Seminar N 10

TOPIC "Corrosion and anti-corrosion protection. Types of corrosion. Characteristics of methods of anticorrosion protection.

Non-metallic materials. Types, general characteristics. Material marking. Glass and ceramic materials used in the manufacture of medical devices. Technological process for the production of glass products».

The main questions to be discussed at the seminar:

1. Non-metallic materials. Concept, types. General characteristics.
2. Glass, characteristics of properties.
3. Glass melting and production of glass products.
4. Types of glasses used in the manufacture of medical devices.
5. ceramic materials. Sitally. General characteristics of properties and scope.
6. Corrosion and anti-corrosion protection. Types of corrosion. Characteristics of methods of anticorrosion protection.

1. Non-metallic materials are a large group of materials made from organic and inorganic (mineral) raw materials.

Organic raw materials include wood and products from it, wool, fibers, bone, rubber, etc.,

to inorganic raw materials - gas, oil, air, water, diamond, clay, quartz, marble and various rocks.

Each type of raw material is used to produce a large group of non-metallic structural materials used in various industries, agriculture, transport, medicine, culture, food industry, everyday life, etc.: plastics, laminates, glass, dyes, adhesives, varnishes, paper, cardboard, woolen and cotton threads and fabrics, building structures made of wood, blanks for furniture, plywood, art products made of bone and horn, etc.

1. Inorganic materials:

1.1. Synthetic (artificial): - minerals; - gases; - inorganic chemicals.

1.2. Silicate materials: - glass; - ceramics (faience, porcelain).

1.3. Natural: - minerals; - gases.

2. Organic materials:

2.1. Natural: - animal materials (polymers, oligomers, monomers); - vegetable (polymers, oligomers, monomers).

2.2 Synthetic (artificial): - monomers; - oligomers; - macromolecular compounds.

By origin, polymers can be:

natural (proteins, polysaccharides, cellulose, starch, natural rubber, mica, asbestos, natural graphite)

synthetic (synthesized macromolecular substances obtained by polymerization or polycondensation (synthetic resins, fibers, rubbers, etc.).

2. Inorganic glass is a homogeneous amorphous substance obtained by solidification of an oxide melt; It does not have a definite melting or solidification point and, upon cooling, passes from a molten, liquid state to a highly viscous state, and then to a solid one, while maintaining the disorder and inhomogeneity of the internal structure.

The main raw materials for glass production are:

quartz sand; nepheline; magnesite (magnesium carbonate); dolomite (magnesium and calcium carbonate); sodium tetraborate;

boric acid; limestone (calcium carbonate); potash (potassium carbonate); soda ash (sodium carbonate); sodium sulfate.

Medical glass is obtained by cooling a molten mixture of silicates, metal oxides, salts and is a solid solution.

Due to the fact that medical glass is made of quartz glass, consisting of 95-98% silicon dioxide, it has a very high thermal and chemical resistance. It is difficult to manufacture and seal ampoules from such glass because of the extremely high melting point (1550–1800°C).

Special modifiers (potassium and sodium oxides) are added to the composition of glass to lower the melting point. The introduction of these substances can reduce the chemical resistance to such an extent that it is possible to obtain liquid or soluble glass (potassium or sodium silicates).

3. Methods for obtaining glass and making products

The melting of medical glasses is carried out in continuous bath furnaces with a capacity of 5-25 tons of glass melt per day.

The cooking temperature is on average 1480-1520 °C, the production temperature is 1200-1250 °C.

GLASS PRODUCTION (excerpt from the OFS)

Glass packaging is obtained from molten glass mass by various methods: blowing, casting, pressing, rolling.

Glass containers (for bottles, bottles, jars) are produced on blow molding machines, semi-automatic machines or manually directly from glass mass. Ampoules, cartridges, vials of small volume are made from medical droit (glass tubes) of a certain diameter, previously obtained from glass mass.

Medical glass consists of a molten mixture of silicates, metal oxides and salts. The main component of medical glass is silicon dioxide, which has a melting point of more than 1700 °C. To give the necessary characteristics to medical glass, various additives are used. To lower the melting point of the glass mass (which is necessary when sealing the ampoules), sodium and potassium oxides are added, but their introduction sharply reduces the chemical stability of the glass. An increase in the chemical stability of glass mass is achieved by the introduction of oxides of aluminum, boron, and calcium. The addition of magnesium oxides to the composition of the glass mass significantly increases the thermal stability. Controlling the content of boron, aluminum and magnesium oxides increases impact strength and reduces glass brittleness.

