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POLYMERS IN SHIP MACHINE BUILDING (POLIMERY V SUDOVOM MACHINOST--ETC(U)  
JUL 77 V Y BAKHAREVA, I A KONTOROVSKAYA

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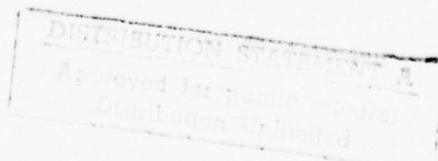
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## POLYMERS IN SHIP MACHINE BUILDING

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### INTRODUCTION

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The Directives of the 24th Congress of the CPSU place primary emphasis on the development of the production and application of polymeric materials in the national economy. This is due to the fact that along with metals, polymeric materials have become one of the basic construction materials, without which further progress in technology and improvement in the standard of living of society are unthinkable.

Polymeric materials have low density, high resistance to corrosive media, nonmagnetic properties, low coefficient of friction and high resistance to wear, workability, etc.

The use of polymeric materials in ship machine building permits the successful solution of such important problems as reducing the mass, increasing the traveling speeds, improving service life and reliability, economizing scarce non-ferrous metals, raising labor productivity, and reducing labor intensity and operating costs. The volume of production and consumption of polymeric materials is increasing each year. While in 1940 the world production of polymeric materials was only 200,000 tons, by 1970 their production had reached 25.0 million tons, i.e., increased 125-fold. Along with the increase in the volume of production of polymeric materials, their assortment expands each year. Thus, while the first plastic, celluloid, was synthesized in 1869, one hundred years later over a thousand brands of polymeric materials were in existence. The polymeric materials known at the present time possess a wide range of properties and belong to different categories of compounds, from polyolefins (polyethylene, etc.) to polyorganosilicoelemental compounds (polybororganosiloxanes, polytitanorganosiloxanes, etc.).

In ship machine building, polymeric materials are used in the manufacture of ship propellers, parts of various mechanisms and devices, sliding bearings, seals, as anticorrosion coatings, etc.

In the Soviet Union, the first screw propellers of textolite (resin-impregnated fabric laminate) and sheet-steel-reinforced textolite, 0.42 m and 0.63 m in diameter, were made back in 1938 under the supervision of Prof. B. A. Arkhangel'skiy. However, tests of these propellers showed that the textolite did not possess the necessary properties and did not make for reliable propellers.

After World War II, the advent of new high-strength plastics started intensive studies aimed at applying plastics to the manufacture of screw propellers. /6

Abroad, plastic screw propellers are produced in Denmark, England, Holland, FRG, Japan, and the USA. Abroad, propellers up to 2 m in diameter are made from polycarbonates, glass-reinforced polyformaldehyde, ABC plastics, nylon, ultramide, and polypropylene.

\* Numbers in the right margin indicate pagination in the original text.

In the USA, lexan polycarbonate is used in the production of 12 standard sizes of propellers. The propeller production amounts to over 150,000 items per year. The cost of lexan propellers is much lower than that of metal ones.

Screw propellers are very difficult to standardize, making it necessary to work out specific methods of manufacture excluding the use of complex and expensive equipment. Thus, to reduce the costs of production, the Dutch companies Lips and Bayer have developed a method of centrifugal casting of articles with a mass up to 200 kg from thermoplasts. This method was used for casting nylon propellers with a diameter of 1.7 m and a mass of 180 kg, and detachable blades for controllable-pitch propellers 4 m in diameter.

To overcome these difficulties, the West German company Basf has proposed ultramide (the Soviet analog of which is caprolon), which is processed into articles by free casting in open molds<sup>78</sup> in the production of propellers.

Thermoplastic propellers are workable in fabrication and have a small mass and high damping properties. However, their scope of application is limited to small-load propellers for low-speed ships because of the relatively low strength and rigidity of thermoplastics (tensile strength, 7.0 kgf/mm<sup>2</sup>; normal elasticity modulus,  $7 \times 10^2$  kgf/mm<sup>2</sup>).

At the present time, the strongest synthetic construction materials are polymers reinforced with glass fibers, i. e., fiber glass plastics. Work aimed at the development of plastics reinforced with carbon fibers, boron fibers and high-strength organic fibers has been conducted in the last few years.

In 1961 in the USSR, propellers were made from fiber glass plastics by the methods of hot pressing and contact and vacuum molding in diameters of 0.3 to 6 m.<sup>7, 24, 37</sup> At the present time, plastic propellers are well established and are being successfully operated on over 200 ships. Soviet plastic propellers have been demonstrated at international expositions in Moscow, Montreal and Rostock.

In Japan, fiber glass plastic propellers are made by contact molding. By 1966, over 300 propellers from 0.3 to 1.9 m in diameter had been installed on ships of the fishing and cargo-passenger fleet. Experience in the operation of these propellers proved successful.<sup>77</sup> It was found that the useful life of fiber glass plastic propellers during navigation in shallow-water Japanese rivers and rivers full of rapids is equivalent to that of bronze propellers, i. e., three years. A substantial reduction in the wear of stern bearings and a decrease in vibration were observed during the operation, this being particularly important for passenger ships.

Polymeric materials are used in foreign shipbuilding in the fabrication of fittings. Heat-resistant polymers such as polyformaldehyde, ABC plastics, or polysulfones<sup>48</sup> are usually employed for this purpose.

A positive effect was obtained by using metallized and fiber glass reinforced thermoplastics. For example, fittings made of thermoplasts with a chromium coating were found to be useful on series-produced superhips built by the Japanese firm Hitachi and Finnish timber carriers.

Polymeric materials are also used in the manufacture of pipes, since they considerably increase the useful life of pipelines. Soviet industry has mastered the production of pipes from low and high density polyethylene. The first plastic pipes were made in 1962 and installed on the VOLGODON motorship.

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The low friction coefficient and low wear of polymers, the possibility of operation without lubricants, resistance to corrosive media, and absence of corrosive action on metals permit the use of polymers in the production of sliding surface bearings of ship shaftings, steering gear, machines and mechanisms. Fluorocarbon plastics, nylon, laminates, polyacetyl resins, polyformaldehyde and polyamides have found application as antifriction materials. /7

The mechanical and antifriction qualities of these materials are considerably improved by introducing glass fiber, graphite, molybdenum disulfide, nonferrous metal powders and other additives. The Polymer Corporation (USA), for example, makes a special antifriction material, "nylon-tron," consisting of nylon 66 with an addition of 30% chopped glass fiber and 3% molybdenum disulfide.<sup>73</sup> Thanks to these additions, the composition obtained has higher heat resistance and stability to hydrolysis than the pure polymer, lower creep under load, and lower friction coefficient. Materials filled with additives make it possible to increase the work loads by a factor of 1.5-2.

As a rule, the bearings are made only from filled materials, which can be produced in a fairly wide assortment.

Special metal-plastic materials consisting of a steel base with porous tin bronze impregnated with fluorocarbon plastic and applied on the steel base have been developed for parts operating under heaviest-duty conditions. Bearings of this material have high resistance to wear and corrosive media, high thermal conductivity, and small thermal expansion, so that they can be used over a wide temperature range, from -200 to 300°C, and at high specific pressures, and also without lubricants. The wear of these bearings is 5-7 times less than that of oil-lubricated bronze bearings.

In the last few years, extensive studies have been conducted by the Soviet industry on the use of polymeric materials such as polyamides, fluoroplastics and polyethylene for the fabrication of bearings; the greatest success was achieved by using caprolon.

The piping of hydraulic and pneumatic systems is sealed with many seals whose role in these systems is extremely important. The pressure, speeds and temperatures of the media as well as the service life and reliability of operation of the actuating mechanisms are largely determined by the state of the seals.

At the present time, rubber is widely used in the manufacture of seals. However, in many mechanisms and devices, rubber cannot meet the stated requirements. In the USA, England, FRG and many other countries, the specific volume of rubber use is being systematically reduced, while the manufacture of seals of polymeric materials correspondingly increases. Polyurethanes, fluorocarbon plastics filled with glass fiber, metal and silicate powders, and glass-filled nylon and polyformaldehyde have been used in the fabrication of seals.

The use of polymeric coatings is required for protection of metal products used in contact with seawater. The use of polymeric coatings makes it possible to replace nonferrous metals, extend the service life, and improve the performance characteristics.

In many cases, when paint and varnish coatings are replaced by polymeric ones, the useful life of the parts increases owing to the characteristics of the technology of application of the coatings and structural and physicomechanical

properties of the polymeric film. The presence of pores in paint and varnish coatings, caused by the evaporation of solvents in the course of film formation, may cause a decrease in the protective characteristics of the coatings under heavy duty operating conditions. Polymeric coatings are more plastic, and are therefore more resistant to impact loads and protect more effectively from various types of chemical, electrochemical and atmospheric corrosion during exposure to mechanical stresses.

The function of individual types of polymers and the selection of the method of application of coatings are determined by considering the characteristics of the articles being protected, their service conditions, and the chemical nature of the polymers and properties of the coatings based on them. Among various high molecular compounds, those that have become most popular in Soviet and foreign shipbuilding have been coatings based on epoxy resins, polyurethanes, chlorinated rubbers, fluorinated hydrocarbons, and various modifications based on them.

Rubbers hold a special place among coatings because of their exceptional resistance to abrasive and hydroabrasive erosion, and also to cavitation effects. Such coatings withstand repeated alternating deformations, strong vibration loads and sharp temperature fluctuations better than other coatings. In their resistance to corrosive media, rubbers surpass most metals and are therefore widely used for the anticorrosion protection of various parts. The greatest effectiveness is achieved when simultaneous protection from corrosive and abrasive wear is required. /8

Urethane coatings, which harden in the presence of moisture, as well as urethane-base film and paint-and-varnish materials have become widespread in shipbuilding.

A valuable category of polymeric materials are fluorinated polymers. Coatings based on Ftorlon lacquers and powdered fluorocarbon plastics find extensive applications thanks to varied dielectric properties and excellent antifriction and anticorrosion characteristics. Depending on the function of the protective coating, powdered fluorocarbon plastics may be used as the base for the development of compositions ensuring the applicability of the coating under specified service conditions. This is achieved by individual preparation of the powder (increasing the bulk density, selecting a definite particle size distribution and shape of the powder particles), introducing stabilizers, plasticizers and fillers providing for the technological and performance characteristics of the coatings, and by using primers of certain compositions.

At the present time, protective coatings based on epoxy resins and possessing the necessary adhesion to metals, mechanical strength and chemical stability have become most popular. Polyepoxides are most frequently used in the form of powder coatings, whose composition includes hardeners, modifiers, and fillers. Increasing the elasticity by modifying with various polymeric compounds, introducing powder fillers to reduce the coefficient of linear expansion, and reinforcing with continuous glass fiber and microglass fiber makes it possible to obtain higher-quality coatings.

The use of antifriction polymeric coatings applied on a metal base makes it possible to improve the removal of heat and promotes the stabilization of the dimensions of mating friction members. The change in dimensions is smaller for members with thin-layer coatings than for monolithic parts from polymers. The best antifriction materials for coatings are polyamides, fluorocarbon plastics, and pentaplast.

Despite their high cost, pentaplast coatings are used rather extensively in many countries, thanks to their exceptional chemical stability, noncombustibility, and attractive mechanical and dielectric properties. The stability of pentaplast-base coatings exposed to the prolonged action of seawater promotes its extensive use in shipbuilding.

Experience shows that in ship machine building, the materials used most extensively for construction articles and anticorrosion coatings are hot-pressed epoxy-glass plastics, caprolon, polycarbonate, polyformaldehyde, polyamides, fluorocarbon plastics, polyethylene, polypropylene and pentaplast.

It is useful in this connection to systematize and correlate the operating experience accumulated thus far, as well as the experimental data on the properties and technology of processing of these materials into articles used in ship machine building.

Chapter 1. BINDERS FOR FIBER GLASS PLASTICS USED IN THE PRODUCTION OF ARTICLES  
FOR SHIP MACHINE BUILDING

1. General Description of Fiber Glass Plastics

Fiber glass plastics are composite materials based on various types of glass fillers (glass fabrics, glass fibers, glass mats, glass roving, etc.) and polymeric binding materials. At the present time, fiber glass plastics are the strongest synthetic materials. Important advantages of fiber glass plastic over other traditional structural materials (metals, alloys, wood) include high specific strength and corrosion resistance, attractive dielectric properties, nonmagnetic character, low sensitivity to microconcentrators, and high vibration and impact resistance. /9

In many cases, fiber glass plastics are irreplaceable materials. Their use for articles in ship machine building permits easy fabrication of parts of diverse geometric complexity with maximum mechanization of the production processes and a substantial reduction of fabrication labor intensity; at the same time, the properties of a fiber glass plastic can be varied over a wide range in accordance with the type of reinforcing and binding materials and the processing method employed.

The mechanical properties of fiber glass plastics are primarily determined by the strength of the glass filler, its content, and the orientation of the reinforcing fibers in the polymeric binder.

A compatible operation of the reinforcing filler is provided for by the polymeric binder. The creation of monolithic fiber glass plastics is possible only through the use of binders possessing sufficient wettability, high cohesive and adhesive strength, and low shrinkage.

On the basis of monolithic conditions for fiber glass plastics of oriented structure (reinforced with fibers and fabrics), several authors\* have formulated the requirements for the mechanical characteristics of binders, taking into consideration the strength properties of the reinforcing fibers (Table 1). /10

Table 1  
Requirements for the mechanical properties of binders for fiber glass plastics

Property	Reinforcement with glass fiber	
	Alkali-free	High-modulus
Strength, kgf/mm <sup>2</sup> :		
tensile	7	12.5
compressive	20	24
shear	3.5	6.3
Elongation, %	5	6
Modulus of tension, kgf/mm <sup>2</sup>	450	570

Low water absorption is also required from binders for fiber glass plastics used in ship building and in seawater or in humid climatic conditions. Practice shows that binders with an intrinsic water absorption no greater than 1-2% ensure an adequate water resistance of fiber glass plastics.



In the production of articles made of fiber glass plastics, the binders used most extensively are polyester, organosilicon, phenol-formaldehyde and epoxy ones.

In each specific case, the choice of the type of fiber glass plastic is determined by the requirements imposed on the articles and by the operating conditions. Thus, for articles operating at elevated temperatures under relatively small loads, use is made of organosilicon fiber glass plastics, which possess high heat resistance. Drawbacks of organosilicon fiber glass plastics include their brittleness, low mechanical strength and considerable cost.

For large-sized articles produced in small quantities, for which the fabrication of expensive equipment is uneconomical, and on which low strength and water resistance requirements are imposed, it is desirable to use polyester fiber glass plastics processed mainly by contact molding.<sup>3</sup>

Phenol-formaldehyde glass plastics, which have high water and heat resistance and considerable rigidity, are used for structural and electrical applications /11 at temperatures up to 200°C, and up to 250°C for short periods, 1-2 h.

The most advantageous combination of high strength properties and water resistance marks fiber glass plastics based on epoxy binders. The application of epoxy binders permits the fullest use of the strength of fiber glass. Sufficient experience with the fabrication and operation of various articles from epoxy-glass plastics has now been accumulated that confirms the promising outlook for the application of these materials.

Almost all existing methods for processing fiber glass plastics into articles are being used in the fabrication of articles for ship machine building. However, the most popular ones are:  
impregnation of the glass filler under pressure;  
vacuum-compression molding;  
pressing.

The choice of the fabrication method depends on many factors, including batch production, strength requirements, service conditions, and shape and size of the article. However, in all cases the selected method should produce a material uniform in density and proportion of the components, and a sufficient stability of the properties during service.

In the first two processing methods indicated above, the binder under pressure is fed into a rigid hermetic mold. In many cases, evacuation of the glass filler is used to reduce porosity. The porosity of the fiber glass plastic decreases with increasing impregnation pressure. However, even under optimum conditions, the porosity of fiber glass plastics obtained by impregnation under pressure or vacuum-compression molding is 6-8%, which results in a significant decrease in the water resistance of the articles.<sup>24</sup>

The pressing method provides for the greatest water resistance and stability of the properties. The use of a high specific pressure makes it possible to obtain intricate-shaped articles of sufficiently dense and homogeneous structure and low porosity (no greater than 3% by volume). Articles made by pressing can be used in water without additional protection against water. The method of hot pressing has found extensive applications in ship machine building. For many years, this method has been used to make blades and cones of ship propellers and other articles.

The individual physicommechanical properties of fiber glass plastics made by these three methods are listed in Table 2.

In connection with increased requirements for the strength and water resistance of materials used for making articles for ship machine building, the widest use has been made of epoxy-glass plastics made by pressing. For this reason, the properties, starting materials and pressing characteristics of articles from epoxy-glass plastics are considered in most detail below. /12

Table 2  
Properties of epoxyamine fiber glass plastics made by different methods

Property	Method of Preparation		
	Vacuum-compression	Impregnation under pressure	Pressing
Binder content, %	40-45	40-45	22-26
Porosity, %	5-8	8-11	1.5-2
Density, g/cm <sup>3</sup>	1.8	1.7	2.0-2.1
Compression strength, kgf/mm <sup>2</sup>	40-45	30-38	50-55
bending strength, kgf/mm <sup>2</sup>	50-65	37-58	70-80
Water absorption in 24 h, %	0.05	0.08	0.005

## 2. Epoxy Resins

Epoxy resins, which are one of the chief components of the binder, are characterized by the presence in their structure of several epoxy groups  $-\text{CH}-\overset{\text{O}}{\text{C}}-\text{CH}-$ , which are

extremely reactive. Epoxy resins are a mixture of oligomers of different molecular masses (from 250 to 4000) and become practically valuable only after their cross-linking, i. e., conversion into a cured polymer of reticulate structure by means of special compounds - curing agents.

Epoxy compounds were first synthesized in 1934 by Shpak, and on the basis of these compounds, Kastan (De-Teril Co., Switzerland) in 1938 prepared a plastic which he used in dental technology.<sup>55</sup>

At the present time, there is almost no area of industry that does not use epoxy resins. In the Soviet Union, epoxy resins have been produced since 1955, and this production has now increased over 30-fold.

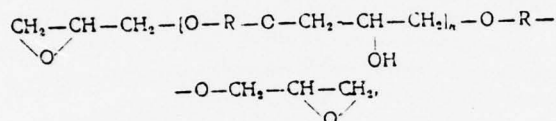
Epoxy compounds are produced in two ways: by direct epoxidation of unsaturated compounds with peracids and by reacting epichlorohydrin or dichlorohydrin with compounds containing a labile hydrogen atom.

Resins obtained by the first method are called cycloaliphatic epoxy resins. Their production on an industrial scale is limited because of the explosiveness of the existing peracids. /13

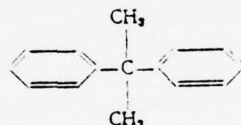
Resins based on epichlorohydrin and obtained by the second method are finding the most extensive uses. Depending on the nature of the component reacting with epichlorohydrin, these epoxy resins may be classified as follows:

polyglycidol ethers (based on diatomic and polyatomic alcohols);  
 polyglycidylamines (based on amine-containing compounds);  
 polyglycidylamides (based on amide-containing compounds).

Diphenylolpropane (diane or bisphenol A) is most frequently used as the diatomic alcohol in the preparation of polyglycidol ethers. The resins obtained by reacting diphenylolpropane with epichlorohydrin comprise 90% of the total production of epoxy resins and are known by the name of epoxydiane resins, of the general formula



where R is



Depending on the conditions of synthesis and ratio of epichlorohydrin to diphenylolpropane, epoxydiane resins with a molecular mass from 250 to 4000 are obtained. The molecular mass of the resin determines the state of aggregation of the resin and its physicochemical properties. Resins with a molecular mass up to 400 are liquid, those with a molecular mass up to 400-800 are viscous (softening point, 15-20°C), and those with a molecular mass above 800 are solid with a softening point above 50°C.

The main characteristics of Soviet and foreign epoxydiane resins are given in Table 3.

In discussing the molecular masses of epoxy resins, one must not forget that these masses are average values. Actual epoxy resins are polydisperse, i. e., mixtures of oligomers of different molecular masses. The fractional composition of some epoxydiane resins is given in Table 4.

Of greatest value are resins with the lowest degree of dispersion and a constant fractional composition from one batch to the next, since they make it possible to obtain reproducible results and hardening products of ordered structure. /14

During the hardening, the highest-molecular oligomers react first, and the majority of unreacted epoxy groups are in the composition of the monomer.

Studies aimed at creating epoxy resins of low dispersity are being conducted in the Soviet industry. A new state standard (GOST 10587-72) was developed in 1972 which stipulates a large number of epoxy resin brands with a narrower gradation of molecular mass, epoxy group content and other qualitative indices.

Table 3.  
Main characteristics of Soviet and foreign epoxydiane resins

Brand of Resin	Average molecular mass	Number of epoxy groups	Softening temperature, °C
Epon-1009 (USA)	3800	1.4	145-155
E-05 (USSR)	3500	1.5-2.5	120
Epon-1007 (USA)	2900	2.2-2.4	127-133
Epon-1004 (USA)	1400	4.3-4.7	95-105
ED-8 (USSR)	800-1000	8-10	-
Araldite B (Switzerland)	1000	9-11	-
Epon-1001 (USA)	900	8.6	64-76
CHS-epoxy-2000 (Czechoslovakia)	850	9-10	65
ED-10 (USSR)	600-800	11-14	-
Epon-864 (USA)	-	13	40-45
ED-14 (USSR)	600	14-16	30
ED-16 (USSR)	460-540	16-18	10
Epon-834 (USA)	470	14.3	20-28
ED-20 (USSR)	340-450	20-22	-
CHS-epoxy-1100 (Czechoslovakia)	380	20-25	-
Epon-828 (USA)	380	22	8-12
ED-22 (USSR)	330	22-24	-
Epon-562 (USA)	319	27	-

Table 4  
Fractional composition of epoxydiane resins<sup>13</sup>

Resin Brand	Content, %, of			
	Monomer n=0	Dimer n=1	Trimer n=2	Higher Fractions n ≥ 3
ED-20	80-90	10-17	2-3	0
ED-16	50-60	15-20	8-10	5-10
ED-10	25-30	13-15	8-10	45-50
ED-8	13-17	12-15	9-12	55-60

In each specific case, the choice of the epoxy resin brand is determined by the technology of fabrication and purpose of the article. Thus, impregnation under pressure and vacuum-compression molding require epoxy resins of low viscosity in order to ensure a quality impregnation of the glass filler with binders without a solvent (from the binder melt). /15

In the pressing method employing preimpregnated glass-reinforcing materials (from a solution of the binder), it is desirable to use resins of high viscosity, which prevents the resin from leaking out at high specific pressures.

However, in selecting the resins for pressing, one must not try to use resins with the highest viscosity and molecular mass, since an increase in molecular mass is inevitably associated with a decrease in specific functionality and hence, a decrease in the number of cross-links and cohesive strength of the hardened product.

In addition, it is necessary to consider the known law governing epoxydiane resins, to the effect that the specific functionality affects not only the quality of the cross links, but also the packing density of the macromolecules. There is a certain value of the molecular mass of the resin corresponding to the optimum packing density, number of cross links and technological viscosity.

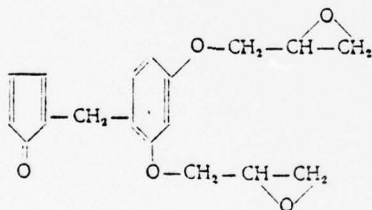
A resin of this type, which satisfies the above requirements, is resin of brand ED-13 TU No. P-267-70, developed for hot pressing. Ed-13 resin is prepared from diphenylolpropane sulfate; it is highly viscous, with an average molecular mass of 700-750 and 13-15% of epoxy groups. ED-13 resin is characterized by a narrow fractional composition with a predominance of oligomers with a degree of polymerization  $n = 3-4$ , providing for a great stability of its properties.

Resorcinol and furfurylresorcinol are also used as diatomic alcohols in the synthesis of polyglycidol ethers. Two methods of synthesis of polyglycidol ethers based on resorcinol are currently in use:

- (a) condensation of resorcinol with epichlorohydrin to form polyglycidol ether of resorcinol (RES-3 resin);
- (b) polycondensation of resorcinol and epoxidation of the oligooxyphenylene obtained with epichlorohydrin to form polyglycidol ether of oligooxyphenylene (EPOF-5 resin).

Polyglycidol ethers based on resorcinol are rigid-chain reactive oligomers with the minimum distance between epoxy groups for aromatic compounds. In comparison with ethers obtained by epoxidation of oligooxyphenylene, polyglycidol ethers obtained by epoxidation of resorcinol have slightly greater elongation (6-8%), but lower heat resistance.<sup>2</sup>

The UP-63 oligomer based on furfurylresorcinol has the following structural formula: /16



The synthesis is carried out in two steps. In the first step, furfuryl alcohol reacts with resorcinol in the presence of acetic acid catalyst to form the intermediate compound furfurylresorcinol. In the second step, furfurylresorcinol in the presence of alkali reacts with epichlorohydrin to form furfurylresorcinol diglycidol ether.

