subsequent operations,
- easily programmable process.

The basis of every device is an efficient pump. Productivity also increases with increasing water pressure. In the case of abrasive water jet, its diameter decreases and the flow velocity increases, so that it supplies a higher power density of the cutting jet, the kinetic energy of the individual parts of abrasive increases. At present, permanent operating pressures of 600 MPa (6,000 bar) are achieved. According to the manufacturers, the jet velocity is then approaching velocities of 1,300 m/s. The systems can also cut to a limited extent in so-called 3D, the water jet can be fed at an angle of up to 60° to the material to be cut. This makes it possible, for example, to chamfer edges. The solution is offered, for example, by the Flow company in the Mach series, which cuts with an accuracy of 0.127 mm at a speed of up to 10.2 m·min^{-1}.

Water jet cutting devices are used for cutting mainly flat glass. Portal CNC machines are used for this purpose. High-precision drives and linear cutting head guides (ball screws or e.g. Nexen Roller Pinion System) are also used for achieving high accuracy.

There are also solutions that allow the cutting heads to be mounted on the arms of industrial robots. The advantage is very flexible cutting. This solution is not used (yet) in glass applications.

11.1.2 Glass drilling

There are several technologies for drilling glass, mainly differing in the diameter of drilled holes and the possibilities of producing non-circular profiles.

Glass drilling machines can be divided according to the drilling tool (medium) as follows:

- flat bottom drill bits,
- diamond drill bits,
- ultrasound,
- laser,
- abrasive water jet.

The individual machines together with the technology are described in the following chapters.

11.1.2.1   Drilling with flat bottom drill bits

Triangular flat bottom drill bits made of sintered WC and TiC carbides, usually of quality H1, are used for drilling small holes, Fig. 11.5. As can be seen from the figure, drill bits with a more pointed tip (smaller apex angle) are used for drilling thinner glasses, and with a tip with a larger apex angle for larger thickness.
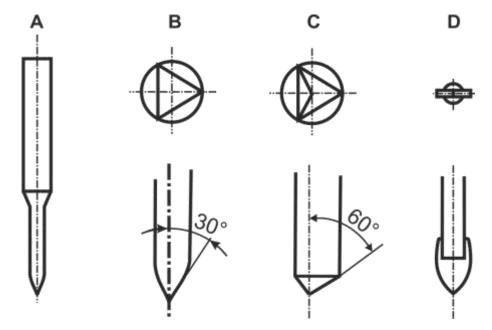
Fig. 11.5 Shape of flat bottom drill bits: A - general view, B - drill bit for drilling of small thickness, C - for drilling of large thickness, D - drill bit with insert

Again, it is necessary to use coolants in machining of glass, which can be water, kerosene, glycerine or turpentine. From the point of view of tool life, the best coolant is turpentine, which, however, ceases to be used for hygienic and ecological reasons, even though it increases tool life 2 to 3 times. Water is most often used.

For drilling with a flat bottom drill bit with an insert, the condition of low speed and the mentioned intensive cooling must be observed. This type of drill bit is manufactured in diameters from 3 to 12 mm.

Flat bottom drilling machines can be universal or single-purpose. An example of a single-purpose device is a machine for drilling holes in chandelier bowls of VM-1 type. The machine drills holes with a diameter of 3 mm, the service life of the drill bit is below 200 drilled holes, the speed of the drill bit is 3,000 min^{-1}, one hole with a depth of 5 mm is drilled within 4 to 8 s.
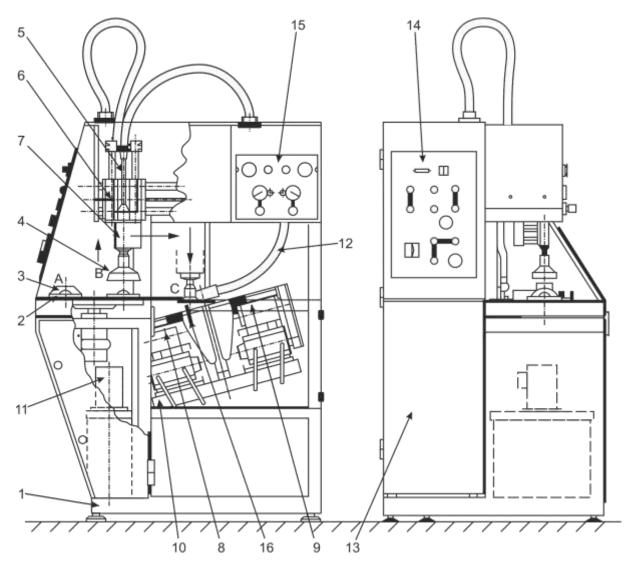
Fig. 11.6 Drilling machine for chandelier bowls of VM-1 type: 1 - frame, 2 - positioner, 3 - chandelier bowl, 4 - gripper, 5 - pneumatic drive, 6 - travel between positions B and C, 7 - turning of the head by the spacing of holes, 8 - left drilling unit (spindle, feed, electric motor), 9 - right drilling unit, 10 - tilting of drilling units, 11 - cooling unit, 12 - cooling water supply to the place of drilling the hole, 13 - distributor, 14, 15 - main and side control panel, 16 - chandelier bowl in the drilling position, A - insertion position, B - transfer position, C - drilling position

11.1.2.2 Drilling with DIA tools

Diamond tools (DIA tools) are also used for making holes in glass. There are basically several types of drill bits. The principle is always to wet and dry cut the glass. In most cases, it concerns drilling of flat glass.

Mini milling cutter can also be used for drilling small diameter holes in glass. These can be in the form of the ball, roller or needle with diamond dust on the surface mounted on a clamping shank. Bar drill bits are used for small diameters from 0.5 to 3 mm. It is an elongated pyramid (needle) from 0.5 to 1.5 mm in diameter (or from 0.6 to 3 mm), which is coated with diamond dust, the speed for drilling with this tool is reported from 400 to 700 min^{-1}. The drill bits are designed for

drilling jewellery and stones. Another type is a roller, which has a diameter from 1 to 2 mm and is coated with diamond dust. The spindle speed should be around 1,000 min⁻¹.
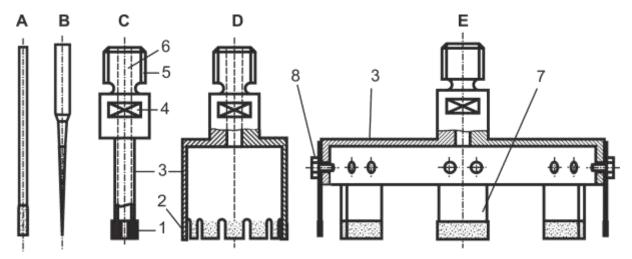
Fig. 11.7 DIA drill bits: A - diamond-coated rod drill bit, B - bar drill bit, C - tubular drill bit with solid crown, D - segmented, E - with screwed segments, 1 - diamond crown, 2 - diamond segment, 3 - tubular part of the drill bit, 4 - double-sided facets for key mounting, 5 - threaded end, 6 - coolant supply hole, 7 - diamond segment, 8 - screw

For drilling, it is also possible to use flat bottom drill bits with a diamond tip, Fig. 11.5, D. In this case, the tip is in the form of a pointed insert with applied diamond grains.

The most commonly used diamond drill bit is currently a tubular drill bit. This is basically the wet and dry cutting of a thin intermediate ring in the glass. The active part of the drill bit is usually formed by a bronze crown containing diamond grains with an average size of 100 - 200 µm. Drill bits usually have a diameter from 3 to 120 mm, they can also have a diameter above 250 mm. From a diameter of 6 mm, they can have a segmented (cut) crown, which improves the removal of coolant with ground glass particles, thus reducing drilling resistance. For industrial applications, the drill bits are cut from a diameter of 14 mm. For drill bits for mechanical production, the coolant is almost always guided through the centre of the drill bit (if allowed by its diameter). Recommended drilling parameters are given in Table 11.1. A pair of drill bits (in the case of drilling flat glass) is commonly used for drilling, which drill the glass from both sides so as to achieve a higher quality of drilled holes without crevices and small shells on the output side. In this case, the drill bits must not come into contact and must be correctly centred.

Table 11.1 Recommended technological drilling parameters

Drill bit diameter [mm]	Speed [min⁻¹]	Water pressure [kPa]	Feed [mm.min⁻¹]
5 – 3	10,000	500 – 200	100
6 – 10	5,500	500 – 200	70
11 – 20	3,500	200 – 100	50
21 – 35	1,500	100 – 50	45
36 – 40	750	100 – 50	40
Above 40	< 600	50 - 20	< 30

Glass drilling machines can be mechanized and automatic. Mechanized machines are used for manual and small series production. These are mostly double-spindle stand drills with a table for laying flat glass. They are flexible, versatile, allow to drill a wide range of different holes, but also require more skills and experience. Modern mechanized machines are characterized by continuously adjustable speed, automatic starting of motors, automatic starting of water into the drill bit, closed water circulation, etc.

11.1.2.3 Ultrasonic drilling

Ultrasound is an acoustic wave, which belongs to the elastic wave with a frequency of 20,000 to 10^9 Hz. Frequencies of 18,000 to 25,000 Hz are used for ultrasonic machining. The basis is a power member sonotrode - concentrator - tool.

The ultrasonic generator is supplied by a piezoceramic transducer, from which oscillations are transmitted via a concentrator to the tool, Fig. 11.8. The principle is based on oscillating the tool and adding a sufficient amount of abrasive suspension (suspension of water and abrasive grains) to the machining location. The process itself is based on disturbing the glass with an abrasive, breaking out small particles, which are then washed out together with the abrasive suspension, while feeding fresh abrasive suspension into their place. The machining process takes place only under the front of the tool, the machining effect is minimal on the walls of the drilled hole. Only a gap of a size, which depends on the grain size of the abrasive used, is created here. The actual hole size is larger than the tool size, 1.6 - 1.8 times the mean size of the grain used.

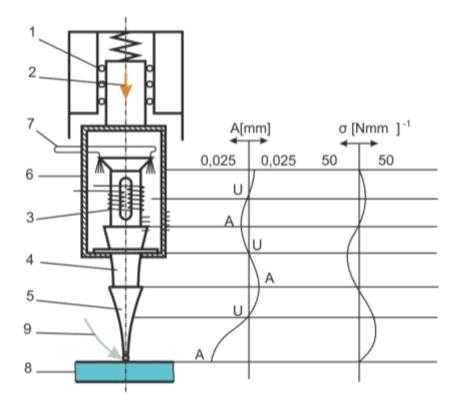*Fig. 11.8 Principle of ultrasonic drilling, electromechanical system, 1 - guiding the whole head in a ball guide, 2 - moving the head hydraulically, servomotor, tongue or weight, 3 - converter, 4 - through cone, 5 - attachment, 6 - housing, 7 - water spray, 8 - drilled glass, 9 - supply of abrasive suspension, A - anti-node distribution, U - node distribution, σ – mechanical stress distribution*

Ultrasound can be used for glass machining, namely drilling, cutting and transfer of embossments. The advantage of ultrasonic drills is the possibility of drilling holes of any profiles and the possibility of using combined tools with minimal thermal, chemical and mechanical stress on the drilled material, which retains its original properties after drilling. For glass, the drilling capacities are reported to be around 250 mm^3.min^{-1} without suction of the contaminated suspension and around 1,200 mm^3.min^{-1} with suction of the suspension.

The glass industry uses ultrasonic machining for processing decorative, domestic and technical glass, as well as, for example, drilling holes in the scales of measuring instruments and parting small discs for optical lenses. Great potential can be seen in the production of glass products in micro dimensions.

There is also the use of ultrasound in the combined method of drilling glass, which uses the already mentioned diamond tools. In this case, the diamond drill bit rotates and oscillates axially at the same time. The grinding tools have a rotary shape with a solid or tubular cross-section and therefore the resulting hole is circular. Like other diamond tools, they must be cooled in this case and the removal of the ground material must be ensured (water is most often used). Compared to conventional rotary drilling, this method has the advantage of increasing the drilling speed (an increase to 2-6 times is reported), improving the accuracy of hole drilling, prolonging the life of the drill bit and reducing the costs of the operation performed.

11.1.3 Grinding and polishing of glass

Grinding is a mechanical method of machining glass with a loose or bonded abrasive on the front face of a wheel rotating about a vertical axis or on the circumference of a wheel rotating about a horizontal axis. During grinding, glass and abrasive rub against each other, most often in the presence of water. Moving sharp grains of the abrasive damage the surface of glass and create a network of lines and cracks, reducing the cohesion of the surface layer. In the further course of the process, small fragments of glass break out of the damaged layer. Mechanically ground surfaces are then polished, products are left matt after grinding only in exceptional cases.

11.1.3.1 Grinding

Two basic parameters are monitored in grinding:

a) Glass abrasion is a process productivity parameter that indicates the amount of glass removed from ground glass. This parameter determines the length of the grinding process.
b) The quality of the ground surface, which includes in particular the degree of roughness and the uniformity of the distribution of surface irregularities. It is proportional to the grinding time and the size of abrasive grains.

Both parameters are closely related and can be influenced by the selection of abrasive and the choice of technological conditions of grinding.

Grinding on the flat face of a wheel with a vertical axis is called surface grinding, also called horizontal grinding - the machine is called horizontal grinding machine. Grinding on the circumference of a wheel with a horizontal axis is called grinding-out, cutting. The common but incorrect name is "rolling". The machine is correctly called - grinding (incorrectly - "rolling machine").

You can find a cylindrical grinder, which also has a horizontal axis, but is much wider than a "rolling machine". It is mainly used for mass grinding of jewellery stones (chatons), Chapter 11.1.3.5.

The actual grinding is often performed in two phases:

- rough grinding,
- fine grinding.

The purpose of rough grinding is to remove the glass from the specified places as quickly as possible or to roughen the surface. This is followed by fine grinding to compensate for scratches caused by rough grinding. Then polishing is performed.

Abrasives

Only natural abrasives were originally used: quartz sand, sandstone, emery, natural corundum, diamond, and others. Today you can find a wide range of synthetic abrasives, such as: silicon carbide (SiC, carborundum), fused corundum (α-Al_2O_3, electro-corundum, sold under the name "Elektrit"), synthetic diamond, and more.

Grinding is performed either with the use of:

- loose abrasive on a cast iron wheel (less common in industrial practice), or
- bonded abrasive (grinding wheels, grains are bonded with a suitable binder).

Loose abrasive grinding

In loose abrasive grinding, a grinding grain (abrasive) with water is fed between the cast iron wheel and the ground glass. The abrasive is most often quartz sand, silicon carbide or fused corundum with a grain size of 5 to 500 µm. The grains between the glass and the cast iron surface cause cracks and chipping of small fragments of glass as the grinder moves. The fragments are chipped from the surface layer of glass 5 - 30 µm thick (so-called embossment layer, Fig. 11.9), but the cracks reach more than double depth (so-called crevice layer). Both layers are referred to as the disturbed layer, which must be removed by subsequent polishing.
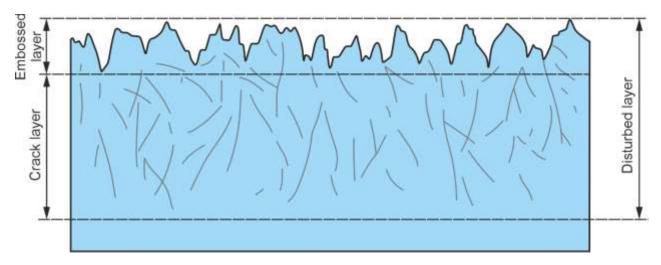

Fig. 11.9 Surface embossment and subsurface disruption of cut glass

The pressure acting in glass grinding cannot exceed the grain strength. This is prevented by crushing of abrasive grains, which accompanies the whole process. Therefore, the grinding process is strongly influenced by the mechanical properties of abrasive, in particular its strength, brittleness and hardness. Due to its mechanical properties, artificial corundum is more effective abrasive than quartz sand and less effective than silicon carbide. The grinding process is also affected by the particle size. Coarse grains are more efficient, but cause larger scratches and cracks, which must be then removed in the next phase (fine grinding). The grinding efficiency of a certain type of abrasive and grain size also depends on the amount of grain supplied, the pressure and the speed of rotation of the grinding wheel. The chemical composition of ground glass also has a significant effect.

Bonded abrasive grinding - grinding wheels

In grinding on grinding wheels, the technology is similar, with the difference that the grinding wheels are already made of their own abrasive bonded with either mineral binders (e.g. sandstone) or artificial binders. These are sandstone, polyurethane and aluminous wheels. This category includes very often recently used diamond grinding wheels and tools already mentioned in Chapter 11.1.1.2 and 11.1.2.2.

The working surface of the grinding wheel is a grouping of a huge amount of sharp abrasive grains. During the grinding process:

- the grains break and the edges are rounded, if this process prevails, then the rough surface of the tool is smoothed and the whole wheel is blunted,
- whole grains are broken out, if this process prevails, then a new rough working surface is created and the tool is sharpened.

The grinding surface must be restored by sharpening using a diamond tip or carborundum tool. Restoration of the geometric shape is performed by dressing with a cast iron, carbide or diamond dresser. However, compared to sharpening, the removal is much greater and the dressing results in large losses of abrasive, which leads to the fact that the working capacity of wheels is only partially used.

11.1.3.2   Polishing

The mechanically ground surfaces are further polished, which turns the matt and only translucent surface into a glossy and transparent surface. The better the polishing, the better and glossier the surface of the product. During polishing, the following parameters are monitored: quality of the polished surface and the polishing efficiency.

Polishing can be:

- mechanical,
- chemical (Chapter 11.3.1),
- thermal (Chapter 11.2.6).

This part of the textbook deals only with mechanical polishing. For mechanical polishing, wheels made of softer material (wood, cork, felt, polyurethane) are used, on which a mixture of water and fine polishing powder is applied. There are also polishing wheels with bonded polishing material. The most important polishing materials are polishing red (α-Fe_2O_3), polishing black

(mixture of partially hydrated iron oxides) and cerium dioxide, CeO_2, which are synthetic polishing materials. The natural polishing material is tripolite (diatomaceous earth containing mainly SiO_2) and pumice (glass foam of volcanic origin).