Light-protective colored glass is obtained by adding small amounts of metal oxides, such as oxides of iron, manganese, selected in accordance with the desired spectral optical density.

Medical glasses are well boiled and clarified (with the exception of glasses of the HC-grades, due to the low content of alkaline oxides, they are poorly clarified).

During the melting of these glasses , the bubbling of the glass mass has an effective effect. When cooking orange glasses, sodium sulfate with an excess of a reducing agent (coal) is introduced into their mixture for coloring. During the melting of such glasses, metal sulfides are formed in them, coloring the glass in an orange color.

The production of medical glass products is carried out on various machines.

A number of products are made from droit, which in these cases is a semi-finished product. These include ampoules and vials.

Medical products are produced mainly from neutral glasses (grades MS-1 and NS-2), from alkaline glass (grades NB-1, MT and OS) and from light-protective orange glass.

The introduction of toxic oxides, such as As 203, Sb203, P205 and fluorine compounds, into the glass composition is not allowed.

Some brands of foreign glasses contain BaO and ZnO.

OFS.1.1.0025.18 General pharmacopoeial monograph “Packaging, labeling and transportation of medicines

Appendix N 1 to the order of the Ministry of Health of the Russian Federation of February 25, 2021 N 133

Glass

Glass is the primary packaging material for the production of one of the main elements of pharmaceutical packaging - glass containers.

Various grades of medical glass are used, differing in chemical composition. The choice of glass brand depends on the physicochemical properties, method of application and other characteristics of the medicinal product and / or dosage form in contact with the primary packaging material - glass.

For parenteral drugs, a colorless glass is usually used, which allows visual inspection of the contents of the package. Similar recommendations have been established for glass primary packaging for parenteral powders.

The chemical composition, physical and chemical properties of medical glass must comply with the established requirements, the list and acceptance criteria of which depend on the brand of medical glass (on the intended use).

The shape (design), appearance, main parameters and dimensions, capacity, weight, as well as other quality indicators of the finished package (packaging element) must comply with the requirements of the current standards for this type of packaging (packaging element).

Packaging made of light-protective glass must meet the established requirements for light-shielding properties.

The outer and inner surface of glass packaging can be specially treated. The inner surface of the glass packaging is treated to increase hydrolytic stability, impart water-repellent properties, while the outer surface is treated to increase abrasion resistance, reduce friction, and increase abrasion resistance. The treatment of the outer surface of the glass packaging must be carried out in such a way as not to affect the inner surface. To protect against light, glass packaging can be covered with a protective layer.

The inner surface of glass packaging can be subjected to delamination - separation of glass in thin layers, flakes. Glass delamination can be influenced by the process of manufacturing glass packaging under stressful conditions (exposure to high temperature for a long time), chemical treatment of the inner surface of the package. The delamination of glass can be caused by a chemical attack called glass corrosion, which occurs due to the processes of dissolution caused by hydrolysis, ion exchange (leaching) when exposed to pH. The susceptibility of glass to delamination is increased by drugs containing glass-destroying buffer components, such as citrates, phosphates, as well as the features of the technological process for the production of drugs in glass packaging: final sterilization, operations carried out on the filling line, etc.

Upon contact of the inner surface of the glass packaging with the contents, depending on the brand of glass, the pH value of the medium and other factors, dissolution or leaching may occur. When dissolved, glass components pass into the contents of the package in the same proportions as in glass; leaching predominantly involves the release of alkali and alkaline earth metal oxides from the glass.

The interaction between the inner surface of the glass package and the medicinal product may have a delayed period and the result of delamination may not be visible until several months after the glass package has been filled.

Glass packaging is the choice for many medicinal products in the form of dosage forms of various physical states (liquid, solid, soft), mode / route of administration and use, including parenteral dosage forms, ophthalmic dosage forms, etc.