Resins based on furfurylresorcinol are characterized by a high content of epoxy groups (21-23%), and hardened binders and fiber glass plastics based on them are characterized by high strength.

The polyatomic alcohol used in the synthesis of polyglycidol ethers is pentaerythritol. The tetraglycidol ether synthesized from it also has high strength in the cured state (UP-635).

Using resorcinol and pentaerythritol, the industry produces resins of brands UP-63, UP-67, RES-3, EPOF-5 and UP-635.

The main characteristics of polyglycidol ethers, binders and fiber glass plastics based on them are listed in Tables 5 and 6.

Table 5  
Principal characteristics of polyglycidic esters based on polyatomic alcohols

Resin Brand	Initial Components	Content of Epoxy Groups, %	Höppler viscosity at 40°C, P	Strength, kgf/mm <sup>2</sup>			Percentage elongation, %	Martens temperature, °C
				Bending	Compressive	Tensile		
UP-63	Resorcinol, epichlorohydrin, furfuryl alcohol	21-23	600	9	20	7.2	2.3	140
RES-3	Resorcinol, epichlorohydrin	22-25	10	11.5	23	7.2	2.2	120
UP-635	Pentaerythritol, epichlorohydrin	27-30	3	13.8	28	9.6	2.4	-
EPOF-5	Polyoxyphenylene, epichlorohydrin	18-22	800	12.5	22	8	1.8	163

Table 6  
Mechanical properties of fiber glass plastics based on polyglycidol ethers

/17

Property	UP-63	RES-3	UP-635	EPOF-5
Strength, kgf/mm <sup>2</sup> :				
compressive	63	62	68	66
bending	92	93	98	97
interlaminar shear	7.8	7.3	9.0	8.0
Impact strength, kgf m/cm <sup>2</sup>	4.3	4.3	4.2	4.0

Polyglycidylamines are obtained from primary and secondary aliphatic and aromatic amines. The synthesis is carried out in two steps: the first step involves the formation of chlorohydrins from epichlorohydrin and the corresponding amine, and the second step consists in dehydrochlorination.

The attention given to polyglycidylamines is due to their high strength combined with heat resistance.

Amine-containing epoxides frequently have low viscosity and are therefore used as active diluents of epoxy binders for fiber glass plastics fabricated by vacuum molding and winding.

Depending on the structure of the initial amino-containing monomer, oligomers with different properties may be obtained. Thus, the use of halogen-containing amines makes it possible to produce fire-resistant epoxy resins. A high fire resistance is exhibited by oligomers synthesized from epichlorohydrin and N-pentachlorophenylethylenediamine and from epichlorohydrin and chlorinated aniline.<sup>63</sup>

Among glycidylmonoamines, the highest adhesive and cohesive strength is exhibited by epoxidized p-aminophenol. Binders based on it, cured with aromatic sulfones or amines, are used for articles made by hot pressing.

The viscosity of polyglycidylamines is considerably increased by using primary diamines as the starting material in the synthesis of epoxy oligomers. The compounds thus obtained are tetrafunctional. Among primary diamines, use is made of 4,4'-diaminodiphenylmethane, 3,3'-dimethoxy-4,4'-diaminodiphenylmethane, 3,3'-dichloro-4,4'-diaminodiphenylmethane, and 3,3'-dibromo-4,4'-diaminodiphenylmethane. The use of 4,4'-diaminodiphenylpropane and metaphenylenediamine has also been proposed.

In the USSR, tetrafunctional glycidylamines based on primary diamines have also been synthesized and are being produced.

Attention is drawn to the high strength characteristics of cured tetrafunctional polyglycidylamines and to their relatively high viscosities. From the standpoint /18 of their properties, tetrafunctional polyglycidylamines are promising materials and may be recommended for use in the composition of binders for hot-pressed fiber glass plastics.

On the industrial scale, polyglycidylamines are made under the following brand designations: EA, UP-610, EKHD, and metolon.<sup>62</sup> The main characteristics of these resins and binders and fiber glass plastics based on them are given in Tables 7 and 8.

Table 7  
Main characteristics of polyfunctional nitrogen-containing epoxy resins

Resin		Initial Components	Content of epoxy groups, %	Hoppler viscosity at 40°C	Strength, kgf/mm <sup>2</sup>			Percent elongation, %	Martens temperature, °C
					Bending	Compressive	Tensile		
Polyglycidylamines	EA	Aniline, epichlorohydrin	30	1.2	8.5	17.5	5	1.8	115
	UP-610	Paraaminophenol, epichlorohydrin	28	11	12	28	8.1	2.6	120
	Metolon	3,3'-dimethoxy-4,4'-diaminodiphenylmethane, epichlorohydrin	30	900	9	26	8	1.9	180
	EKHD	3,3'-dichloro-4,4'-diaminodiphenylmethane, epichlorohydrin	26	20	13	27	9	2.3	165
Polyglycidylamides	ETs	Cyanuric acid, epichlorohydrin	30	Solid product	7.5	18	4.2	1.5	180
	ETsD-13	Cyanuric acid, diphenylolpropane, epichlorohydrin	20	750	9	21	6.8	2.1	160

Table 8  
Mechanical properties of fiber glass plastics based on nitrogen-containing epoxy resins

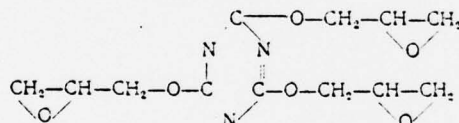
Property	EA	UP-610	Metolon	EKhD	ETs	ETsD-13
Strength, kgf/mm <sup>2</sup> :						
compressive	48	68	69	69	42	60
bending	79	96	97	98	68	90
interlaminar shear	6.9	9.2	9.0	9.8	6.5	7.8
Impact strength, kgf m/cm <sup>2</sup>	4.1	4.1	4.3	4.0	4.0	4.0

A general method of preparation of polyglycidylamides is the reaction of amides /19 with epichlorohydrin, sometimes in the presence of catalysts (for example, complexes of borontrifluoride), followed by dehydrochlorination.

Among glycidylamides, the best known are derivatives of cyanuric acid (cyanurates). The domestic industry produces triglycidyl isocyanurate (ETs-K), a mixture of mono- and diglycidyl isocyanurates (ETs-N), a mixture of mono-, di- and triglycidyl isocyanurates (ETs), as well as composites of epoxycyanurate and epoxydiane resins.

The main characteristics of the indicated compounds as well as those of binders and fiber glass plastics based on them are given in Tables 7 and 8.

Triglycidyl isocyanurate (ETs-K)




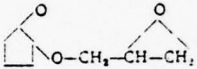
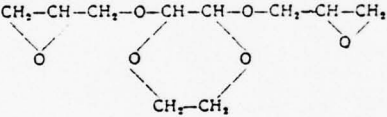
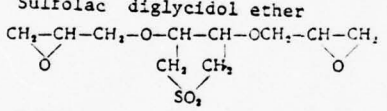
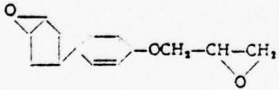
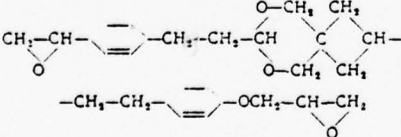
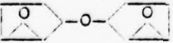
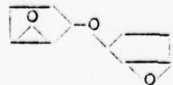
is a monomeric crystalline product with a melting point of 156°C, marked by a comparatively high specific functionality (content of epoxy groups, 41-42%). Along with a compact molecular structure and the presence of a symmetric isocyanurate heterocycle, the high specific functionality provides for the formation of a reticulate polymer with a high cross-linking density, rigidity and heat resistance.

The glass transition point of cured triglycidyl isocyanurate is 195°C, and the Martens temperature is 230°C. The reactivity of triglycidyl isocyanurate with amines is so high that it is practically impossible to process compositions based on it. In addition, at room temperature it does not dissolve in any of the known solvents, and partially crystallizes on cooling from solutions obtained at 90-100°C.

A mixture of mono- and diglycidyl isocyanurates (ETs-N) cured with amines or anhydrides is inferior to triglycidyl isocyanurate in heat resistance and strength, but is conveniently characterized by lower activity and solubility in ordinary solvents. Therefore, ETs-N resin is widely employed in various branches of industry for the fabrication of articles used at high temperatures. The use of ETs-N resin for the fabrication of fiber glass plastics for shipbuilding applications is undesirable because of high brittleness and low water resistance as compared to those of epoxydiane oligomers. In order to obtain a composition of satisfactory heat



Table 9.  
Properties of cycloaliphatic epoxy resins developed abroad

Brand	Chemical Composition	Curing temperature, °C	Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>	Tensile strength, kgf/mm <sup>2</sup>	Percentage elongation, %	Modulus of compression, 10 <sup>3</sup> kgf/mm <sup>2</sup>	Compressive strength, kgf/mm <sup>2</sup>
ER-2114	Diepoxide based on 1,4-cyclohexadiene 	160	0.62	9.5	1.5	0.72	26.5
ER-291	2,3-epoxycyclopentylglycidol ether 	160	0.51	4.5	0.6	0.5	—
ER-2189	Dioxane diglycidol ether 	160	0.46	12.0	6.9	—	—
ERZ-2772	Sulfolac diglycidol ether 	160	0.320	9.0	6.6	0.308	13.5
ERNA-0256	Epoxy cyclopentylphenylglycidol ether 	160	0.415	10.0	3.1	0.401	16.0
EXPP-1259	Bisphenol diglycidol ether 	160	0.262	7.0	8.8	0.247	10.5
ERRA-0300		160	0.612	11.5	2.6	—	—
ERLA-0460		160	0.480	12.3	4.6	0.478	19.5

resistance combined with a high strength and reactivity, the ETS-13 composition was developed, based on ETS epoxycyanurate resin and ED-13 epoxydiane resin. /22

In the oligomers discussed above, the epoxide  $\alpha$ -oxy ring and nitrogen-containing group were separated by a methylene group. Sometimes the epoxy and nitrogen-containing groups are so far apart that their mutual influence on the reactivity of the oligomers is absent.<sup>65</sup> In this case, the nitrogen-containing group is an internal modifier that improves the properties of the oligomers. This group of oligomers includes polyglycidylamides, the synthesis of which is based on aminolysis of methyl esters of epoxidized fatty acids or on the epoxidation of unsaturated aliphatic polyamides. Curing with compounds of boron trifluoride forms elastic polymers for electrical insulation coatings. A disadvantage of epoxidized polyamides which limits their application in shipbuilding is reduced water resistance.

As was noted above, cycloaliphatic epoxy resins are prepared by direct epoxidation of unsaturated compounds.

The unsaturated compounds used may be both aliphatic and aromatic. On curing, cycloaliphatic epoxy resins form three-dimensional structures with a large number of cross-links. The latter directly join the rings, causing the high strength and heat resistance of the cured products.

Cycloaliphatic resins also possess high thermal stability, dielectric properties which are maintained at high temperatures, and high atmospheric resistance, which permits their use as binders for fiber glass plastics used at high temperatures and sealing compounds.

All cycloaliphatic epoxy resins are marked by low reactivity and are cured at high temperatures by polycarboxylic acid anhydrides in the presence of accelerators - boron trifluoride complexes.

Among rigid cycloaliphatic resins, those developed by Union Carbide Corp. (USA) and Ciba are well known.<sup>1, 62</sup>

In order to obtain more elastic structures, cycloaliphatic resins are modified by increasing the distance between the aromatic rings and thereby decreasing the heat resistance to some extent.

The properties of the best-known cycloaliphatic resins cured with metaphenylenediamine are given in Table 9.

### 3. Curing Agents

The presence of two types of functional groups - epoxy and hydroxyl - in epoxy oligomers makes it possible to cure them with various substances. Depending on the nature of the curing agent, the curing may take place with the predominant participation of epoxy groups, hydroxyl groups, or both simultaneously. Curing agents reacting with epoxy groups include polyamines and polycarboxylic acids and their anhydrides. Curing agents curing through hydroxyl groups include compounds with isocyanate groups. Curing with phenol-formaldehyde resins involves the participation of both epoxy and hydroxyl groups. /23

Depending on the type of curing agent, curing may take place at room or higher temperature. For articles used in ship machine building, it is preferable to use so-called hot-curing agents, which provide for the highest strength properties of the structures and an adequate period of storage of the press materials.

The increased useful life of the composites is an important factor which makes it possible to use the highly productive mechanized impregnation of glass fabrics.

The selection of a given curing agent is determined in each case by the fabrication technology, structure, and set of requirements placed on the article.

Curing with amines. At the present time, a large number of amine type curing agents are known, including primary, secondary and tertiary amines of the aliphatic and aromatic series.

The rates of reactions with primary and secondary amino groups differ only slightly. Side reactions, for example between epoxy and hydroxyl groups, are practically absent. Curing with amines is a bimolecular reaction. Theoretical calculations of the reaction rate are in good agreement with the experimental data. Optimum properties of the compositions are achieved when one hydrogen atom of the amine corresponds to one epoxy group.

Aliphatic amines have low viscosity at room temperature (0.1 P at 25°C), easily mix with epoxy oligomers, and cure them even at room temperature.

Disadvantages of aliphatic amines include their high toxicity, low water resistance and heat resistance of the binders during their use.

Typical representatives of aromatic amines are m-phenylenediamine; 4,4' and 3,3'-diaminodiphenyl sulfone, 4,4'-diaminodiphenylmethane and its derivatives. Compositions based on epoxy oligomers with aromatic amines have high strength characteristics and water and heat resistance.<sup>6, 2, 65</sup> Aromatic amines cure at high temperature (140-180°C). Compositions of epoxy oligomers with such products as 4,4'-diaminodiphenyl sulfone remain stable for several months at room temperature, and hence, molding materials and binders may be stored for long periods of time at room temperature.

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In addition to aromatic amines, eutectic mixtures of aromatic amines are also used as curing agents. The mixtures are liquid at room temperature or have a low melting temperature, and therefore compositions based on them are easier to process than compositions with individual aromatic amines.

The properties of aromatic amines synthesized in the Soviet Union are listed in Table 10.

Aromatic amines constitute a promising group of curing agents providing for high strength and heat and water resistance of fiber glass plastics (Table 11). However, their use for series-produced articles for ship machine building is currently limited by their high cost, which results in a considerable increase in the prices of the articles, since the content of amines in an epoxy binder is at least 20%.

In contrast to primary and secondary amines, tertiary amines do not contain reactive hydrogen atoms, and curing with their participation follows a catalytic

mechanism. Cross-linking of the molecules takes place by polymerization through epoxy groups.

Curing with tertiary amines takes place at temperatures of 120-160°.

Table 10.  
Principal properties of amine type curing agents

Curing Agent	Physical State	Melting Point, °C	Molecular Mass
3,3'-diaminodiphenyl sulfone	White crystalline substance	110	248
4,4'-diaminodiphenyl sulfone	Same	150	248
4,4'-diaminodiphenylmethane	Same	92.5	80
3,3'-dichloro-4,4'-diaminodiphenylmethane	Brown powder	101	267
Metaphenylenediamine	Gray powder	63	136.2
Triethanolamine titanate	Thick viscous liquid, yellow to brown	-	-
3,3'-dimethoxy-4,4'-diaminodiphenylmethane	Gray crystalline substance	150	258
Triethanolamine	Transparent liquid	-	149.2

Table 11  
Properties of fiber glass plastics cured with aromatic amines

Property	Curing Agents		
	4,4'-diaminodiphenyl sulfone	3,3'-dichloro-4,4'-diaminodiphenylmethane	Meta-phenylenediamine
Strength, kgf/mm <sup>2</sup> :			
tensile	60	60	44
compressive	54	48	39.3
bending	75	68	54.1
interlaminar shear	7.4	6.5	6.5
Impact strength, kgf m/cm <sup>2</sup>	4.4	4.3	4.0

A considerable number of curing agents are known among tertiary amines: trimethylamine, triethylamine, triethanolamine, dimethylbenzylamine. In the Soviet industry, triethanolamine is most frequently used in the production of hot-pressed fiber glass plastics.

Triethanolamine is obtained by reacting an aqueous solution of ammonia with ethylene oxide. Triethanolamine has the appearance of a transparent, viscous liquid. It is convenient to handle, nontoxic, and mixes readily with resin. A disadvantage of triethanolamine is its high hygroscopicity. Fiber glass plastics

cured with triethanolamine are characterized by unstable strength properties, although individual samples of the plastic have relatively high mechanical characteristics.

Curing with polyamide resins. Epoxy resins are cured with low-molecular polyamide resins and methylol derivatives of polyamides with a high molecular mass. Epoxypolyamide resins are marked by high elasticity. The increase in elasticity in this case is due to the comparatively low cross-linking density and the introduction of flexible aliphatic linkages into the polymer structure. Polyamide resins are nontoxic and provide for a comparatively long useful life. The curing reaction is not very exothermic and takes place without the evolution of volatile substances.

"Oligoamides," low-molecular polyamide resins similar to "versamide" foreign resins, have been developed by a group of workers under the supervision of K. N. Vlasova.<sup>15</sup> They are prepared by using polymerized esters of fatty acids from soy and linseed oils and diamines, isolated from technical-grade polyethylene polyamine by vacuum distillation.

Low molecular polyamides are viscous liquids.

The physicomechanical properties of epoxypolyamide resins change with the proportion of the components, and the best properties are achieved with a 40-50% oligoamide content. Glass fabric resin laminates based on them (of brand EN-50) are prepared at specific pressures of 1-3 kgf/cm<sup>2</sup> and 120-160°C.

/26

Methylol derivatives of polyamides are obtained by reacting formaldehyde with high-molecular polyamides.<sup>16</sup>

Glass fabric resin laminate based on methylolpolyamidoepoxy resin (of brand PEM-2) is obtained by impregnating glass fabric with an alcohol-acetone solution of the resin, then drying at 60-70°C. The impregnated fabric is pressed at 160°C and a specific pressure of 30-50 kgf/cm<sup>2</sup>.

Another type of epoxypolyamide fiber glass plastic is material of brand EDP-2, in which methylolpolyamide resin enters into the block copolymer with epoxydimethylresorcinol resin. Fiber glass plastic of brand EDP-2 is prepared similarly to PEM-2 material.

The use of epoxypolyamide elastic binders makes it possible to increase the resistance of glass fabric resin laminates to dynamic loads and to reduce their delamination. Epoxypolyamide binders have reduced water resistance and heat resistance. The most water-resistant of this group of materials is EDP-2 fiber glass plastic (Table 12).

Curing with isocyanates. Isocyanates (derivatives of N-isocyanic acid) are characterized by the presence of a highly reactive radical which reacts with the hydroxyl groups present in the epoxy resins. To extend the storage life of the compositions and reduce their toxicity during the production of the fiber glass plastics, pure isocyanates are usually replaced by their derivatives, for example, products of the reaction of toluylene diisocyanate and polybutanediol or toluylene diisocyanate and diphenylolpropane (polyphenylurethane resin).

Table 12.  
Physicomechanical properties of epoxy polyamide fiber glass plastics

Property	Brand of Binder		
	EDP-2	PEM-2	EN-5L
Strength, kgf/mm <sup>2</sup> :			
tensile	52.0	45.0	50.0
bending	54.2	42.6	39.5
compressive	43.4	33.0	32.6
Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>	3.0	2.9	3.1
Impact strength, kgf m/cm <sup>2</sup>	4.5	3.4	3.2
Water absorption after 30 days, %	1.3	2.2	3.3

Note. Water absorption was determined on specimens 120 x 15 x 10 mm.

An epoxy polyurethane binder has been developed from a binder consisting of an epoxy and a polyphenylurethane resin taken in the proportion of 1:1. On curing, the polyphenylurethane resin breaks down into its initial components, so that diphenylolpropane and toluylene diisocyanate react with the epoxy resin. /27

The curing reaction of the epoxy resin with isocyanates takes place without the evolution of volatile substances. However, the main reaction is accompanied by the reaction of isocyanate with moisture, a certain amount of which is inevitably present in the components of the fiber glass plastic. This side reaction takes place with a substantial liberation of carbon dioxide, which is a major technological disadvantage of epoxy polyurethane binders. Fiber glass plastics based on epoxy polyurethane binders are processed by hot pressing at 170-180°C and a specific pressure of 50-70 kgf/cm<sup>2</sup>.

Epoxy polyurethane fiber glass plastics are characterized by excellent water resistance, heat resistance, strength properties, and impact resistance.

Properties of epoxy polyurethane fiber glass plastics

Strength, kgf/mm <sup>2</sup> :	
tensile .....	54.0
bending .....	62.0
interlaminar shear.....	7.3
compressive .....	43.0
Impact strength, kgf m/cm <sup>2</sup> .....	5.3
Water absorption, %:	
after 30 days .....	0.24
after 365 days .....	0.49

Curing with phenol-formaldehyde resins. Phenol-formaldehyde resins constitute low-toxicity, inexpensive and technologically effective curing agents. Phenol-formaldehyde resins of both resol and novolac type are used for curing. Fiber glass plastics based on them possess a relatively high short-time, fatigue and stress-rupture strength, as well as water and heat resistance.

This section discusses the mechanism of curing of epoxy resins by resol type phenolic resins. The mechanism of curing with novolac resins is described in Ch. 10.

Experimental studies have established that the optimum ratio of epoxy resin to resol-type phenolic resin is 70:30. In view of the complexity of the process of curing with phenolic resins, this ratio cannot be established by calculation.

Curing of epoxy resins with phenol resins forms rigid products of reticulate structure which provide for a high strength and water resistance of the fiber glass plastic.

Curing with a resol type phenolic resin containing phenol and methylol hydroxyl /28 groups takes place simultaneously in the following directions:<sup>7, 28, 47</sup>  
reaction of the epoxy group with the methylol hydroxyl group (reaction 1);  
reaction of the epoxy group with the phenol hydroxyl group (reaction 2);  
condensation of the resol resin with the splitting off of water without the participation of the epoxy component (reaction 3);  
reaction of the methylol group with the secondary hydroxyl group of the polymeric epoxy compound (reaction 4);  
reaction of the epoxy group with the secondary hydroxyl group of the polymeric epoxy compound (reaction 5).

Reactions 1, 2 and 3 determine the quality of the end product; the rate of reactions 1 and 2 should be much higher than that of reaction 3 - the condensation of the resol resin itself. Violation of this condition results in the formation of insufficiently cured products.

Because of steric hindrance, reactions 4 and 5 take place at slow rates and do not effectively determine the quality of the end product. Reaction 3 is undesirable, since it involves the evolution of water and causes a decrease in the number of functional groups of the curing agent and hence, the formation of an inhomogeneous, insufficiently cured product of increased porosity.

Studies have shown that the optimum curing conditions chosen for a given batch of phenol resin (bakelite lacquer) do not provide for the formation of products of the required strength as one passes to another batch of the lacquer. As we know, bakelite lacquer is a solution of a phenolic resin in alcohol. When bakelite lacquer is stored for a long time, partial polycondensation of the phenolic resin takes place, inevitably resulting in a decrease of its activity and hence, a decline of the quality of the cured fiber glass plastic. The activity of the phenolic resin as a curing agent also depends on the conditions of its synthesis and presence of various uncontrollable impurities.

The instability and multistep character of the process of curing with phenolic resins, due to the formation of undesirable by-products, make it necessary to control the starting materials carefully and select individual pressing conditions according to the geometry and dimensions of the article and characteristics of the raw material.

Catalytic curing. The catalytic curing of epoxy oligomers is a fairly complex process that has been inadequately studied. The following compounds may be used as catalytic type curing agents:

- chelate nitrogen or oxygen-containing compounds;
- complexes of esters or amines with Lewis acids, etc;
- alkyl and cyclopentadienyl derivatives of metals;
- metal salts;
- alcoholates, phenolates, mercaptides;
- finely divided nickel, iron, copper, chromium, molybdenum, lead;
- metal oxides and hydroxides.

/29

Historically, the first compounds used as curing catalysts were chelate compounds, in which the metal atoms are linked by a coordinate bond to the oxygen or nitrogen included in the composition of the same molecule as the metal. The use of these chelates for curing or for accelerating the curing of epoxy oligomers has been described in many patents. Aluminum and cobalt derivatives of acetoacetic ester and nickel and chromium derivatives of acetylacetone may be used for these purposes.

A comparatively short curing time at elevated temperatures is exhibited by epoxy compositions with the same catalysts as chelate compounds of divalent and trivalent cobalt, magnesium, nickel, and molybdenum and vanadium oxides with dicarbonyl compounds.

In 1960, Elbling and Thomas patented the use of compounds in which the metal atom is linked by a coordinate bond to the nitrogen atom as curing agents.