Grinding is mainly a mechanical process, but the following effects apply in polishing:

a) Mechanical - the same principle as in grinding.
b) Chemical - when the ground surface comes into contact with the aqueous suspension of polishing material, the glass is constantly corroded to form a silica gel, which is entrained and carried away by the polishing grains. This explains the dependence of the polishing efficiency on the type of suspension used and its acidity. According to the literature, the pH of the polishing suspension should be in the range of 4 to 10, higher and lower values reduce the removal of glass and thus the efficiency of polishing.
c) Thermal - the glass surface heats up and softens as the polishing material moves. The pressure of the grains then causes the glass to flow in a thin layer (Beibly layer) and the surface tension subsequently smooths the surface. This process thus contributes to the levelling of the surface, in particular in the final stage.

Furthermore, the process is influenced by the type of polishing powder, the amount of polishing suspension, its concentration and temperature, pressure and speed of the wheel, and other factors. Even here, the composition of glass has a significant effect on the polishing process. Glass with a lower grinding hardness, such as lead crystal, is easier to polish.

Grinding and polishing are usually performed in the presence of water, which has several important functions: it cools the products during the grinding or polishing process, washes away loose glass particles, cleans the grinder and is a carrier medium for loose abrasive or polishing material. A small amount of water causes so-called firing, a large amount washes away abrasive particles too quickly. If diamond is used, water cools the tool (abrasive).

There are many machines and whole facilities that use the above grinding and polishing technologies. The following are just examples for some of the most common types of glass products.

11.1.3.3   Grinding and polishing of flat glass

In the past, it was necessary to grind and polish entire surfaces of sheet glass for the production of mirrors. Special machines were used, which made it possible to grind and subsequently polish large formats. These were carousel machines, machines with a linear feed or automated lines for double-sided grinding and polishing, so-called continuous grinders and polishers. These lines are no longer used, because the quality of flat glass produced by FLOAT technology is so high that this glass can be used for the production of mirrors without mechanical grinding and polishing.

Machines for grinding and polishing of cutting surfaces and edges are often used in the production of flat glass products. In this way, the surfaces are most often machined after separation by breaking, but also after other methods of separating glass. There are technologies specially for grinding linear, circular or curvilinear shapes of flat glass.

Machines (Fig. 11.10) with diamond tools in the form of grinding wheels are used for grinding linear surfaces. The machines are designed as modular with one to six pairs of grinding units. Grinding may be followed by a polishing machine and, conversely, may be preceded by a glass cutting machine (Chapter 11.1.1). Linear grinding and polishing of edges are performed on glass for the furniture industry, the production of mirrors and other products.
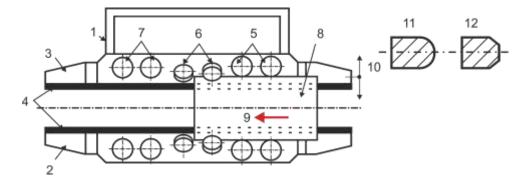
Fig. 11.10 Diagram of machine for linear grinding of cutting surfaces and edges of flat glass sheets, 1 - machine frame, 2 - fixed side with grinding stations, 3 - adjustable side with grinding stations, 4 - belt conveyor, 5 - grinders for rounded or vertical grinding of the cutting surface (according to notes 11 and 12), 6 - pot grinders for chamfering, 7 - polishing wheels 8 - glass sheet, 9 - direction of feed of the sheet, 10 - adjustment of the machine to a given width of glass, 11 and 12 - options for choosing the shape of ground cutting surfaces of glass sheet

Especially in the production of automobile glazing closures, grinding (edge grinding) and possibly also polishing are performed on machines for machining uneven contours. An example is shown in Fig. 11.11. The edges are also chamfered, bevelled or rounded. For grinding curvilinear cutting surfaces, the machines are controlled by a computer or a control unit with a processor, thus ensuring accuracy, reproducibility and operability of production.
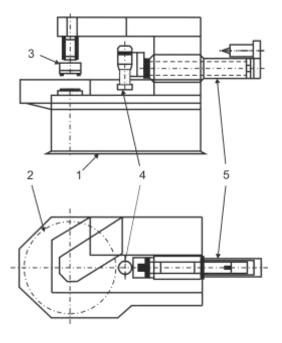
Fig. 11.11 Diagram of automatic machine for grinding edges of automobile glazing closures: 1 - machine frame, 2 - rotary table, 3 - rotary feed clamping head, 4 - grinding head, 5 - sliding arm

Flat glass can also be ground and polished on flat glass decorating machines. Machines can only grind grooves (Fig. 11.12) or grind out freely shapes. The aim may be finishing for technical purposes (e.g. fastening of rubber bands) or it may be of aesthetic significance.
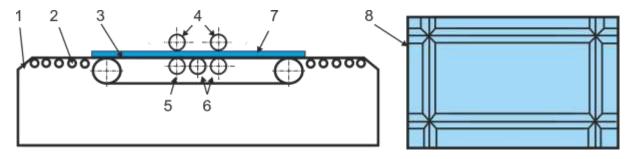
Fig. 11.12 Diagram of groove grinding machine: 1 - frame, 2 - roller table, 3 - belt conveyor, 4 - pressure roller, 5 - diamond grinding wheel, 6 - polishing wheel, 7 - glass sheet, 8 - glass sheet with ground-out decorative grooves

For machines that grind and polish only the groove, a double construction can be encountered. The glass sheet is either placed on the machine table and there is a bridge above the table along which the grinding heads move or the glass sheet is placed on two parallel belt conveyors which move it to grinding wheels located stationary in the machine frame under the glass sheet.

Modern grinding and polishing machines are based on the principle of CNC machining centres. They use diamond grinding wheels, which are stored in a magazine and are selected by the grinding head according to the required shapes and sizes of grooves. Data is exported from common CAD formats and allows grinding of virtually any pattern.

11.1.3.4   Grinding and polishing of domestic glass

Machines for manual, mechanized or automatic grinding and polishing of surfaces, cuts, edges, décors, conical cuts, etc., are used for processing of domestic glass. According to the operations performed on them, they are divided into horizontal, rolling, engraving, decorating and grinding machines.

The horizontal grinding machine for manual surface grinding and polishing of flat glass surfaces with loose or bonded abrasive/polishing material is shown in Fig. 11.13. The grinding wheel of the HS 600 machine is mounted on a vertical spindle, which is driven by a flange motor. The individual speeds are given by a number of exchangeable pulleys. The mentioned machine is manufactured in a version with speeds of 280, 335, 450 and 560 min^{-1} or with increased speeds of 710 and 1,120 min^{-1}.

The so-called rolling machine is often used for the manual production of domestic, decorative and art glassware. Today's machines are often made as modular systems, the basis of which is a fitted steel weldment, which can be incorporated into any unit. The machine is often delivered in an assembly that includes the machine placed on a concrete base and the laminate tank with stand is separate. The transmission is performed by means of a belt, for example a "POLY-V" belt, the pulleys are multi-stage, for example five-stage. The assembly is often supplemented with lighting, a work bench and a spray cover.
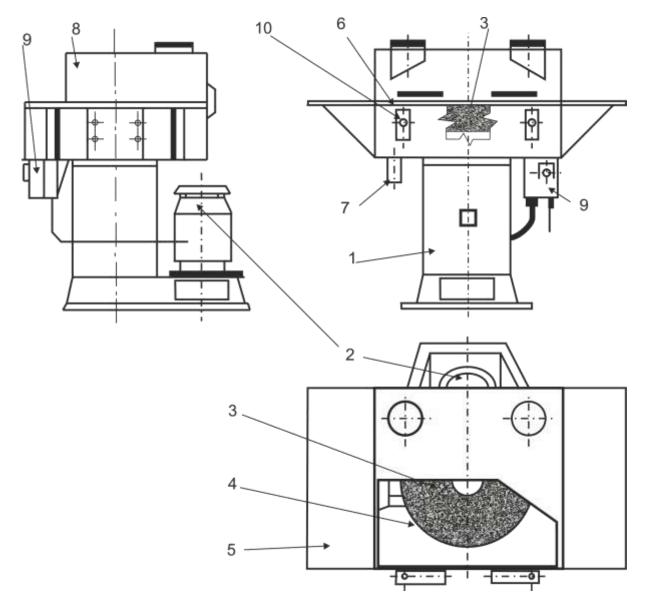
Fig. 11.13 Horizontal grinding machine HS 600: 1 - frame, 2 - electric motor, 3 - grinding wheel, 4 - safety cover, 5 - storage platform, 6 - tank, 7 - waste, 8 - suction cover, 9 - switch with circuit breaker, 10 - mounting

In the case of automatically produced thin-walled domestic glass, the cracked-off edge is ground after cracking-off (Chapter 11.2.1). Belt grinders are often used and the speed of the grinding belt is about 6 m.s^{-1}. Some machines use grinders with flat diamond wheels. In some cases, the cracked-off edges are also bevelled on both sides.

Decorating machines for automatic production are most often designed as individual section machines, which have 4 to 8 separate stations. They mainly grind simpler decorations, which, however, can be very diverse. An older version of the machine is shown in Fig. 11.14. The control of modern machines is via a computer or a control unit with a processor. These are often automatic machines based on the principle of CNC machines with their own magazine of several tools.
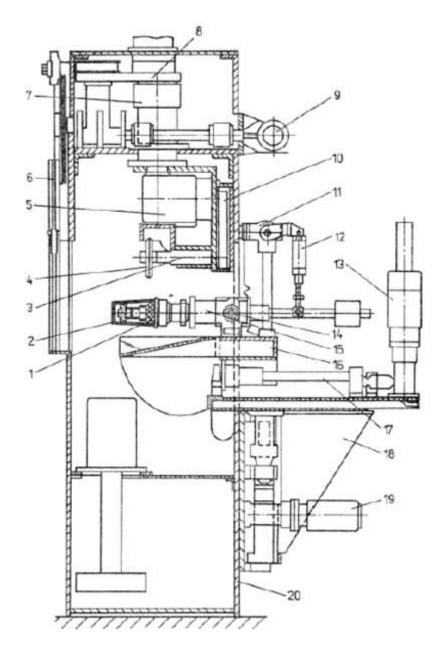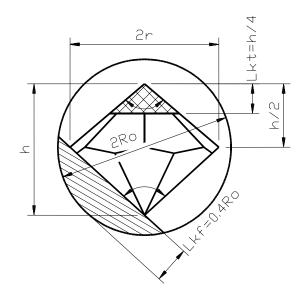
Fig. 11.14 Section of individual section 8-station machine: 1 - rubber handle for vacuum-sucked glass, 2 - glass, 3 - grinding wheel shaft, 4 - diamond grinding wheel, 5 - electric motor, 6 - sliding transparent cover, 7 - bearing body enabling rotation of the grinding wheel, 8 - toothed belt, 9 - drive for turning the grinding wheel, 10 - belt driving the grinding wheel shaft, 11 - tilting mechanism, 12 - air cylinder, 13 - electric motor for table drive, 14 - tilting pivot point, 15 - rotating holder along its axis, 16 - sliding table, 17 - shaft driving the table feed, 18 - fixed table, 19 - electric motor for height adjustment of the sliding table, 20 - machine frame

11.1.3.5   Grinding and polishing of glass jewellery

Today, grinding of glass jewellery is performed on flat-surface or cylindrical grinders by mass grinding, in which the individual semi-finished products are bonded on sticks placed on apparatuses, which are inserted through a flap into the grinding machine. Grinding is performed on grinding machines - grinders. Polishing is performed on polishing machines - polishers.

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The most important representatives of jewellery stones are the so-called chatons (Fig. 11.15) and therefore the principle of production will be described herein.

Fig. 11.15 Basic parameters of the chaton

A diagram of the principle of grinding on a flat-surface grinder is shown in Fig. 11.16 and a diagram of grinding on a cylindrical grinder is shown in Fig. 11.17. The grinding wheels move not only about their axes during grinding, but eccentrically in the case of surface grinding and back and forth in the case of cylindrical grinding in the axial direction. This prevents the tracks on the grinding wheels from being ground through, thus prolonging the time after which the wheels need to be dressed and thus extending their service life. Ground surfaces in grinding on cylindrical grinders are not flat, but for small products this defect is negligible. For larger products, such as larger chatons or chandelier trimmings, grinding is performed exclusively on surface grinders. Mass grinding based on both described principles is enabled by the use of grinding apparatuses, on which the so-called sticks are attached and the semi-finished products are bonded on them during grinding and polishing. The sticks are arranged so that they can be rotated by the angle needed to grind the individual surfaces, the so-called facets. The bonding agent is prepared according to special recipes and its main components are rosin and shellac. The bonding equipment (bonding-on and bonding-off) and the re-bonding section are used for bonding-on of the raw material. In grinding on a surface grinder, the exchange of apparatuses, bonding and re-bonding are automated in current equipment. In the case of cylindrical grinder, the apparatuses are removed manually, as well as bonding and re-bonding are manual.

For surface grinding, the flaps of the apparatuses are mounted on a plate, on which eight flaps with the apparatuses are placed, Fig. 11.16. The process of bonding, grinding, re-modelling and bonding-off is shown in Fig. 11.18.

In grinding and polishing on cylindrical grinders and polishers, so-called "grinding assemblies" (also "compositions") are used, Fig. 11.17 at the bottom, consisting of grinder, polisher, bonding and re-bonding machine, and cleaning equipment to remove residual bonding agent from the sticks. Assemblies differ in their arrangement according to the number and type of operations. The machines are operated by two to three workers, the process of bonding, grinding, re-bonding and bonding-off is shown in Fig. 11.18.
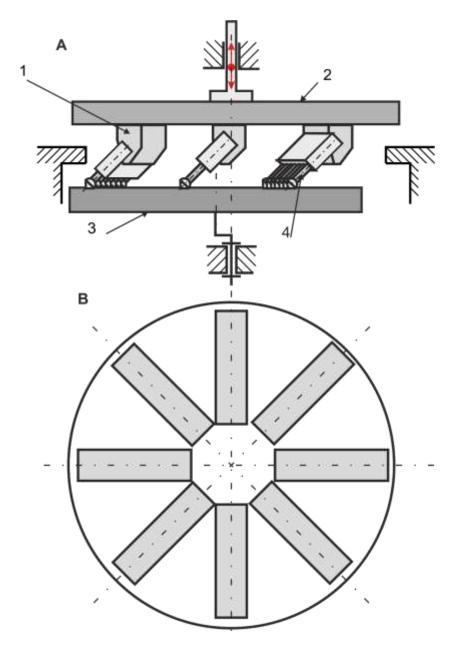
Fig. 11.16 Diagram of grinding of chatons on surface grinder: A - principle of technology, B - placement of flaps on the plate, 1 - flap with apparatus and sticks, 2 - plate, 3 - horizontal grinder, 4 - sticks with bonded-on semi-finished products for the production of chatons

In the next production phase, the semi-finished products are bonded off at higher temperatures, washed in dilute hydrochloric acid and cleaned by ultrasound. In the case of chatons, the surfaces are ground, so-called "faceting" in the next technological step.

Grinding and polishing of chatons, doublets and chandelier trimmings are carried out with almost identical technological procedures from grinding raw material on assemblies of several single-purpose machines and now often on automatic production machines and lines up to final polishing.

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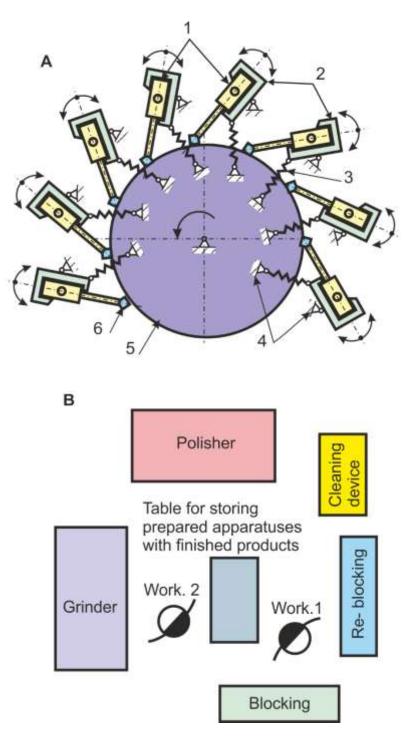
Fig. 11.17 Diagram of cylindrical grinder: A - principle of technology, B - grinding assembly ("composition"), 1 - apparatuses, 2 - flaps with tilting of apparatuses, 3 - spring, 4 - machine frame, 5 - cylindrical grinder, 6 - ground chaton
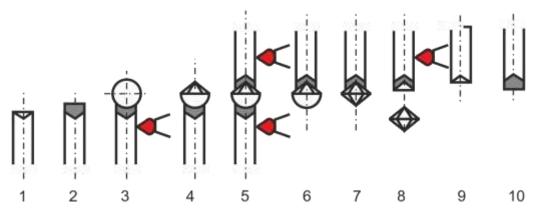
Fig. 11.18 Bonding and re-bonding of ground and polished chatons. 1 - cleaned stick, 2 - applying bonding agent to the stick, 3 - gluing (fixing) of the glass semi-finished product in the form of a ball or in the form of a formed chaton on a rotary presser, 4 - grinding and polishing of the top side of the chaton, 5 - re-bonding, 6 - re-bonded semi-finished product on another apparatus, 7 - grinding and polishing of the underside of the chaton, 8 - bonding-off of the chaton, 9 - cleaning of the stick, 10 - application of the bonding agent, thus preparing the stick for another bonding and re-bonding operation as in position 3 or 5

11.1.3.6 Grinding and polishing of optical glass

Optical glass grinding and polishing machines must ensure the final dimensional and shape accuracy of optical glass product. They can be divided into machines for grinding and polishing flat (Fig. 11.19, A, B, C, D), circular (Fig. 11.19, E) and spherical optical glass (Fig. 11.19, F, G, H).
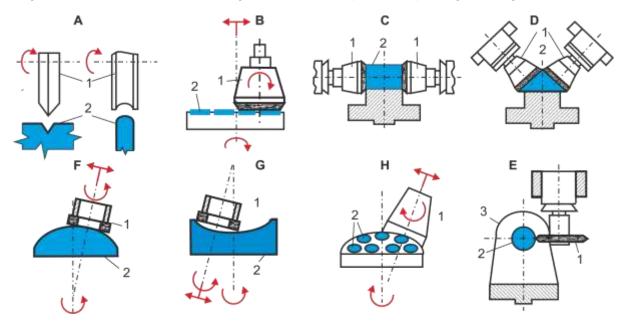
Fig. 11.19 Main principles of grinding of optical glass: A, B, C, D - surface grinding, E - circular grinding, F, G, H - spherical grinding, 1 - grinding tool, 2 - ground glass product, 3 - holding device

Universal grinding machines for spherical grinding, as shown in Fig. 11.19, are used for grinding individual lenses or even flat surfaces with ring or tablet tools. In grinding, tools with

bonded diamond grains or carborundum and aluminous wheels are mainly used. Kerosene or aqueous emulsions with the addition of sulphonic oils are used as coolants.