Glass packaging has high chemical and thermal resistance, allows for the sterilization of medicines, can be hermetically sealed or sealed, can contain aggressive substances, ensure the safety of perishable substances, etc. Glass packaging is characterized by a variety of shapes and sizes, its capacity varies from a few milliliters to 20 or more liters. If necessary, glass packaging may be transparent to provide visual control of drugs, or colored to protect from light.

4. Brands of medical glass used for the production of various types of glass containers for packaging medicines, including those listed in the OFS OFS.1.1.0025.18

The brand of medical glass, as a rule, is indicated in the pharmacopoeial monograph or regulatory documentation for the medicinal product.

Glass grade XT and XT-1 is chemically and thermally resistant and is used for the production of syringes. XT-1 glass can also be used for the production of bottles for storing blood, transfusion and infusion drugs and ampoules.

Glass grades HC is a neutral glass. **Grades NS-1, NS-1A and NS-3** are used for the production of ampoules and vials, while glass of the NS-3 brand can be used for solutions of substances subjected to hydrolysis, oxidation and similar changes, including in syringes, and glass of the NS brand -1 - for solutions of substances less sensitive to alkalis. Colorless medical glass grades NS-2 and NS-2A is intended, as a rule, for the production of glass bottles for storing blood, transfusion and infusion drugs and aerosol cans.

AB-1 brand glass is ampoule, boron-free, alkaline glass, used mainly for the production of ampoules, vials.

Glass brand SNS-1 - light-protective neutral glass for the production of ampoules for solutions of light-sensitive substances.

For the production of jars and vials used as the primary packaging of medicines that do not require sterilization, aseptic preparation and are not intended for parenteral use, as a rule, medical glass grades MTO (discolored medical packaging) are used, and for photosensitive substances - colored glass grades **OS, OS-1 (orange container).**

5. Ceramics is a group of materials that occupy an intermediate position between metals and non-metallic elements, this class includes oxides, nitrides and carbides.

Sitalls (glass-ceramic materials) *are* artificial materials based on inorganic glass, obtained by complete or partially controlled crystallization in them.

As a general rule, the class of ceramics includes oxides, nitrides and carbides. So, for example, some of the most popular types of ceramics consist of aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), silicon nitride (Si_3N_4).

In addition, among those substances that many call traditional ceramic materials are various clays (in particular those used to make porcelain), as well as concrete and glass.

The mechanical properties of ceramics are relatively rigid and durable materials comparable in these characteristics to metals.

Typical types of ceramics are very hard.

However, ceramics is an exceptionally brittle material (almost complete lack of ductility) and does not resist fracture well.

All typical types of ceramics do not conduct heat and electricity (i.e. their electrical conductivity is very low).

6. Corrosion is **understood** as the destruction of a material due to exposure to the external environment.

Corrosion of metals and products from them has a chemical or electrochemical nature.

Corrosion of non-metallic materials (organic and synthetic) is caused by microorganisms and is called microbiological corrosion, or biocorrosion.

Corrosion is usually accompanied by changes in the appearance of products, since it begins with surfaces that are in direct contact with the external environment.

Chemical corrosion is the result of exposure to the metal of various chemicals with the formation of chemical compounds on its surface, i.e., corrosion products.

So, carbon steel products are covered with rust, which is iron hydroxide; products made of copper and its alloys turn green, covered with copper oxides and salts.

All metallic materials undergo corrosion to some extent over time, but its degree depends on the resistance of metals in certain environments.

So, aluminum and its alloys in the air are covered with a thin film of oxide, which protects them from further destruction, however, under the action of alkaline solutions, the corrosion process is accelerated many times over.

The need to protect medical products from corrosion is caused by the fact that these products undergo thermal or chemical sterilization or treatment with antiseptic solutions before use.

In addition, medical devices come into contact with aggressive corrosive media in the form of pus, blood, etc., which accelerate corrosion processes.

To increase the service life of products, it is necessary to protect them from corrosion by one method or another, depending on the operating conditions.

Various coatings are used for this purpose.

No need for additional protective coating: noble metals and some stainless steels, the surface of which must be well polished to increase corrosion resistance.

To protect medical products and their metal parts from corrosion, three types of coatings are used:

metal

non-metallic inorganic

non-metallic coatings with paints and varnishes.

Metallic coatings. In order to protect against corrosion, medical instruments made of carbon steels and brass are usually coated with a layer of nickel or chromium, or both at the same time, using the galvanic method.