In addition to chelate compounds, complexes of esters or amines with Lewis acids have good curing properties. Compositions which are cold-resistant and cure readily on heating can be obtained by using complexes of tin tetrachloride with 1,2-dithioethylene glycol dibutyl ester for curing.

Curing catalysts of the third group - alkyl and cyclopentadienyl derivatives of metals - have begun to be used very recently. The principal studies are being conducted in Japan on compounds of zinc and aluminum. The use of this group of curing agents is complicated by their self-ignitability.

In Japan and the USA, zinc, cadmium, cobalt, and nickel salts of organic acids (acetic, propionic, benzoic) are being extensively used as catalysts.

Of great interest are epoxy compositions cured by metal alcoholates and mercaptides. Their properties are unique - the compositions can be stored for long periods of time at room temperature, and they cure in a few minutes at 100°C.

In recent years, studies have been conducted in the USA on the curing of epoxy compounds by finely divided metal powders - nickel, iron, copper, chromium, lead, and their oxides and hydroxides.

Among curing catalysts, triethanolamine titanate is being produced on an industrial scale in the Soviet Union. The properties of binders with different contents of triethanolamine titanate are shown in Table 13. Their curing kinetics are represented in Fig. 1.

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#### 4. Plasticization of Epoxy Binders

A disadvantage of epoxy binders is the brittleness due to strong intermolecular interaction and rigidity of the trimer chains formed during the curing.

The elasticity of the binders can be increased by introducing flexible linkages into the trimer network, reducing the intermolecular interaction, and blending with polymers having a low modulus of elasticity. Such an effect is achieved by using inert plasticizers (external or physical plasticization) and introducing special types of compounds compatible with epoxy oligomers (structural plasticization).



Table 13  
 Physicomechanical properties of epoxyamine binders with different contents of triethanolamine titanate /30

Property	Triethanolamine titanate content of the composition, %													
	0.5		1		2		5		10		15		20	
	ED-13	EKHD	ED-13	EKHD	ED-13	EKHD	ED-13	EKHD	ED-13	EKHD	ED-13	EKHD	ED-13	EKHD
Strength, kgf/mm <sup>2</sup> :														
compressive	2.0	2.0	3.0	3.8	9.0	12.4	14.0	12.9	18	27	17	21	15.0	12.7
bending	—	—	4.8	—	7.0	4.6	9.0	6.5	11	13	10	11	9.4	7.8
Elongation in tension, %	—	—	—	—	2.0	1.95	2.7	2.0	2.9	2.7	3.2	2.9	3.4	2.58
Adhesion strength, kgf/mm <sup>2</sup>	0.5	0.2	1.4	1.2	2.3	2.4	2.9	3.8	3.5	4.6	3.8	4.9	3.1	4.0
Deformation temperature, °C	—	—	58	60	70	106	80	125	106	155	102	148	95	136
Water absorption after boiling for 1 h, %	0.55	0.38	0.38	0.31	0.27	0.23	0.16	0.12	0.18	0.16	0.18	0.21	1.5	1.01

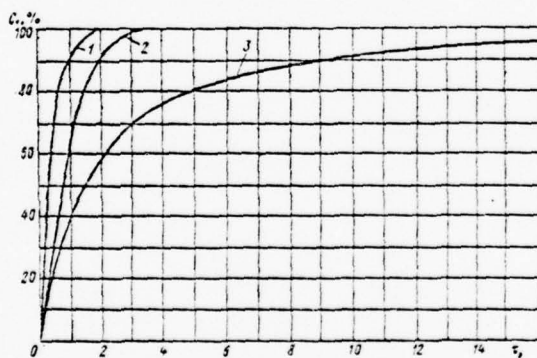


Fig. 1. Curing kinetics of epoxyamine binder based on ED-13 epoxy resin at 160°C /31 for different contents of the curing agent - triethanolamine titanate. 1 - 5%; 2 - 10%; 3 - 15%. C<sub>1</sub> - amount of unreacted epoxy groups, %; τ - curing time, h.

In addition, many authors<sup>65</sup> propose to increase the elasticity by decreasing the density of the cross-linkages. However, in practice, a substantial change in cross linking density results in only a slight change in the modulus of elasticity, and in many cases also leads to an increase of this modulus, since the high flexibility of the chains promotes a denser packing of them. This is confirmed by studies of the dynamic modulus of elasticity of epoxydiane resins with different contents of epoxy groups (10, 16, 21%); the lowest modulus of elasticity is exhibited by the resin with 21% of epoxy groups.

/32

One of the methods of structural plasticization involves blending with polymers having flexible aliphatic chains and terminal functional groups capable of reacting with the epoxy groups of resins. Strong bonds are thus formed between the plasticizing polymers and epoxy oligomers.

Such plasticization causes an increase in the percentage elongation of the resin, but on the other hand, it is inevitably related to a decrease in the cohesive strength of the resin and its heat stability. The magnitude of the plasticization effect depends not so much on the nature of the plasticizer as on the degree of the loosening of the trimer network caused by it, i. e., on the amount of plasticizer. Usually, 10-20% of plasticizer is introduced into the composition of the binder.

Among plasticizers of this type, the ones most closely studied have been low-molecular polysulfide rubbers - thiokols. Thiokols are liquids with a pungent odor and a viscosity of 150-300 cP.

Epoxy resins are capable of reacting with liquid thiokols in the presence of organic amines and phenolic resins.

Increasing the thiokol content above 20% in the composition of the binder causes a sharp decline of the strength properties of cured binders and fiber glass plastics.

In addition to polysulfide rubbers, plasticization of epoxy fiber glass plastics is accomplished by means of butadiene-nitrile carboxylated rubbers of brands SKN-10-5, SKN-18-1, and SKN-26-1, with viscosities from 400 to 3000 cP.

However, because of the relatively high molecular mass and low reactivity of the rubbers, the end products of curing consist mainly of a mechanical mixture of polymers and have a low cohesive strength (Table 14).

Plasticizers with terminal functional groups also include polyester acrylate resins, which are very compatible with an epoxy resin. Polyester acrylate plasticizers are employed most extensively in connection with the use of epoxy resins as sealing compounds. Such plasticizers have limited use for hot-pressed fiber glass plastics.

One of the methods of structural plasticization involves the use as curing agents of polymers containing flexible aliphatic linkages. Such curing agents include the above-described oligoamides, and also a curing agent consisting of triethanolamine titanate, modified with the product of transesterification of castor oil and triethylene glycol.

The most effective structural plasticizers are aliphatic polyglycidyl ethers created in the USSR by a group of co-workers under the supervision of Blyakhman

and Skrylova.<sup>13</sup> Aliphatic polyglycidol ethers are obtained by condensing polyatomic alcohols - ethylene glycol, diethylene glycol and triethylene glycol with epichlorohydrin in the presence of alkali catalysts. They are low-viscosity liquids with an epoxy group content of 25-30%.

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Table 14  
Effect of plasticization with rubbers on the physicomechanical properties of epoxy-phenol fiber glass plastics

Property	Brand of Rubber		
	Thiokol (20%)	SKD-10 (20%)	SKN-10-5 (40%)
Strength along warp of fabric, kgf/mm			
tensile	64.0	58.0	46.0
compressive	40.5	39.2	38.0
bending	63.0	57.5	56.0
interlaminar shear	6.2	5.6	5.4
Tensile strength at 45° angle to warp, kgf/mm <sup>2</sup>	22.3	12.4	-
Elongation, %			
along warp	2.0	2.3	2.7
at 45° angle to warp	5.8	5.9	6.0

Note. The content of rubbers is given in percent of mass of epoxy resin.

The possibility of using aliphatic polyglycidol ethers in epoxy fiber glass plastics and their plasticizing effect are determined by their structure and properties.

When aliphatic ethers are introduced into an epoxy composition, on the one hand, the density of the network increases, since the ethers are characterized by a high content of epoxy groups, and on the other hand, the flexibility of the resin macromolecule increases because of the presence of flexible aliphatic chains. When the content of aliphatic components is 10-30%, the indicated opposite effects probably offset each other, and therefore the induced elasticity limit and glass transition temperature change insignificantly. At the same time, the tensile, compressive and bending strengths of the resin and fiber glass plastics increase. Further increase of the content of glycidol ether to 40% in the composition causes a rapid decrease of the cohesive strength of the binder, and when the ether content is 60-70%, the polymers become rubberlike. The elongation at rupture of such modified binders is 100-150%, and the induced elasticity limit is 20-25 kgf/cm<sup>2</sup>.

Table 15 gives the properties of epoxy fiber glass plastics with phenol-formaldehyde resin curing agent modified with DEG-1 aliphatic ether. As expected, materials containing 10-20% of DEG-1 aliphatic ether have a higher strength.

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A disadvantage of fiber glass plastics modified with DEG type aliphatic ethers in comparison with unplasticized binders is their reduced water resistance, due to the presence of a large amount of hydrophilic polar group in the cured resin. As

the relative content of DEG-1 resin increases in the composition, the water resistance of the fiber glass plastic decreases, and therefore, an epoxy fiber glass plastic containing no more than 10% of DEG-1 plasticizer should be used in shipbuilding.

Table 15  
Effect of plasticization with DEG-1 aliphatic epoxy resin on the physicommechanical properties of epoxyphenol fiber glass plastics.

Property	Content of DEG Resin, %			
	0	10	20	50
Strength along warp of fabric, kgf/mm <sup>2</sup> :				
tensile	64.0	64.3	63.5	54.1
bending	69.0	72.0	71.0	60.0
compressive	43.1	44.5	44.0	25.2
interlaminar shear	6.9	7.1	7.4	5.5
Elongation of fiber glass plastic, %				
Tensile strength at 45° angle to warp, kgf/mm <sup>2</sup>	25.5	27.5	28.2	15.6
Elongation of specimens at 45° angle to warp, %	5.2	5.8	6.0	-
Water absorption after 7 days of exposure to water, %	0.33	0.68	1.0	3.8
Bending strength after 730 days of exposure to water	55.0/78	50.0/70	39.0/50	10.0/20
Remarks.	1. Content of DEG-1 resin given in percent of mass of epoxy resin. 2. Water absorption determined on samples measuring 120 x 15 x 10 mm. 3. Numerator indicates absolute value of strength in kgf/mm <sup>2</sup> ; denominator gives percentage of initial value.			

More water resistant are glycidyl esters of brands DEG-F and DEG-Zh, obtained by esterifying DEG-1 resin with dimethyl phthalate or methyl esters of fatty acids (Table 16).

The strength properties of fiber glass plastics modified with DEG-F and DEG-Zh resins are somewhat lower than in the case of modification with DEG-1 resin. In the case of plasticizers, polymers with a low modulus of elasticity and higher elongation are also used, for example, polyvinylbutyral and modified fluorocarbon plastics and polyamides.<sup>45, 54</sup>

For plasticizing, it is preferable to use lacquer and adhesive polyvinylbutyral of brands LA, LB, KA and KB, which blend better with resin. Plasticization of the binder with a small dose of polyvinylbutyral (up to 5%) decreases the internal stresses and increases the impact strength of the material. Up to 30% concentration, polyvinylbutyral is uniformly distributed among the macromolecules, so that the modulus of elasticity and the strain of the structure decrease. As the polyvinylbutyral content increases further, fine irregular inclusions appear which adversely affect the properties of the binder (Table 17).

Table 16  
Properties of aliphatic epoxy resins

Property	DEG-1	DEG-F	DEG-Zh
External appearance	Low-viscosity liquid		
Color	From light-yellow to brown		
Content of epoxy groups, %	24-26	11-14	6-10

Table 17  
Effect of plasticization with polyvinylbutyral on the physicommechanical properties of epoxyphenol fiber glass plastics

Property	Polyvinylbutyral content, %		
	0	5	10
Strength along warp, $\text{kgf/mm}^2$ :			
tensile	66.0	65.8	58.0
bending	69.0	70.4	64.1
compressive	43.1	45.5	42.0
interlaminar shear	6.9	7.3	7.1
Elongation %	1.8	2.1	2.4
Tensile strength at 45° angle to warp, $\text{kgf/mm}^2$	25.5	25.0	22.1
Percentage elongation of specimen at 45° angle to warp, %	5.2	5.75	6.0
Water absorption after 4 h of boiling in water, %	0.33	0.36	0.40
Bending strength after 4 h of boiling in water	61/68	59.1/84	48.6/76
Remarks.	1. Polyvinylbutyral content given in percent of mass of epoxy resin. 2. Water absorption determined on specimens measuring 120 x 15 x 10 mm. 3. Numerator indicates absolute value of strength in $\text{kgf/mm}^2$ ; denominator indicates percent of initial value.		

## Chapter 2. REINFORCING MATERIALS

### 5. Composition of Glass and its Influence on the Properties of Fiber Glass

According to the adopted classification, fiber glass is divided into the following groups:

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- (a) with increased strength and high strength;
- (b) with altered cross sectional geometry;
- (c) heat-resistant;
- (d) semiconducting and current-conducting.

According to their strength, glass fibers may be divided into three groups:

- (a) high-strength ( $\sigma_e = 370-470 \text{ kgf/mm}^2$  or higher);
- (b) increased strength ( $\sigma_e = 250-350 \text{ kgf/mm}^2$ );
- (c) normal strength ( $\sigma_e = 150-250 \text{ kgf/mm}^2$ ).

The chief component of glass is silicon dioxide  $\text{SiO}_2$ . Its content is usually no less than 50%. During the melting, various components are added to the glass: aluminum oxide ( $\text{Al}_2\text{O}_3$ ), calcium oxide ( $\text{CaO}$ ), boric anhydride ( $\text{B}_2\text{O}_3$ ). The proportion of these components, i. e., the chemical composition of the glass, determines the principal strength and technological properties of the glass fiber. Thus, the introduction of boric anhydride and aluminum oxide increases the atmospheric and water resistance of the glass fiber and improves its textile properties. The addition of calcium oxide also increases the water resistance as well as the hardness. The presence of copper, beryllium and titanium oxides in the glass composition improves the elastic properties of the fiber glass and its adhesion to the binder. With rising percent content of alkali metal oxides, the water resistance and elastic properties decrease.

At the present time, aluminoborosilicate glass containing no more than 1% alkali metal oxides and conventionally designated alkali-free is usually employed in the production of structural fiber glass plastics. The glass has a relatively low fusion temperature; its modulus of elasticity is  $7.8 \times 10^3 \text{ kgf/mm}^2$ , and the tensile strength is  $280 \text{ kgf/mm}^2$ .

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Alkali-free glass fibers are also characterized by high heat resistance and excellent electrical insulating properties. The composition of alkali-free glass includes the relatively scarce and expensive boric anhydride, whose cost accounts for up to 80% of the cost of the glass.

For this reason, instead of alkali-free glass, boron-free alkali glass containing 5 to 15% alkali metal oxides is used in many cases. Alkali fiber glass has lower tensile strength (by 15-20%) and modulus of elasticity (by 10-15%), and reduced torsional resistance (by 12%). Its cost is 35% lower than that of alkali-free glass.<sup>70</sup>

Studies currently being conducted are aimed at finding new compositions of boron-free or low-boron water-resistant glasses with properties equivalent to those of aluminoborosilicate glass. A whole series of glass compositions have been developed in which the absence of boric anhydride is compensated by introducing zirconium and manganese oxide and other components while increasing the content of silicon dioxide.

New glass compositions containing 8% boric acid instead of 10% have been created to reduce the cost. At the present time, as much as 30% of all continuous glass fiber is prepared with an 8% boric anhydride content. The quality of these fibers is equivalent to that of fibers based on aluminoborosilicate glass, the cost being 10-12% lower.

The steadily increasing demand for high-strength fiber glass plastics has made it necessary to develop new glass compositions for fiber glass whose tensile strength and modulus of elasticity considerably exceed those of alkali-free fiber glass.

Among the many studies aimed at the creation of new fibers, one should note the development of quartz fibers. Continuous quartz fiber has the highest mechanical strength, high melting point, dielectric properties which are high and stable at various temperatures, low coefficient of thermal expansion, and low thermal conductivity. Various studies have shown that the modulus of elasticity of glass fiber increases by introducing metal oxides of groups II and III of the periodic system into the glass composition. Thus, Aerojet General Corporation (USA) has developed glass fibers of brands 29-A and 4H-1, with a high aluminum oxide content; their modulus of tension and tensile strength are  $11.9 \times 10^3$  kgf/mm<sup>2</sup> and 562-708 kgf/mm<sup>2</sup> (for 29-A glass) and  $9.8 \times 10^3$  kgf/mm<sup>2</sup> and 482 kgf/mm<sup>2</sup> (for 4H-1 glass), respectively, versus  $7.8 \times 10^3$  kgf/mm<sup>2</sup> and 280 kgf/mm<sup>2</sup> for aluminoborosilicate glass. Fibers with a higher aluminum oxide content as well as zirconia-silicate fibers are currently made only under laboratory conditions. /38

The elastic modulus of glass is increased most effectively by beryllium oxide. In the USA, beryllium oxide has been used in the manufacture of glasses of brands 905 (Imperial Glass Co.) and UM 31A (Owens Corning Fiberglas).<sup>61</sup> Beryllium glass fibers are no different in strength from aluminoborosilicate glass, but have an elastic modulus of  $(11.8-12.6) \times 10^3$  kgf/mm<sup>2</sup>. The chief disadvantage of beryllium glasses is the high toxicity of beryllium, which limits the scope of its industrial application.

Of considerable interest are studies aimed at the development of nontoxic high-modulus glasses containing copper, titanium and zirconium oxides.

Glass fiber containing cuprous oxide has an elastic modulus of  $9 \times 10^3$  kgf/mm<sup>2</sup>.<sup>72</sup> According to the data of the US Naval Ordnance Office, fiber glass plastic based on copper-containing glass fiber has a modulus of tension of  $5.5 \times 10^3$  kgf/mm<sup>2</sup> for parallel arrangement of the fibers.

Fibers of aluminotitanosilicate glass have a strength of 30%, elastic modulus of 15%, and heat resistance 60° higher than fibers of aluminoborosilicate glass. These fibers are stable to water, acids, and alkalis.

A promising new glass fiber is one with a high content of silicon, aluminum and magnesium oxides and has a high tensile strength (370-425 kgf/mm<sup>2</sup>) combined with a high elastic modulus ( $9.5 \times 10^3$  kgf/mm<sup>2</sup>).

With further sharp increase in elastic modulus of the glasses, the density of the fibers increases ( $2.9$  g/cm<sup>3</sup>) and the strength decreases to 250 kgf/mm<sup>2</sup>, this being due to the microcrystalline structure of this type of fiber. Because of low viscosity, high surface tension and tendency to crystallize on cooling, high-modulus glasses are more difficult to convert into fibers.

In addition to enhancing the elastic properties of fiber glass plastics by changing the chemical composition of the glass, studies are now being aimed at increasing the rigidity of structures by using hollow glass fibers.

The first reports of tests of hollow fiber in a fiber glass plastic date back to 1961. The use of hollow fibers makes it possible to:

- increase the flexural rigidity of the fiber glass plastic;
- create a fiber glass plastic with higher heat-insulating properties due to the lower thermal conductivity of hollow glass fiber in comparison to solid fiber;
- create a fiber glass plastic of low density and improved dielectric properties.

Abroad, research on fiber glass plastics based on hollow fibers is being conducted by the General Electric Co., Thompson Fiber Glass, and others. /39

However, there are considerable difficulties and limitations on the uses of hollow fiber. Primarily, they include the:

- difficulty in producing a hollow fiber yarn of uniform quality with a constant coefficient of capillarity, so that one cannot definitively predict the strength properties of the fiber glass plastic;

- high sensitivity to the penetration of liquids into the internal cavity of the fibers. The problem of capillary penetration of liquids into unprotected ends or cracks of the composites is as complex as the problem of penetration of the binder into the fiber capillaries during fabrication, and makes it necessary to use substantial thicknesses of the surface protective coating.

The physicomachanical properties of fiber glass plastic based on hollow glass fiber produced in the Soviet Union are:

Tensile strength, $\text{kgf/mm}^2$ .....	46.0
Bending strength, $\text{kgf/mm}^2$ .....	72.0
Impact strength, $\text{kgf m/cm}^2$ .....	2.00
Modulus of normal elasticity, $\text{kgf/mm}^2$ .....	$2.8 \times 10^3$
Density, $\text{g/cm}^3$ .....	1.4

## 6. Woven and Nonwoven Glass-Reinforcing Fabrics

According to their mode of fabrication, reinforcing fabrics used in the production of fiber glass plastics may be divided into two types: nonwoven and woven. The nonwoven ones include fibers, filaments, yarn, and lapse. Woven ones include all glass fabrics of different types of weave.

Woven Fabrics. The industry produces a large number of glass fabrics differing in strength, mass, thickness and type of weave. Each type of glass fabrics has its distinctive technological characteristics, which must be considered when selecting a fabric for each type of article.

Fiber glass plastics are usually produced from glass fabric of calico (linen) serge (twill) and satin weaves based on twisted or untwisted threads.

Of major importance for glass fabrics used in the production of structural fiber glass plastics is the waviness of the threads, i. e., the extent to which



the threads deviate from the straight line when they are interwoven with perpendicular threads. The less the waviness of the glass fabric threads, the greater the mechanical strength of the fiber glass plastics based on these fabrics. The extent of the waviness depends on the type of fabric weave and degree of twist. Linen-woven glass fabrics have the maximum waviness; the overlap of threads in these fabrics takes place at a 90° angle. The fibers in serge-woven fabrics are somewhat straighter than in linen-woven ones, and this has a positive effect on the mechanical properties of the fiber glass plastic articles. /40

In satin-woven fabrics, the waviness of the threads is much less. This is due to the fact that each thread of the warp or weft passes under five, eight or other number of threads of the weft or warp.

Satin fabrics have a comparatively high density. Their formability and flexibility are greater than those of linen and serge fabrics. Satin fabrics are widely used as the reinforcing material in the production of articles for ship machine building.

The assortment of fabrics adopted by the Soviet industry has been based chiefly on the use of primary threads from glass spinners equipped with 100- and 200-spinneret glass melters producing fiber 5-7  $\mu\text{m}$  in diameter.

At the same time, foreign experience shows the promise of using glass fabrics from fibers 8-10  $\mu\text{m}$  in diameter and from thicker primary threads consisting of 400 to 800 filaments.

The development of a new glass-fabric manufacturing technology is aimed at reducing the cost and increasing the strength is being conducted along the lines of accelerating the glass-fiber-forming process and reducing the degree of twist or eliminating it entirely.

An acceleration of the glass-fiber-forming process is achieved by increasing the fiber diameter and number of spinnerets of the glass-melting container. With increasing diameter of the elementary glass fiber, the output of glass-spinning assemblies sharply increases. When the optimum forming conditions and a high degree of homogeneity of the glass mass are achieved, the strength of a glass fiber 9-11  $\mu\text{m}$  in diameter is essentially the same as that of glass fiber 5-7  $\mu\text{m}$  in diameter. The use of glass fiber 9-11  $\mu\text{m}$  instead of 5-7  $\mu\text{m}$  in diameter for fiber glass plastics makes it possible to increase the volume of production of primary glass thread from existing production areas by 50-60%.<sup>70</sup>

The output of a glass-spinning assembly is practically directly proportional to the number of spinnerets of the glass-melting container. In the last few years, the use of 400- and 800-spinneret containers has sharply increased. Twelve-hundred-spinneret containers are now being tested.

Fabrics have been made from threads thickened by using 400-spinneret containers with a fiber diameter of 5-7  $\mu\text{m}$  (400-filament primary thread instead of a 200-filament one), and by simultaneously increasing the fiber diameter to 9-11  $\mu\text{m}$  and using 400-filament primary threads.

In the first case, in the production of glass fabric from a 400-filament primary thread without a change in fiber diameter, the final structural indices of the glass fabrics (numbers of the threads, density of the fabric) remain unchanged. In order to ensure a constancy of the final structural indices of the glass fiber, the number of ends during the twisting of the thickened primary thread is decreased. /41

Thus, the most popular satin-woven fabric, of brand ASTT(b)-S<sub>2</sub>-8/3, with a thickness of 0.29-0.32 mm, had previously been made from glass fiber 5-7 μm in diameter and a 200-filament primary thread. During twisting and folding, a "balanced" thread with a metric number of 9, twist of 100 and number of ends 6 has been obtained. A new technology of production of ASTT(b)-S<sub>2</sub> fabric has been developed, using a 400-filament thread with an elementary fiber diameter of 5-7 μm. In order to obtain a "balanced" thread of the same thickness, as before, the number of ends is decreased from 6 to 3. The use of such a fabric provides for the preservation of the quality characteristics of fiber glass plastics based on it, with a 13-17% decrease in the cost of the fabric.

Much more effective is the use of glass fabrics in which the fiber diameter and filament content of the primary threads are simultaneously increased. Such fabrics are made from 400-filament primary threads with a fiber diameter of 9-11 μm and are thicker than those they replace. At the same time, the structures of the new fabrics have been corrected, and the twist of the threads decreased (from 100 t/m to 50 t/m). The principal characteristics of the fabrics devised are given in Table 18.