Universal surface grinding machines, as shown in Fig. 11.19, have either one or more grinding heads. They are used for grinding glass prisms, blocks, etc.

Polishing machines are similar in construction to grinding machines, polishing tools are usually made of felt or resin. Their working speed is lower than in grinding and the polishing pressure is also lower (about 10 kPa). Polishing suspensions are used for polishing.

11.1.4 Sandblasting and mechanical frosting

Sandblasting is in fact mechanical frosting and is used for decorative purposes, such as interior equipment, and also for marking of products. The technology consists in blasting of the abrasive at high speed against the surface to be worked, which does not only have to be made of glass. The result is a rough surface that reduces the transmittance of glass and scatters the light. The surface characteristics are determined by the type of abrasive, the blasting time, the speed of abrasive parts and the type of glass to be worked. Corundum (brown and white - for lead glass, because it does not stain), silicon carbide, garnet, silica sand, ballotini (soda-lime silicate glass balls) are often used as abrasives for glass. Sandblasting systems can be divided into:

- compressed-air (pneumatic) - blasting of abrasive under air pressure onto the glass surface, either injector or pressure system is applied,
- mechanical (throwing) - the abrasive is thrown by the blades of throwing wheels.

The depth of the disturbed layer ranges from 10 to 30 μm. The most widespread is probably sandblasting for flat glass, which is either sandblasted in closed or through booths, table or chamber blasters, if necessary, it is possible to sandblast in the open area. The sandblasting device is mostly closed with extraction of dust and abrasive from the blasted surface. The extracted abrasive is sucked back into the unit and the dust is separated into the bin.

In the case of flat glass, sandblasting is often replaced by silk screen printing, with regard to the costs and subsequent maintenance of the glass thus finished (fingerprints are formed on the sandblasted surface when touched).

The mechanical treatment of the surface of flat glass with the new Eco Sphere technology is based on brushing of the surface with plastic bristles containing diamond grains. It is a sophisticated environmentally friendly solution. The technology enables mechanical frosting and patterning of glass without the use of chemicals, while the only waste product is environmentally friendly grinding sludge.

11.1.5 Engraving

Glass engraving technology is mainly manual technology and is one of the most laborious finishing techniques. Its essence is close to grinding and polishing of glass. Compared to grinding, harder glasses are more suitable for engraving, which put more resistance on the tool and the abrasive, so highly lead crystals are not suitable. Fine-grained abrasives (most often electro-corundum or silicon carbide) are used for the actual engraving, which are applied to the tool as a suspension in oil, kerosene or mixture thereof. Copper wheels with a diameter of 2 to 200 mm and

a thickness of 0.5 to 6 mm are most often used as tools. The tools do not engrave themselves, they serve as a carrying element for the abrasive suspension.

11.1.6 Tumbling, tumbling in water and chopping

There are many mechanical processes in the manufacture of glass jewellery components, typical only for this commodity. Examples of the most common other procedures are tumbling, tumbling in water and chopping.

In manual or mechanical squeezing and moulding of glass pressings, excess glass melt often leaves during forming at the place of clamping of the mould into flash, the so-called excess glass. For larger pressed objects (trimmings), the excess glass is removed individually by shearing (trimming). Excess glass is separated by shears - in particular for semi-finished products with straight edges or by means of a trimming machine, which consists of two sharp steel wheels rotating against each other.

For minor and small semi-finished products, e.g. after pressing on a rotary presser, Matur's presser and Kopal's presser (Chapter 9.3.3), the excess glass is removed in bulk by tumbling of pressed objects in rotating closed drums with a horizontal axis of rotation (mass tumbling - this is processing as defined herein). The drums can have various shapes, most often five- to ten-sided with dimensions of approximately 1,000 mm (diameter) and 300-500 mm (width). They are made of wood or sheet metal, they can have a rubber-coated inner surface. The common name for this operation is **tumbling** (dry tumbling), Fig. 11.20. The drive is realized by means of an electric motor.
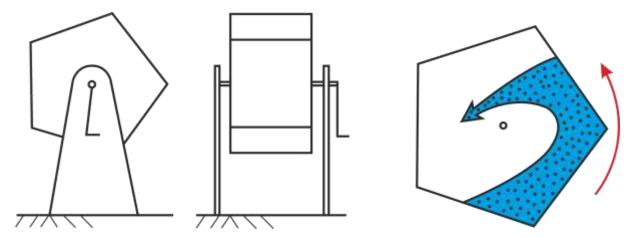
Fig. 11.20 Five-sided drum for tumbling and movement of pressed objects as it rotates

The correct circumferential speed is important in rotation of these drums. Pressed objects must be brought to such a height that they fall and thus the flashes are knocked off. Drums are filled to approximately 1/5 of volume, when the path of free-falling pressed objects is the longest.

After tumbling, the products are separated (excess glass-blasted) on vibrating screens from cullet, which is one of the auxiliary operations, which further follows some finishing technologies.

At present, tumbling lines are beginning to appear, which can perform the entire operation independently. In this case, no drum is used for removing flashes, but the semi-finished products pass through a tumbling chamber lined with ceramics with rotating brushes with plastic bristles.

Due to their rotation, the excess glass is removed. Subsequently, excess glass blasting is performed on the line using a series of screens.

Finishing can also include tumbling, for which the name **tumbling in water** is used. It is a surface treatment of glassware in rotating barrels in the presence of water and silica sand or polishing material. In tumbling with polishing material, the name "mechanical frosting" is also used, which is an environmental option for chemical frosting, in which, however, the hole is not polished. For tumbling only in water without other substances, the name "watering" is common and used.

Silica sand with a grain size in the range of 120 - 200 μm is used for tumbling and is prepared by washing it through a screen with a stream of water. It is then filled into tumbling barrels together with the goods. The weight of the goods is 5 - 10 times larger than the weight of sand and about 50 - 60 kg of goods, 5 to 15 kg of sand and about 30 l of water are filled per barrel. Barrels can have (as with tumbling) different shapes. They are usually polygons, typically 700 or 800 mm in diameter and 500 mm wide, they are made of soft or hard wood (beech and pine) and are used for all types of tumbling, i.e. from roughing to polishing. Metal barrels with an inner lining made of molten basalt or a layer of concrete are exclusively intended for roughing, which are used for roughing of smaller products. Barrels lined with rubber are also used. The speed of rotation depends on the size of the products and the technology performed. The speed ranges from 15 to 80 revolutions per minute, smaller products rotate faster and larger products rotate slower. During polishing, all products rotate slowly, the barrel is driven by an electric motor.

Tumbling achieves the desired size of glass products, the desired surface quality, or both. Products with a size of about 6 - 8 mm are the most suitable for tumbling. Smaller products are too light, so the pressing forces acting in tumbling are small and the tumbling effect is not significant. Larger products, on the other hand, are too heavy and could beat. For these reasons, mixtures are often prepared, i.e. small and large products are mixed together. Mixtures are also prepared for those types of products where there is a risk of breaking (in particular thin or long narrow shapes) or where the design needs to be refined. The composition of glass is also important, because rich colours tumble faster than transparent colours.

The operation requires knowledge of the operator in terms of the composition of wet-tumbling mixture, the fineness of sand, the composition of beads in the barrel and the total wet-tumbling time, etc. Depending on the required nature of the surface, the wet-tumbling process may be followed by polishing and watering.

Mechanical **separation by chopping** is used for chopped beads and seed beads. Chopping is performed on chopping machines, which often have different constructional arrangements but essentially work on the same principle (Fig. 11.21). The chopping machine consists of a chopping stand and a machine attached to it, which is provided with two opposed carbide or sintered carbide blades, Fig. 11.21 A. To eliminate longitudinal cracking, the upper movable blade is straight, the fixed lower blade is provided with teeth. This achieves contact at 3 points and the upper blade lowers only to 1/3 of diameter of the tube, the rest of the tube breaks cross fire ly. The upper blade moves vertically at a frequency of up to 1,000 chops per minute, is driven via a cam by an electric motor and the speed can be regulated according to the required length of the beads. The blades must often be sharpened to chop off the tubes in high quality.
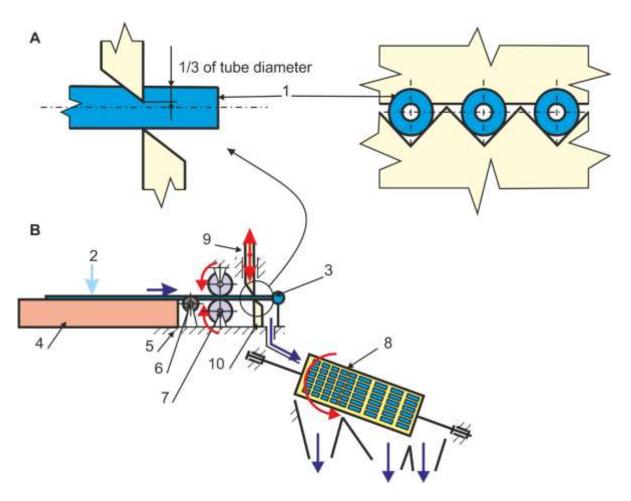
Fig. 11.21 Diagram and principle of chopping machine: A - tube loading, B - machine diagram, 1 - tube, 2 - pressure on tubes by hand, 3 - stop in the form of a roller, 4 - table, 5 - machine frame, 6 - roll with grooves, 7 - hard rubber rolls, 8 - screen to separate the chopping product from the cullet and long tubes, 9 - movable knife, 10 - fixed serrated knife

Tubes are first evenly distributed by hand on the table so as to fit into the grooves in the grooved roll (or grooved travel), the grooves corresponding to the grooves of the fixed lower blade (Fig. 11.21 B). Tubes are then pressed against the table by hand and loaded between rubber rolls, which move the tubes between the blades all the way to the stop. The upper blade then lowers into the chop. The number of tubes chopped at a time is determined by their cross-section and the length of knives, which is 200 to 240 mm depending on the design of the machine. The gaps between the individual tubes represent about 10% of their diameter.

The chopping product (product of the chopping of seed bead tubes) falls into a rotating cylindrical screen, where the semi-finished products are sorted from waste (short, long and cullet). The screen is often provided with extraction because fine glass dust is generated during chopping. The movement of knives and feed rollers is controlled by a cam and the length of chopped goods is regulated by the feed speed of tubes.

In the past, there have been several attempts to automate the chopping process, but the devices have not achieved yield, quality and reliability as mechanized chopping.

Chopping is followed by another technological operation. As far as the production of seed beads is concerned, the chopping product is mixed with the filling material and rounded (Chapter 11.2.7), other products may be tumbled or ground.

11.2 Thermal processes

Thermal processes can be divided according to the purpose to be achieved. It can be a separation of glass, where a controlled fracture or local reduction of viscosity is used to allow two parts of glass to be separated. Thermal processes can include cutting, drilling and laser decorating. They also include bending and tempering of flat glass. Furthermore, it can be an improvement of the surface properties of glass such as polishing, surface tension is also used in edging. Heat treatment also includes striking and opacification.

11.2.1 Cracking

Cracking technologies are used for separating the heads (so-called moils, Fig. 11.22) of blown glass cups, goblets, vases, separating glass tubes, etc. In cracking, the phenomenon is used when rapid local heating of the surface disturbed in advanced (scratched with diamond or carbide) creates a tensile stress, which increases the line created by scratching until the two parts are completely separated. Heating is usually performed by means of a multi-flame burner with a jet flame.
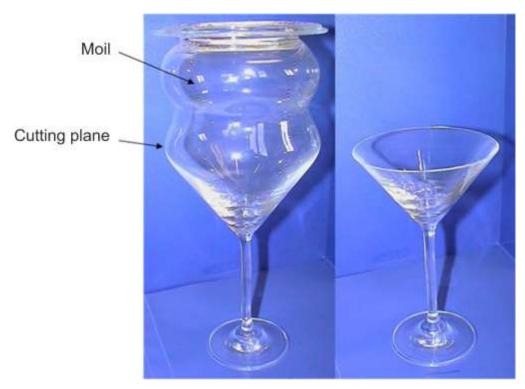
Fig. 11.22 Principle of the separation of moil

The generation of compressive and tensile stress on the surface of the rotating vessel after its heating and cooling is shown in Fig. 11.23. The principle of cracking with a multi-flame burner is shown in Fig. 11.24.
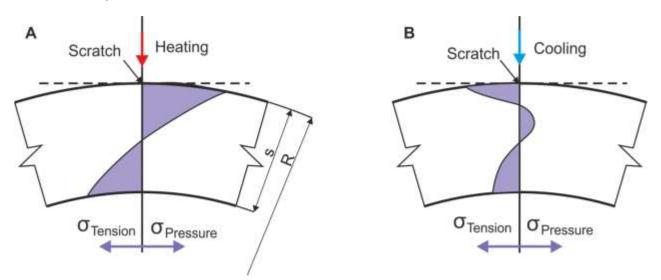
Fig. 11.23 Stress generation on the surface of the rotating vessel: A - after local heating, B - after local cooling
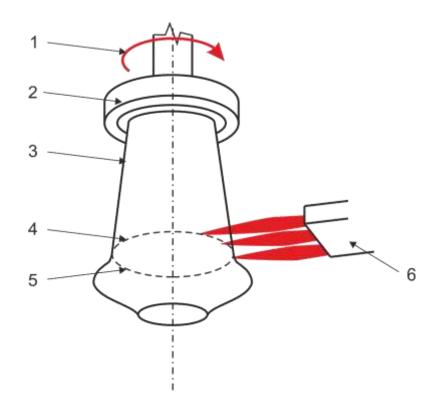
Fig. 11.24 Principle of cracking-off with a multi-flame burner: 1 - direction of movement of glass semi-finished products, 2 - vacuum clamping element, 3 - product, 4 - notch, 5 - moil, 6 - burner

An example of a carousel cracking-off machine is shown in Fig. 11.25. The glass blank with moil is usually clamped in this machine by means of a vacuum or mechanical-pneumatic clamping head, which rotates about its axis. The advantage of this embodiment is that the cracked-off moils can fall freely into the hopper or onto the conveyor belt and that the cracked-off edges are ground in the machine by means of an integrated belt grinder. The above mentioned cracking-off machine is twelve-position machine, but 36-position machines are commonly used in automated production. Their average output is 1,200 pcs.h^{-1}.

In cases of difficult cracking of the glass, which is inherent in glass with a low coefficient of thermal expansion (SIMAX cooking glass), it is necessary to create more drastic heating and cooling conditions at the place of cracking. A hydrogen-oxygen jet flame is used and rapid efficient cooling is performed by a narrow liquid jet concentrated at the line of fracture.
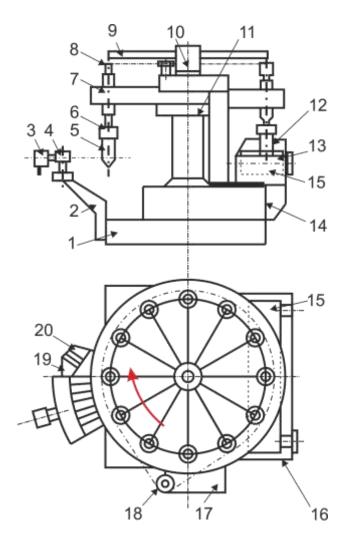
Fig. 11.25 Cracking-off machine with belt grinder for grinding cracked-off surfaces: 1 - frame, 2 - arm, 3 - mixer, 4 - burner segment of multi-flame burner, 5 - glass semi-finished product with moil, 6 - clamping head, 7 - carousel, 8, 18 - sprocket, 9 - roller chain, 10 - distributor for media, 11 - column, 12 - cracked-off ground glass product, 13 - sanding belt, 14 - drive housing of the machine, 15 - belt grinder roll, 16 - protective water screen, 17 - chain drive, 18 - sprocket, 19 - device for making notches, 20 - carbide wheel

11.2.2 Edge melting

The ground cracked-off edges of glass products are sharp and matt (after grinding) and must therefore be rounded and polished. For thin-walled glass, so-called "edge melting" is performed. The ground edges of glass products, which rotate about their axis, are heated by efficient burners to the softening temperature, and due to surface tension, the matt ground surface is polished and the sharp edges are rounded. Edge-melting machines are usually either carousel machines with movement along a circular path or with a chain conveyor with linear movement. Machines with a chain conveyor are newer constructions and their output varies according to the size and wall thickness of burnt-off products from 1,100 to 3,000 pcs.h^{-1}.

11.2.3 Burning-off

In the case of less demands on the appearance of the edges of glass products in the place of separation of the moil, it is possible to replace the production operations of cracking-off, grinding and edge melting by a single operation - burning-off. The principle of burning-off is given in Fig. 11.26.
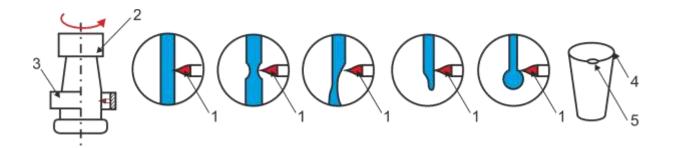
Fig. 11.26 Principle of moil burning-off operation: 1 - flame, 2 - clamping head, 3 - circular burner, 4 - reinforced edge, 5 - tear

The clamping head is usually either mechanical-pneumatic or vacuum head. The circular burner is usually multi-arm or with a slot nozzle. Carousel burning-off machines usually have 6 to 32 stations. Their output is up to 1,500 pcs.h^{-1}.