At the same time, it is taken into account that the appearance of the coating must correspond to the functional purpose of the products.

The finish can be glossy or matte.

Matte nickel plating is not used, as it does not give the product a good decorative look.

Chrome plating is performed both shiny and matte. In recent years, matte black chrome has become quite widespread.

For metal coatings there is GOST:

- installing multilayer coatings for steel products (copper + nickel + chromium);
- Operating conditions for coated products are divided into four groups: light, medium, hard and very hard.

Medical devices are exposed to very aggressive substances during operation.

For products that have contact with body tissues, medicines, drugs and are subject to disinfection, pre-sterilization cleaning and sterilization, a special group of operating conditions has been established: M-1.

It includes all surgical instruments.

The thickness of the coating for surgical instruments is prescribed taking into account the operating conditions:

- surgical needles are coated with a minimum layer of chromium of 1-5 microns,
- knives and scalpels - with a chromium layer of 3-6 microns,
- the rest of the instruments are covered with a layer of nickel (12 μm) and chromium (3 μm).

Nickel coatings are supplemented with chromium coatings due to the fact that it tends to tarnish, and also to reduce the porosity of the coating, since the pores of the nickel coating are blocked by a layer of chromium.

Equipment parts that are operated in a humid environment are coated with tin (tinned) or zinc, and the brass parts are coated with a layer, tin directly, and the rest are pre-coated with a layer of nickel (3 microns) and copper (10 microns).

Details of disinfection equipment exposed to steam-formalin and other mixtures used in disinfection chambers are coated with a layer of zinc up to 42 microns.

To protect parts of medical equipment, as a rule, a three-layer coating (copper + nickel + chromium) with a total layer thickness of 24 to 40 microns, or a two-layer coating (nickel + chromium) - up to 18 microns is used.

To cover some products (tracheotomy tubes, spectacle frames, etc.), noble metals are used - silver and gold.

Metallic and non-metallic inorganic coatings

They consist of inorganic metal compounds (oxide, oxide-phosphate, phosphate, etc.) and are obtained by chemical processing of products.

Oxide films on steel products are black in color and are used on instruments, including stainless steel, intended for operating under a microscope (otosclerosis surgery kit), as well as on light-absorbing surfaces of optical instrument parts. These films are obtained by oxidation, i.e. processing in a boiling solution of alkalis (temperature 135-145 ° C): caustic soda NaOH , sodium nitrite Na_2NO_3 (or trisodium phosphate Na_2PO_3). The oxide coating has low protective properties. These properties are enhanced when the coating is treated with neutral oils.

Oxidation of non-ferrous metals (parts made of copper and its alloys, tools made of titanium). Titanium alloy tools are electrochemically oxidized in an electrolyte containing oxalic acid at normal temperature by applying direct current. The color of the resulting film depends on the grade of the alloy and can vary from light green with a reddish tint to dark gray with a greenish tint.

Protective and decorative oxide films on aluminum and its alloys are obtained by anodizing, that is, by processing in an electrolytic bath containing a solution of sulfuric acid (180-200 g per 1 liter of water) at normal temperature. The oxide film obtained in this way can be dyed in various colors (black, blue, light green, red and yellow, as well as the color "gold"), as it easily adsorbs organic and inorganic dyes. Anodizing provides protection for products operating in a water vapor environment, as well as against atmospheric corrosion.

Wear-resistant anodic oxide coating, which is characterized by high hardness (770 kgf/mm^2) and high abrasion resistance, especially when impregnated with lubricating oils, has found application for parts of medical products. Its color is dark gray to black.

To improve the corrosion resistance of parts coated with zinc and cadmium, especially for tropical conditions, these parts are subjected to phosphating. Phosphate coatings are films of insoluble zinc phosphate salts firmly adhered to the metal surface. The film is painted in a gray-smoky color and has a fine-grained structure.

The disadvantages of this coating include the fact that fingerprints are stored on it.

Surface treatment.

Electroplated coating obtained in electrolytes without special additives, as a rule, turns out to be matte. It does not have a good enough decorative appearance, it is easily soiled and poorly cleaned.

To give the coating a decorative look, it is polished.

A brilliant coating can be obtained mechanically, chemically or electrochemically, as well as in special electrolytes with the addition of brighteners.