Use of the new structures makes it possible to reduce the cost of the fabrics considerably by increasing the productivity of the equipment. Thus, in the manufacture of fabric of brand T-22-78, which can be substituted for ASTT(b)-S<sub>2</sub> fabric, a 1.5-fold reduction in labor cost per kg of mass is achieved by using existing equipment. Adoption of new textile equipment specially designed for the manufacture of the new fabric structures can reduce the labor costs by a factor of nine.<sup>79</sup>

Research aimed at the complete elimination of the twisting operation has led to the creation of a new type of fabrics - braid fabrics. Glass braid fabrics are also made on weaving machines from untwisted elementary fibers 9-11 μm in diameter and have a dense or serge weave. The cost of braid fabrics is 2-2.5 times lower than that of fabrics from twisted threads.

The use of braid fabrics permits the fullest utilization of the theoretical strength of the glass fiber, since twisting of the thread is inevitably associated with a loss of strength due to the mechanical destruction of some of the fibers and their nonuniform tension in the threads. The use of braid fabrics permits the most effective application of the strength and elastic properties of fibers of high-modulus glass.

The fraction of braid fabrics in the total volume of glass fabric production increases each year.

In the case of manufacture of articles with a predominant strength in a given direction, it is desirable to use so-called cord or unidirectional fabrics possessing high mechanical strength in one of the directions in comparison with the strength in the perpendicular direction. To enhance this effect, threads of higher strength are included in certain cord fabrics in one of the directions. Cord fabrics may be made from both twisted and untwisted threads. The latter provide for a 10-15% increase in the strength of glass fabric resin laminates and a substantial decrease of their cost.

The fabrics described above have a two-dimensional weave, and their thickness does not exceed 1.5-2.0 mm. A promising trend is the creation of fabrics with

a three-dimensional weave, i. e., multilayered fabrics. The latter can be formed by using any glass fabric, then bonding the layers.

The breaking strength of a specimen of multilayered glass fabric is determined by the strength of the fiber, density, and angle made by the threads with the fabric surface. By changing this angle, i. e., the fabric structure, one can increase the degree of utilization of the strength of the thread in the fabric.

Table 13  
Properties of glass fabrics

Structure	Brand	Density (number of threads per cm)		Mass of 1 m <sup>2</sup> , g	Thickness, mm	Tensile strength, kgf		Diameter of glass fiber, $\mu$ m
		warp	weave			Warp	Weft	
Satin weave	TS-8/3-250	36	20	290	0.23	250	145	5-7
	ASTT(b)-S <sub>2</sub> -8/3	24	10	390	0.36	230	160	5-7
	T-22-78 <sup>2</sup>	11	8	620	0.53	410	330	9-11
Linen weave	T-18-78	6	6	400	0.40	230	230	9-11
	T-20-78	5	5	500	0.50	380	380	9-11
Braid, linen weave	TZhS-0, 7	19	19	780	0.72	400	300	9-11
Braid, cord weave	T-25-78	10	10	320	0.26	380	25	9-11
Multiple	MTBS-1, 8	34	5.4	1600	1.8	550	700	9-11

However, in any structure of a multilayered glass fabric substantial distortions of the threads of the warp and weft are inevitable, causing a regular decrease in the rupture strength of the glass fabric and in the tensile, compressive and bending strengths of the fiber glass plastics. /43

For hot pressing, use may be made of multilayered glass fabrics no more than 1.8-2 mm thick, because of the technological difficulties arising during the impregnation of multilayered glass fabrics of large thicknesses.

Multilayered fabrics up to 2 mm thick find limited application in the production of hot-pressed fiber glass plastics because of their high cost (5-10 times higher than the cost of analogous fabric with a two-dimensional weave). The principal characteristics of these fiber glass plastics based on various glass fabrics are shown in Table 19.

Nonwoven fabrics. Nonwoven fiber glass fabrics are made chiefly from untwisted primary threads with a fiber diameter of 10-14  $\mu$ m instead of 5-9  $\mu$ m; as a result, the productivity of glass-spinning equipment increases threefold.

Table 19  
Properties of epoxyamine fiber glass plastics based on different glass fabrics

Property	ASTI(b)-S <sub>2</sub> - 8/3 <sup>2</sup>		T-22-78		TZnS-0, 7		T-25-78		MTBS-1, 8	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
Strength, kgf/mm <sup>2</sup> :										
tensile	75	65	78	66	82	65	96	9.3	60	51
bending	78	65	83	70	85	70	101	20	70	54
compressive	52	40	54	42	56	40	60	15	38	35
interlaminar shear	7.2	7.2	7.2	7.2	6.9	6.9	6.8	6.8	6.2	6.2
Impact strength, kgf m/cm <sup>2</sup>	4.5	3.4	4.5	3.5	4.6	3.6	7.0	1.2	4.4	4.2
Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>	3.0	2.4	3.0	2.4	3.2	2.5	4.7	1.7	2.5	2.1

In the production of nonwoven fabrics, twisting and weaving are completely eliminated, so that all the operations of the technological process of their manufacture can be mechanized and automated, and the cost can be reduced by a factor of two-three in comparison with woven fabrics.

Among nonwoven fabrics in ship machine building, use is made of glass fiber press materials AG-4S, 27-63s and 33-18s based on suitably modified aniline-formaldehyde, epoxy-phenol and epoxy-polyurethane binders. The properties of fiber glass plastics based on unidirectional press materials are presented in Table 20.

Table 20  
Mechanical properties of fiber glass plastics

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Property	27-63S	33-18S	AG-4S
Strength, kgf/mm <sup>2</sup> :			
tensile	92.0	90.0	85.0
compressive	50.0	52.0	40.0
bending	95.5	97.4	80.0
Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>	4.8	4.7	4.3

Another type of nonwoven material is SVAM. The method of fabrication of a press material based on it consists in orienting the glass monofilaments parallel to each other while applying the binder on them. A material analogous to SVAM has found extensive applications in many countries, for example, the Scotchply material is produced in the United States.<sup>75</sup>

SVAM is produced in the form of sheets with a unidirectional or crosswise structure of the glass fibers. It is used as an electrical and structural material and has high mechanical strength. The mechanical properties of this fiber glass plastic are given in Table 21.

Table 21  
Mechanical properties of SVAM fiber glass plastic and fiber glass plastic with alternating layers of laminated fiber glass sheet and glass fabric ASTT(b)-S<sub>2</sub> based on epoxyphenol binder

Fiber Glass Plastic	Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>		Strength, kgf/mm <sup>2</sup>					
			Tensile		Bending		Compressive	
	Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
SVAM with 10:1 structure	4.8	1.8	80.0	9.5	96.0	16.0	58.0	19.5
With alternating layers of laminated fiber glass sheet and ASTT(b)-S <sub>2</sub> glass fabric	4.0	2.1	80.0	27.0	85.0	39.0	53.0	24.0

Certain researchers<sup>32</sup> indicate the following drawbacks of SVAM material: presence of internal stresses due to different lengths of the fibers and upper layers, more difficult conditions of removal of volatiles during the production of SVAM, a considerable spread of the physicochemical properties due to distortion of the fiber direction during the removal of the fiber glass sheet, lower fatigue strength of SVAM, and, in comparison with glass fabric resin laminates, greater brittleness of monofil 14 μm in diameter.

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Among nonwoven fiberglas fabrics in rolls, of interest is a cross-type rigid fabric of braided or twisted threads. The output of the equipment during its fabrication increases by a factor of 10-15 in comparison with woven fiber glass fabrics. According to the calculations of Ref. 70, cross-type rigid fiber glass fabric produced on an industrial scale can be one-half or one-third as expensive as similar braid fabrics. The position of the threads relative to each other is fixed by bonding. With nonwoven cross-type fabric used as the base, articles are made by methods of hot pressing, contact molding and winding.

One of the modifications of cross-type fiber glass fabric is VPR-10 knitted-sewn reinforcing fabric. This type of fabric is characterized by the fact that the perpendicular systems of untwisted threads are not bonded but tied by the weft knitting method. It is more flexible and elastic than rigid cross-type fabric while at the same time retaining all of its advantages.

The production of knitted-sewn fabrics has been mastered by the Soviet industry. The strength properties of fiber glass plastics based on VPR-10 are 25-30% below those of fiber glass plastics based on glass fabrics.

Combined reinforcement. The quantity of reinforcing fabrics now in production does not effectively provide for the ratio of warp to weft strength required in structures. In some cases, to achieve this ratio in structures, it is desirable to use industrially produced satin or linen glass fabrics combined with cord-weave

Table 22  
Physicochemical properties of epoxyphenol fiber glass plastics with a composite filler /45

Arrangement of glass fabrics (specimen 10 mm thick)	Ratio of glass fabrics (% of copolymer)	Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>		Tensile strength, kgf/mm <sup>2</sup>		Modulus of flexure, 10 <sup>3</sup> kgf/mm <sup>2</sup>		Bending strength, kgf/mm <sup>2</sup>	
		Warp	Weft	Warp	Weft	Warp	Weft	Warp	Weft
	20	3.7/3.6	2.3/2.3	76.5/75.4	12.1/11.1	4.2/4.1	2.1/2.2	88.0/89.3	35.4/34.2
	40	4.0/3.9	2.1/2.2	81.0/80.1	33.8/34.6	4.5/4.4	1.9/2.0	91.0/95.1	23.8/24.7
	50	4.1/4.0	2.0/2.1	83.5/81.6	29.5/28.5	4.4/4.2	1.9/2.0	92.0/90.1	26.0/24.8
	50	4.1/3.9	2.6/2.1	83.5/81.0	29.5/30.7	4.2/2.1	2.2/2.2	88.0/86.9	35.0/36.4

Remarks. 1. Numerator gives calculated values, and denominator, experimental values.

2. Notation: - T-25-78 glass fabric; - TS-8/3-250;

- filler layer with alternating glass fabrics of brands T-25-78 and TS-8/3-250.

glass fabrics or nonwoven fabrics. Such a combination in suitable proportions makes it possible to obtain the required ratio of mechanical properties. Knowing the mechanical properties of fiber glass plastics based on each brand of reinforcing fabric used individually, one can calculate, with an accuracy adequate for practical purposes, the expected strength properties of the combined fabric by using formulas (1)-(4), on the basis of the percentage ratio of the materials (or on the basis of areas occupied in the cross section of the structure):

$$\sigma_t = \frac{1}{F} \sum_{i=1}^n \sigma_i F_i, \quad (1)$$

where  $\sigma_t$ ,  $\sigma_i$  are the tensile strengths of the composite and individual component, respectively;

$F$ ,  $F_i$  are the cross-sectional areas of the specimen and component; /47

$$E_t = \frac{1}{F} \sum_{i=1}^n E_i F_i, \quad (2)$$

where  $E_t$ ,  $E_i$  are the moduli of tension of the composite and individual component;

$$\sigma_b = \frac{1}{J} \sum_{i=1}^n \sigma_i J_i, \quad (3)$$

where  $\sigma_b$ ,  $\sigma_i$  are the bending strengths of the composite and individual component;

$J$ ,  $J_i$  are the moments of inertia of the cross sections of the specimen and individual component;

$$E_b = \frac{1}{J} \sum_{i=1}^n E_i J_i, \quad (4)$$

where  $E_b$ ,  $E_i$  are the moduli of flexure of the composite and individual component.

Table 22 presents data characterizing the mechanical properties of composite fiber glass plastics prepared by using TS-8/3-250 satin glass fabric and cord braid glass fabric. To obtain a more homogeneous composition, satin and cord-weave glass fabric layers alternate regularly.

Particularly desirable is the use of composite reinforcement when high-modulus glasses are used. It is well known that the strength and elastic properties of high-modulus fiber are preserved most fully when the fabrics are made from untwisted threads. It is therefore uneconomical to make them from

Table 23  
Strength and elastic properties of epoxyamine fiber glass plastics based on cord glass fabric

Property	Glass		
	Copper-containing	Aluminoborosilicate	High-modulus
Warp strength, kgf/mm <sup>2</sup> :			
tensile	93.0	96.0	102.0
compressive	63.0	60.0	63.0
bending	107.0	101.0	110.0
Impact strength, kgf m/cm <sup>2</sup>	7.4	6.8	7.2
Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>			

Table 24  
Strength and elastic properties of epoxyphenol fiber glass plastics based on  
glass fabrics ASTT(b)S<sub>2</sub> and T-25-78 with alternating layers

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Property	Glass	
	Copper-containing	Aluminoborosili- cate
Strength, kgf/mm <sup>2</sup> :		
tensile	88.0/31.0	83.0/29.0
compressive	49.0/27.0	46.0/25.0
bending	93.0/38.0	88.0/35.0
Modulus of tension, 10 <sup>3</sup> kgf/mm <sup>2</sup>	4.8/2.4	4.0/2.0
Note. Numerator - warp data; denominator - weft data.		

high-modulus glasses of satin weave fabric, since the cost is considerably in-  
creased for a slight gain in strength.

Tables 23 and 24 show the strength and elastic properties of composite fiber  
glass plastics based on cord and satin glass fabrics of high-modulus and  
aluminoborosilicate glass in a ratio of 1:1 with alternating layers.

#### 7. New Types of Reinforcing Materials

New types of reinforcing materials are developed for the purpose of expanding  
the assortment of composites having either lower density or better strength and  
elastic properties as well as higher heat stability.

Inorganic materials. Among new fibers, of considerable interest are boron  
fibers, produced abroad in a diameter of 0.07-0.1 mm under the brand name borofil.  
Borofil fibers have a tensile strength up to 300 kgf/mm<sup>2</sup> and elastic modulus up  
to 41 x 10<sup>3</sup> kgf/mm<sup>2</sup>. After fatigue tests with a base of 10<sup>7</sup> cycles, boron fibers  
retain up to 50% of their initial strength.

Borofil is produced by depositing boron from the gaseous phase on a tungsten  
wire 0.01-0.012 mm in diameter heated to 1110°C. The fiber obtained contains  
intermediate tungsten boride W<sub>2</sub>B<sub>5</sub> type compounds between the tungsten core and the  
rough outer cellular surface of amorphous boron. The fiber surface has no micro-  
cracks, pits, or other defects.<sup>1</sup>

Because of different coefficients of linear thermal expansion of boron  
(8.14 x 10<sup>-5</sup> °C<sup>-1</sup>) and tungsten (4.16 x 10<sup>-5</sup> °C<sup>-1</sup>), radial cracks running from  
the center to the periphery are formed inside borofil fibers. Studies aimed at  
perfecting boron fibers are being conducted. In particular, treatment of the fiber  
with nitric acid increases the tensile strength by a factor of three to four.

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The high cost of boron plastics limits their application as an independent  
structural material. A combination of boron and glass plastics is frequently  
employed in constructions. Thus, successful tests have been completed in the USA



on blades of a helicopter rotor whose spar and trailing edge are made of boron plastic, and the remaining part of the blade is made of fiber glass plastic.<sup>1</sup>

The Teyko\* Co. (USA) has produced a single-crystal sapphire fiber 30.5 m long from aluminum oxide. The sapphire fiber is equivalent to glass fiber in strength, but is much superior to it in elastic properties [ $E_c = (45-49) \times 10^3 \text{ kgf/mm}^2$ ].

Carbon (or graphite) fibers are made by carbonizing organic textile fibers, for example acrylonitrile ones. Because of their low density (1.7-2.0 g/cm<sup>3</sup>), they greatly surpass all other fibers in tensile strength weight ratio and rigidity. Carbon fibers are resistant to water, chemicals and wear at high temperatures. They are compatible with epoxy and polyimide binders.<sup>1</sup>

Carbon fibers have a polycrystalline structure thanks to heat treatment and stretching of the atoms, providing for the highest strength and rigidity along the fiber axis.

Carbon fibers obtained by heat treatment at 1000°C have a tensile strength of the order of 200 kgf/mm<sup>2</sup> and an elastic modulus of  $42 \times 10^3 \text{ kgf/mm}^2$ .

At a heat treatment temperature of 2500-2700°C, graphite fibers are obtained which possess a better structure and better properties, with a strength of 290-300 kgf/mm<sup>2</sup>.

In the near future, a substantial expansion of the use of graphite fibers is expected as a result of a marked anticipated drop of prices of this material. Graphite fibers made by the Great Lakes Carbon Co. have an elastic modulus ranging from 21000 to 42,000 kgf/mm<sup>2</sup>. The material is made as a continuous filament, which makes it possible to produce long ribbons for reinforcing epoxy resins. An epoxy laminate with a filler of graphite fibers having an elastic modulus of about 42,000 kgf/mm<sup>2</sup> has a bending strength of 120 kgf/mm<sup>2</sup>, tensile strength of 105 kgf/mm<sup>2</sup>, and compressive strength of 84 kgf/mm<sup>2</sup>.

Most widely used at the present time are graphite fibers for reinforcing epoxy resins in aviation and space technology; they are also beginning to be used in shipbuilding. US Navy researchers have come to the conclusion that an epoxy plastic reinforced with graphite is more promising than fiber glass plastics, since it is marked by a higher modulus, lower density, and high fatigue strength. /50

British experts are planning to use graphite fibers in the production of rotating parts of compressors, centrifuges and various electromechanical devices, as well as in the textile industry. Using the Hifil carbon fiber reinforced plastic, the Rolls Royce Co. makes fan blades 2400 mm in diameter and compressor parts.

Organic materials. In recent years, studies have been made indicating the possibility of using organic fibers for reinforcing polyester and epoxy binders. Laminates based on organic fibers (organic plastics) have low density (1.15-1.25 g/cm<sup>3</sup>), attractive dielectric properties (at 10<sup>6</sup> Hz,  $\epsilon = 2.2-2.8$ ;  $\tan \delta = 0.0115$ ), vibration resistance, and high fatigue strength.

\*Transliteration of Russian spelling.

The reinforcing materials used may be fabrics from fibers - capron, lavsan, nitron (acrylonitrile) and polypropylene. Of these, capron fabrics are the strongest ones. Minimum elongation (13-14%) and strength are exhibited by nitron fabric.

Reinforcing materials based on organic fibers differ considerably in water resistance. Results of determination of the strength of fabrics after 2 hours' boiling in seawater are given in Table 25. In nitron fabrics, the loss of strength is 14-15%. The strength of lavsan fabrics remains practically unchanged.

Table 25  
Properties of fabrics made of organic and glass fibers

Fiber and Fabric Article	Breaking load of fabric strip, 25 x 100 mm, kgf		Elongation of strip at rupture, %		Shrinkage after boiling, %	
	Initial	After boiling	Initial	After boiling	Width-wise	Length-wise
Polypropylene, art. 23352	190.0	225.8	41.6	54.8	6.7	7.3
Nitron art. 23455/1	134.5	143.8	13.4	21.0	2.0	4.8
Lavsan art. 23372/1	200.5	198.0	19.4	25.0	2.0	0.5
Lavsan art. 23372/2	206.5	211.8	23.6	25.0	1.5	4.5
Capron art. 22338	379.2	323.0	4.76	53.6	-	4.8
Glass fabric ASTT(b)-S <sub>2</sub> (a/f glass)	249.2	107.6	3.2	1.0	-	-
Glass fabric ASTT(b)-S <sub>2</sub> (T-273A glass)	204.6	166.8	3.2	2.0	-	-

In polypropylene and nitron fabrics, the strength increases\* by 19% and 7%, respectively, after boiling in seawater. For comparison, one can note that under similar testing conditions, glass fabric of alkali-free glass (a/f) loses 50% of its initial strength. In all organic fiber fabrics, shrinkage and an increase in breaking elongation are observed. The greatest shrinkage (7-7.5%) is exhibited by samples of polypropylene fabrics.

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The use of organic fibers makes it possible to increase the water resistance of an organic plastic in comparison with a fiber glass plastic. The strength and water resistance of an organic plastic are determined not only by the chemical structure of the organic fibers, but also by the structure of the fabric. The best mechanical properties and water resistance are those of organic plastics based on satin weave, since this structure provides for higher-quality impregnation with the binder and better solidity of the organic plastic.

Fabrics made of organic fibers are impregnated with epoxy binders on standard vertical-type impregnating machines. A 30-34% resin content of the binder is

\*Sic [translator].

provided for at the same binder concentrations as in the impregnation of glass fabric. The conditions of pressing for organic plastics are analogous to those for fiber glass plastics based on the same binders.

During the pressing of organic fiber fabrics, it is necessary to consider the shrinkage, which for lavsan fabrics is as high as 15-20%. Fabric shrinkage accounts for the formation of internal stresses. To reduce it in the course of pressing, the fabric prior to the impregnation should be subjected to heat treatment at a temperature close to the pressing temperature. In comparison with the initial fabric, the strength of the heat-treated fabric decreases by only 1-3%, and the elongation at rupture remains practically unchanged.

A characteristic feature of organic plastics is their capacity for high deformations - the elongation at rupture is 17-20%. The proportionality limit in extension in the direction of the warp is 3.7-3.9 kgf/mm<sup>2</sup>, in the direction of the weft 2.7-3.0 kgf/mm<sup>2</sup>, and at a 45° angle, 2.4-2.6 kgf/mm<sup>2</sup>.

In tensile deformations up to 3-3.5%, the main load is borne by the binder, which acts as a rigid matrix that redistributes the stresses among the fibers. As the elongation increases further, the rigid matrix cracks, and its function begins to be assumed by the boundary layer between the filler and the binder, formed during the pressing and consisting of a block copolymer of the binder and lavsan.<sup>1,2</sup>

The block copolymer is formed by the reaction of epoxy groups of the binder and terminal hydroxyl groups of polyethylene terephthalate (lavsan).

At elongations of 8-10%, which cause rupture of this elastic block copolymer, delamination of the sample takes place. Further load is received by individual layers of the plastic, which break under the load. /52

In compression tests, organic plastic is capable of functioning as a monolithic material up to stresses of 8.0-10.0 kgf/mm<sup>2</sup>, the deformation being 10%. As the stresses increase, flow of the organic plastic begins. In static bending tests, specimens of organic plastic also show considerable deformations.

When the maximum load is reached, the specimens bend without breaking. Microstructural analysis has shown that no destruction of the fabric takes place in the region of maximum flexure of the specimens. The thermal recovery capacity of organic plastics has been noted.<sup>1,2</sup> After being kept for 2 hours at an elevated temperature, specimens bent during testing recover their shape and strength. Heating of the specimens accelerates relaxation processes, leading to a rapid recovery of the shape and strength of the specimens.

In contrast to fiber glass plastics, organic plastics are characterized by appreciable creep. Thus, after 500 h under tensile stresses of 2.0-3.0 kgf/mm<sup>2</sup>, the elongation is 1.96%, and under stresses of 9.0 kgf/mm<sup>2</sup>, it increases to 20% (at 20°C).

The use of composite fillers based on organic and glass fibers is effective for many structures. Glass fibers impart strength and rigidity to a composite material. Depending on the proportion of the components and mode of their arrangement, combined plastics change their strength characteristics over wide limits.

As an example, Table 26 gives the strength and elastic properties of combined plastics made from epoxyamine binder, glass fabric and lavsan fabric. As is evident from the table, with increasing glass content, all the strength properties of the material increase regularly from values characteristic of organic plastics to those characteristic of fiber glass plastics, and the density also increases, from 1.26 to 1.95 g/cm<sup>3</sup>.

Table 26  
Properties of composite plastics based on lavsan and fiber glass fabric

Reinforcement scheme	Strength, kgf/mm <sup>2</sup>		
	tensile	compressive	bending
Lavsan (100%)	20.0	14.0	13.8
Fiber glass fabric (100%)	80.0	55.0	35.0
Lavsan outer layers (70%)	31.0	18.0	18.2
" " " (50%)	41.3	25.3	28.6
" " " (30%)	55.4	36.6	43.4
Fiber glass fabric outer layers (30%)	27.8	19.5	49.6
" " " " " (50%)	40.2	27.3	64.3
" " " " " (70%)	50.0	40.0	78.0
Alternating layers	45.0	28.0	42.6

### 8. Water-Repellent Adhesive Treatment of Reinforcing Fabrics

One of the decisive factors affecting the physicochemical properties of a fiber glass plastic is the strength of the adhesive bond between the fiber and the polymer binder. The interaction of the binder with the glass fiber is a fairly complex process that is determined by many physicochemical and physicochemical factors: the actual contact area, internal stresses, friction, surface tension, and effect of the glass fiber on the curing processes. /53

There are two basic points of view regarding the nature of adhesion between the binder and the glass fiber.<sup>2, 4, 10, 20</sup> According to the first, adhesion strength is almost completely determined by the physical contact resulting from shrinkage of the binder on curing. Adherents to the second point of view assert the possibility of formation of a chemical bond in the glass fiber-binder system. In the interaction of epoxy binders with glass fiber, a chemical reaction is postulated between the epoxy groups of the binder and the hydroxyl groups on the surface of the glass fiber, with the formation of strong bonds.