11.2.4 Laser cutting, drilling and decorating

Like water jet cutting, laser cutting allows the production of any shape. In this case, the technology is so-called waste-free, i.e. no waste is generated during the process (e.g. cullet in water jet cutting or wet and dry cutting of glass). Compared to separation by breaking, the cut has a higher quality and usually does not need to be further worked.

In essence, laser cutting machines can work on three basic principles:

1. The laser beam creates a scratch on the surface of the glass, at the root of which there is a tensile stress. The glass is then cut mechanically by breaking, similar to cutting after marking by scratching.

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2. The laser beam induces a tensile stress in glass exceeding the strength limit of glass and, as a result, a crack propagates in the glass. It is a separation by a controlled fracture without secondary cracks.

3. The laser beam melts and evaporates the glass due to the high energy density that is concentrated in the cutting line.

The individual principles differ mainly in the energy needed for separation, the lowest energy is needed for the first method and the highest for the third method. The most commonly used principle at present is the latter. CO_2 or diode lasers are used, but they require subsequent cooling. Another technique is MLBA (Multiple Laser Beam Absorption). Unlike CO_2 lasers, the radiation of solid-state lasers is absorbed by the entire thickness of the glass. Following the method, where the laser beam is absorbed by glass several times by a suitable arrangement of reflectors, sufficient energy is accumulated in the primary laser-shaped contours to induce an induced thermal stress in the whole cross-section of the glass. No additional coolant is required to separate it. This one-stage process is the most productive, compared to the mechanical process by about 50%.

Laser cutting technology can be described as a very promising and productive glass cutting technology. Very often you can find the separation of glass blanks for modern devices such as mobile phones, tablets, camera covers, and more. An example is the separation of thin glasses. Ultra-short pulse (in the order of picoseconds) lasers are used. The result is a cut with low roughness, which leads to higher flexural strengths and tempered glass can also be cut. In general, high cutting speeds and associated high productivity can be achieved.

Laser drilling is based on the evaporation of material from the cutting point. Pulsed lasers with a pulse length of less than 1 ms are used for this purpose. However, shortening of the pulse time is not enough, a suitable laser drilling method must be also chosen. Laser drilling is possible with single pulses, repeated pulses, cutting holes, etc. The advantage of the laser is the creation of small holes even in places where it is difficult or impossible using other methods. Metals, plastics, wood, ceramics, glass and other natural materials can be drilled. In industry, Nd:YAG[16] lasers with a power output of 100 to 500 W are mainly used for drilling holes.

For laser drilling, the longer the hole, the more its shape deviates from the exact geometry, which is caused by energy distribution of the beam. The advantage of laser drilling is the creation of small holes with a diameter of 10 μm to 100 μm. The holes can be circular or shaped, the length of the drilled hole can be up to 50 mm.

The laser is today also used for welding small glass parts and finishing glass products by decorating.

Laser marking of glass or internal decorative engraving has also been recently growing in popularity. On the one hand, the laser can burn on the glass surface a certain, perhaps even a colour motif, prepared by another technology (e.g. silk screen printing), but a more frequent use of the laser in the marking of glass is a method with a change in surface topography. At the point of incidence of the focused laser radiation on the glass surface, the glass melt partially evaporates

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[16] The most used solid-state laser. The active medium is neodymium doped yttrium-aluminium garnet $Y_3Al_5O_{12}$.. It works with a wavelength of 1.06 μm in pulsed and continuous mode.

and cracks on its surface. Light is scattered on the cracks, thus achieving a bright appearance of the pattern.

Pulsed lasers with a short pulse time and power density are suitable for markings and decoration of glass. These can be TEA-CO_2 lasers, excimer lasers or diode-pumped solid-state Nd:YAG lasers. More expensive excimer lasers, due to their shorter wavelength in the UV region of the spectrum and higher beam quality, are more suitable for marking of fine, brittle parts, such as optical glass. When marking with an Nd:YAG laser, a high speed of marking is achieved by oscillating the focused beam with a scanner.

In internal (mostly decorative) engraving, the focus point of the beam lies inside the glass object, where the concentrated energy input creates locally limited cracks, while the surface remains undamaged. Due to light scattering, microcracks appear as bright points. By moving the laser beam and the glass object in 2D or 3D coordinates, it is then possible to create entire shapes from single points.

Laser can be used for bonding glass tubes, glass with metal, close glass ampoules and one of the latest innovations from the Laser Zentrum Hannover is the polishing of glass, especially optical glass.

11.2.5 Tempering and bending of flat glass

Safety tempered glass (incorrectly called hardened) is produced by heating the glass to a temperature close to the softening point and then rapid and uniform cooling. This creates a uniform permanent compressive stress in the surface layer of glass, which increases the mechanical strength and heat resistance. When broken, tempered glass breaks into a large number of blunt-edged fragments that do not have sharp cutting edges, thus reducing the risk of injury. Tempered glass is subsequently difficult to machine mechanically, and therefore all mechanical treatment must be carried out before it is tempered.

This finishing technology is used mainly for flat glass and domestic glass in the form of glasses (e.g. so-called "Duritka"). The following text is focused on the production of flat safety tempered glass, which can be flat or bent. The technology is applied to automobile glazing closures and to building exterior and interior glass.

The technology is based on a heating furnace, cooling equipment and mechanisms enabling the handling of tempered blanks. The possible arrangement of the equipment is shown in Fig. 11.27. The treated flat glass is transported by the device in a horizontal position on a roller conveyor. It passes smoothly through the heating section, where radiation or radiation-convection heating is used. After reaching the required temperature, the glass is cooled by air sprays, which perform the necessary rapid cooling. In this case, it is cooling by blast of air driven by efficient fans. Devices for tempering sheet glass in a vertical position are also designed.

Flat glass can also be bent and subsequently tempered. Bending is performed on gravity moulds or by pressing.
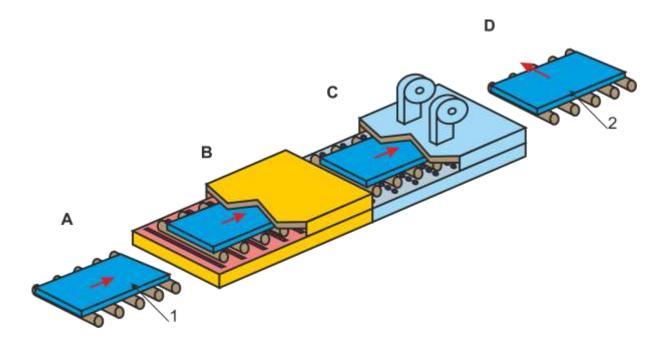
Fig. 11.27 Diagram of the line for thermal tempering and strengthening of flat glass: A - loading position, B - heating station, C - tempering station, D - glass removal, 1 - glass blank, 2 - tempered glass

As mentioned, bent glass can be untempered and tempered. In the case of untempered glass, the technology is based on subsequent cooling according to the cooling curve so that no excessive permanent stress is created in the glass. In the case of tempered glass, uniform rapid cooling is used instead of gradual cooling. The bending technology can be purely spontaneous (so-called gravitational forming) or with a mechanical action (using moulds).

In gravitation forming, the glass is placed on a mould in a horizontal position, heated, and after reaching the required temperature (around 600°C for ordinary flat glass), the glass is formed by its own weight. The mould may form a whole, then the surface of the glass may be affected by contact with the surface of the mould. However, the mould can also be in the form of a frame on which the glass is placed, and by means of precise control of the temperature regime in the furnace, the glass is formed without contact with the mould (except for the peripheral frame). This principle is applied to automobile glazing closures, on one side of the tunnel furnace the glass is loaded on metal frames, which are carried on a trolley and passes gradually through the individual sections of the furnace, in which the temperature is precisely controlled. The finished products leave the furnace and are still air-cooled.

Modern bending devices can, for example, be designed with a software-controlled flexible conveyor which directly forms the flat glass during the oscillating movement, Fig. 11.28. The above mentioned system does not require any moulds, which leads to a significant increase in capacity and flexibility of the device. The shape of the bend changes based on software intervention.
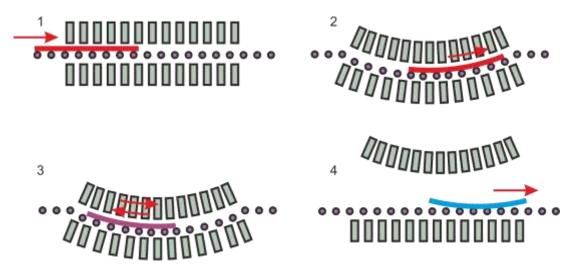
Fig. 11.28 Diagram of forming glass with one radius of curvature in a furnace without moulds (forming axis across the movement of the conveyor): 1 - supply of flat blank, 2 - forming by readjusting the flexible conveyor, 3 - cooling in reciprocating oscillating movement of the glass, 4 - setting the roller conveyor into a plane and moving the formed glass into the annealing section

In the case of tempered glass, a section for tempering of glass is included after the forming device. Special moulds are used for this method, enabling air cooling of both glass surfaces.

11.2.6 Heat polishing

A smooth surface of products, rounding of sharp edges, etc., is sometimes made by locally raising the temperature to such a value to achieve the desired effect by the action of surface tension forces. This can be achieved by using flames of the burners located on the burning-off devices or directly on the burner at the table from free hand. Special electric furnaces are more often (for mass production of jewellery) used for this purpose. The process is called heat polishing (also called flame polishing).

Polishing (the action of surface tension forces) takes place in a thin surface layer and the temperature must be higher than the softening temperature. Heating must be fast enough that the glass becomes "liquid" only on the surface of the polished part or the surface of the whole product, but the inside must have a lower temperature to prevent the product from deforming. In this case, the low thermal conductivity of glass is preferably used. In fact, heat polishing can be referred to as reannealing of glass, which serves to compensate for any irregularities in the surface layer, which occurred in previous operations or as a result of careless handling (scratches, small pinches, etc.), or technological process (grinding). Some defects can be thus "hot" removed immediately after the product is made. However, the product can go through a annealing process, then it is cold processed, e.g. by grinding, and defects are removed by heating up and heat polishing. This is how some types of beads, cheaper trimmings, buttons, doublets are finished. Large products such as vases, etc., can also be heat polished.

Polishing furnaces for jewellery are belt tunnel or chamber (pallet with sheets) furnaces. Wood-fired furnaces were formerly used for polishing, then gas-fired furnaces, and today electric furnaces are used exclusively, which enable precise setting of the temperature regime and thus achieving a stable quality of polished products. In chamber furnaces, the temperature regime is set

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by the temperature and its time curve. For tunnel furnaces, the regime is set by the temperature of the individual sections and the travel speed of the belt.

An example is a tunnel furnace with three sections: 1. start-up 500 to 650°C, 2. polishing 650 to 800°C, 3. cooling 500 to 650°C, where the exact temperatures are determined with respect to the type of glass and its viscosity curve. Semi-finished products for polishing (sizes 3 to 8 mm) are fed either by hand or by means of vibrating feeders onto rectangular sibral plates, which well maintain the temperature. These plates pass through a tunnel furnace and the products are emptied into containers and sorted on vibrating screens at the end of the furnace. For proper polishing, the speed of the conveyor, which carries the plates, is set on the furnace in addition to the temperatures of the individual sections.

In the case of heat polishing of decorative and domestic glass, automation and the use of robots can also be encountered. An example is the line with the industrial angular Kuka robot, Fig. 11.29. In order for the robot to work, it is necessary, among other things, to solve the gripping of hot semi-finished products (around 500°C), which are segmented and diverse in shape.

Fig. 11.29 Angular Kuka robot for handling in vase polishing

11.2.7 Edging

Edging is performed for jewellery products, which are called seed beads. It is a mass heat treatment of the surface of chopped seed bead tube of given dimensions (chopping technology, Chapter 11.1.6), which leads to rounding of the outer surface while maintaining the hole within the appropriate tolerance dimensions. The surface of the beads will be bright.

The mechanically chopped and sorted chopping products are mixed with the filling material and edged at elevated temperatures into seed beads. The filling material consists of ground dolomite and kaolin, where the ratio of these components is important for the successful course of edging. The chopping products with the filling material form an edging mixture and prevents the beads from "sticking" and sealing of the hole. Dolomite ($CaMg(CO_3)_2$ magnesium calcium carbonate) decomposes at a temperature of 650 to 750°C and releases carbon dioxide, which disintegrates the edging mixture and creates so-called fluidized state. This state reduces the possibility of direct contact of the beads and thus their sticking. Because the reaction consumes heat, dolomite also acts as a stabilizer for temperature conditions during edging. Edging takes place in a furnace at temperatures of 600 to 800°C. At these temperatures, the viscosity of a given glass composition is so low that a surface tension is applied and, as a result, the beads are edged. Certain products are edged also repeatedly (so-called fine polishing), or with an intermediate step of acid pickling of the surface.

The following furnaces are mainly used for edging of seed beads:

- mechanized gas furnaces,
- electric continuous furnaces.

The type of furnace is chosen with regard to quantity, size of assortment and colour.

Continuous **e**lectric **ed**ging **f**urnaces (so-called "ekup") are two rolls about 3 m long inserted into each other, made of heat-resistant steel with an internal helical path. They are placed in a space heated by electrical resistance elements (Fig. 11.30). The edging mixture is loaded into the inner tube and by rotating it (the movement is reversible) it is moved to the other end, where it falls into the outer tube, which is moved in the opposite direction and falls through the mouth of the outer tube into the rotating hexagonal screen separating the filling material from the beads.

In the next phase after edging, the residues of filling material are removed by washing in dilute hydrochloric acid while stirring, then by washing in water. The articles are dried in heated centrifuges and then in an electric continuous furnace (belt furnace). This is followed by sorting, hole punching and sorting for roundness.
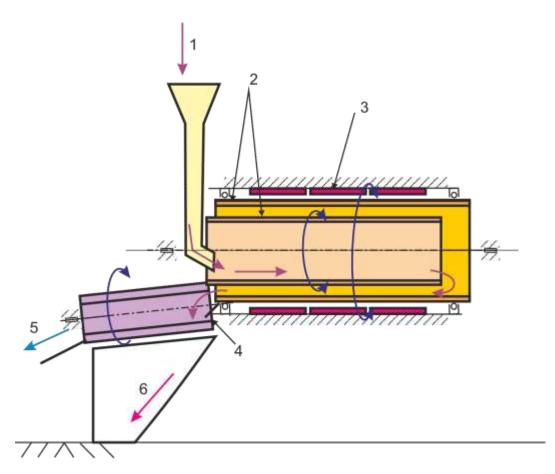
Fig. 11.30 Automatic edging in electric furnace, so-called EKUP: 1 - hopper for edging mixture, 2 - inner and outer drum with spiral grooving with reversible rotation, 3 - electric resistance heating, 4 - separation of the chopping products from the filling material in a hexagonal rotating screen, 5 - edged semi-finished products with residues of filling material, 6 - separate filling material falling onto the conveyor belt towards the regeneration of the edging mixture

11.2.8 Striking and opacification

Some thermally unstable glasses must be heat-treated once more after melting to achieve the desired colour or opacity. A frequent case is the production of semi-finished products for glass jewellery. This operation is called striking, to obtain the desired colouration and opacification, to obtain the desired opacity. If this operation is not performed on the raw material, it must be performed additionally in the production of articles as one of the technological operations for which the so-called striking and opacifying furnaces are used. The required colouration (opacification) of the product is achieved by a controlled temperature regime for a certain exposure time. Therefore, these furnaces must make it possible to set the exact regime of heating the products to temperatures at which the colouration is stabilized or the necessary opacification is achieved by the prescribed characteristic of the temperature curve, the so-called temperature gradient. Therefore, these furnaces are also sometimes called "gradient" furnaces. This technological operation is performed twice. Two types of these furnaces are designed - tunnel or rotary. In the mentioned furnaces, it is also possible to opacify, i.e. to process thermally unstable glasses from the point of view of opacification.

Tunnel furnaces are heated tunnels made of refractory insulated brickwork, divided into several sections with separate temperature control. The articles are carried through the tunnel mostly by means of a steel refractory conveyor belt, depending on the size of the products either loosely or on a suitable refractory pad. The travel speed of the belt is continuously adjustable, so that together with the control of temperatures of the individual sections, the prescribed temperature exposure can be ensured in terms of temperature and time.

Rotary striking furnaces are only suitable for processing glass marbles, when the temperatures of the striking process are higher than the deformation temperature of glass and when the articles would be deformed in stationary placement of the articles on the pad.

11.3 Chemical processes

In the case of chemical processes, these are mainly final surface treatments of products that can be combined with each other. Virtually all product groups can be chemically treated. It is most often flat glass, domestic glass and semi-finished products for glass jewellery.

In chemical finishing, the quality of the resulting surface is often determined by the quality and purity of all raw materials. One of the basic raw materials is water, which is treated from drinking water from the water supply network by means of a demineralization column, which removes chlorine, fluorine, calcium, etc., from water. Water is then referred to as demineralized or demi water.

Chemical processes involve a generally wide range of processes with different specializations. In general, chemical processes can be divided into:

- chemical polishing, etching and frosting,
- strengthening of glass by ion exchange,
- vacuum evaporation,
- magnetron sputtering,
- pyrolytic plating,
- varnishing, painting and glazing,
- silk screen printing,
- layers on the glass.

11.3.1 Chemical polishing, etching and frosting

Chemical **polishing of glass** means removing unevenness of the glass surface until smoothing. A mixture of hydrofluoric acid together with sulphuric acid is used for polishing. The structure of the glass is disturbed by hydrofluoric acid, and during reactions with the glass surface, fluorides are formed on the surface, which, as products of a chemical reaction, adhere firmly to the glass surface. Further action of hydrofluoric acid allows the presence of sulphuric acid, which dissolves the resulting reaction products. The process is also supported by the removal of reaction products from the glass surface during the reaction by relative movement of the glass and bath.

Chemical polishing is used after rough grinding, especially for décors where mechanical polishing would be difficult. Glossy etching occurs - the mixture etches off protruding microscopic irregularities. The advantage is the extremely high gloss of the glass after completion, there is no rounding of the inner edges of the grind and it is possible to polish several products at once.