The main active principle of microbiological corrosion is fungi, and for some materials, bacteria. The main factor in the vital activity of mold fungi is the presence of water. Low temperatures hinder their development, however, in the presence of water, some types of mushrooms grow well even at temperatures close to 0 ° C. Mold spores are widespread in the atmosphere, but they are especially numerous in the surface layers of the soil. Mold relatively easily adapts to various physical and chemical environmental conditions.

Mold feeds on materials containing carbon and nitrogen, but molds are known to assimilate phenol and rubber. The optimum temperature for the development of all types of mold is in the range of 26-30°C. With an increase or decrease in temperature, their development slows down. Spore forms of mold fungi endure temperatures of 100 ° C and above.

Under the influence of mold, materials of organic origin are destroyed, and their decay products can cause chemical corrosion of metals. This is especially dangerous for electrical products (wires with a cotton or silk braid). As a result of microbiological corrosion, the electrical strength of the insulation sharply decreases and breakdowns and short circuits can occur . Cases are known when As a result of microbiological corrosion, the functioning of mechanical devices, such as a mirror galvanometer, was completely disrupted.

Biocorrosion protection measures. The best protection during storage and operation of products is the creation of conditions that prevent the development of mold. The operating conditions - of medical equipment products are unfavorable for the occurrence of mold, since the products are repeatedly sterilized or subjected to wet sanitization during operation . In this regard, favorable conditions for the development of mold can appear mainly when products are stored in warehouses . However, at normal storage temperatures and under ultraviolet irradiation, the product will be reliably protected from mold .

Inorganic glass is a homogeneous amorphous substance obtained by solidification of an oxide melt. It does not have a specific melting point or solidification point and, upon cooling, it passes from a molten, liquid state to a highly viscous state, and then to a solid state, while maintaining the disorder and inhomogeneity of the internal structure.

Glass can contain three types of oxides:

- glass formers
- modifying
- intermediate.

Glass-forming oxides are oxides of silicon, boron, phosphorus, germanium, arsenic.

The modifying oxides include oxides of alkali (Na, K) and alkaline earth (Ca, Mg, Ba) metals.

Modifying oxides are introduced during the glass melting process.

Alumina $A1_2O_3$ increases the mechanical strength, as well as the thermal and chemical resistance of glasses.

With the addition of B_2O_3, the rate of glass melting increases, clarification improves and the tendency to crystallization decreases.

Lead oxide PbO, introduced mainly in the manufacture of optical glass and crystal, increases the refractive index.

Zinc oxide ZnO lowers the temperature coefficient of linear expansion of glass, thereby increasing its thermal stability.

Intermediates are oxides of aluminium, lead, titanium, and iron, which can replace some of the glass-forming oxides.

The chemical composition of glass can be changed over a wide range, and therefore the properties of glass can be different.

According to the chemical composition, depending on the nature of the glass forming oxides, there are

- silicate
- aluminosilicate
- borosilicate
- aluminoborosilicate

and other types of glass.

Depending on the content of modifiers, glass can be:

- alkaline
- alkali-free
- quartz inorganic glass.

By purpose, glass is distinguished:

- building (window, glass blocks)
- household (glass containers, dishes)
- technical (optical, electrical, chemical, etc.).

According to optical properties, glasses are distinguished:
- transparent
- painted
- colorless
- scattering light.

Consumer properties of inorganic glasses include:
- about transparency
- high weather resistance
- water and air tightness
- heat resistance.

Glass-ceramic materials (glass-ceramic materials) are an artificial material based on inorganic glass obtained by complete or partially controlled crystallization in them.

The term "sitalls" is derived from the words: "glass" and "crystals". According to the structure and production technology, sitalls occupy an intermediate position between conventional glass and ceramics.

They differ from inorganic glass in their crystalline structure, while they differ from ceramic materials in their finer grained and homogeneous microcrystalline structure.

Ceramics is a group of materials that occupy an intermediate position between metals and non-metallic elements.

As a general rule, the class of ceramics includes oxides, nitrides and carbides. So, for example, some of the most popular types of ceramics consist of aluminum oxide (Al_2O_3), silicon dioxide (SiO_2), silicon nitride (Si_3N_4).

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