The properties of polymers present in thin layers on the solid surface of the filler differ markedly from those of polymers in the volume.<sup>53</sup> On the surface of the filler, the glass transition temperature of the polymer rises, and the relaxation properties change as a result of the limitation of the segmental mobility of macromolecules by the solid surface. Glass fiber may also considerably affect the curing of the binder, catalyzing or inhibiting the rate of the curing reaction.

In the course of curing of the binder, because of the difference in the coefficients of thermal expansion of glass and binder, internal stresses arise at

their interface. The concentration of residual stresses and stresses due to external loads is one of the causes of crack formation in the fiber glass plastic. If the adhesion between the glass fiber and binder is similar to the cohesive strength of the binder, the fibers will block the propagation of cracks, and the surface of contact between the binder and glass will remain intact. If however the adhesive strength of this system is much lower than the cohesive strength of the binder, the tensile stresses will cause the breakdown of the contact surface.

In view of the fact that in the overwhelming majority of cases, the fiber is treated with technological lubricants, major importance is assumed by the chemical reactions between the binder and lubricant and between the latter and the glass fiber.

The technological lubricant applied during the drawing of glass fiber protects /54 the fibers from wear, bonds the monofilaments to form a thread, and protects the threads from mechanical damage during textile processing and from the action of moisture.

The nature of their interaction is of course determined primarily by the chemical composition of the lubricant. Thus, when paraffin emulsion, which is an aqueous emulsion of the chemically inert substances paraffin, stearin, transformer oil and vaseline, and is widely employed in industry, is used as the technological lubricant, the wettability of glass fiber is reduced, and chemical interaction at the interface is practically absent. When surfactants and water-repellent adhesive substances (sizing agents) are used for treating the glass fiber, hydrolytically stable chemical bonds are formed between the binder, sizing agent and glass fiber, the wetting conditions improve considerably, and there is formed a continuous transition from the binder to the glass fiber through the surface layer of sizing agent.

Depending on the polarity of the sizing agent, the adhesive strength between the binder and glass fiber passes through a maximum and, as the polarity increases above a certain limit, falls off. In this case, the orientation of the molecules of the sizing agent on the surface of the glass fiber is very important.

The sizing agents used are monomeric organosilicon compounds whose composition includes various reactive functional groups (vinyl, methacryl, phenyl, epoxy, amino and imino groups, etc.), chromium complexes of methacrylic acid, or organophosphorus compounds.

The formation of bonds stable to the action of solar radiation has been established during the interaction of functional phosphorus-containing groups with the glass surface. Fiber glass plastics based on glass fiber treated with an organophosphorus sizing agent exhibit high bending strength but low water resistance, due to the hydrolyzability of organophosphorus compounds.

Salts of polyvalent metals have recently been widely employed as sizing agents. Salts of such metals as aluminum, titanium, copper, iron, etc., are employed. Good results have been obtained by treating glass fiber with chromium chloride. The chromium oxide formed on the surface of the glass is not only strongly bonded to the glass fiber, but also interacts with the polar groups of the binder. The increase in the strength of fiber glass plastics due to treatment of the glass fiber with aluminum and titanium chlorides is particularly appreciable at higher temperatures. Treatment with titanium tetrachloride promotes the attachment of epoxy groups to the surface of the glass fiber.

In each individual case, the choice of the sizing agent composition is determined by the type of binder employed. /55

Monomeric organosilicon compounds containing amino groups are used for epoxy-glass plastics in the USSR and abroad. The amine groups of the sizing agent react with the epoxy groups, forming interfacial bonds stable in a neutral aqueous medium.

Among organosilicon sizing agents, of interest are the following compounds:  $\gamma$ -aminopropyltriethoxysilane (AGM-9), aminohexamethylenaminomethyltriethoxysilane (AGM-3) and N-diethylmethylenetriethoxysilane (ADE-3). Abroad, compounds similar in structure to AGM-9 are known under the designations A-1100 (USA) and 3100-W (France). In addition to these compounds, epoxy derivatives of silanes are employed. In the USSR, the product ES, epoxypropoxypropyltriethoxysilane, is employed.

At the present time, all known methods of treatment of fiber with water-repellent adhesive products may be divided into three groups:

- thermochemical treatment;
- introduction of water-repellent adhesive products into the composition of the binder;
- introduction of water-repellent adhesive products into the composition of the sizing agent.

Thermochemical treatment. This treatment consists of two basic operations - removal of inert lubricant (paraffin emulsion) and application of sizing agent.

Removal of the lubricant may be carried out by caramelization, thermal purification, and washing.

The caramelization method consists in thermal treatment of the glass fabric at a temperature up to 300°C, part of the lubricant being volatilized. The caramelized glass fabric has a golden brown color, and its residual lubricant content is up to 0.5% (instead of 2-3% in the original glass fabric).

Thermal purification of glass fabrics is achieved by treating them at 350-500°C, thus obtaining a more complete removal of the lubricant, down to 0.1-0.2%. Thermal purification is the most common method of lubricant removal and is usually accomplished by the continuous method in vertical ovens.

The washing method consists in treating the glass fabric with special compositions (benzine, oleic acid, etc.). The glass fabric is passed through a series of baths with solvents, washed with water, and dried. The lubricant content of the washed glass fabric is 0.3-0.5%. The use of ultrasound during the washing makes it possible to replace the toxic solvent compositions with water.

After the lubricant has been removed, the fabric is hygroscopic and should therefore be immediately treated with water-repellent adhesive compositions (sizing agents). The chemical treatment is carried out with dilute aqueous solutions (concentration, 0.5-5%) of sizing agents followed by washing with water and drying. The content of the sizing agent is 0.25%. The chief disadvantage of the thermochemical treatment is the reduction in fabric strength from 25 to 50%. /56

Addition of water-repellent adhesive products to the binder composition. This method is easy to apply technologically, and can be carried out by using a wide assortment of compounds, whereas the thermochemical treatment is confined only to compounds soluble in water or alcohol. However, as in the thermochemical treat-

ment, it is first necessary to remove the lubricant, i. e., paraffin emulsion. The chemically active compounds used for introduction into the binder are organo-silicon products containing amino groups (AGM-9, AM-2, ADE-3), hydroxyl groups (MR-1) and epoxy groups (ES). In the ideal case, the introduction of organo-silicon products into the binder involves their migration to the surface of the glass fibers, hydrolysis of alkoxy groups by moisture present on this surface or in the binder, and interaction of the sizing agents with the glass.<sup>31</sup> The introduction of sizing agents into the binder decreases the residual stresses at the glass fiber - binder interface. It has been found<sup>31</sup> that the best water-repellent effect is achieved by introducing the sizing agents in the amount of 3%.

Introduction of water-repellent adhesive products into the composition of the lubricant. This method is the most advanced and considerably simplifies the technology of production of reinforcing materials, since the operations of application of technological lubricants and water-repellent adhesive treatment are combined, and the operation of removal of the inert lubricant, associated with a loss of strength of the glass fabric, is excluded.

Lubricants based on the products AGM-3 (lubricant 652), ADE-3 (lubricant 752) and AGM-9 (lubricants 78 and 80) have been developed for epoxy-glass plastics. Product OS-20 is added as the emulsifier, and dibutyl sebacate is added as the plasticizer. A mixture of these products is applied on the fibers from a 5% aqueous solution. The content of adhesive lubricant on the fabric is about 1%.

The effectiveness of the waterproofing may be estimated from the strength and dielectric properties of the fiber glass plastics.

Considering that the chief purpose of the waterproofing adhesive treatment is the stabilization of the properties of the fiber glass plastic in a moist medium, of greatest interest are data on the change in these characteristics after exposure to water. The greatest stability of the properties of fiber glass plastics in water is provided by waterproofing adhesive lubricants 652, 78 and 80. Thus, whereas the decrease in strength after 240 days in water is 25-30% when paraffin emulsion is used, it is about 14-15% when lubricant 652 is employed (Table 27). /57

Particularly appreciable is the positive effect of waterproofing on the change in the dielectric properties in water (Figs. 2 and 3). Thus, even a 30-minute boiling of epoxyphenol fiber glass plastic with paraffin lubricant increases the dielectric loss tangent from  $1.72 \times 10^{-2}$  to  $8.9 \times 10^{-2}$ , whereas for sized fiber glass plastics (AGM-9 sizing agent), after 6 hours' boiling, this value is  $4.15 \times 10^{-2}$ . /58

An important property of fiber glass plastics for shipbuilding applications is their durability in water. Tests have shown<sup>32</sup> that durability in water in pure bending is the most sensitive method of estimating the effectiveness of waterproofing adhesive treatment. The long-time strength in water in bending with a base of 1000 h for epoxyphenol fiber glass plastics with a paraffin lubricant is 0.45 of the long-time bending strength, and for analogous fiber glass plastics with lubricant 652, 0.65 of the short-time strength (Table 28, Fig. 4).

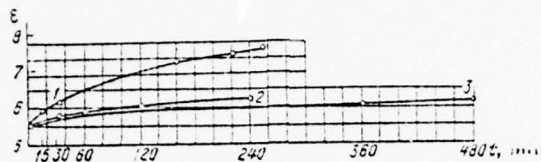
Creep tests (Fig. 5) have shown that the deformation produced after 1000 h of testing is relatively small and rather insensitive to the method of treatment and to the influence of water. /59

Table 27  
Water resistance of waterproof epoxyphenol fiber glass plastics

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Property	Nature of glass fabric treatment					Addition of ES additive to binder
	Lubricants			Sizing		
	Paraffin emulsion	652	752	AGM-9 product	AGM-3 product	
Water absorption, %:						
after 4 h boiling in water	0.39	0.29	0.31	0.33	0.36	0.36
after 240 days in water	0.32	0.24	0.25	0.27	0.31	0.30
Tensile strength, kgf/mm <sup>2</sup> :						
after 4 h boiling in water	$\frac{59}{92}$	$\frac{64}{99}$	$\frac{60}{97}$	$\frac{63.5}{100}$	$\frac{59.6}{96}$	$\frac{63.6}{98}$
after 240 days in water	$\frac{61}{96}$	$\frac{65}{100}$	$\frac{60.5}{98}$	$\frac{63}{99}$	$\frac{61}{99}$	$\frac{63.5}{98}$
Bending strength, kgf/mm <sup>2</sup> :						
after 4 h boiling in water	$\frac{51.5}{75}$	$\frac{67}{90}$	$\frac{66}{88}$	$\frac{67.5}{90}$	$\frac{61}{85}$	$\frac{60}{86}$
after 240 days in water	$\frac{55}{80}$	$\frac{69.5}{93}$	$\frac{71}{95}$	$\frac{69}{92}$	$\frac{61.5}{86}$	$\frac{60}{86}$
Compressive strength, kgf/mm <sup>2</sup> :						
after 4 h boiling in water	$\frac{30}{70}$	$\frac{40.4}{86}$	$\frac{40}{82}$	$\frac{37}{80}$	$\frac{33}{75}$	$\frac{33}{72}$
after 240 days in water	$\frac{31.4}{73}$	$\frac{40}{85}$	$\frac{43}{85}$	$\frac{38.5}{85}$	$\frac{33.5}{77}$	$\frac{36}{78}$
Remarks. 1. Water absorption was determined on specimens measuring 120 x 15 x 10 mm.						
2. Numerator - absolute values of strength in kgf/mm <sup>2</sup> ; denominator - percent of initial value.						





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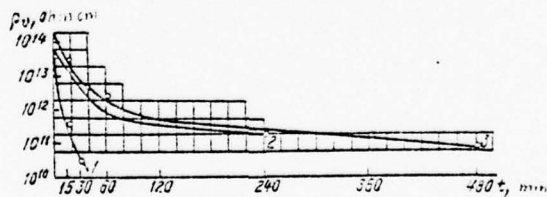
Fig. 2. Dielectric constant  $\epsilon$  of waterproofed epoxyphenol fiber glass plastics vs boiling time in water.

1 - glass fabric with lubricant - paraffin emulsion; 2 - glass fabric with lubricant 752; 3 - glass fabric treated with AGM-9 sizing agent.

Table 28

Long-term strength in pure bending of waterproofed epoxyphenol fiber glass plastics in air and water<sup>1, 2</sup>

Nature of glass fabric treatment	Medium	Long-time strength, kgf/mm <sup>2</sup>		
		1000 h base	100,000 h base	
Lubricant: paraffin emulsion	Air	45.8	40.9	
	Water	22.6	13.5	
	652	Air	51.0	44.7
		Water	42.3	30.5
Sizing agent: AGM-9	Air	48.5	40.5	
	Water	47.8	40.4	
	AGM-3	"	34.1	27.0
		ES product introduced into binder	"	31.3



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Fig. 3. Volume resistivity  $\rho_v$  of waterproofed epoxyphenol fiber glass plastics vs boiling time in water.

1 - glass fabric with lubricant - paraffin emulsion; 2 - glass fabric with lubricant 752; 3 - glass fabric treated with sizing agent 752.

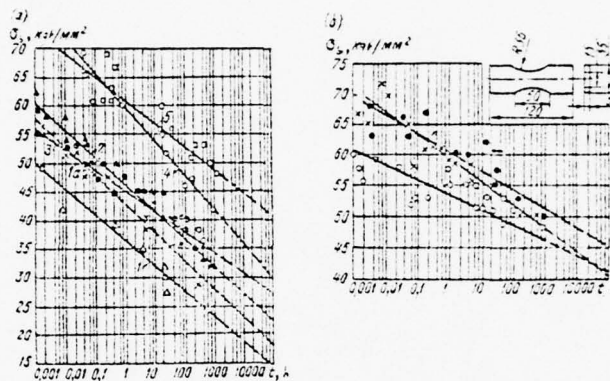


Fig. 4. Time dependence of strength of sized epoxyphenol fiber glass plastics in pure bending in water (a) and air (b).

1 - glass fabric with lubricant - paraffin emulsion; 1a - same, with isolated ends; 2 - heat-treated glass fabric; 1% ES added to binder; 3 - glass fabric treated with AGM-3 sizing agent; 4 - glass fabric treated with AGM-9 sizing agent; 5 - glass fabric with lubricant 652.

The tests performed clearly indicate the advantage of the introduction of the sizing agent into the lubricant over methods of thermochemical treatment of the glass fabric and particularly over the introduction of the sizing agent into the binder; this may be explained as follows. Lubricants 78, 80, 652 and 752 applied on the glass fiber leaving the spinneret are more strongly bonded to its surface chemically by hydrolysis-resistant siloxane bonds than the sizing agents, which are applied on the fiber surface with residues of the paraffin emulsion. Moreover, the amount of the lubricants on the fibers is 3 to 4 times greater than in other methods, promoting the formation of a uniform water-repellent film on the fibers. During the thermochemical treatment, the distribution of the sizing agents (type AGM-9) over the glass fabric is very irregular. Their concentration is particularly high at the points of contact of the fibers; however, a considerable portion of the glass fiber surface remains bare.

To obtain a comprehensive estimate of the behavior of waterproofed fiber glass plastics, the short-time and long-time strength, creep and dielectric properties were determined by testing the specimens in air. As expected, the influence of sizing on the dielectric properties and strength in ordinary short-time tests in air was relatively slight and independent of the sizing method. The influence of the time factor on the strength of fiber glass plastics in air, determined by the ratio of long-time strengths with a time base of  $10^5$  h to the short-time strength, also depended little on the sizing conditions.

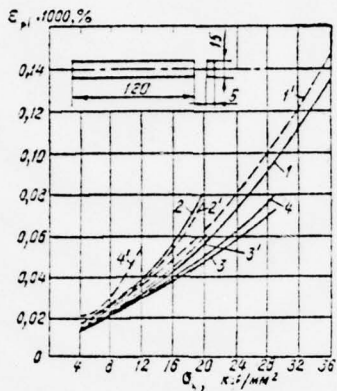


Fig. 5. Deformation developed after 1000 h of testing vs effective stress  $\sigma_b$  in bending for sized epoxyphenol fiber glass plastics.

1, 1' - glass fabric with lubricant 652; 2, 2' - glass fabric treated with AGM-3 sizing agent; 3, 3' - heat-treated glass fabric, 1% ES added to binder; 4, 4' - glass fabric with lubricant - paraffin emulsion;

- - - tests in water;

— tests in air.

Chapter 3

PROPERTIES OF EPOXY-GLASS PLASTICS

9. Mechanical Properties

The successful use of fiber glass plastics in primary structures depends on a detailed knowledge of the physicomaterial properties and their effective consideration in the design. /61

The mechanical properties and methods of testing of epoxy-glass plastics are described in detail below, and data are given on the static strength in short-time and long-time application of loads, fatigue strength, and shock resistance.

Static tensile tests. Tensile strength is determined chiefly by the strength and amount of the fiber glass reinforcing material, since during extension of the fiber glass plastic along the principal direction of reinforcement, mainly the fiber glass, which is an elastic body, is operating. At the same time, the binder is subjected to considerable deformations until the start of failure.

In tensile tests, the quantities determined are the ultimate strength, modulus of normal elasticity, percentage elongation and Poisson's ratio, and the nature of the functional relationship between the load acting on the specimen and the deformation it produces is also determined. In tests along the principal direction of reinforcement, the diagram of the functional relationship is usually represented in the form of a straight line (Fig. 6), i. e., it may be assumed with a sufficient degree of accuracy that the fiber glass plastic obeys Hooke's law in this case. However, as was shown by Smirnova, Sokolov, Ya. S. Sidoren et al.,<sup>51</sup> Hooke's law is obeyed only at loads amounting to 30-40% of the ultimate strength of the fiber glass plastic. In contrast to most metals, the stress-strain curve of a glass fabric resin laminate does not show a yield plateau, indicating brittle failure of the material. /62

Absolute values of the ultimate strength and elongation depend on the rate of relative deformation, size and shape of the specimens. The above values were obtained in tests at a loading rate of 20 mm/min on standard blades measuring 235 x 25 x 5 mm. As the rate of relative deformation increases, an increase in these values is observed.

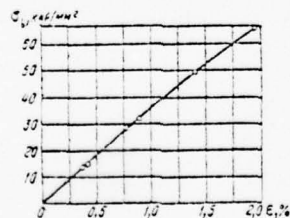


Fig. 6. Stress-strain curve of epoxyphenol fiber glass plastic (composite glass filler).

$\sigma_t$  - effective stress, kgf/mm<sup>2</sup>;

$\epsilon$  - strain, %.

A disadvantage of standard specimens is the presence of flutes, which are stress raisers and decrease the strength. In testing of specimens with unidirectional reinforcing fabrics, such a decrease in strength is appreciable, since failure takes place with shearing in the region of the flutes. Testing of unidirectional fabrics is usually carried out on rectangular specimens measuring 250 x 20 x 5 mm.

Static compression tests. The compressive strength is determined to a considerable extent by the adhesive and cohesive strength of the resin. The magnitude of this characteristic is particularly dependent on the quality of the binder, type of waterproofing adhesion treatment of the reinforcing fabric, and conditions of pressing of the fiber glass plastic.

Compression as well as tension tests involve the determination of ultimate strength, percentage elongation, elastic modulus, Poisson's ratio and nature of the stress-strain relation. From the start of loading to the instant of failure of the specimen, the compression curve of the fiber glass plastic closely follows Hooke's law (Fig. 7). The ultimate strength and percentage elongation in compression of a fiber glass plastic usually differ from the corresponding quantities in tensile tests. The elastic constants in compression, i. e., the elastic modulus and Poisson's ratio, are practically the same as the corresponding characteristics determined in tension.

The magnitude of the mechanical properties in compression as well as tension is affected by the deformation rate, scale factor, and shape of the specimens.

In compression tests, standard specimens (10 x 10 x 15 mm) fail prematurely owing to crumpling at the ends. New shapes of specimens have been proposed along with devices for compression testing of fiber glass plastics, whose failure takes place in the region of homogeneous stress.

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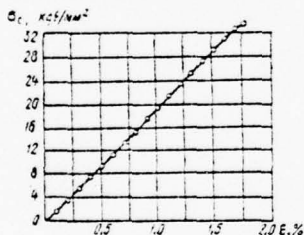


Fig. 7. Compression curve of epoxy-phenol fiber glass plastic (reinforcing fabric - ASTT(b)-S<sub>2</sub> glass fabric).

$\sigma_c$  - effective stresses, kgf/mm<sup>2</sup>;  
 $\epsilon$  - strain, %.

Table 29 shows the properties of fiber glass plastics in compression.

Static bending tests. Static bending tests involve the simultaneous presence in the fiber glass plastic of tensile, compressive and shearing stresses, and therefore, bending strength is a complex property of the fiber glass plastic, convenient for estimating the quality of the plastic and suitability of the material for service under certain specified conditions.

It should be kept in mind that the value of the cross-breaking strength<sup>3-4</sup> is somewhat high and surpasses the tensile and compressive strength indices. This is

Table 29  
Physicomechanical properties of epoxy-glass plastics in compression

Property	Orientation of reinforcing fabric	
	Warp	Weft
Compression strength, $\text{kgf/mm}^2$ : parallel to the layers	40 52	28 40
	50 65	40 52
perpendicular to the layers	2.9 3.0	2.1 2.2
	1.6 1.9	1.6 1.9
Elastic modulus, $10^3 \text{ kgf/mm}^2$		
Percentage elongation, %		
Poisson's ratio	0.18 0.2	-

Note. Numerator - values for epoxyphenol fiber glass plastics;  
denominator - epoxyamine plastics.

due to the fact that in fiber glass plastics, the distribution of stresses over the height of the specimen's cross section does not correspond to the linear law of stress distribution, whereas the formula for calculating this characteristic of the material,  $\sigma_b = M/W$  (M being the bending moment and W the cross sectional resistance moment), has been derived by assuming that this law is obeyed. The deflection  $\delta$  of fiber glass plastic specimens as a function of bending stress is shown in Fig. 8. Table 30 gives the physicomechanical properties of fiber glass plastics in static bending tests.

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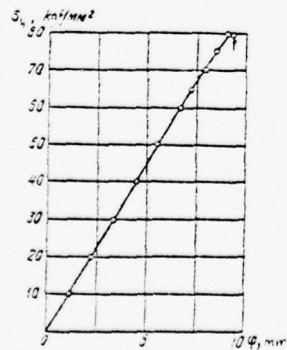


Fig. 8. Deflection  $\delta$  vs bending stress  $\sigma_b$  for epoxyphenol fiber glass plastic with composite glass filler.

Static shearing tests. Depending on the manner in which the forces are applied to the specimen, three types of shear are distinguished:  
 in the plane of the reinforcing fabric;  
 perpendicular to the plane of the sheet;  
 along the layers of the fiber glass plastic (interlaminar shear or shear along the layer).<sup>31</sup>

Table 30  
 Physicomechanical properties of epoxy-glass plastics in bending

Property	Orientation of reinforcing material	
	Warp	Weft
Ultimate strength, kgf/mm <sup>2</sup>	$\frac{70}{78}$	$\frac{56}{65}$
Elastic modulus, 10 <sup>3</sup> kgf/mm <sup>2</sup>	$\frac{2.8}{3.0}$	$\frac{2.0}{2.2}$
Percentage elongation, %	$\frac{2.0}{2.4}$	-
See note in Table 29.		

Shearing tests in the plane of the reinforcing fabric make it possible to determine the strength and elastic properties of the fiber glass plastic: ultimate strength of the material, elastic modulus, and maximum angle of torsion, and to plot the shearing stress-strain diagram. To provide for pure shear conditions, the specimens are tested in special hinged four-link chains which convert the tensile forces into shearing ones by stretching the specimens along one of the diagonals. The shearing stress-strain diagram of the fiber glass plastic is represented as a straight line in a rectangular coordinate system, where the shearing stresses are laid off along the ordinate, and the shearing angle is laid off along the abscissa (Fig. 9). The magnitude of the shearing strength depends on the angle formed by the warp of the glass fabric with the direction in which the shearing load is acting, and depends little on the type of binder.

/65

The shearing strength values for an epoxyphenol fiber glass plastic are given as an example (Table 31).

Shear perpendicular to the plane of the reinforcing fabric is determined by the resistance of the glass fiber to transverse forces; for epoxy-glass plastics, the shear strength is 13-15 kgf/mm<sup>2</sup>.

The strength of fiber glass plastics in interlaminar shear characterizes the adhesion strength of individual layers of reinforcing fabrics. It is determined by subjecting specimens measuring 60 x 10 x 15 mm to bending tests with a load concentrated at the center. The distance between the supports is 40 mm, which provides for failure of the specimens due to shearing stresses through their delamination along the neutral layer.

Table 32 gives data characterizing the interlaminar shear strength of epoxy fiber glass plastics of different compositions. The highest characteristics are those of fiber glass plastics based on a chlorine-containing tetrafunctional epoxy resin (EKHD).