Polishing takes place by alternating immersion of the product in the polishing bath (for 15 to 20 sec) and in the rinsing water. The number of immersions depends on the composition of the glass melt and the depletion of the bath, as some of the ongoing reactions are irreversible. In the past, during polishing, the products were placed in baskets, which were immersed in the solution by means of a pulley, automatic drum polishers are used today. In these polishers, the glass is polished in a closed bath in the rotary movement of the drum, by the alternating action of the polishing bath and the rinsing bath. After polishing, the glass is washed with clean water in one or two open tanks. The facility also includes working bath tanks, acid feeding equipment and sludge sedimentation tanks. The facilities are supplied in various modifications according to the required polishing technology and the needs of the operator.

The overall disadvantage of this technology is the difficult handling of hydrofluoric acid, which is highly harmful to health, the need for efficient extraction and capture of gaseous products, costly neutralization, the need for special treatment of sludge and, in general, high costs of technology due to strict environmental and hygiene regulations.

Etching and chemical frosting of glass (matt etching) are decorative techniques that use the action of hydrofluoric acid and its salts on the glass surface, where some components of the glass dissolve and the final surface is covered with fine crystals of insoluble fluorides.

If the glass surface is covered with an acid-resistant layer (e.g. wax), it is partially exposed in some places and thus exposed to the effects of an etching bath, the surface is etched in these places, called "deep etching", which is mainly used in decorative glass and is performed in order to create a matt surface. Hydrogen fluoride baths or pastes are most often used, e.g. ammonium hydrogen fluoride $(NH_4)HF_2$. Chemical frosting is today being replaced by mechanical frosting.

Partial automated **etching technology** can be found in the area of domestic glassware. These are devices such as wax-engraving tools and the etching lines. Machines for mass engraving in wax are based on relatively old principles (so-called needle machines). They have several positions in which wax-coated articles rotate, mostly goblets or tumblers. Mechanically operated tips engrave embossment into the wax, which is then exposed to the etching bath. The tips move vertically up and down and their movement is mechanically coupled with the rotation of semi-finished products. The drive of all moving parts of the machine is realized by means of one electric motor with a gearbox. The movements of the tips and rotating positions are derived via cam.

The **frosting baths** contain ammonium salts for the coarse matt and potassium salts for the fine matt. The concentration of free hydrofluoric acid in the bath is important. Too high concentration of hydrofluoric acid causes a coarse to uneven matt, a low concentration causes a silky matt.

The nature of the matt depends on the composition of the frosting bath, the composition of glass, the temperature of the bath and the exposure time. In frosting baths, the products are usually frosted over the entire surface area.

Paste frosting is more commonly used than bath frosting, frosting entire surface areas of sheet or lighting glass and some types of pressed or blown glass. Paste frosting is widely used in decorative glass, often as a supplement to painting techniques.

Frosting décors are transferred to the glass surface by various reproduction techniques (stamping and writing, pantographing and needle etching) or by decorating the glass surface using protective covers.

The time required to create a matt is usually 5-10 minutes. The paste is washed with warm water or wiped back on a pallet and then the matt surface is washed with water. However, the paste thus wiped gradually loses its effectiveness.

Finishing of flat glass can be mentioned as representatives of the automatic glass frosting technology. The line is often built in the shape of the letter L or U. The glass is supplied to the line in the required dimensions, maximum dimensions of the jumbo format (3210 x 6000 mm) and the thickness is usually in the range of 3 - 12 mm. In the case of one-sided frosting, the side of the sheet which was not in contact with the tin bath during the production of the basic semi-finished product (flat glass FLOAT) is frosted. The reason is the residual tin after the production of flat glass by floating, when the reaction with the frosting solution would produce an undesirable product (tin fluoride - SnF_4) degrading the surface (a grey map would be created). The non-frosted side is protected by an adhesive polyethylene (PE) film of different thickness depending on the thickness of the frosted glass, which is resistant to the effects of chemical solution and at the same time does not leave marks on the glass surface after its application and later removal.

The frosting line (Fig. 11.31) is formed by individual positions and the movement of the glass sheet between them is performed by means of a driven roller conveyor. The line starts with a loading robot, followed by washing the sheet. Cleaning takes place with brushes and demineralized water, followed by air drying. In the next step, the film is applied, trimmed and a protective tape is applied to the edges of the glass. This is followed by frosting in a closed tunnel separated by ventilation, the frosting time is stated to be around 10 minutes. The second washer included in the line is used for cleaning the glass sheet from frosting solution. In the next step, the film is scanned and the whole process ends with an control station (output matt quality control).
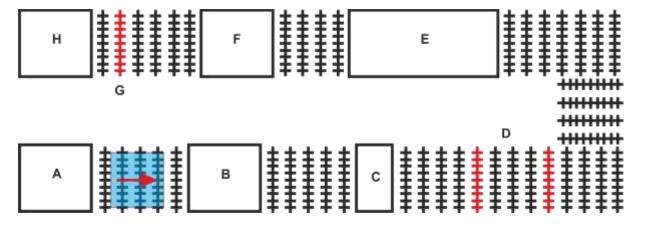

Fig. 11.31 Diagram of frosting line: A - loading robot, B - washer, C - film application, D - manual trimming and protective tape application, E - frosting bath, F - washer, G - film scanning, H - control and dispatch

11.3.2 Strengthening of glass by ion exchange stuffing

In addition to the thermal process (mentioned in Chapter 11.2.5), it is also possible to chemically strengthen safety tempered glass by means of the compressive stress created in the surface layer. The most frequently mentioned procedure is ion exchange stuffing below the lower cooling temperature.

Ion exchange on the glass surface is a diffusion process governed by Fick's laws. The number of ions exchanged at a constant temperature is directly proportional to the square root of the processing time, and the thickness of the treated layer increases in the same way. The tests were performed on samples of Float flat glass which had been in contact with the melt of potassium nitrate, KNO_3, for some time at temperatures ranging from 300 to 500°C. Under these conditions, the exchange of Na^+ ions from the glass surface for K^+ ions from the potassium nitrate melt takes place. Due to the larger ionic radius of the potassium ion, a compressive stress is created in the thin surface layer, the release of which is prevented by the inner cold layer of glass, which does not allow the stress to be equalized by the viscous flow. The described ion exchange stuffing creates a compressive stress of up to 700 MPa in the surface layer of the glass, the small tensile stress in the inner layer of the glass is virtually constant. The thickness of the strengthened surface layer usually ranges from 10 to 100 μm. In experiments, an increase in the strength of 3 mm thick glass samples was found to be about 1.3 to 4.2 times compared to the starting unstrengthened glass. Unlike thermally tempered glass, which also has the character of safety glass, glass strengthened chemically by ion exchange stuffing lacks this characteristic. The strengthened glass may have a modified chemical composition particularly suitable for this process.

In the production of chemically strengthened glass, a container with unstrengthened glass is inserted into the KNO_3 melt in a strengthening furnace. Due to the relatively high melt temperature (more than 380°C), it is necessary to first temper the glass in an electric tempering furnace to prevent cracking due to temporary stress. After placing the tempered glass in the melt, it is necessary to strictly observe the technological conditions of the process within the prescribed limits. The strengthening process lasts from 4 to 48 hours, depending on the required degree of prestress, bath temperature and type of glass. At the end of the strengthening process, the container with finished products is removed from the bath and allowed to cool freely to ambient temperature. A residual film of used salt remains on the surface of the glass sheets, which must be removed in the washer. The described method of strengthening does not leave any optical or deformation effect on the glass surface, which can be a certain advantage compared to thermally tempered glass for applications with high demands on quality (e.g. laminated fronts of high-speed trains).

The application of chemically strengthened glass can be encountered in the glazing of vehicle windows, especially in the windscreens of trains and aircraft. Also for mobile phone and tablet displays (Gorilla Glass, Dragontrail and others). In addition to the limited possibilities of continuous production, the fact that it is not safety glass also prevents the wider expansion of the application. However, this requirement can be solved by laminating this glass, for example with a polyvinyl butyral film.

11.3.3 Application of layers on glass

This is the creation of layers on the glass surface, causing the desired effect and can be created by various technologies. In the following text, only a selection of the most used finishing technologies is given.

11.3.3.1 Silvering, gilding and platinum plating

These are techniques for applying layers of these precious metals to glass for domestic and decorative purposes. The first is the application of a mixture of fine metal powder (Ag, Au) and flux (bismuth oxide with borax or lead borate). When fired, the flux fixes the metal to the surface of the glass, but its appearance is matt and it is necessary to mechanically polish it. The mixture is usually applied in the form of a suspension in lavender oil.

A completely different silvering process is chosen in the production of mirrors and mirror surfaces in general, including the silvering of jewellery stones for simulating and silvering the holes of seed beads. The basic condition is the surface of the glass polished and perfectly cleaned, without any grease and other impurities. Prior to silvering, the surface is activated by a solution of stannous chloride, which forms a network of reduction centres on the surface of the glass. A freshly prepared mixture of an ammonia solution of silver nitrate containing a silver diamine complex $[Ag(NH_3)_2]^+$ and a glucose solution is applied to the surface thus prepared. The said complex is easily reduced to metallic silver by simple sugars with an aldehyde group, for example glucose $(C_6H_{12}O_6)$. Very simply, this process can be expressed by a chemical reaction:

$$2[Ag(NH_3)_2]OH + R - COH \rightarrow 2Ag + 3NH_3 + R - COONH_4 + H_2O \quad (11.1)$$

After the chemical reactions, a thin layer of metallic silver is deposited on the surface of the glass, which must be covered with a protective layer of suitable varnish after the process, which prevents the action of air and protects the silver from oxidation and mechanical damage.

The bright metallic gold coating gives its organic compound resinate applied in lavender or other suitable oil to the glass, which, after drying and firing to about 550°C, is reduced to metal, adhering firmly to the glass surface. The bright platinum layer is formed in a similar manner from platinum resinate. Other metal resinates (Rh, Ag, Bi, Co, Cr…) are often added to both resinates, which improve the adhesion and properties of the resulting layer and change its colour.

Luxury articles can also be decorated with gold leaves, which are films of pure gold, which are glued to the surface of the glass using colourless adhesives with a refractive index similar to that of glass.

Silvering is most commonly used in the production of mirrors and in the production of glass jewellery components.

11.3.3.2 Production of mirrors

The vast majority of mirrors are made by chemical application of metals, especially silver, to the treated glass surface. The already mentioned reaction of an ammoniacal solution of silver nitrate with a reducing agent is used, followed by the application of a protective layer. In the past, copper was used, which was abandoned due to its toxicity. The current lines of the so-called third generation are made up of technological units that enable continuous production with gradual steps:

1. ***Loading semi-finished products on a silvering line.*** The sheets already have the size required by the customer.

2. ***Cleaning and polishing the surface of the glass sheet*** is first by rinsing with water, followed by cleaning with roller rotating brushes. The surface of the glass is then polished by means of polishing bridges, for the actual polishing a mixture based on cerium dioxide in aqueous suspension at a temperature of 40 to 50°C is used. After polishing, rinsing with nozzles follows. The cleaning is completed with rotating roller brushes sprinkled with demineralized water.

3. ***Activation of the glass surface*** before silvering is carried out with a solution of stannous chloride through a row of nozzles, left to act for about 5 minutes, followed by rinsing with demineralized water.

4. ***Silvering*** is performed using two rows of nozzles. In one row a silvering solution is fed and in the other row a reducing solution is fed. Mixing with each other occurs only on the surface of the glass. This is followed by rinsing with demineralized water at a temperature of 25 to 30°C supplied by nozzles arranged in a row. At the same time, a visual inspection of the uniformity and quality of the applied layer is performed.

5. ***Passivation and silanization*** form a coating on the silver layer, ensuring its protection against damage. The passivation solution is applied by spraying by means of a row of nozzles on a silver-plated surface, where it is left to act for some time. This is followed by rinsing with demineralized water. In the next step, the silanizing solution is applied again by means of a row of nozzles, which also requires a certain exposure time. This step is completed by rinsing with demineralized water.

6. ***Heating*** is performed in order to remove residual water and preheat the sheet before applying the protective layer of varnish. The system consists of a system of heating heaters arranged in sections, the switching on and off of which can regulate the temperature so as to reach approximately 60°C.

7. **Varnishing** is performed in two steps and the aim is to create protection against mechanical and chemical damage. In the first step, the primer is applied using a varnishing head, which creates a continuous curtain. The plated sheet passes through this curtain at a certain speed, so that a layer of primer with the required and uniform thickness is formed (Chapter 11.3.3.7). In the same way, the topcoat layer is applied in the second step.

8. **Cooling, washing and drying of the finished product.** Cooling is primarily done by fans that suck in air from the surrounding environment and blow the glass sheet from both sides. The final cooling and simultaneous washing of the sheet take place in boxes with a separate function. First, the upper surface of the sheet is washed with water using a system of nozzles (while being cooled at the same time). This is followed by washing (and cooling) with rotating rollers made of soft material. The rollers are soaked in the tanks first in water, then in a solution of ferric sulphate (which removes silver residues on the edges of the mirror) and again in water (rinsing of residues after the reactions of the previous solution). The final washing of the sheet is performed by spraying the bottom and top surface of the sheet with

the simultaneous action of rotating brushes. The drying of the finished products is performed by the effect of compressed air supplied by nozzles.

After the completion of technological operations, the individual sheets are usually printed with identification data, followed by inspection and removal of finished products from the line.

11.3.3.3   Similization of jewellery stones

Another example is similization. Because the ground, polished and cleaned glass stone does not have such a perfect optical effect (gloss, brilliance and play of colours) as a well-ground natural stone, the lower part of the stones is similizated (covered with a silver mirror layer) to improve the effect, since the 1970s. Similization is collectively called the whole process by which a reflective silver layer is formed on the surface of the lower part of glass stone (e.g. chaton), protected from the outside by a protective layer of varnish with pigment. This is again the principle of creating a mirror, which in this case consists of a number of sub-operations and special work procedures, which can be divided into preparatory work, treatment and finishing operations. The preparatory work includes cleaning of the articles before similization, placing the stones in the fixative and its preparation, embedding the stones in the fixative, or cooling the plates with embedded stones. The fixative enables mass silvering and bronzing, where the embedded tops of the stones are protected against silvering by this fixative. In the past, gutta-percha (rubber-related material) was used for fixation of the stones, but today film made of softened polyvinyl chloride in the shape of a circular plate or strip (in the case of a continuous automatic line) is mainly used. The film is heated to soften in the embedding space and, after inserting the sieve with stones into this space, air is sucked out of it. The stones are embedded in the PVC by the effect of vacuum and the empty sieve is removed.

The actual treatment operations are: washing the surface and activating it for silvering, silvering, drying of silver-plated stones, bronzing and drying. Before silvering, the stones must be washed and then their surface is activated with a 0.1% solution of stannous chloride. Silvering is performed by spraying with compressed air. The spray gun is equipped with two nozzles, one of which sprays an ammonia solution of silver nitrate and the other a reducing solution. The silver-plated stones on the plates are usually dried in a tunnel drier, followed by the application of a protective varnish with metallic pigment by spraying. The pigment is bronze, brass (gold imitation) or aluminium (silver imitation). After the protective layer has dried, the stones are loosened (broken) and fall by bending the plates or strip.

Treatment operations are followed by finishing operation, which is firing of the protective layer at a temperature of 150 to 200°C. All operations follow each other in a similization line that is automated. At the exit of the line, the stones are checked and sorted.

11.3.3.4   Vacuum evaporation

Vacuum evaporation is the domain of jewellery in glass production. The principle of vacuum evaporation (vacuum plating) is the evaporation of materials in a high vacuum and the condensation of their vapours on the surface of objects. The modified steamed object with a perfectly clean surface is placed in an enclosed space, from which air is exhausted to a pressure of 1.10^{-2} Pa. The substance which is to form a coating on the object is heated under this vacuum by an evaporation source to the evaporation temperature in so-called "trays". The evaporation temperature of a given substance must be lower than its melting temperature. Due to the increased kinetic energy of the particles in the surface of the evaporated substance, atoms or molecules are released, which propagate linearly in a vacuum, unless they collide with the remaining gas

molecules. The evaporated material condenses on the surface of objects with a lower temperature (steamed object, but also walls and all internal equipment of the device). At a sufficiently high vacuum, most of the evaporated molecules fall on the surface of the object without colliding with the molecules of the residual gases. Due to the kinetic energy that the evaporated molecules have, a continuous coating with good adhesion is formed on the object. The vapour-deposited layer can cover the entire product, the so-called **all-metal** or only a part, **semi-metal.**

One vapour-deposited layer is very thin, usually 30 to 50 nm, and always several layers (typically 7 to 10 layers) are applied, which can be of different composition. The layers can be formed by one or more metals, so-called **metallic décors**. Aluminium, chromium, nickel, copper, silver, gold, chrome-nickel and others are mainly used. The resulting décors have a typical metallic lustre and if the thickness exceeds 100 nm, they also have a metallic appearance.

The layers can also be formed by oxides (titanium monoxide is used for achieving a similar effect as in the irisation), but layers of different composition can also be applied and these layers can be combined and alternated to achieve the desired optical and colour effect. An example is interference layers, where layers with a high and a low refractive index of a precisely determined thickness are applied alternately. This creates **interference décors**, where the most famous is the décor created from a combination of layers of titanium oxide and silicon Aurora borealis (also called AB – décor, formerly Titania). Fluorides, such as magnesium fluoride and many others, are also vaporized from non-metallic substances.

Combined décors are composed of a combination of metal and interference layers. The metal layer in this case usually serves as reflective and the interference layers create their own decorative effect.

Vacuum-vapour-deposited layers have sufficient resistance and only in some cases (layers of soft metals - aluminium, copper) are protected by a layer of resistant oxide also applied in a vacuum or a layer of varnish.

Vacuum evaporation is performed in vacuum evaporation apparatuses. The device consists of several parts: vapour-depositing device, vacuum system consisting of a rotary pump, a Roots pump, a diffusion pump and a control system. After vapour plating, the products are fired at 200 to 400°C (depending on the type of articles) to improve adhesion and mechanical properties.