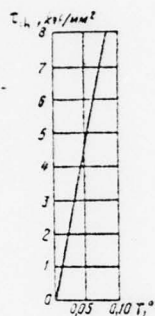


Fig. 9. Shearing stress-strain diagram of epoxyphenol fiber glass plastic (reinforcing material - ASTT(b)-S<sub>2</sub> glass fabric).

Table 31  
Physicomechanical properties of epoxyphenol fiber glass plastics in shear

Direction of reinforcement	Shear strength, kgf/mm <sup>2</sup>	Shear modulus, 10 <sup>3</sup> kgf/mm <sup>2</sup>	Maximum shear angle, °
Warp	19.0	1.4	0.43
Weft	11.5	1.3	-
At 45° angle	15.0	0.95	3.25

Creep and long-time static strength. Short-time tests of specimens do not reproduce the service conditions and do not provide an exhaustive characterization of the material. The performance of the fiber glass plastic may be estimated much more fully from the long-time strength and creep characteristics. /66

The method of testing for long-time strength consists in determining the stress at which the specimen fails at constant temperature at the end of a given time interval. When a constant load is applied for a long period of time, the strain of the material increases, i. e., creep is observed. The phenomenon of creep is closely related to the decrease in strength, and fiber glass plastics are characterized by the fact that creep of the material is already observed at room temperature and at relatively small loads, whereas in the case of metals, creep is chiefly observed at elevated temperatures or at loads close to the yield point. The creep process is subdivided into three periods: period of unsteady creep, period of steady creep during which the rate remains unchanged, and the period preceding the breakdown of the specimen, characterized by a sharp increase in creep rate.<sup>51</sup>

The tensile creep curves characteristic of an epoxyphenol glass laminate are shown in Fig. 10. It is evident from the figure that the duration of the first



period is short, about 50 h. The strain buildup rate of the steady creep process in the stress interval of 0.1-0.66 of the short-time strength is slow and does not affect the performance of the material.<sup>51</sup> The total creep strain in tension is 5-6% of the instantaneous strain corresponding to each stress level; in bending, it is slightly higher and equal to 8%.

Table 32  
Properties of epoxy-glass plastics in interlaminar shear

Resin	Curing Agent	Ultimate strength, kgf/mm <sup>2</sup>
Epoxydiane (ED-13)	Resol type phenol-formaldehyde resin	6.2
Same	Triethanolamine titanate	7.2
Purfurylresorcinol glycidol ether (UP-63)	" "	7.5
Diaminodichlorodiphenylmethane glycidol ether (EKHD)	" "	9.8
Same	Diaminodichlorodiphenylmethane	8.0
Aminophenol glycidol ether (UP-610)	Diaminodiphenyl sulfone	8.4

Curves representing instantaneous strain and strain developing toward the end of the tests versus effective tensile and bending stresses are shown in Figs. 11

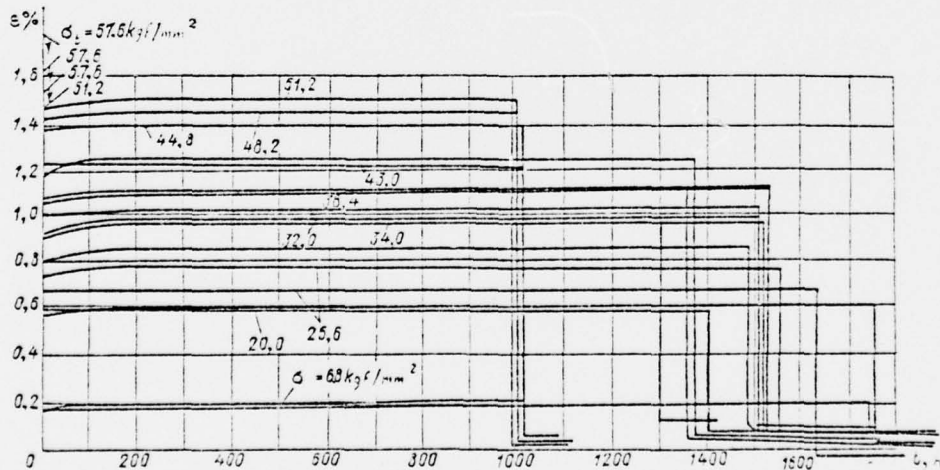


Fig. 10. Creep curves of epoxyphenol glass laminate with composite glass filler in tension.

and 12. Similar curves characterize other compositions of hot-pressed epoxy-glass plastics.

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Practically no residual strains are observed in hot-pressed fiber glass plastics; prolonged action of tensile stresses amounting to 0.1-0.6 of the short-time strength gives rise to residual strains that do not exceed 0.04%.

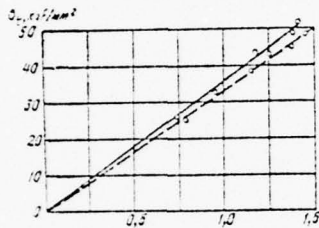


Fig. 11. Strain during short-time application of load,  $\epsilon$ , %, and strain developing toward the end of the tests vs effective stress  $\sigma_t$  in tension for epoxyphenol glass laminate with composite glass filler.

———— strain during short-time application of load;  
 - - - - strain accumulated after 1000 h under load.

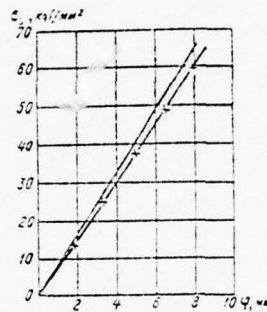


Fig. 12. Deflection during short-time application of load  $\delta$  and deflection accumulated by the end of the tests vs effective stress  $\sigma_b$  in bending.

———— deflection during short time application of load;  
 - - - X — deflection after 1000 h.

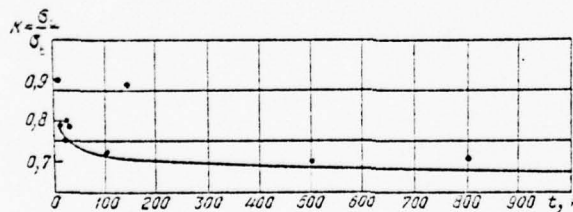


Fig. 13 Curve of long-time tensile strength of epoxyphenol glass laminate with composite glass filler.  
 $t$  - duration of tests, h;  $\sigma_s$  - effective tensile stress,  $\text{kgf}/\text{mm}^2$ ;  $\sigma_t$  - short-time tensile strength of glass plastic,  $\text{kgf}/\text{mm}^2$ .

The test results were used to plot long-time strength curves of materials in tension (Fig. 13) and to determine the long-time strength of fiber glass plastic. The value of the long-time strength is usually expressed in fractions of the corresponding short-time strength. For epoxy-glass plastics with different types of reinforcing material, the long-time strength in tension is 0.6-0.75, and in bending, 0.6-0.7 of the short-time strength.

Results of tests of epoxy-glass plastic specimens, performed to determine the long-time compression strength, are given in Table 33.

Table 33  
Long-time strength of fiber glass plastics

Resin	Curing Agent	Conventional long-time strength with a base of 1000 h
Epoxydiane (ED-13)	Triethanolamine titanate	$0.660\sigma_c$
Epoxycyanurate (ETsD-13)	Same	$0.687\sigma_c$
Epoxydiane (ED-13)	Phenol-formaldehyde resin	$0.660\sigma_c$

The values of conventional long-time compression strength with a base of 1000 h amount to 0.66-0.68 of the short-time strength for epoxy glass plastics based on various binders.

Static fatigue. Fiber glass plastics are characterized by sensitivity to a repeatedly applied static load of the same magnitude, i. e., so-called static fatigue of the material.

The conventional static fatigue limit of epoxy-glass plastics with a base of 1000 cycles amounts to 0.6-0.7 of the short-time strength. Moreover, thanks to the attractive elastic properties of the glass plastic almost no increase in deflection takes place under these conditions. Figure 14 shows characteristic curves representing the change in the deflection of specimens with increasing number of cycles of repeated static tension. Another confirmation of the attractive elastic properties of the material are the characteristic hysteresis curves, plotted after the first and the one-thousandth cycle of repeated static loading. The hysteresis loops practically coincide, with the unloading branch differing only slightly from the loading branch (Fig. 15). The residual strain accumulated by the end of the tests after one thousand cycles of stresses amounting to 0.6-0.7 of the short-time strength is of very small magnitude, on the order of 0.2-0.3 mm.

Figure 16 shows curves of static compressive fatigue for epoxy-glass plastics. /70  
The ultimate strength values of the glass plastics in repeated static compression based on 10,000 cycles amount to 0.66-0.72 of the short-time strength (Table 34).

Also of interest are certain data permitting an evaluation of the performance of a glass plastic under repeated loading conditions. Thus, for example, in repeated long-time bending, specimens of epoxyphenol plastic withstand a 7-tuple cycle

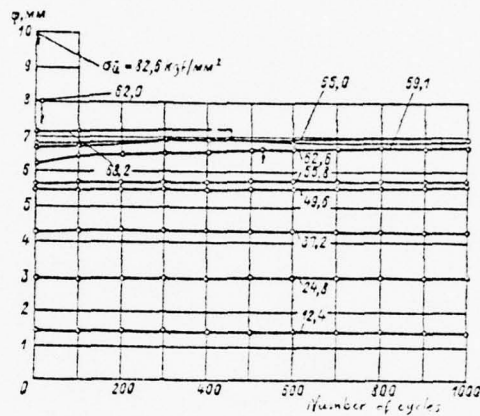
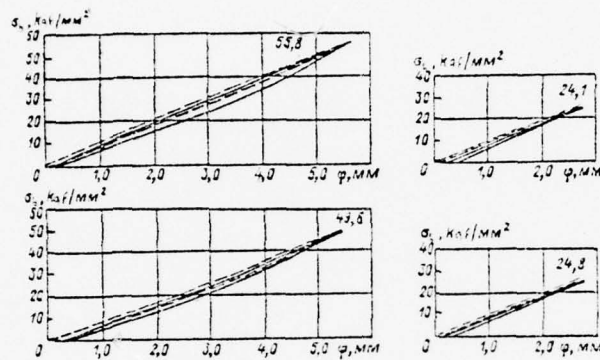


Fig. 14. Deflection  $\delta$  of specimens as a function of effective stress with increasing number of repeated static loading cycles for an epoxyphenol glass plastic with composite glass filler

Table 34  
Fatigue strength of fiber glass plastics

Resin	Curing Agent	Number of specimens	Correlation factor	Correlation equation	Measure of dissipation, $\text{kgf/mm}^2$	Limited fatigue strength based on 10,000 cycles
Epoxydiane (ED-13)	Triethanolamine titanate	28	-0.96	$R = 12 - 0.0026\sigma_c$	2.00	$0.68\sigma_c$
Epoxycyanurate (ETSD-13)	Same	17	-0.90	$R = 13.53 - 0.0026\sigma_c$	1.50	$0.69\sigma_c$
Epoxydiane (ED-13)	Phenol-formaldehyde resin	16	-0.85	$R = 12.45 - 0.0026\sigma_c$	1.98	$0.72\sigma_c$



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Fig. 15. Area of hysteresis loop as a function of the number of repeated static bending cycles for different values of maximum effective stresses.

$\sigma_b$  - effective stress,  $\text{kgf/mm}^2$ ;  $\phi$  - deflection, mm;

----- 1 - cycle - 1000 cycles.

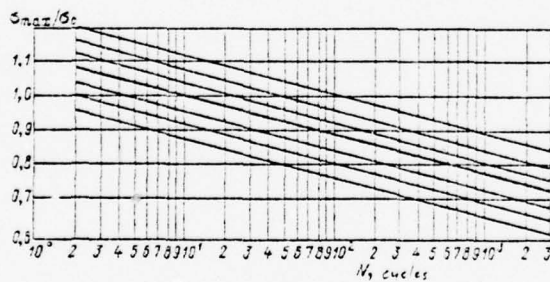


Fig. 16. Curves of static fatigue in repeated static compression of epoxyamine glass plastic based on satin-weave glass fabric.

$\sigma_{\max}$  - maximum stress of cycle,  $\text{kgf/mm}^2$ ;  $\sigma_c$  - long-time strength of glass plastic in compression,  $\text{kgf/mm}^2$ .

of 150 h of operation and 50 h of relaxation at stresses no greater than 0.7 of the short-time bending strength. In tests for repeated long-time tension, the specimens withstood two cycles (1000 h of operation, 50 h of relaxation) at stresses not exceeding 0.4 of the short-time strength. It is of interest that an increase in relaxation time from 50 to 500 h did not appreciably alter the experimental results.

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Dynamic fatigue strength. The resistance of a fiber glass plastic to fatigue failure is represented by a fatigue curve. As the stress amplitude decreases, this curve becomes increasingly more level, but in contrast to the curves of metals, has no asymptote. Thus, according to the data of Ref. 51, even with a test base up to  $10^{10}$  cycles, the horizontal portion of the fatigue curve is not reached. It is possible therefore to speak only of a conventional fatigue limit of fiber glass plastics, limited by a certain test base, i. e., by the highest stress withstood by the specimen without fatigue failure in the course of a predetermined number of cycles. The fatigue strength test base is usually assumed to be  $1 \times 10^6 - 5 \times 10^8$  cycles.

A qualitative criterion of the fatigue failure of a specimen is the appearance of a visible fatigue crack. However, specimens which have undergone tests and developed cracks have very high strength and other properties and it may therefore be assumed that the value of the conventional fatigue limit for a fiber glass plastic is somewhat low.

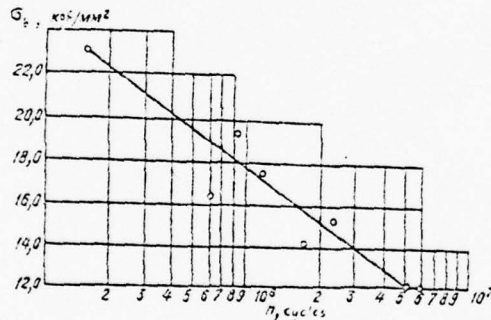


Fig. 17. Fatigue strength in cyclic bending vs number of cycles n for epoxyphenol glass plastic with composite glass filler.

According to the loading scheme, one distinguishes fatigue strength in pure bending, bending through an angle, and pulsating tension. A fiber glass plastic is characterized by a marked dependence of the ultimate strength on the frequency of load changes. The fatigue curves (Fig. 17) were plotted at a loading frequency of 900 oscillations per minute, the fatigue limit being  $0.20 \sigma_b$ . As the loading frequency decreases to 300 oscillations per minute, the fatigue strength increases to  $0.26 \sigma_b$ .

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A marked heating up of fiber glass plastic specimens, dependent on the oscillation frequency and amplitude, is observed in dynamic tests. The material of the specimen heats up because the fiber glass plastics have large hysteresis losses in comparison with metals. An increase in the frequency of load alternation or oscillation amplitude leads to a corresponding increase in the amount of heat evolved per unit time, whereas the heat transfer to the ambient medium changes insignificantly. As a result, the temperature of the specimen rises. Thus, at a frequency of 1000 oscillations per minute, the overheating of the specimen amounts to 50-75°C, and at 300 oscillations per minute, only 25-30°C.

An important feature of the dynamic properties of a material is the internal dissipation of energy (damping capacity), which along with the fatigue limit determines the strength of the part during its operation under near-resonance conditions. Resonance conditions are the most dangerous ones, since they frequently lead to ruptures and breakdowns at comparatively moderate work loads.

The damping capacity of a material is usually represented by the logarithmic decrement,<sup>40</sup> which is the rate of damping of free transverse oscillations of a cantilever specimen. As compared to metals, fiber glass plastics have more pronounced damping properties, which permit their successful application to operating conditions involving vibration loads and resonance phenomena.

The higher resistance of fiber glass plastic structures to vibration loads in comparison with an aluminum alloy may be illustrated by the following example.<sup>70</sup> One of the two stators of helicopter fans was made of aluminum alloy, and the other, of fiber glass plastic. Both stators were tested with a vibration load at a frequency equal to the natural frequency (for fiber glass plastic, 75 cycles/sec, and for the metal, 100 cycles/sec). The metal stator broke down after  $3.1 \times 10^5$  cycles, whereas the fiber glass plastic stator did not break down after  $15 \times 10^6$  cycles and exhibited a satisfactory damping capacity (the amplitude was 1/3 of the amplitude of the metal stator).

Shock resistance testing methods. At the present time, shock resistance is characterized by standards (GOST 4647-62) specifying tests of plastics for transverse impact bending with determination of impact strength, i. e., work done in breaking the specimen, referred to its cross sectional area. The quantity "a" obtained by this method is largely conventional and cannot be directly applied to the design of articles or their parts from the standpoint of impact loads. The value of impact strength is usually employed only for a comparative estimation of the quality of a material. /74

The behavior of a fiber glass plastic exposed to impact loads can be estimated more reliably by means of the characteristics of general and local strength proposed by L. N. Kositskiy.<sup>35</sup>

The overall strength of a fiber glass plastic under impact load is determined by means of specific work or specific energy capacity R, i. e., the work done in breaking the specimen, referred to a unit volume. The adoption of specific energy capacity as the basis for the characteristics of a material under impact loads makes it possible to describe the behavior of the material under impact bending, tension and compression. Table 35 gives the characteristics of overall strength under impact loads for an epoxyphenol glass plastic in comparison with the corresponding characteristics of certain other materials.

Table 35  
 Characteristics of overall strength under impact loads for certain structural materials<sup>1,2</sup>

Material	Strength, kgf cm/cm <sup>3</sup>		
	Bending	Tensile	Compressive
Epoxyphenol glass plastic:			
along warp fibers	65	78	61
along weft fibers	56	64	53
across warp fibers	49	-	-
across weft fibers	34	-	-
Structural steel	8.8-13	17	-
Stainless steel	76-90	110	-
Gray cast iron	4.8-6.0	9	-
Tin bronze	10.5-14.0	17	-
Wood laminate	26.5-30.0	35	-
Wood (pine)	8.0-12.0	15	-

The overall strength of epoxy-glass plastics under impact loads is higher than that of many structural materials in use at the present time, and is inferior only to that of alloy steels. However, the high overall strength of a glass fabric resin laminate cannot be utilized under repeated impact loads because the material is anisotropic and because of its appreciable energy capacity of local contact strain.

By energy of local contact strain is meant the energy of local failure of the material, associated with the formation of cracks and delaminations disrupting the continuity of the material. Even under single impacts, the fiber glass plastic becomes delaminated in some cases. In impacts lasting a long time, the concentration of strain energy in the weakest areas of bonding of the glass fabric creates favorable conditions for delamination. This phenomenon is typical of all laminates /75 and causes the relative energy of local strain  $r$ , corresponding to the beginning of general failure, to be much higher than in structural steels, cast iron, or bronze. Thus, for fiber glass plastics,  $r$  is 1700 and 4250 kgf cm cm<sup>3</sup> in impact bending along the fibers and across them, respectively, whereas for structural steel it is 110 kgf cm/cm<sup>3</sup> and for bronze, 200 kgf cm/cm<sup>3</sup>.

Of interest are the experimental data obtained by B. A. Antonov and A. A. Kognovitskiy, who studied the local strength of edges of articles. The data are comparative in nature and make it possible to compare the impact resistance of the edges of specimens of a glass fabric laminate and metals. If the impact resistance of the edge of a specimen of St. 3 steel 10 mm thick is taken as unity, the impact resistance of the edges of the other materials studied with the same thickness may be expressed in the following relative values: 0.82 - LMsZh-55-3-1 brass; 0.52 - 1Kh1N89T stainless steel; 0.42 - fiber glass plastic.

The impact resistance of the edges of fiber glass plastic specimens decreases even more under repeated impact, and after the third impact it drops by a factor of four as compared to the initial resistance, then remains practically unchanged. The insufficient impact resistance of the edges may be partially offset by increasing the relative thickness of the edge. Thus, while in the case of impact on a specimen 10 mm thick, the test leaves only a slight mark of the pendulum hammer



on the edge, and the surface layer of the material is not broken, in the case of impact with the same initial potential energy of the hammer on a specimen 5 mm thick, the edge splits.

#### 10. Aging of Fiber Glass Plastics

Aging is the term applied to the change in the properties of a fiber glass plastic with time under the influence of several factors: humidity, temperature, solar radiation. The decline in the mechanical and dielectric properties observed during aging is the result of complex chemical and physical processes taking place in the material. The chief purpose of the study of the influence of various factors on the properties of fiber glass plastics is to determine the service life of the products under various service conditions.

Effect of temperature on the properties of fiber glass plastics. Ship machine building products are used over a wide temperature range, from  $-40^{\circ}\text{C}$  to  $200^{\circ}\text{C}$ . The most severe conditions arise at elevated temperatures.

The ability of a material to perform at elevated temperatures is usually characterized by the Martens temperature, i. e., the temperature at which the deformation of the tested specimen under a bending load of  $50\text{ kgf/cm}^2$  is 6 mm. For epoxyphenol glass plastics, the Martens temperature is  $240-280^{\circ}\text{C}$ , and for epoxyamine glass plastics,  $180-220^{\circ}\text{C}$ . However, experience with the use of fiber glass plastics for articles operating at elevated temperatures has shown that this index is not sufficient in selecting the maximum working temperature for a specific article. A correct selection of the working temperature of a fiber glass plastic makes it necessary to know its strength at different temperatures, the glass transition temperature, and the degradation temperature of the binder.

The glass transition temperatures of the binders may be determined from the temperature dependence of the deformation or hardness of the polymer at constant load. As an example, Figs. 18 and 19 show thermomechanical curves of epoxyamine binders of different compositions.

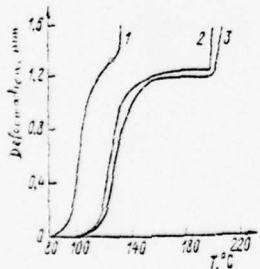


Fig. 18. Thermomechanical curves of epoxyamine binder based on ED-13 resin under different curing conditions.

1 -  $160^{\circ}\text{C}$ , 2 h; 2 -  $160^{\circ}\text{C}$ , 6 h;  
3 -  $160^{\circ}\text{C}$ , 12 h.

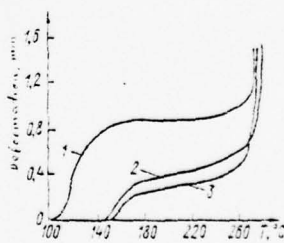


Fig. 19. Thermomechanical curves of epoxyamine binder based on EKbD resin under different curing conditions.

1 -  $160^{\circ}\text{C}$ , 2 h; 2 -  $160^{\circ}\text{C}$ , 6 h;  
3 -  $160^{\circ}\text{C}$ , 12 h.

The thermomechanical curves of epoxy binders show two distinct portions. The first portion corresponds to the vitreous state, characterized by small deformations, and the second portion, to a hyperelastic state with large reversible deformations. The temperature of transition of the vitreous to the hyperelastic state is termed the glass transition temperature of a polymer. In view of the fact that the transition from the hyperelastic to the vitreous state for epoxy binders is not clear-cut, the glass transition temperature is determined from the point of intersection of the tangents to the thermomechanical curve in the regions of the vitreous and hyperelastic states.

The glass transition temperature of a cured binder makes it possible to estimate the rigidity of the reticulate structure obtained and degree of curing, and is one of the most important characteristics of the binder. The glass transition temperature depends on the chemical structure of the epoxy resin, curing agent, and degree of curing. As a rule, cured polyfunctional epoxy resins have a higher glass transition temperature than bifunctional ones. For example, in curing with triethanolamine titanate, EKhd resin has a glass transition temperature of 153°C, EPOF resin, 155°C, and ED-13 bifunctional epoxydiane resin, 98°C. In curing with methyltetrahydrophthalic anhydride, ETs-K polyfunctional resin (triglycidyl isocyanurate) has a glass transition temperature of 300°C, and ED-20 bifunctional epoxydiane resin, 145°C.

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Table 36  
Physicomechanical properties of epoxyphenol glass plastic vs temperature

Property	In initial state	After 720-hour exposure to 200°C	In initial state, testing temperature 120°C
	Testing temperature 20°C		
Impact strength, kgf m/cm <sup>2</sup>	3.22	3.36	5.30
Strength, kgf/mm <sup>2</sup> :			
bending	42.30	46.40	9.43
compressive	51.10	62.66	41.60
Splitting resistance, kgf	412	316	274
Note. Reinforcing material - brand E fabric.			

The curing agent has a major effect on the glass transition temperature. In curing with anhydrides, aromatic amines or phenol resins, more heat-resistant compositions are obtained than in curing with tertiary amines.

With increasing degree of curing in long exposures to temperatures of 140-180°C, additional cross-linking of the binder takes place as a result of the interaction of secondary hydroxyls of the epoxy compound with epoxy groups or methylol hydroxyls (in curing with phenol-formaldehyde resin); at the same time, the glass transition temperature increases.