11.3.3.5 Magnetron sputtering

Although conventional thermal vacuum evaporation has already found its stable application in the glass and jewellery industry, there are currently more progressive methods of applying layers. Cathodic sputtering, especially magnetron sputtering, occupies a significant place among them. This technology is used especially for flat glass for glazing windows with two or more panes (insulating glass). These are coatings that are relatively soft (compared to pyrolytic plating, Chapter 11.3.3.6) and are easily scratched. Therefore, these glasses are used exclusively for insulating glazing (double and multiple glazing), where the surfaces treated in this way are oriented towards the glazing cavity. The whole system is closed with a circumferential seal and an expansion profile containing a desiccant.

The process of magnetron sputtering consists in bombardment of a target with particles of ionized gas in vacuum chambers. The energy of the particles is large enough to be able to release

particles of material to be applied from the target. These particles fall on the surface of the glass, where they form a thin layer, the diagram of the process is shown in Fig. 11.32.
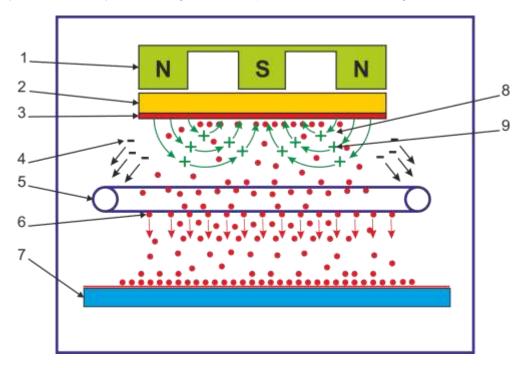

Fig. 11.32 Diagram of magnetron sputtering: 1 - permanent magnet, 2 - cathode, 3 - target - deposited material, 4 - electrons, 5 - anode, 6 - atoms sputtered away, 7 - glass sheets (substrate), 8 - magnetic field, 9 - cations

An inert gas, most often argon, is introduced into the vacuum chamber, which is ionized in a glow discharge. The action of permanent magnets creates a strong magnetic field, which causes the resulting plasma to be concentrated immediately in front of the cathode. The secondary electrodes deflect to the auxiliary anode or to the recipient wall, thereby greatly reducing the temperature of the substrate. Argon ions increase their kinetic energy and bombard the target mounted on a water-cooled copper cathode. The target is sputtered to form the desired coating on the substrate. The working pressure is usually from 0.1 to 1 Pa, the substrate temperature from 50 to 250°C. The rate of increase of the thickness of the formed layer can be up to ten times higher than in vacuum evaporation.

The sputtered layers are structurally homogeneous with high adhesion and reproducible composition, which is important especially for alloys. Direct magnetrons enable the sputtering of all refractory metals (W, Ta, Mo, Zr, Hf, etc.), the use of high-frequency magnetrons and the sputtering of dielectrics (SiO_2, Al_2O_3, ZrO_2, etc.). Another advantage is the uniform coating of large areas (e.g. glass sheets), therefore some magnetrons reach considerable dimensions.

Magnetrons also allow for reactive sputtering of layers, in which the base metal or compound reacts during the process with reactive gases admitted to the recipient for this purpose. In this way it is possible to prepare a whole range of decorative and functional very hard layers (TiN, TiAlN, WC, CrN, WN, etc.). Working conditions in reactive sputtering are very demanding not only in terms of geometric arrangement, but also require strict adherence to set conditions, such as the degree

of ionization, the intensity of the magnetic field and the regulation of ionized and reactive gas. For these purposes, the device is equipped with a control unit.

Sputtering technology can be used for both monolithic layers and multilayer systems. The order of the layers then corresponds to the order of the targets placed on the line in the individual chambers, thus also determining the variability of the device in terms of the production of different types of coatings. There can be several tens of layers on the glass. At present, there are also sputtered layers, which are also suitable for subsequent thermal tempering.

For large outputs, large-capacity in-line devices are manufactured, consisting of a series of separate chambers placed one after the other, Fig. 11.33. The device is called a coater and is operated continuously with a conveyor on which flat glass is placed.
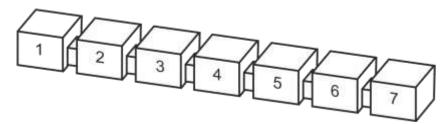

Fig. 11.33 Diagram of magnetron sputtering line: 1 - loading of glass sheets, 2 - washer, 3 - inspection, 4 - vacuuming, 5 - sputtering zone, 6 - gradual increase of pressure, 7 - output of sheets with formed layer

In the first phase, the glass is placed on a conveyor, washed and inspected. Furthermore, the glass continues to the decompression zones, where the pressure is gradually reduced to the working pressure. In the sputtering zone, the desired coating is formed on the glass surface. This is followed by a gradual increase in pressure through the chamber system. An inspection is performed during the process. In particular, the quality of the glass, the thickness of individual layers, the homogeneity of the formed coating, the colour of the coating and others are checked.

11.3.3.6   Pyrolytic plating

Pyrolytic-plated glass is glass plated with a hard layer of metal oxide applied by spray or CVD technology[17]. This technology allows the application of a perfectly uniform protective layer of metal oxides due to the reaction of gas on the glass sheet. The gas comes into contact with the glass at high temperatures and forms a hard "pyrolytic" protective layer, which is firmly bonded to the glass surface. These layers are resistant to mechanical damage and often also to climatic effects in exposure to the external environment. Thus, products with this treatment are used in monolithic glazing, and the advantage is also easy further processing such as grinding and thermal tempering.

The device is often part of the FLOAT line (Fig. 11.34) for the production of flat glass, Chapter 9.6.3. When applying the active layer by spraying, the used preparation comes into contact with the hot surface of the bolster at the beginning of the annealing furnace; when using CVD, the effective layer is formed in the space of the tin bath, which is a more modern method that allows the formation of multilayer coatings.

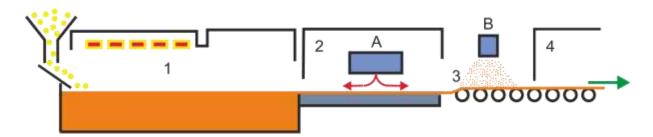---

[17] Chemical vapour deposition.

Fig. 11.34 Diagram of pyrolytic coating: A - CVD application, B - spray application, 1 - melting and working ends of the furnace, 2 - tin bath, 3 - lifting rolls, 4 - annealing furnace

11.3.3.7   Glass with functional coatings

In particular, flat glass for architecture is provided with a surface layer in order to improve its functional properties. Since it is not possible or economically efficient to develop new glasses with special properties by changing their chemical composition and also the flexibility of today's flat glass production lines from the point of view of changing the glass composition is not high, coatings are being developed to improve glass properties. Functional coatings on flat glass are applied mainly by the above-mentioned technologies of magnetron sputtering and pyrolytic plating. These generally transparent layers in the visible region of radiation are used mainly to change the reflectance and absorb part of the spectrum, which improves the thermal insulation properties of the glass and the ability to selectively transmit the individual components of solar radiation. In addition, the coatings on the glass may have antibacterial effects, change the degree of reflection of the surfaces or may be modified for easier processing and cleaning. The properties of coated glasses are always considered as a whole, because the properties of the base glass - substrate also affect the overall properties of this coated glass.

Low emissivity glass is called glass with a thermal insulation function. Such glasses used for glazing reduce the heat loss of the building to a minimum in the winter, by minimizing heat leakage through glass from inside the buildings while allowing direct sunlight to pass through. It is used for low-energy and passive buildings. The basic parameter determining the thermal insulation properties is the normal emissivity of the coating, which is crucial to achieving a high degree of thermal insulation. The coefficient of heat transfer U [W·m^{-2}·K^{-1}] expresses how much heat escapes through a glass surface with a surface area of 1 m^2 at a surface temperature difference of 1 K. Lower values of the coefficient represent better insulation. For example, a separate float glass without functional coatings has the coefficient of heat transfer of 5.8 W·m^{-2}·K^{-1} for glass with a thickness of 4 mm. For high-quality double glazing units with functional coatings, values around 1.1 W·m^{-2}·K^{-1} are given, for triple glazing units, the values can approach up to 0.6 W·m^{-2}·K^{-1}.

Selective glass makes it possible to reduce the heat gain caused by the penetration of sunlight in summer. Conventional glasses transmit optical radiation in the range of λ ≈ 300 nm (UV radiation) to λ ≈ 5,000 nm (IR radiation), i.e. part of ultraviolet and a wide range of infra-red radiation (Chapter 3.9.3). This radiation brings heat into the interiors. The aim of the selective layer is to minimize the transmission of UV and IR radiation and to transmit visible radiation at the same time. The selectivity of glazing can be expressed by the ratio of the light transmission factor (L_T) and the total solar transmission factor (S_F). Visible light makes up 50% of the total range of the solar spectrum. Therefore, for example, for glazing with $L_T = 50$ % the best possible $S_F = 25$ % was considered. Until recently, the selectivity of coated glass was able to range from 0 to 2. With

the advent of new materials and technologies, selectivity values higher than 2 can be achieved. Only the best glasses meet the maximum selectivity value.

Other types of coatings with specific properties are applied by a number of other different technologies, such as sol-gel process. **Sol-gel process** is used for the preparation of mainly inorganic oxide materials in the form of layers and is based on the preparation of colloidal solution (sol), which is converted into a gel and subsequently into a solid material. **Nanotechnologies** are also being developed to create scratch-resistant coatings, water-repellent and non-stick coatings (which do not adhere dirt, grease, scale, fingerprints, etc.), other applications can be encountered in surface painting, in the production of photovoltaic solar cells, when increasing the fire resistance of glass, etc. There are also other technologies, which are, however, mostly part of the production know-how.

An example of other functional coatings is the **antibacterial surface of glass**, which is modified so that the diffused silver ions are part of the glass structure. Thanks to this treatment, the glass surface destroys harmful bacteria (99.9%) for a long time and prevents the formation and growth of many fungi.

Coatings for easier maintenance aim to simplify the care of the glass surface. These are mainly coatings with hydrophobic, hydrophilic and photo-catalytic properties. There are two basic approaches to easy surface maintenance.

The first is to provide the glass surface with a hydrophobic layer, which repels grease and water, protects the glass surface from corrosion and damage, such as graffiti. The layers are most often applied to the surface by spray or CVD method is used, the layers are further cured by a chemical reaction or high temperature. For example, polymers (silane or fluoropolymer) can be used as the material. The main disadvantage of these layers is the lower resistance to mechanical damage.

The second approach represents the use of a hydrophilic coating with photovoltaic properties. In this coating, nanoparticles TiO_2 are used as catalysts, which show photo-catalytic activity (triggered by UV-A radiation). The principle of the coating function can be divided into two processes:

- UV radiation, which is part of sunlight, starts a photo-catalytic reaction, which decomposes organic impurities on the glass surface and at the same time the glass surface becomes hydrophilic (the required intensity of UV radiation penetrates through the clouds).
- In subsequent rain, due to the hydrophilic properties of the surface, a thin film is formed on the glass, which evenly washes away the decomposed organic impurities and the remaining inorganic particles. This water film dries easily and quickly.

Since not all organic particles are decomposed and the effect depends on many factors (intensity of UV radiation, location on the building, orientation to the cardinal points, the level of air pollution with inorganic dust), this is not so-called "self-cleaning", as is sometimes stated for marketing reasons, but it is a surface with easier maintenance. The durability of surfaces, their compatibility with other materials used (e.g. for sealing of insulating glass) and the fact that it is necessary to apply coatings also on the other side of the sheet, which is technically very demanding, remains a problem.

Anti-reflective coatings can reduce the reflectivity of glass from 7.7% to less than 1% (in perpendicular incidence of light). For this purpose, anti-reflective sol-gel coatings applied as dip-coating (soaking in a sol bath and subsequent heat treatment) or by sputtering are used.

Windows with controlled permeability (chromaticity) have two basic variants, the first is the principle based on a layer placed in a liquid crystal film, the principle is described in Chapter 11.4.1.1. The second principle uses the so-called electro-chromic glass, which can change the colour from the usual colourless through light blue to dark blue by regulating the stress. It is based on two sheets of glass covered with a very thin transparent electrically conductive layer (ITO layers, indium doped tin dioxide), between which there is a layer of polymeric material, which is a good electrolyte, so that lithium ions can move in it. One part of this layer is provided with a very thin layer of tungsten oxide, WO_3, applied under defined atmosphere, the other layer contains lithium ions. An external source of direct voltage is connected to the electrically conductive layers on the surface of the glasses, the effect of which can create colour centres. Dimming is controlled by a reversible electrochemical reaction associated with the diffusion of lithium ions into the layer WO_3:

$$WO_3 + Li^+ + e^- \rightleftarrows LiWO_3 \qquad (11.2)$$

$LiWO_3$ is dark blue. The intensity of the dark blue shade depends on the duration of the stimulation. The resulting $LiWO_3$ is dark blue. Deactivation of the colouration is performed by reversing the polarity, which causes feedback and return to the original clear state.

11.3.3.8   Staining of the glass surface

The staining of the glass surface can be divided into varnishing, painting and glazing. The largest volumes of products are varnished. It is the application of thin coloured layers on glass in one of the "mechanical" ways. Varnishing has two basic purposes. The first aims to create a protective layer, especially on silver-plated glass surfaces. The second application is the decorating function, where both transparent and rich colours are applied.

Varnishing goes across the application of glass. It is most common in jewellery, generally in architectural glass (e.g. flat glass, glass building blocks,…), in domestic glassware, but also in Christmas decorations.

Varnishing can also include silk screen printing, roller coating, curtain coating, spraying, digital printing, etc.

Silk screen printing

The silk screen printing technology is based on extruding the colour paste through a silk screen printing matrix attached to the glass surface, followed by drying and firing of the ink. The silk screen printing matrix is prepared on the basis of a design, which is photographically transferred to a fine (often nylon) mesh, which is clamped to the frame. The mesh is permeable only in the place of the photographed design and otherwise the entire surface of the mesh is impermeable.

The clear glass is precisely placed under the matrix-carrying frame in accordance with the requirement for pattern placement and is always in a horizontal position, then the matrix with the required pattern placement is lowered on it and the pre-prepared ink from the container is deposited on the screen from above. The ink is then extruded with a spatula, which passes over the matrix.

The quality of ink application and the thickness of the applied layer is determined by the viscosity of the ink, the pressure of the spatula and in particular the density of the screen.

Silk screen printing inks are ceramic frits, today free of heavy metals and harmful components that were part of inks in the past. The inks are applied by dispersing the colourant into a carrier liquid medium, which consists of either a printing oil (based on terpene, pine oil and binders soluble therein), or water-soluble liquids (water-soluble organic solvents and binders) or water-based liquids.

Large-scale prints are used for façade glazing or interior partitions. Fully automated lines for smaller dimensions and large series are used, for example, for printing automobile glazing closures. Silk screen printing is also used for domestic and decorative glassware, for the production of cheaper products, on container glass, where it replaces labels, but also for Christmas decorations. The whole process can be manual, semi-automatic to fully automated using one or more inks and motifs. Multicolour prints take place gradually, the inks are dried between applications.

During drying, volatiles are removed and performed either with hot air or infra-red radiation. This is followed by firing, which bonds the layers of ink to the surface of the glass. An example of a flat glass printing line is shown in Fig. 11.35.
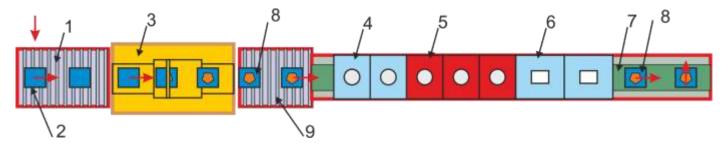

Fig. 11.35 Example of flat glass printing line: 1 - loading on a roller conveyor, 2 - glass, 3 - silk screen printing machine, 4 - drying, 5 - firing, 6 - cooling zone, 7 - conveyor, 8 - printed glass, 9 - conveyor for print control

Roller coating

The ink used for silk screen printing can also be applied by cylinder on flat glass, so-called Roller Coating. Roller coating can create separate colour effects or a print created by silk screen printing can be added.

The application principle is schematically shown in Fig. 11.36. The glass moves in a horizontal position on the conveyor, from the upper side it is adjacent to the application roller, which rotates in the direction of glass movement. By moving the application roller, the ink from the container is transferred to the surface of the glass sheet, creating a homogeneous film with a well-controllable thickness (approximately 30 to 200 μm). The layers applied by this technology can be full-area or can have a décor that is repeated in accordance with the rotation of the application roller. As with silk screen printing, application is followed by drying and firing.
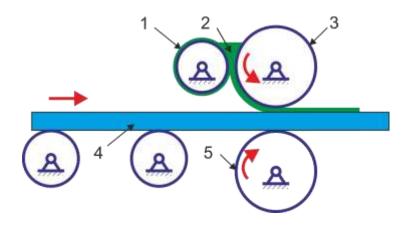
Fig. 11.36 Principle of roller coating, 1 - container, 2 - ink, 3 - application roller, 4 - glass, 5 - transport roller

Curtain coating

Curtain coating is again applied to flat glass, e.g. in the production of mirrors. In this coating technology, a thin layer of paint flows through the longitudinal slit of the applicator (head) and forms a continuous curtain, Fig. 11.37. The glass sheet passes through this curtain at a certain speed, thus creating a layer of varnish of the desired and uniform thickness. A certain disadvantage of this process may be that the leading edge of the glass passing through the curtain is also coloured and, if necessary, its cleaning can be difficult.
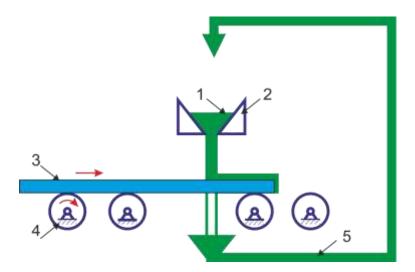
Fig. 11.37 Principle of curtain coating, 1 - ink, 2 - outlet slit, 3 - glass sheet, 4 - transport rollers, 5 - circulation

Spraying

Spray gun systems are used for decorating small products, which also allow flexible colour change. The paints used can be of various compositions, from modern water-based, to pastes used for roller coating or for curtain coating. It is important to keep a constant thickness of the applied layer of paint. The disadvantage of this technology is the significant loss of colour. An

automated coating device is a conveyor that carries glass semi-finished products. The nozzle system itself is located above the conveyor and moves across.