At operating temperatures below the glass transition temperature of the binder, fiber glass plastic articles retain relatively high strength characteristics (Table 36). At a service temperature above the glass transition temperature of the binder, the mobility of macromolecular segments increases, the intermolecular interaction

of the segments weakens, and deformations of the binder develop. These processes are inevitably associated with a marked decrease in strength and increase in creep of the fiber glass plastic.

The change in the strength of a fiber glass plastic as a function of temperature depends on the type of stressed state. /78

The effect of temperature on the strength of fiber glass plastics is apparently related not only to the loss of strength of the binder, but also to the change in the mechanism of transfer of forces in the system. In the case of appreciable shearing stresses, when the main load is borne by the binder, the decrease in strength is more appreciable than in the case of tension, when the main load is received by the reinforcing material. As the temperature increases, the tensile strength (homogeneous stressed state) changes much less than the bending strength (inhomogeneous stressed state). The bending strength decreases by a factor of 10-12, and the tensile strength, three-four. When fiber glass plastics are loaded at an angle to the warp, the effect of temperature on strength increases, since the working area of the polymer binder is enlarged. Poisson's ratio also increases with rising temperature. The process of decrease in strength is reversible, and the intermolecular interaction is restored after the temperature drops.

Thus, loaded articles of fiber glass plastic can serve for long periods of time only at temperatures below the glass transition temperature of the binder, and unloaded ones, above the glass transition temperature, but below the binder degradation temperature. The temperature at which degradation begins for epoxy-phenol binders is 250-280°C, and for epoxyamine binders, 190-210°C.

Above the degradation temperature of the binder, a decrease in the strength of the fiber glass plastic takes place which progresses rapidly and is irreversible. Thermal degradation starts with the detachment and decomposition of the epoxy groups, and involves the formation of gaseous products, aldehydes, and water. In addition, bonds between carbon atoms in aliphatic portions of the chains may be broken.

Above 300°C, decomposition of the glass fiber begins in the fiber glass plastic, involving the formation of not only longitudinal but also transverse cracks, which cause a decrease in the effective length of the fiber. After 200 h of aging at 400°C, the effective fiber length decreases so much that the fracture of the specimen after the bending test does not even have a fibrous structure, and the fiber is actually converted into a powdery filler.<sup>32</sup>

The service life of fiber glass plastic articles at temperatures above 300°C is determined by the time required for the temperature of the ambient medium to be reached throughout the glass, i. e., by the thickness and thermophysical properties of the article (Table 37). The action of a medium at 350-400°C for 1-2 min does not cause any appreciable decrease in strength. As the temperature increases further to 730°C, a specimen of epoxyphenol fiber glass laminate ignites spontaneously in 18 sec.

Fiber glass plastic articles are successfully used at low temperatures, from -40 to -60°C, where even a certain improvement in the properties of the fiber glass plastics is observed. Apparently, the rigidity and plastic strain resistance of the vitrified binder and the strength of the glass fiber increase at low temperatures. /79

Table 37  
Thermophysical properties of epoxyphenol glass plastics<sup>1,2</sup>

Testing temperature, °C	Coefficient of linear expansion $\alpha$ , °C <sup>-1</sup>	Coefficient of thermal conductivity $\lambda$ , W/(m K)	Thermal diffusivity $a$ , 10 <sup>-11</sup> m <sup>2</sup> /h	Specific heat capacity $c$ , kJ/(kg K)
20-100	$6.2 \times 10^{-5}$	0.32-0.39	7.5	0.90-1.2
100-200	-	0.36-0.40	6.8-7.1	1.15-1.3

Effect of atmospheric conditions on the properties of fiber glass plastics. When articles are used at atmospheric conditions, aging of fiber glass plastics takes place under the influence of such factors as solar radiation, abrupt temperature change, humidity, precipitation in the form of rain, snow and fog, etc.

The factor responsible for the most pronounced aging of fiber glass plastics is the ultraviolet portion of solar radiation (3000-4000 Å), which alters the supermolecular structure of the binder and accelerates the cracking of the surface layer and its mechanical shelling ("chalking"). An abrupt temperature change intensifies the processes of microcrack formation in the binder. By penetrating into the microcracks, moisture produces a splitting pressure which leads to a gradual increase in the surface of the defects. Finally, wind and precipitation remove individual binder particles from the surface, considerably accelerating the processes of erosion of the resin film on fiber glass plastic articles.

At the present time, the atmospheric stability of a fiber glass plastic is estimated by means of field tests and laboratory tests in artificial weather chambers using various techniques. The laboratory testing techniques involve an intensification of the aging process for the purpose of reducing the testing periods. In one such technique of accelerated aging, developed by the Institute of Metallo-polymer Systems, Academy of Sciences of the Belorussian SSR,<sup>3,3</sup> the specimens are subjected to the combined action of irradiation in the 3000-10,000 Å wavelength range at elevated and low temperatures, and variable humidity with thermal shocks from 55°C to -45°C.

The character of the structural changes and changes in mechanical properties in tests under laboratory conditions is identical to analogous changes under natural conditions. 400-600 h of accelerated tests correspond to 6-9 months of tests under tropical conditions or 15-18 months of tests under the conditions prevailing in Leningrad. /80

As a result of aging, the irradiated side of the specimens and articles made of fiber glass plastics shows a loss of surface luster and erosion of the surface layer of the binder in prolonged tests, revealing the structure of the glass fabric and causing an increase in the roughness of the surface. However, the depth of penetration of ultraviolet radiation does not exceed 0.5-0.6 mm; all the structural changes take place in the surface layer of the binder, and the atmospheric resistance of the fiber glass plastic is determined primarily by the properties of the binder.

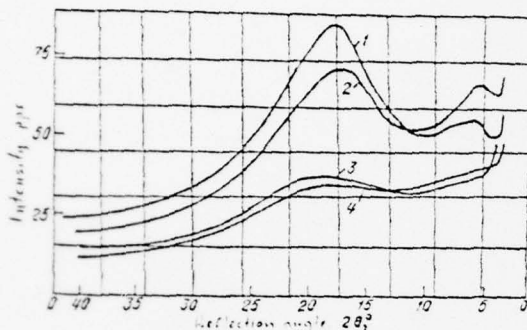


Fig. 20. X-ray powder pattern of epoxyamine binders.

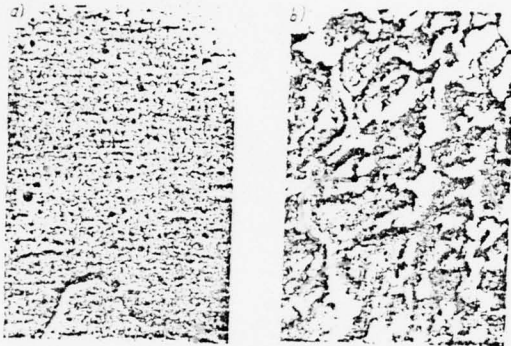
1, 2 - binder based on ED-13 resin before and after atmospheric aging;  
 3, 4 - binder based on EKHD resin before and after atmospheric aging.

On the irradiated side of binder specimens, in a study of their atmospheric resistance, the appearance of a dense network of surface cracks visible under the microscope is observed. Studies of the supermolecular structure of epoxy binders make it possible to explain the erosion of the surface layer of fiber glass plastic articles. The atmospheric aging process involves a redistribution of the relative arrangement of the binder macromolecules and disruption of the previously existing short-range order in their arrangement (Fig. 20).

Solar radiation causes a change in the globular structure of epoxy binders and a peculiar "enlargement" of elements of the supermolecular structure. Microcracks appear at the boundary between these elements. The bonding between individual enlarged structural elements is substantially weakened. Changes in the globular structure are observed with the aid of an UEMV-100 electron microscope at a magnification of 3000-14,000 (Fig. 21).

The formation of an extensive microcrack network under the influence of solar radiation is particularly manifest when one observes a low-temperature fracture of the surface layer of the specimens before and after atmospheric aging under an MIM-8 microscope in reflected light. /82

Before atmospheric aging, the surface of the low-temperature fracture of the specimens has a peculiar "banded" structure characteristic of glassy polymers. After atmospheric aging, the surface of the fracture has a "reticulate" structure. The observed structure is formed by the intersection of the front of the primary crack (during fracture) with the front of secondary cracks formed under the influence of solar radiation. When the distribution of microcracks is relatively uniform, a reticulate structure with rectangular or more intricate-shaped cells is formed (Fig. 22).



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Fig. 21. Supermolecular structure of cured epoxyamine binder based on ED-V epoxydiane resin in an electron microscope at a magnification of 8000: a - in the initial state; b - after four months' exposure to natural atmospheric conditions.

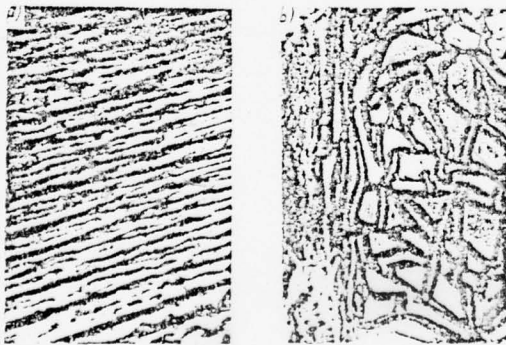


Fig. 22. Fracture surface of specimen of cured epoxyamine binder based on ED-13 epoxydiane resin under a microscope at a magnification of 250 in reflected light: a - in the initial state; b - after 500-h exposure in an artificial weather chamber.

After 400 h of exposure under laboratory conditions, the network of surface cracks becomes so extensive that the mechanical strain causes free particles to become detached from the surface of the specimens, i. e., chalking takes place. The mass of binder specimens initially increases somewhat as a result of moisture absorption, then decreases because of the chalking process (Fig. 23).

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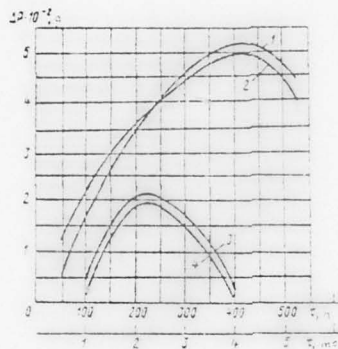


Fig. 23. Effect of atmospheric aging on the mass of specimens  $\Delta p$  of cured epoxyamine binders.

1, 2 - atmospheric aging in an artificial weather chamber ( $\tau$ , h); 3, 4 - atmospheric aging under natural conditions ( $\tau$ , months); 1, 3 - binder based on EXhD resin; 2, 4 - binder based on ED-13 resin.

On the basis of existing data, one can postulate that under the influence of solar radiation, oxidative degradation and secondary cross-linking take place in the surface layer of the binder. The degradation creates free spaces due to the volatilization of gaseous products. It promotes the disruption of short-range order in the arrangement of the macromolecules, formation of a secondary supermolecular structure made up of enlarged elements, and appearance of micro-cracks at the interface of these elements.

The mechanical action of wind, raindrops and snow causes free particles to detach themselves from the surface, resulting in surface erosion of the binders.

One of the ways of slowing down the erosion of the surface layer is to introduce photo- and thermostabilizers into the composition of the binders of fiber glass plastics. Their action is based on their strong absorption of ultraviolet light and inertness to thermal and photodegradation. Such compounds, which absorb the entire range of ultraviolet light, include a powdery filler - diffusion gas black. It has been found that the effectiveness of carbon black as a stabilizer increases with the introduction of certain polymeric sulfur-containing compounds: thioethers, thiols, disulfides. Into the binder of the shaping layers of stabilized

/83

fiber glass plastics are introduced 5% of DC-100 gas black and 0.5% of thiuram disulfide (the percentage is calculated from the mass of the resin).

In the presence of surface erosion of articles in the course of atmospheric aging and an appreciable increase in roughness, it is desirable to apply a protective organic coating on the articles. EP-525 epoxy paint, KhV-113 perchloro-vinyl paint, etc., are recommended as atmosphere- and water-resistant paints. Before the articles are painted, they should first be degreased.

If the protective organic coating is periodically renewed, the articles can be used under atmospheric conditions for long periods of time. The strength characteristics of fiber glass plastic specimens change insignificantly during exposure to atmospheric conditions (Table 33).

Table 33  
Strength limits,  $\text{kgf/mm}^2$ , in compression of epoxyamine glass plastics after exposure to atmospheric conditions

Resin	Months			
	0	12	24	36
ED-13 epoxydiane	55.0	52.0	51.2	49.5
ETsD-13 epoxycyanurate	58.0	54.1	52.6	53.1
UP-63 epoxyresorcinol	57.5	53.8	51.4	52.1

Effect of water on the properties of fiber glass plastics. Establishing the nature of the change in the properties of a fiber glass plastic due to the action of water is of major practical importance in determining the substantiated reserve strength factors in the design of articles.

The water resistance of materials is estimated from the values of water absorption, change in mechanical characteristics after exposure to water, and diffusion (moisture) constants.

The water absorption, i. e., moisture content per unit mass, is determined by weighing the specimens after certain periods of exposure to water. The kinetics of the water absorption process is usually described in the form of sorption curves, which asymptotically approach the maximum value of equilibrium water absorption.

The change in mechanical properties is determined after the specimens remain in water under laboratory and natural conditions (on underwater stands and in different climatic zones). /84

The water absorption kinetics and change in properties in water depend on the dimensions of the specimens being tested. Absolute characteristics independent of the dimensions of the specimens are the diffusion constants (permeability coefficient, diffusion coefficient, solubility coefficient). They make it possible to calculate the times of water filtration through fiber glass plastics of any thicknesses and to compare different materials with one another.

The permeability coefficient  $P$ ,  $\text{g}/(\text{cm Torr h})$ , quantitatively characterizes the passage of water vapor through the material; the diffusion coefficient  $D$ ,  $\text{cm}^2/\text{h}$ ,



characterizes the rate of filtration; the solubility coefficient  $h$ ,  $g/(cm^3 \text{ Torr})$ , characterizes the dissolution of water in the material.<sup>3</sup>

The diffusion constants of fiber glass plastics are determined in two ways: by coulometry and by sorption.<sup>3</sup> In the coulometric method, the tested specimen is placed in a chamber where a given water vapor pressure is established on one side, and a vacuum of  $10^{-3}$ - $10^{-7}$  Torr is produced on the other side.

The moisture constants are calculated from Berrer's formulas:<sup>11</sup>

$$D = \frac{d^2}{\theta^2}; \quad (5)$$

$$P = \frac{Qd}{S\Delta p}; \quad (6)$$

$$h = \frac{P}{D}. \quad (7)$$

where  $d$  is the thickness of the specimen, cm;  
 $\theta$  is the time lag (before the appearance of moisture), h;  
 $Q$  is the amount of moisture which has passed through the specimen in a given time interval  $t$ , h;  
 $S$  is the area of the specimen,  $cm^2$ ;  
 $\Delta p$  is the pressure difference, Torr.

In the sorption method, the specimens are placed in water, and equilibrium water absorption is determined.

The diffusion coefficient is calculated from a formula obtained from Fick's equation<sup>11, 43</sup>

$$D = \frac{d^2}{4t^2} \frac{\Delta \ln(Q_\infty - Q)}{\Delta t}, \quad (8)$$

where  $d$  is the thickness of the specimen, cm;  
 $Q$  is the amount of moisture absorbed by the specimen during a certain time interval  $\Delta t$ , g;  
 $Q_\infty$  is the amount of moisture absorbed by the specimen in a state close to equilibrium, g. /85

The permeability coefficient  $P$  is determined from formula (7), and the solubility coefficient is

$$h = \frac{Q_\infty}{vp}, \quad (9)$$

where  $p$  is the partial vapor pressure, Torr, at specified temperature and pressure;  
 $v$  is the volume of the specimen,  $cm^3$ .

The water resistance of fiber glass plastics is determined by many factors: thickness of protective film of binder, composition of binder, composition of glass, structure of reinforcing material and method of its waterproofing treatment, and technology of fabrication.

The influence of the binder during the diffusion is determined by its water permeability and the decrease in strength after exposure to moisture. The epoxy binders used in the production of articles from hot-pressed fiber glass plastics

are relatively water-resistant; their diffusion coefficients are  $(1.3-4.2) \times 10^{-6}$   $\text{cm}^2/\text{h}$  and are at the level of the most water-resistant polymers. For example, the diffusion coefficient of polypropylene is  $2 \times 10^{-6}$   $\text{cm}^2/\text{h}$ .

The diffusion coefficient of the binder correlates with the degree of curing and functionality of its components. Thus, the diffusion coefficient of a binder based on the tetrafunctional resin EKHD is 3.5-4 times smaller than the diffusion coefficient of the binder based on the bifunctional epoxy resin ED-13. Increasing the curing time of epoxy binders from 2 to 15 h causes a certain deceleration of the diffusion process (Table 39).

The solubility coefficients of binders are determined primarily by the content of polar groups in the cured polymer. Owing to the fact that practically all epoxy binders have a certain number of polar groups (hydroxyls), the magnitude of their solubility coefficient and of the associated equilibrium water absorption considerably exceeds the corresponding characteristics of such nonpolar polymers as polyolefins and fluoroplastics. This is confirmed by a comparative analysis of such binders as epoxyphenol and epoxyamine ones. The latter, because of the presence of free hydroxyls in the cured structure, are inferior to epoxyphenol ones in water resistance, and as the content of triethanolamine titanate rises, water absorption increases from 0.18 (at 10% triethanolamine titanate) to 1.5% (at 20% triethanolamine titanate in the composition).

The introduction of plasticizers such as aliphatic hydroxyl-containing epoxy resins DEG-1, DEG-Zh, etc. into the composition of epoxy composites also leads to a decline in water resistance. In this case as well, as their relative content rises, water absorption increases and the strength decreases (Fig. 24, Table 40). The polarity of the nitrile groups entering into the composition of epoxycyanurate resin and of the hydroxyls in the composition of UP-63 epoxyresorcinol resin explains the reduced water resistance of binders and fiber glass plastics based on them in comparison with binders and fiber glass plastics based on type ED-13 epoxydiane resins (Fig. 25). The moisture which has passed through the film of binder to the glass-binder interface disrupts the adhesion bonds between them.

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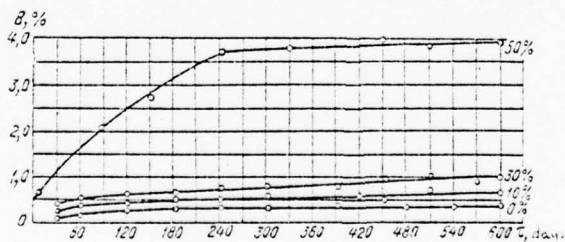


Fig. 24. Water absorption B of epoxyphenol glass plastics with different contents of DEG-1 plasticizer vs duration  $\tau$  of exposure to water. Numerical values given in the figure represent the plasticizer content (%).

The change in adhesion strength of the binder after prolonged exposure to water is shown in Figs. 26 and 27. The decrease in adhesion strength in accelerated tests is as high as 30-35%. Under actual conditions, this value is much lower, but the tests performed show that the main decrease in the strength of the fiber glass plastic in water is determined by the rupture of the adhesion bonds between glass and binder.

When the waterproofing adhesive lubricants 752, 652, 78 and 80 are used, the process slows down. Sorption curves of sized fiber glass plastics are shown in Fig. 28. The processes of moisture diffusion through the binder and along the glass-binder interface are reversible, and after the removal of moisture, the strength of the fiber glass plastic is restored.

The decrease in the strength of the fiber glass plastic also takes place as a result of the decrease in the strength of the glass fiber, when water penetrates through the lubricant film. The decrease in strength is specific precisely for glass fibers, whereas for other types of natural and synthetic fibers (cotton, capron, etc.) the strength in the moist state increases somewhat. The decrease in the strength of glass fiber under the influence of moisture is explained by an adsorption effect and a process of chemical breakdown. While the adsorption effect is reversible, the chemical attack of the glass fiber is irreversible.

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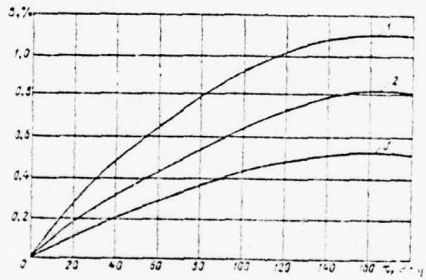
Table 39  
Diffusion coefficients of epoxyamine binders,  $10^6 \text{ cm}^2/\text{h}$

Resin	Curing time, h	Temperature, °C	Pressure, 1 kgf/cm <sup>2</sup>	Increased pressure
ED-13 epoxydiane	2	20	4.5	3.9
		40	7.1	6.9
		60	11.2	17
		80	16.4	56
	15	20	4.2	3.6
		40	6.0	6.3
		60	10.2	16.0
		80	14.4	46.9
EKhd epoxy	2	20	1.3	1.1
		40	3.8	3.6
		60	5.2	8.1
		80	15.0	23
	15	20	1.1	1.0
		40	2.8	2.4
		60	5.1	7.6
		80	13.2	21

The extent to which the strength of glass fiber decreases depends considerably on its chemical composition. With decreasing amount of alkalis in the composition of the glass, its water resistance increases. An increase in water resistance also

Table 40  
Effect of the content of DEG-1 aliphatic resin on the water resistance of epoxy-phenol glass plastic

Content of DEG-1, %	Bending strength, kgf/mm <sup>2</sup>	Bending strength after 2 years of exposure to water, kgf/mm <sup>2</sup>	Loss of strength after 2 years of exposure to water, %
0	69.0	55.0	22
10	71.0	50.0	30
20	71.0	39.0	45
50	50.0	10.0	80



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Fig. 25. Water absorption of specimens of epoxyamine glass plastics 1 mm thick (at atmospheric pressure) vs duration  $\tau$  of exposure to water.

1 - based on ED-13 resin; 2 - based on UP-63 resin; 3 - based on ETsD-13 resin.

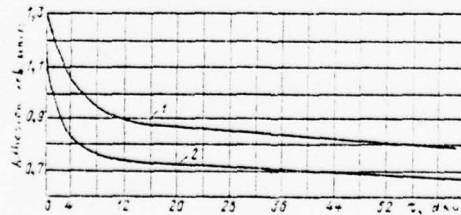


Fig. 26. Effect of prolonged exposure to water on the adhesion of cured epoxyamine binders based on ED-13 and EKd epoxy resins (curing for 2 h at 160°C).

1 - EKd resin; 2 - ED-13 resin

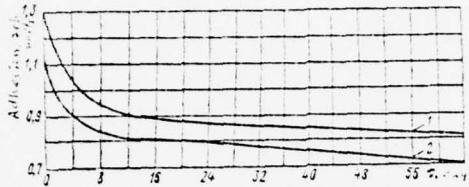
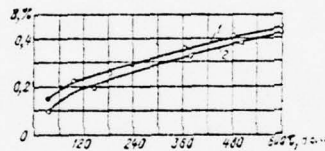


Fig. 27. Effect of prolonged exposure to water on the adhesion of cured epoxyamine binder based on EKHD resin.

1 - curing for 2 h at 160°C; 2 - curing for 6 h at 160°C.



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Fig. 28. Water absorption of epoxyphenol glass plastics vs duration  $\tau$  of exposure to water for specimens with different lubricants.

1 - glass fabric with paraffin emulsion lubricant; 2 - glass fabric with lubricant 652.

results from the introduction of such oxides as cuprous and titanium oxides into the glass composition.

Figure 29 shows the properties of epoxyphenol glass plastics based on aluminoborosilicate, titanium-containing and copper-containing glass. The highest water resistance is exhibited by glass plastics based on glass fiber containing cuprous oxide.

The hygroscopicity of the threads is 5-10 times greater than that of the monofilament because of additional sorption in the gaps between the fibers, and it increases from untwisted to twisted threads. The hygroscopicity of glass fabrics depends on the weave type. Other things being equal, the least hygroscopicity is exhibited by cord glass fabrics from untwisted threads. This is clearly illustrated by data on the sorption of fiber glass plastics based on satin and cord glass fabrics (Table 41).

Naturally, moisture diffusion processes are greatly affected by the quality of the glass plastic and the presence of cavities and microdefects therein, which are determined by the technological conditions of fabrication. Thus, at

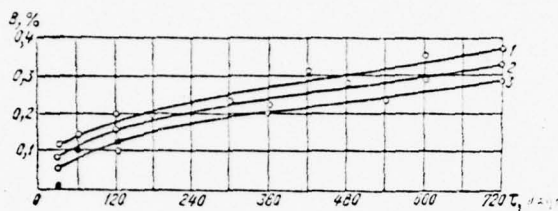


Fig. 29. Water absorption  $B$  of epoxyphenol glass plastics based on glass fibers of different compositions vs duration  $\tau$  of exposure to water.