Varnishing of beads

Light-fast paints are also used for varnishing some types of beads (e.g. seed beads, double beads, pipes, pins, satin beads, ...). Paints are applied to heated semi-finished products and some of them are subsequently fired. The process is often automated today. They are painted in barrels and the applied paints are water-soluble. In the past, alcohol paints were used.

Digital printing

Digital printing is currently expanding, allowing for high flexibility of motifs and print speed. Applications are mainly for flat glass for construction purposes (interiors and exteriors) and automobile glazing closure.

 The range of colours in the form of inks is also diverse, from transparent to opaque. Printed glass can be cooled (often laminated) or tempered. Inks can be ceramic and need firing when applied to glass, but have a longer life and colour fastness. Inks can also be cured by UV radiation.

The ink is applied by a print head placed on a portal beam, which allows movement in two axes (similar to cutting heads for cutting flat glass). At present, it is possible to achieve a resolution of up to 720 dpi and the size of the glass can be up to 18 x 3.3 m.

Painting

Painting is a typical finishing process for domestic and especially decorative glassware. It is mainly manual production. Painting techniques can be divided into painting with baking paints, painting with glazing mixtures, painting with cold paints, painting with metals, line drawing, icing and frosting with frosting salt.

When painting with baking paints, flat, relief, and transparent topcoat paints are used. Topcoats have three basic components: flux, pigment and opacifier. Fluxes are low-melting colourless glasses (frits), containing lead oxide, boron oxide, sodium oxide and small amounts of silica. In new types of fluxes, lead oxide is replaced by safer non-toxic oxides, such as bismuth oxide. Pigments (ceramic pigments) are mostly simple or double metal oxides, which give the glass melt (frit) the necessary colouration. If the pigments dissolve perfectly in the flux, it is an ionic colouration and transparent colours are formed. If the flux reacts with the pigments only to a limited extent, or not at all, topcoats - pigments - are formed. Opacifiers are substances that cause opacity of paints. These are mainly sparingly soluble oxides or oxides causing recrystallization (tin oxides, titanium dioxide, zirconium dioxide, cerium dioxide, antimony oxide, etc.). The actual production of paints is very long, especially grinding of frits in ball mills, which lasts on the order of several days. In order for the fine powder paints to adhere to the glass surface, they must be mixed with binders and treated with thinners. These are substances of organic origin; thinners are volatile oils, and balms and resins are used as binders. An example of a known substance which is already ready for use is turpentine. The treated paint is applied to the glass surface with various painting aids and, after drying, fired at temperatures of 500 to 600°C, i.e. at a temperature which is lower than the softening temperature of the base glass (approximately at the lower cooling temperature) but higher than the softening temperature of the coloured powder. At this temperature, the paint softens enough to form a continuous layer that bonds well with the glass product.

Glazing

Glazing is one of the oldest painting techniques in glassmaking (since the 14th century). The essence of this process is the penetration of the colouring agent by diffusion into the glass surface at elevated temperature. This is done by applying a colouring component to the glass together with a carrier, which is usually a slurry of kaolin and water. The colouring component is either silver chloride, AgCl or copper sulfate, $CuSO_4$, or a mixture thereof. Metal ions diffuse into the glass surface at a temperature of 500 to 600°C and colour it. Thus, by diffusion of Ag^+ a yellow glaze is formed, by diffusion of Cu^{2+} first a faint yellow-green colouration (1st firing), which by burning in a reducing atmosphere acquires a black colour (2nd firing) and then in an oxidizing atmosphere changes to the desired red glaze (3rd firing). By combining both ions, green glaze can also be obtained [23, 38].

The glazing technology is used mainly for finishing domestic and decorative glassware, but it can also be used for pressed beads, so-called glazing. The technology is difficult to automate.

Layers used in glass jewellery

Layers can be created by different technologies:

- lustering,
- irization,
- silvering, gilding and platinum plating, similization (Chapter 11.3.3.1),
- vacuum evaporation (vacuum plating, Chapter 11.3.3.4),
- waxing,
- varnishing (mentioned above in this Chapter),
- painting and glazing.

The layers in jewellery are very diverse, they are described in the literature, there is only one representative herein, and that is irization.

The most common is warm iris of titanium tetrachloride, where metal salt vapours are deposited on heated glass. Deep coloured glasses are hot-iridescent, causing an increased colour effect by perfect reflection at the air-layer and layer-glass interface. Titanium tetrachloride ($TiCl_4$) is supplied in a liquid state and vapours are obtained by bubbling dry air through a liquid, which allows an arbitrarily long exposure time. Dry air is used due to the risk of reaction with air humidity. Different exposure time can achieve different layer thickness and thus different colouration, which can be divided according to increasing thickness into the following successive degrees: grey, brown, blue, green, red, bright green, bright red.

The process is mostly performed on attended semi-automatic machines, Fig. 11.38. The products are fed on plates placed on a conveyor that moves intermittently. They are transported to the furnace and heated to temperatures from 300 to 350°C, then fall through a chute onto a sieve. The vapours flow from a bottle to which dry air is supplied under mild pressure. The vapours act on the products on a sieve placed in a furnace at a temperature of approximately 100°C. The sieve moves back and forth to make the décor even. After the required time, the sieve is tilted and the products are emptied from the machine into the box and then washed in water to remove chlorides from their surface.
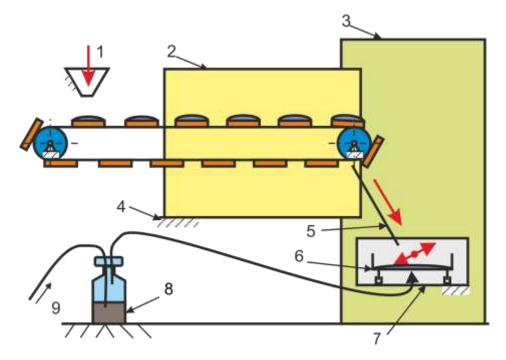
Fig. 11.38 Diagram of finishing technology by irization with warm TiCl₄: 1 - feeding, 2 - heating to 300 to 350°C, 3 - furnace, 4 - machine frame, 5 - shoot, 6 - sieve, 7 - opening for emptying products, 8 - bottle containing titanium tetrachloride, 9 - compressed air supply

11.3.4 Bonding - gluing

Chemical processes can also include glass gluing. Three groups of adhesives can generally be used for bonding glass:

- silicones - one-component sealants and adhesives which harden via a reaction with air moisture,
- two-component adhesives - which harden after precise mixing of the base material with the hardener,
- one-component adhesives - which cure via UV radiation or surface activation, the resulting bond is transparent and very strong.

The creation of "invisible" bonds, for example in the case of glued pendant figures, is now carried out mainly by means of UV adhesives, which polymerize photochemically after exposure to UV light. The hardening of the layer is performed by illumination with a UV lamp with radiation with a wavelength of 315 - 400 nm. These adhesives can be used for creating not only glass-glass bonds, but also glass-metal, glass-plastic, or glass-wood, glass-stone bonds. They can be two-component, clear or pigmented, and special adhesives do not even require a UV lamp and cure even in daylight. Adhesives with different viscosities (low, medium, high), refractive index and strength are produced for different applications. Curing usually takes place within a few seconds.

These binders are not suitable where an elastic joint is required or where the joint is exposed to permanent action of water. For objects located outdoors, the joint must be covered with a protective layer of neutral silicone.

11.4 Special processing and finishing techniques

Another technology that cannot be included among the mechanical or thermal methods of processing is the lamination (sticking) of glass using plastic films and other types of laminated glass. In essence, it does not have to be just flat glass, but flat glass is the most common for the technologies mentioned below.

11.4.1 Laminated flat glass

Laminated flat glass is used in architecture and automobile glazing closures (the term "safety laminated glass" can also be found). Laminated flat glass consists of at least two sheets of glass and their bonding by means of an adhesive elastic layer (most often polyvinyl butyral - PVB or ethylene vinyl acetate - EVA). The glass used can be made using the FLOAT technology or can be ornamental cast glass as well as bent, stained, printed, chemically frosted, and more. The elastic layers can be stained, printed, with anti-noise properties, and the like.

The basic operations in the production of laminated glass are preparation of a glass sheet, interleaving of film, preforming, sometimes cutting of glass and final pressing at elevated temperature in an autoclave, the line diagram is shown in Fig. 11.39. The production process follows very strict rules for cleanliness, because any impurities that would get between the glass sheets and the film reduce the quality of the product.
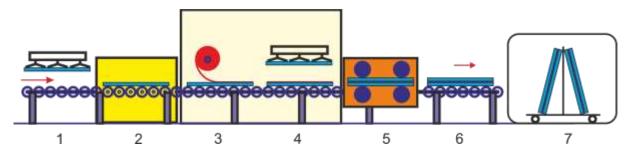

Fig. 11.39 Diagram of automatic production line for laminated glass production: 1 - laying of glass, 2 - washing, 3 - application of PVB film, 4 - laying of upper glass, 5 - preforming, 6 - folding on a stand, 7 - autoclave

At the beginning of the process, the blanks of the desired shape are first washed with demineralized water at a slightly elevated temperature and using rotating roller brushes. Subsequently, they are completely dried with preheated air.

The most commonly used PVB film is supplied in special packaging that prevents the ingress of moisture. PVB film binds part of the moisture, thus changing some of its properties. The film is also stored at 8 to 10°C. The interleaving is often handled manually, and with modern lines this is the only production step that is not automated. Interleaving automation can also be encountered, but it has its specific problems. In the case of manual interleaving, it is often an air-conditioned room where the temperature is maintained at 25°C, the humidity at 30% and the room is maintained at a slight overpressure. After placing the film on the glass and placing the top glass on the film, the excess film will be cut off. For the production of laminated glass, a PVB film 0.38 mm or 0.76 mm thick is used, in special cases it is possible to apply the film in several layers.

The preform is made by several technologies, one of which is the use of rubber rolls. During preforming, the residual air between the glass sheets and the film is expelled as much as possible and the glass sheets are pre-bonded.

The glass sheets can be cut before or after the final pressing. In both cases they are cut by breaking the glass after marking by scratching (Chapter 11.1.1.1). However, the cut must be made from both sides, and very precisely. The breaking takes place by means of breaker rolls, which gradually break off the lower and upper sheet of the double glass. During breaking, the parts to be cut are pulled apart (to prevent damage to the edges of the glass), while being heated by resistance wire, during which the PVB film is remelted. If the laminated glass consists of more than two layers of flat glass, it is necessary to use a diamond wheel or other technologies for separation.

The pressing is carried out in an autoclave, in which a perfect bonding of glass sheets with the PVB film is achieved. After preforming (and possible separation), the glasses are stacked in a stand, which allows transport and also perfect filling of the autoclave. Glasses on the stand are hermetically sealed in an autoclave and the temperature is raised to 140°C and the pressure to 1 MPa (10 bar). The pressure and temperature are maintained in the autoclave for 5.5 to 6.5 hours based on the set cycle. The pressing time is determined by the thickness of the PVB film used. Finally, the temperature in the autoclave is gradually reduced by means of water coolers, the pressure is reduced and after opening the lid of the working zone, the stand with the finished products is taken out.

11.4.1.1 Laminated glass with other properties

In addition to improved mechanical properties, safety properties and increased protection, laminated glass also provides further improvement in the properties of the composite itself.

It is a **glass that regulates the transmittance of radiation**, which can be achieved by using glass coloured throughout the mass, by using reflective glasses or by using PVB film with properties regulating the transmittance of radiation.

Anti-noise laminated glass is provided with a film that improves the acoustic properties of the glass.

Laminating glass, usually with more than two glasses and more than one film, is used for the production of **bulletproof glass**. The composite is composed of glasses of larger thickness, which are on the side where a possible attack is expected (greater thickness absorbs more energy), several PVB films laminated on top of each other and thinner glass to prevent cullet from penetrating onto the protected person. The composite is often supplemented with compound glass (from two sheets bonded by one film) to a distance of 50 mm to prevent any penetration of cullet onto the protected person. In addition to bulletproof glass, there are glasses with protection against forced entry, which are less resistant compared to bulletproof glass. On the other hand, there are glasses with protection against shooting through and explosion, which are more resistant than bulletproof glass.

Compound glasses may have liquid crystals placed in the film, which rotate as the electric field passes to allow light to pass through. This creates glass that allows to **change the transparency** as needed. If the electric field stops acting, the liquid crystals rotate randomly and cause opacity. Such a solution already allows for complete opacity today. This glass is used in interiors, for example in separating the water closet and the bathroom. Furthermore, for example,

for high-speed trains for separating the cockpit and the passengers. The use of this glass can also be found in the glass roofs of cars. Shading is thus a matter of switching on and off the control element on the dashboard.

Integrated LED lighting can also be in the film. These can be separate LEDs connected by thin wires or a transparent conductive layer. It is very likely that integrated LED lighting and subsequently OLED[18] technology in double glazing with independent control of each RGB diode (pixel) will be used in the near future.

11.4.2 Glass with increased fire resistance

Fire retardant glass is often called fire resistant glass due to its high resistance to fire effects. The purpose and primary function of this product is to maintain the optical properties of ordinary clear glass during normal operation and, in the event of a fire, to protect the user from its effects for a known period of time. The aim is to allow users to escape safely from the fire area and to effectively slow down its spread. In addition to basic protection against the penetration of smoke or flames, fireproof glass today offers a high degree of thermal insulation as protection against penetrating heat or opacity of the glass due to high temperature to reduce panic behaviour of users. The main performance parameter is always the time for which the glass retains the required function when tested according to applicable standards.

Fireproof glass with a thermally reactive layer is based on the principle of laminated glass bonded by clear interlayers which can swell and in the event of a fire the interlayers expand at about 120°C and turn into an opaque shield. At the same time, this glazing meets the criterion of integrity, where the glazing does not crack or let combustion products pass through, and, in addition, it meets the criterion of insulation, where such glass does not transmit radiant heat or conduction. The specificity of transparent fireproof designs is that the glazing and the frame in combination create a fire-resistant construction. Therefore, the glass is always tested with a specific type of mounting or profile. The installation of glass is also very important for this type of glazing, which is usually subject to a detailed installation manual.

11.4.3 Glass for solar applications

Glass for solar applications is used in many forms, the main ones being the use for the construction of installations for obtaining environmentally "clean" energy. The basic applications are:

- solar panels for hot water heating,
- solar photovoltaic panels,
- mirrors for solar thermal (concentrator) power plants.

The capacities of **solar panels for water heating** were 406 GW of heated hot water in 2014 (below 100 GW in 2004). These panels are several times more efficient (60% compared to the reported 15% of photovoltaic cells). The predominant part consisted of glass panels made of flat glass or tubes (over 95%). Flat glass used for the production of solar panels is either produced by floating technology (Chapter 9.6.3) or casting technology (Chapter 9.6.2). In casting technology, glass is often provided with a structure (often quadrilateral pyramid-shaped projections) on the

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[18] OLED - Organic Light-Emitting Device, a type of display using organic light emitting diode technology.

underside that improves the reflection of sunlight towards the collector. Tubular solar panels are made of several tubes in a row. Vacuum solar collectors consisting of two thin-walled tubes (wall thickness about 1 mm) are common, between which there is a vacuum, which reduces heat loss.

The capacities of **solar photovoltaic (PV) power plants** are still growing. This type of power plant generated 3.7 GW of electricity worldwide in 2004 and already 177 GW in 2014. Such a sharp increase is mainly due to the policy of supporting the purchase of electricity produced by this technology. The efficiency of standard PV panels that use monocrystalline or polycrystalline silicon cells is about 15% (for grid connection). Generating electricity in this way would not be able to compete with other less environmentally friendly "clean" electricity generation technologies without legislative support. The aim is therefore to achieve an efficiency of industrially produced PV panels approaching 40% and it is mainly assumed the use of broad-spectrum solar cells, processing radiation in the visible, but also partly in the infra-red spectrum (the current record for laboratory equipment is 46% efficiency per cell). It is a system that uses up to 900 times concentrated radiation incident on the surface area of a multiple semiconductor cell, e.g. gallium-indium-phosphide/gallium-indium-arsenide/germanium. Thin films or organic PV cells are also being developed that are less efficient than silicon PV cells but are relatively cheap. All these cells use mainly glass as a very durable, strong, transparent material, which not only protects photovoltaic technology, but also allows its easy installation and navigation relative to the position of the sun.

The increase in the world's capacity of power plants is thus associated with the demand for glass for the production of PV panels. The glass used for the panels is exclusively flat float or cast glass, clear with a low iron content, often provided with an anti-reflective coating or with a special structured surface enabling the capture of the maximum amount of sunlight. Glass is often tempered to have sufficient puncture resistance at a thickness of normally 3 mm and to withstand significant temperature differences. Adapted production technologies used for laminated safety glass are used for placing the cells under the protective glass. The interlayer used for these products is EVA and PVB in the vast majority of cases. In general, the EVA film has better properties for the production of PV cells, as it has a lower viscosity during lamination and is thus able to better fill all the gaps and irregularities created between the PV cell and the glass. The glass with cells can be mounted in a frame with a covered perimeter of the sheet or, increasingly, with the edge exposed to achieve the maximum energy-efficient surface area. In this case, the long-term stability of the edge against the effects of water and temperature changes is very important.

Glass for solar photovoltaic panels currently follows three trends: thin float glass (maximizing transparency), extra clear float glass with a minimum of colouring oxides, cast glass with a surface structure that reduces reflectivity and increases the efficiency of solar panels.

Solar thermal power plants use concentrated solar radiation to heat a liquid medium which is used for generating steam in the exchanger, which rotates the turbines (usually in combination with a gas or coal-fired power plant). There are 3 basic types of these power plants

- centrally located energy absorber (mirrors are placed around the tower, the so-called absorber), to the top of which the reflected solar radiation is directed; in the absorber, heat is usually transferred to the primary liquid, which generates steam by heating water, which then drives a conventional steam turbine),

- parabolic troughs (mirrors are in the form of a part of a cylinder and concentrate energy on a tube with a flowing liquid, which, as in the previous type, heats the water which drives the turbine), and
- parabolic discs (Stirling engine is located in the focus of the disc, which allows to achieve efficiency over 31%).

Solar thermal power plants use glass both for the production of reflectors and, for example, tubes for the distribution of heated medium at the parabolic trough.

11.4.4 Automobile glazing closures

A very important production technology is the production of automobile glazing closures, which has a high added value. These are products that are constantly innovated and individual production operations are also undergoing innovation. Production is thus highly automated for most types. The semi-finished product for the production of these glasses is flat glass made by floating technology (Chapter 9.6.3) iron-coloured throughout the mass (glasses are thus blue-green).

Products can be divided into two types:

- tempered safety glass,
- laminated safety glass.

It is stated that tempered glass is about ten times cheaper than laminated glass and is used for side and rear glazing of cars. However, for safety reasons, laminated glass must be used on the windscreen. Glass is often bent (Chapter 11.2.5), has a print applied by silk screen printing technology (Chapter 11.3.3.8), can have heating, antennas, and more applied to the surface. The technology of tempered glass production is presented in Chapter 11.2.5. The diagram of the production process of tempered automobile glazing closure is shown in Fig. 11.40.

The production process begins by placing the blanks on the transport section. The size of the blanks is usually already adapted to the cut-out size of automobile glazing closures and is thus delivered directly from the FLOAT flat glass production line. In the first phase, glasses are cut by breaking. They are first cut with a carbide wheel and then separated mechanically or thermally by heating selected places with burners (Chapter 11.1.1.1). This is followed by precise clamping of the semi-finished product on a grinding machine, which grinds the edges to the required quality. Grinding is followed by washing and drying. The next step can be printing of edges using silk screen printing, or applying other elements to the surface such as GPS antennas, radio antennas, TV antennas, or heating of glass. The next step is to bend the glass by gravity or using a press forming element and a mould. This is followed by rapid but uniform cooling, which induces the desired permanent compressive stress in the glass surface. After cooling to a temperature close to ambient temperature, the products are removed from the line and stacked on racks. Quality control is performed either for each piece (optical defects) or after several pieces before removing the glass or subsequently for contact verification of the correct shape.
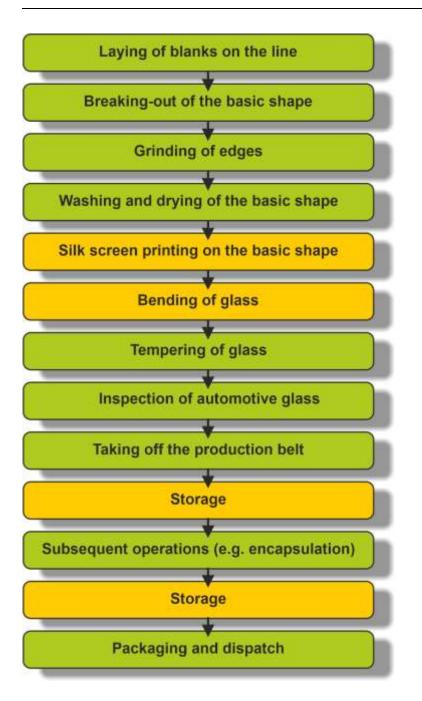
Fig. 11.40 Diagram of the production process of tempered automobile glazing closure

Laminated safety glass (also called safety compound glass, Chapter 11.4.1) is used for car windscreens. Nevertheless, it can be assumed that it will be increasingly used in the higher class of cars as well as in side and rear glazing, due to better acoustic-thermal-insulation properties and the integration of new functions. The diagram of the production of laminated glass for cars is indicated in Fig. 11.41.

The laminated windscreens are bent, the sheet forming the outer surface is slightly larger than the inner sheet. Uneven edges are difficult to even out by subsequent machining, so it is more advantageous to prepare the shape of both glasses during cutting. The line for breaking out semi-finished products and grinding is thus often doubled. The outer edges of the glass are then printed

using the silk screen printing technology. Glasses are covered with a fine powder to prevent them from sticking together and folded before the gravity forming process. Both glasses (inner and outer) then travel together through the production process of bending on the moulds. After forming, the glass is gradually cooled to avoid permanent stress to the glass. Glasses are disintegrated, washed and dried again. This is followed by the insertion of PVB films, their cutting and preforming, which is already performed on bent glass with film using profiled rolls. The required profile is formed by rubber wheels of various diameters assembled so that the preforming "rolls" copy the curvature of the surface of the bent glass. The next step is autoclaving at elevated temperature and pressure. This is followed by inspection, which may also be followed by attaching the bracket to the rear-view mirror.

Both types of glass are subsequently processed. This is most often the so-called encapsulation, when the entire glass is sealed in plastic frames, which are used for glueing or mounting the glass in the car. Glasses can also be provided with various holders and jigs which are glued or fixed as part of the mentioned encapsulation. The glass produced in this way is delivered to car assembly lines, where it is mounted or glued directly to the car body.

11.4.5   Other technologies and products

The trend is the integration of other functions into automobile glazing closures. These are, for example, transparent layers for glass heating, communication elements (radio, TV or GPS antenna), rain sensors, rear-view mirror brackets, hydrophobic coatings preventing water droplets from sticking to the glass during rain, heated parts for the view of increasingly frequent cameras, special films for windscreen for head-up displays (HUD), self-opacifying glass that changes transparency when the controller is pressed, electrochromic glass, surface finishing to prevent glass from freezing and dewing, and more.

Head-Up displays are being introduced today and are based on the reflection of useful data for drivers on the windscreen. They consist of a projection unit and a transparent layer between the panes that allows information to be reflected into the driver's eyes. Important information (current speed, permitted speed, navigation, etc.) is thus displayed in the driver's field of vision, which increases driving safety, as the driver does not take his/her eyes off the road ahead.

At present, the glass designated "POWERGLAS" is already sold. These are specially modified double glazed units, which are provided with a film providing heating. An electric current is applied to the specially laminated glass plates, which is converted into thermal energy due to the resistance of the semiconductor layers. With the help of a heat-reflecting layer, up to 90% of thermal energy is evenly reflected back into the living space. This removes cold zones from places near windows. This method of using radiant heat is comparable to floor or wall heating.

Other products are laminated glasses with an interlayer consisting of or containing glass fibres of variable cross-section intended for diffuse lighting, e.g. galleries and spaces requiring uniform lighting, insulating glasses with integrated blinds, gas-chromic insulating glasses to change the light and energy properties of glazing, insulating glasses with chamber filled with air-gel to increase thermal insulation properties. Glass here serves either primarily to provide a certain function, or as a covering material or a material improving the function of any device or material.
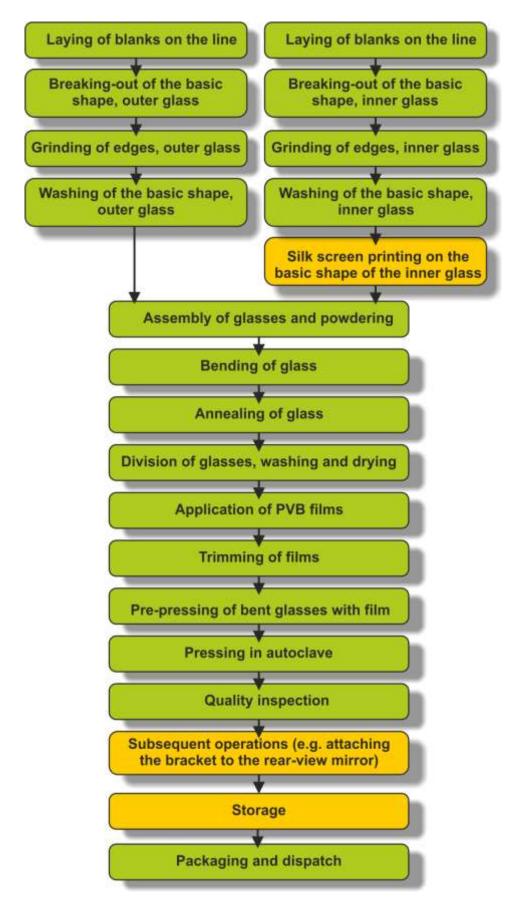
Fig. 11.41 Diagram of the production process of laminated automobile glazing closure

12 Defects of glass and glass products

Experience gained in monitoring of the glass production shows that no industrially produced glass can avoid the risk of the presence of some of the common defects. Defects arise and appear gradually in all phases of glass production and their early identification allows such interventions in the technological process to be carried out, which help to eliminate or at least minimize these defects. In the following chapter, these defects will be briefly classified and specific examples that can be encountered in practice will be given.

12.1 Defects arising during the production of glass melt up to its preparation for forming

12.1.1 Stones

This is the presence of a crystalline phase, which can have various causes.

Stones of refractory materials, which are most often released in the melting phase (melting, fining, homogenization), the source can be corrosion of refractory materials most often at the phase interface (lining, surface level of glass melt, furnace atmosphere), but also at other places of the melting unit, e.g. release of stones from the crown, etc. The chemical composition and crystalline phase correspond to the refractory material used, so we distinguish between stones of siliceous materials (dinas, melted quartz, other siliceous refractory materials), stones of aluminosilicate materials (fireclay), stones of high-alumina materials (mullite, silimanite), stones of Al_2O_3-based materials, where the content of aluminium oxide generally exceeds 90% (corundum materials), stones of alumina-zirconium-silica materials (designated "AZS"), stones of zirconium-silica (zirconium) materials, stones of Cr_2O_3-containing materials, and possible others,

Stones from the charge, the most common source here is the most difficult to dissolve raw material - quartz sand, as well as other sources. As already mentioned, these are most often stones of non-melted sand, stones of accompanying minerals found in the sand (e.g. kyanite, chromite), stones of aluminium hydrate and finally stones from contaminated charge (transport, use of own and foreign cullet, etc.),

Stones formed by crystallization of glass (products of devitrification). Examples are β-cristobalite, γ-tridymite, devitrite, β-wollastonite, diopside and other glass crystallization products.

If stones reach the finished product, they do not only appear visually as an unacceptable defect, but due to the different chemical composition from the surrounding glass, an internal stress occurs at the phase interface, which can also cause product failure.

12.1.2 Glass inhomogeneities - striae

Striae are glass inhomogeneities in glass. It is the glass that differs in its properties from the surrounding glass and is therefore visible. The striae that differ in their chemical composition from the surrounding glass are called chemical striae, the striae that do not differ in their composition from the surrounding glass are thermal striae (some authors refuse the existence of thermal striae).

Internal stress can also develop between striae and surrounding glass even in well- annealed products. This happens when the chemical composition and thus the thermal expansion of striae

differs from the surrounding glass. This difference in thermal expansion causes the two glasses to shrink differently in annealing, which can lead not only to internal stress but also to cracking.

12.1.3 Gaseous inhomogeneities in glass - bubbles

Bubbles play a dual role in the production of glass. In the melting process itself, their action is usually favourable (they support convection and thus contribute to the homogenization of the melt), but if they are not removed from the glass in time, they cause an unacceptable defect.

The very small bubbles (D=0.1-0.4 mm) are called seeds, the larger bubbles are called blisters. Bubbles with diameters smaller than 0.1 are often called micro-seeds.

In the melting phase, the origin of gases and their solubility in glass melt (both physical and chemical) are important, as well as kinetics of bubble behaviour in glass melt (especially the rate of rise), the growth and dissolution of bubbles in glass melts and, in summary, the effect of temperature, pressure and composition of glass melt on the rate of removal of bubbles. The most common origin is bubbles formed by chemical and electrochemical reactions and finally bubbles formed mechanically. These include bubbles created from the surrounding atmosphere (mixing of glass melt, feeding of glass melt, cutting-off of the gob, etc.), bubbles coming from refractory materials and bubbles coming from cooling water. For final quality of the glass product, it is necessary to limit the sources of bubbles and their growth and, if possible, suppress their existence.

12.1.4 Defects in colouration of glass melt

These defects can be caused by inaccuracy in the calculation of the composition of charge, overfeeding of colouring components or, conversely, a lack of decolourizing agents. The release of colouring components (for example chromium compounds) from the refractory material can also have a negative effect, as well as inappropriate use of "foreign" cullet as raw material in the charge. These defects are absolutely unacceptable in the production of flat glass, optical glass, but also in the production of glass jewellery. To some extent, they can be tolerated in melting glass for container glass (brown or green bottles). Discolouration of glass (suppression of the colour shade caused by the content of iron oxides in glass melting sand) can also be included here.

12.2 Defects arising during forming

This includes defects arising during the forming of glass melt up to the beginning of cooling (defects caused by cutting-off of gob, too high or low temperature of the mould, defects caused by deformation of the product due to non-compliance with the technology, defects caused by insufficient heat removal and more). A specific example of this defect is the non-standard thickness of the produced FLOAT bolster during the transition from one value of strip thickness to another value (all produced glass between the dimensions of original and new thickness must be discarded).

12.3 Defects arising during glass annealing

Improper annealing of glass products can cause various defects. Some are immediately obvious (deformation, cracking, discolouration), others cannot be seen at first glance (internal stress, increased fragility).

Good or bad product annealing refers to the amount of internal stress. A well-cooled product contains internal stress of allowable size, a poorly cooled product has internal stress exceeding the allowable size.

12.4 Defects arising during processing and finishing of glass

This group includes, among others, secondary devitrification, secondary formation of bubbles, cracking and all defects caused by non-compliance with the technological procedure in the processing or finishing of glass.

12.5 Additional defects

This group includes defects manifesting themselves during handling, transport, storage and use of the glass product (spontaneous cracking, surface defects such as weathering, solarization, etc.).

Defects are divided into repairable and irreparable defects, and defects classifying the product in a lower quality class. Defects must be detected in good time, if possible, so as not to increase the loss by further processing of a low-quality product, which will be finally discarded anyway. Quality control is thus an essential part of the production process, from manual production to fully automated production.

13 Quality control

During the production process, product defects can occur that are undesirable. Quality control can be generally performed:

- by contact,
    - without damage to the product,
    - with damage to the product,
- without contact.

Contact methods are based on direct contact with the test jig or device. They are often focused on mechanical testing of products, but they can also be used for testing the correct shape (e.g. using so-called car window mock-ups).

A visual inspection (mostly without contact) is virtually always performed for glass products, which can be performed:

- only by operator - his/her knowledge allows to evaluate the quality of the product, it is a relatively easiest inspection method, which is burdened by experience of the operator and, for example, his/her tiredness,
- only by operator while comparing with the standard - again, experience of the operator is important, but the standard allows to partially eliminate differences in evaluation,
- by digital comparison with the standard/pattern - industrial cameras are used, which perform a comparison with the standard/pattern stored in the computer's memory and evaluate deviations from the required state,
- by comprehensive automatic evaluation (or defect recognition) - these are advanced quality control systems that comprehensively evaluate product quality, use lasers and industrial cameras.

13.1 Quality control in the production of flat glass by floating technology

The quality system varies according to products and technologies. An example of the application of very comprehensive control is the production of flat glass by floating technology.

Core quality defect detectors are used on the principle of lasers or industrial cameras and are located behind the glass washer. Detectors must be able to provide information not only on the magnitude/severity of the defect, its position, but also on the density of defects for the given size and time. In general, the value of the number of defects is used in relation to the surface area of glass, e.g. per 10 m^2, in relation to the specified production time, e.g. in 6 minutes, one hour and one day. Current detectors can also divide defects into basic categories, such as lens, thread, bubble, sulphate, tin, etc. Information on defects is immediately passed to the metallurgical staff as feedback for intervention to eliminate the defects.

In the case of flat glass, the optical quality is further controlled, where the basic parameters are:

- light transmittance - to be performed for the regions of visible optical radiation, ultraviolet and infra-red radiation,
- zebra test - it is important especially for automobile glazing closure, where the glass must not distort the driver's view,
- corrugation test - it is focused on optical quality in reflection and is important in the production of mirrors,
- striae test - it detects unacceptable striae in glass caused by inhomogeneity of glass melt or flow of tin in the bath.

Surface quality control is an equally important parameter of glass quality, in particular for the automotive industry. These are mainly scratches, abrasions, cullet, etc.

13.2 Quality control in the production of container glass

Another example of the use of advanced quality control methods is the production of container glass. Both non-contact optical inspection using industrial cameras and contact inspection are performed. The inspection is often performed on all bottles.

Optical inspection can use 20 or more cameras that scan the bottle from various angles, including neck and bottom. Very often, the device is designed in the form of boxes, which are included on a belt conveyor for the transport of finished bottles after finishing at the cold end. The rate of bottle inspection is even more than 500 wine bottles per minute. In the case of other types of bottles and higher production volumes, the device is doubled, i.e. the bottles are divided into two conveyors and controlled in two boxes at the same time.

Contact inspection is often used for lateral pressure testing and neck leak testing.

14 Conclusion

Today, modern glass lines are fully automated and use the latest knowledge of science and research. More than 99% of all glass production in volume units is produced on fully automated equipment, where glassmakers perform the role of adjusters, technical supervision, quality control or sit at computers in the so-called control room. Glass-blowing pipe is today rather a symbol than a production tool. However, glass-blowing pipes can be found on many machines, they are transformed into equipment as a necessary technological part of production.

Knowledge of glass technologies is thus very important for current graduates in the field of the glass industry. The general overview given in this textbook is only an introduction to the knowledge of glass technologies, mechanization and automation in the production in question. The information provided here should also not be used as a basis for memorizing the text. It should rather serve to understand the basic principles and as a general starting point for further study.

If we focus on the state of glassmaking in the Czech Republic, there is no reason to jump to conclusions about the end of this industry in our country. The development of glass production and its trends in the Czech Republic must be seen in the context of the European glass industry and, thanks to the strong influence of market globalization, also in the global context. The justification of this view is also supported by the fact that most Czech glass companies are owned by global companies. Compared to world production, glass production in the Czech Republic represents 1.5% of the total glass production in the world (beer production 0.9%, automotive production 1.6%). The glass industry has a strongly pro-export character and, due to the converted amount of glass per capita, is more important for the national economy than in most European countries. It follows from the above that Czech glassmaking has maintained its level not by clinging to traditions, but thanks to the abilities to introduce new knowledge, technologies and machines into production.

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