1 - aluminoborosilicate glass; 2 - titanium-containing glass;  
3 - copper-containing glass.

specific pressures from 1 to 10 kgf/cm<sup>2</sup>, the porosity in the fiber glass plastic is 10-11%, and at a pressure above 20 kgf/cm<sup>2</sup>, the porosity is 2.5-3.0%. With increasing porosity, the water absorption and rate of diffusion in the fiber glass plastic increase correspondingly (Fig. 30). At a porosity above 4%, water absorption and diffusion rate increase sharply because, along with activated diffusion, which has a slow rate, the most active process of capillary filtration begins. /90

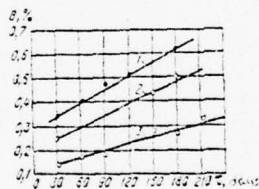


Fig. 30. Water absorption  $B$  of specimens of epoxyphenol glass plastic pressed at different specific pressures.

1 - 1 kgf/cm<sup>2</sup>; 2 - 5 kgf/cm<sup>2</sup>;  
3 - 50 kgf/cm<sup>2</sup>.

This phenomenon accounts for the high water resistance of fiber glass plastics fabricated by pressing at high specific pressures in comparison with those fabricated by other methods (winding, vacuum compression molding, etc.), despite the analogous composition of the binding, sizing and reinforcing materials employed. The most dangerous process of penetration of water molecules through the capillaries and pores in hot-pressed fiber glass plastics is minimized. The rate of water diffusion through a hot-pressed fiber glass plastic is actually determined by the rate of activated water diffusion through the film of binder. The diffusion coefficients of hot-pressed epoxy-glass plastics are  $(1.1-2) \times 10^{-6}$  cm<sup>2</sup>/h, whereas they are  $10^{-3}-10^{-4}$  cm<sup>2</sup>/h for epoxy-glass plastics made with the same binders by the methods of winding and vacuum and contact molding, the porosity of which is three to four times that of hot-pressed glass plastics.

Table 41  
Effect of glass fabric weave type on the water resistance of epoxyphenol glass plastic

Glass Fabric	Bending strength, kgf/mm <sup>2</sup>		
	After boiling for 4 h	After exposure to water, days	
		90	365
Cord T-25	$\frac{92.0}{94}$	$\frac{97.0}{99}$	$\frac{92.0}{94}$
Satin ASTT(b)-S <sub>2</sub>	$\frac{56.7}{86}$	$\frac{64.0}{93}$	$\frac{62.0}{90}$

Remarks. 1. The properties are given for specimens 10 mm thick obtained by mechanical treatment of epoxyphenol glass plastic based on glass fabric with lubricant 652.  
2. Numerator indicates absolute value of strength; numerator gives percentage of initial value.

The rate of diffusion processes increases with temperature, while the water vapor pressure gradient increases exponentially. For example, as the water temperature rises to 80°C, the diffusion coefficient of epoxyamine glass plastic based on ED-13 epoxy resin increases from  $1.9 \times 10^{-6}$  cm<sup>2</sup>/h to  $12.6 \times 10^{-6}$  cm<sup>2</sup>/h (Table 42). The linear relation  $\ln D - \frac{1}{T}$ , where D is the diffusion coefficient at a given temperature, cm<sup>2</sup>/h, and T is the absolute temperature, K, holds for epoxy binders and glass plastics in the 20-80°C range.

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This linear relation makes it possible to state that epoxy binders and glass plastics at a hydrostatic pressure of 1 kgf/cm<sup>2</sup> obey the Arrhenius equation

$$D = D_0 e^{-\frac{E_D}{RT}} \quad (10)$$

where

$$E_D = \frac{RT_1 T_2}{\Delta T_{1,2}} \ln \frac{D_1}{D_2} \quad (11)$$

D<sub>0</sub>, D<sub>1</sub>, D<sub>2</sub> are the diffusion coefficients of water in the polymers at standard conditions and temperatures T<sub>1</sub> and T<sub>2</sub>, respectively;

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ΔT<sub>1,2</sub> is the difference in temperatures at which the diffusion coefficients were determined;

R is the universal gas constant;

E<sub>D</sub> is the activation energy of the diffusion process.

By activation energy is meant the energy necessary to separate the polymer chains from each other and create a "free volume" into which penetrates the diffusing substance - water. The activation energy for epoxy binders at a hydrostatic pressure of 1 kgf/cm<sup>2</sup> is 6-7 kcal/mole.<sup>10</sup>

Table 42  
Effect of hydrostatic pressure, temperature and curing time on the diffusion coefficient of water in fiber glass plastics.

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Fiber glass plastic	Curing time, h	Temperature, °C	D, 10 <sup>9</sup> cm <sup>2</sup> /h	
			pressure, 1 kgf/cm <sup>2</sup>	elevated pressure
Epoxyamine plastic based on ED-13 resin	2	20	1.9	1.4
		40	3.7	2.9
		60	7.0	8.8
		80	12.6	68.6
	15	20	1.7	1.2
		40	2.6	2.3
		60	5.5	7.1
		80	10.6	47.0
Epoxyamine plastic based on EKHD resin	2	20	1.1	1.0
		40	1.9	1.8
		60	4.1	5.5
		80	7.5	19.0
	15	20	1.0	0.9
		40	1.8	1.6
		60	3.8	5.2
		80	6.4	11.9

Studies of the diffusion of water through binders and fiber glass plastics at different temperatures show that it is most desirable to use epoxy glass plastics for vehicles employed in water at temperatures not above 40-50°C. Even at temperatures of 60 and 80°C, the diffusion of water is sharply accelerated, and is associated, though to a very slight degree, with the washing out of the low-molecular fraction of the binder and leaching out of the glass fiber.

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The boiling of fiber glass plastic specimens subjected to the combined action of temperature and boiling water, involves several processes simultaneously: diffusion of moisture at an increased rate, softening and partial washing out of the low molecular fraction of binder, and intensive leaching out of glass fiber. If the diffusion process is associated with an increase in the mass of the specimens, the latter two processes lead to a loss of mass. This is also confirmed by data obtained by the authors in a study of the porosity of a fiber glass plastic. The porosity was determined from the difference between the calculated and experimental densities using the formula

$$\frac{a}{\rho_{res}} + \frac{b}{\rho_{st}} = \frac{100 - c}{\rho_{st}} \quad (12)$$



where  $a$  is the resin content, %;  
 $b$  is the glass content, %;  
 $c$  is the content of air inclusions, %;  
 $\rho_{res}$ ,  $\rho_{gl}$ ,  $\rho_{pl}$  are the densities of the resin, glass, and fiber glass plastic,  
 respectively, in  $g/cm^3$ .

The porosity of the fiber glass plastic remains practically unchanged during exposure to water at 20°C for up to 720 days. After boiling for 4 h, the porosity of the glass plastic increases to 5-7%. In view of the above, the magnitude of the water absorption and diffusion coefficient, determined during boiling, cannot be used to estimate the true water resistance of the fiber glass plastic. The magnitude of water absorption obtained during boiling is low (Table 43).

At 20°C, hydrostatic pressure slows down the diffusion process and has little effect on the magnitude of equilibrium water absorption of the binders and fiber glass plastics. As the hydrostatic pressure increases, the diffusion coefficient /93

Table 43  
 Properties of fiber glass plastics after prolonged exposure to water and boiling

Binder	Water absorption, %		Bending strength, $kgf/mm^2$	
	After 240 days of exposure to water	After 4 h of boiling	After 240 days of exposure to water	After 4 h of boiling
Epoxyphenol binder based on ED-13 resin	0.29	0.24	$\frac{67.0}{95.0}$	$\frac{64.0}{90.0}$
Epoxyamine binder based on ED-13 resin	0.33	0.28	$\frac{73.6}{92.0}$	$\frac{64.0}{80.0}$
Epoxyamine binder based on ETS-13 resin	0.57	0.45	$\frac{75.0}{89.0}$	$\frac{63.0}{75.0}$
Epoxyamine binder based on UP-63 resin	0.37	0.32	$\frac{74.7}{90.0}$	$\frac{64.0}{77.0}$

Remarks. 1. Properties given for specimens 10 mm thick without mechanical treatment.  
 2. Numerator indicates absolute value of strength; denominator gives percentage of initial value.

decreases by a factor of 1.2-2. At the same time, raising the pressure by 100  $kgf/cm^2$  has the same effect as lowering the water temperature by 3°C. The water diffusion rate in the presence of increasing hydrostatic pressure is affected by two factors with opposite effects. On the one hand, as the pressure increases, the

polymer material is compressed, the cohesive forces between individual segments of the polar chains increase, and additional obstacles to the motion of the diffusing water molecules arise. On the other hand, the water vapor pressure gradient increases, promoting an increase in the diffusion rate and in the swelling of polymers. For the majority of known polymers at 20°C, the effect of compression caused by pressure surpasses the increase in volume (swelling) caused by the increase in water vapor pressure. Therefore, at normal temperature, as the hydrostatic pressure increases, the diffusion process slows down.

As the water temperature is raised to 40°C, the nature of the effect of hydrostatic pressure on the diffusion process remains the same, but is less pronounced. In the 40-50°C range, the pressure begins to accelerate the diffusion. The pressure has its greatest effect at 60-80°C. Thus, the simultaneous action of temperature and hydrostatic pressure leads to not only quantitative but also qualitative changes in the process of water diffusion through polymeric materials. Diffusion in this case has a more complex, nonlinear character. /94

The diffusion coefficient ceases to be a constant of the material - it depends on the concentration of the diffusing substance (water) and swelling time of the polymeric material. The swelling process itself under the combined action of 60-80°C temperatures and increased hydrostatic pressures goes through several successive stages. Prolonged exposure of the specimens to these conditions leads to a "loosening" of the structure of the material and to a nonlinear sorption of moisture. The character of the change in the mechanical properties of fiber glass plastics in water is illustrated by the data of Table 44.

Table 44  
Change in the properties of epoxyamine glass plastics exposed to seawater.

Glass plastic	Hydrostatic pressure, kgf/cm <sup>2</sup>	Compressive strength, kgf/mm <sup>2</sup>							
		Duration of exposure to water, days							
		0	30	60	90	120	180	270	400
Epoxyamine glass plastic based on ED-13 resin	1	55	55	54	54	52	52	49	48
	Increased	54.5	55	54	53.5	52	52	48.5	48.5
Epoxyamine glass plastic based on EKHD resin	1	69	68	68	64	63	61	60	59
	Increased	68.5	68	69	63	62.5	62	60	60

After one year of exposure to water at 20°C, the strength of fiber glass plastic specimens 5 mm thick decreases by not more than 15%. The process of decline in strength characteristics due to exposure to water is reversible. After the specimens are kept in air, the mechanical strength of the fiber glass plastics is restored, attesting to the absence of their chemical breakdown at 20-40°C. The decrease in strength due to exposure to water (at 20°C) is independent of hydrostatic pressure.

Exposure of fiber glass plastic specimens to hot water (at 70°C) leads to a sharp decrease of their strength even at normal hydrostatic pressure; this is particularly characteristic of epoxyamine glass plastics. It is noteworthy that whereas at 20°C epoxyphenol glass plastics surpass epoxyamine ones only slightly in water resistance, this difference is multiplied severalfold at 80°C. Thus, after 100 days of exposure to water at 70°C, the bending strength of epoxyphenol glass plastics decreases by 20-25%, and that of epoxyamine plastics, by 40-45%. The strength of such specimens after their exposure to air is not completely restored.

Even more abrupt is the decrease in the strength of fiber glass plastic specimens during boiling. After only 4 h of boiling, the bending strength of epoxyphenol glass plastic specimens is reduced by 10%, and that of epoxyamine specimens, by 20%.

The values obtained by Bakhareva and Mirkin<sup>3</sup> for the diffusion coefficients and their dependence on the water temperature and hydrostatic pressure permit a tentative calculation of the water absorption for this type of glass plastic as a function of the thickness of the article, time of exposure to water, water temperature, and hydrostatic pressure, and on the basis of a comparison of experimental data obtained on the specimens, permit a determination of the loss of strength corresponding to any magnitude of water absorption during a given time period.

The water absorption is calculated from a formula derived from Fick's equation:

$$Q = Q_{\infty} \left( 1 - \frac{3}{\pi^2} e^{-\frac{D\pi^2 \tau}{d^2}} \right), \quad (13)$$

where  $Q$  is the amount of moisture, %, absorbed by the specimen in time  $\tau$ , h;  
 $Q_{\infty}$  is the amount of moisture absorbed by the specimen in a state close to equilibrium, %;  
 $D$  is the diffusion coefficient,  $\text{cm}^2/\text{h}$ ;  
 $d$  is the thickness of the specimen, cm.

For articles of epoxyamine glass plastics, a water absorption of 0.3-0.4% and corresponding 10-16% decrease in strength will take place at a pressure of 1  $\text{kgf}/\text{cm}^2$  and 20°C.

Thickness, mm	5	10	20	40
Time, years	0.7	2.5	10	38

Field tests of articles confirm the calculations. After 1500 days of exposure to water, ship propellers 1.5-2 m in diameter with a thickness of 20 mm in the critical section did not undergo any change in dimensions and showed practically no change in their strength properties.

#### 11. Electrical Insulation Properties of Fiber Glass Plastics

In addition to high mechanical strength, hot-pressed epoxy glass plastics possess attractive electrical and electronic properties, which account for their extensive use as insulating materials.

The principal indices characterizing the electrical insulation properties of fiber glass plastics are the surface electrical resistivity, volume electrical resistivity, breakdown voltage, and dielectric loss tangent. Epoxy glass plastics

retain relatively high electrical insulation properties on aging and may be used as reliable insulation. /96

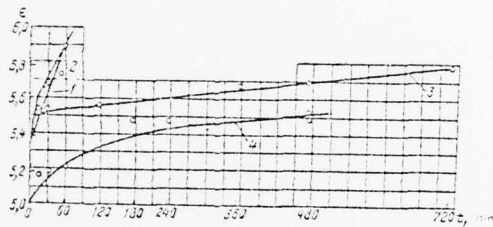


Fig. 31. Permittivity  $\epsilon$  of fiber glass plastics vs time  $t$  of boiling in water for specimens based on various binders.

- 1 - fiber glass plastic with epoxyamine binder plasticized with DEG-1 resin;
- 2 - fiber glass plastic with epoxyphenol binder plasticized with DEG-1 resin;
- 3 - fiber glass plastic with epoxyphenol binder (unplasticized);
- 4 - fiber glass plastic with epoxyamine binder (unplasticized).

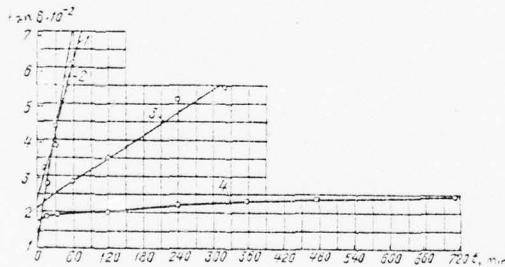


Fig. 32. Dielectric loss tangent  $\tan \delta \times 10^{-2}$  of fiber glass plastics vs time  $t$  of boiling in water for specimens based on different binders.

Notation same as in Fig. 31.

The electrical insulation properties of fiber glass plastics change even when the moisture content is negligible, and decline considerably when the plastics are exposed to high humidity. This decline in properties is due to a high permittivity ( $\epsilon = 81$ ) and substantial electrical conductivity of water. Even the conductivity of completely pure water is  $4.2 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-3}$ , and therefore, when epoxy glass plastics are used in electronic equipment, in order to increase the stability of their properties, it is necessary to use unplasticized binders, sized glass fabrics, as well as long-term curing, and to increase the specific pressure. /98

Table 45  
Effect of long exposure to water on electrical insulation properties of epoxy glass plastics (frequency,  $10^5$  Hz)

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Time of exposure to water, days	Epoxyphenol glass plastic				Epoxyamine glass plastic			
	$\epsilon$	$\tan \delta \cdot 10^{-2}$	$\rho_{1000} \cdot 10^{12}$	$\mu, \nu$	$\epsilon$	$\tan \delta \cdot 10^{-2}$	$\rho_{1000} \cdot 10^{12}$	$\mu, \nu$
0	5.71	1.52	$3 \cdot 10^{14}$	—	5.55	1.6	$3.5 \cdot 10^{14}$	—
10	5.72	1.59	$3 \cdot 10^{14}$	0.06	5.55	1.71	—	0.06
20	5.77	1.63	$1 \cdot 10^{14}$	0.08	5.57	1.71	—	0.07
30	5.77	1.63	—	0.1	5.59	1.71	—	0.11
40	5.81	1.65	$8 \cdot 10^{14}$	0.11	5.65	1.80	—	0.125
50	5.84	1.73	$1.5 \cdot 10^{14}$	0.14	5.68	1.98	$1.4 \cdot 10^{14}$	0.171
60	5.84	1.82	$5.6 \cdot 10^{13}$	0.29	5.77	2.53	$4.8 \cdot 10^{13}$	0.256
90	5.88	1.80	$3.6 \cdot 10^{13}$	0.37	5.80	2.88	$2 \cdot 10^{13}$	0.385
120	5.06	1.60	$8.7 \cdot 10^{12}$	0.28	5.92	3.37	$1.7 \cdot 10^{13}$	0.40
225	5.06	1.98	$8.0 \cdot 10^{12}$	0.41	5.97	3.77	$6.8 \cdot 10^{11}$	—
270	5.07	1.95	—	0.43	6.11	3.77	$1.3 \cdot 10^{11}$	0.63
360	5.09	1.95	$4.4 \cdot 10^{12}$	0.46	6.23	4.22	$2.2 \cdot 10^{11}$	0.76
720	5.27	2.52	$1.1 \cdot 10^{12}$	0.56	6.9	11.1	$3 \cdot 10^{10}$	1.2
900	5.40	3.23	$7.5 \cdot 10^{11}$	0.5	—	—	—	—

Note. Specimens measuring 100 x 100 x 3 mm were tested.

Table 46  
Effect of boiling on the electrical insulation properties of epoxyphenol glass plastics (frequency,  $10^5$  Hz)

Property	Glass	
	Aluminoborosilicate, ACM-9 sizing agent	Copper-containing, 652 Lubricant
Dielectric loss tangent	$\frac{4.6 \times 10^{-4}}{(3-3.5) \times 10^{-4}}$	$\frac{1.92 \times 10^{-4}}{(2.6-2.7) \times 10^{-4}}$
Permittivity	$\frac{5.0-5.7}{6.0-6.4}$	$\frac{5.5-5.8}{6.0-6.1}$
Volume resistivity, ohm cm	$\frac{(2-3) \times 10^{14}}{(1-2) \times 10^{14}}$	$\frac{9.5 \times 10^{12}}{8.0 \times 10^{12}}$

Note. Numerator - values at standard conditions; denominator - after boiling for 6 h.

The electrical insulation properties of epoxy glass plastics of different compositions during long-term exposure to water and boiling are shown in Tables 45 and 46 and Figs. 31 and 32.

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## 12. Erosion Resistance and Methods of its Determination

Abrasion resistance. Wear in a flow of abrasive particles is observed during the operation of such ship machine building parts as fan blades and the air propellers of air cushion ships.

Despite the large number of experimental studies, there is as yet no definitive theory to account completely for the process of wear in a flow of abrasive particles. In the view of certain researchers,<sup>29</sup> the wear is caused by the impact of the abrasive flow. V. I. Briginov and I. K. Lebedev have attempted to correlate abrasive wear with the laws of cutting or fatigue phenomena. I. Kleys\* discusses the process of wear in a flow of abrasive particles as a complex process that may involve the cutting of microshavings by the abrasive particles, and contact fatigue and breakdown of the surface due to high contact stresses. The rate of wear is also affected by the shape and size of the abrasive particles, their velocity, and their angle of incidence.

The wear of a surface element per unit time is proportional to the kinetic energy of the acting particle and to the number of collision of the particles.

A centrifugal type rotor device is used for abrasive wear tests (Fig. 33). Specimens 10 are mounted in special brackets 8 in the stator part of the device around the rotor. The tests are performed at different angles of incidence. The

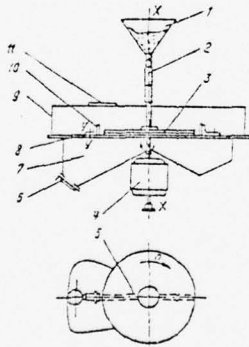


Fig. 33. Diagram of centrifugal type rotor.

- 1 - hopper; 2 - flexible tubing; 3 - rotor;
- 4 - motor; 5 - channels; 6 - two-step gate;
- 7 - collecting bin; 8 - brackets; 9 - chamber;
- 10 - specimens; 11 - glass-covered opening.

angle of incidence is varied by changing the position of the brackets. The abrasive particles falling into the center of the rotor move along channels 5

\*Russian transliterated spelling.

under the influence of centrifugal force. The speed of rotation of the rotor is adjusted over a wide range by means of an autotransformer. The necessary rotational speeds are adjusted to within  $\pm 1\%$  by means of a tachometer. A pinchcock is used to adjust the concentration of the abrasive jet.

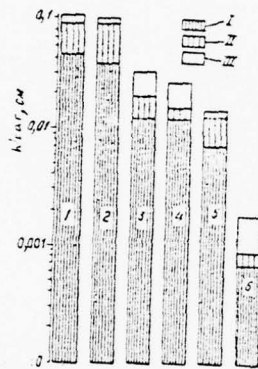


Fig. 34. Diagram of relative resistance of epoxy-amine glass plastic to abrasive wear.

1 - without coating; 2 - with polypropylene coating; 3 - with coating of polyethylene modified with molybdenum disulfide; 4 - with coating of fluoroplastic 42; 5 - with polyethylene coating; 6 - with polyurethane coating. I - flow velocity, 80 m/sec; II - flow velocity, 100 m/sec; III - flow velocity 130 m/sec.

The index of abrasive wear represents the extent of damage to the surface layer  $\Delta V$  during tests of the material studied.

$$\Delta V = \frac{G_1 - G_2}{\rho} \quad (14)$$

where  $G_1$  and  $G_2$  are the mass of the specimen before and after the test;  $\rho$  is the density of the coating material.

The results of the tests of fiber glass plastics with different protective coatings are shown in Table 47 and Fig. 34. The properties of the glass plastic without the coating are also given for comparison. The tests show that the wear resistance of polymeric materials is determined by their elasticity: the lower the elastic modulus and higher Poisson's ratio, the better the resistance of the material to the impact of abrasive particles. The highest abrasive resistance is exhibited by the elastomer polyurethane.

Table 47  
Resistance of polymeric materials to abrasive wear

Material of Coating	Volume wear $\Delta V$ , cm <sup>3</sup> , at velocity, m/sec		
	130	100	80
Fiber glass plastic	0.273	0.22	0.12
Polyethylene	0.037	0.033	0.018
Fluoroplastic 42	0.066	0.043	0.029
Polyurethane	0.005	0.0025	0.0015

The elasticity and hardness of the coating depend substantially on its thickness. When the thickness of the coating is small, its elastic properties are not fully manifested, and the energy capacity of the coating decreases, increasing its wear.

Hydroabrasive resistance. The conditions of operation in a hydroabrasive medium are characteristic of parts of pumps and ship propellers. The intensity of the hydroabrasive action also depends on the speed of the abrasive mixture, its concentration, and also on the particle size and mineralogical composition of the abrasive components.

The wear resistance of materials is estimated by relative comparison, in which the quantitative index is the dimensionless coefficient  $E$ , calculated from the formula

$$E = \frac{g_1 \rho_2}{g_2 \rho_1}, \quad (15)$$

where  $g_1$ ,  $g_2$  are the mass losses of the standard and investigated material, respectively;  
 $\rho_1$ ,  $\rho_2$  are the densities of the standard and investigated material.

The wear resistance of protective coatings of fiber glass plastic under certain testing conditions is shown in Tables 48 and 49. The standard material used is epoxy glass plastic without a coating. The tabulated data clearly demonstrate the effectiveness of the protective coatings. In a hydroabrasive medium with sand, the resistance of fiber glass plastics with a coating based on rubbers and fluoroplastic 26 surpasses the resistance of carbon steel.

If the data on the hydroabrasive resistance of polymers are compared with their physicochemical properties, a certain trend can be observed: the resistance to hydroabrasive wear in the water-sand medium is proportional to the elasticity of the polymer. In the water-gravel medium, where impact of large particles is observed, the nature of the breakdown (breaking away or detachment of individual particles of the coating) changes, and the wear is inversely proportional to the mechanical strength of the coating material. The stability of the coating to the impact of gravel particles increases with increasing thickness of the coating. The greatest stability in the water-gravel medium is exhibited by coatings based on the strongest thermoplasts such as pentaplast and fluoroplastic 2. This pattern is clearly illustrated by results of tests of specimens with a coating based



Table 48  
Resistance to hydroabrasive wear in the water-sand medium

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Material	Volume losses, cm <sup>3</sup> , after 6 h of tests	Wear resistance coefficient
NO-68 rubber	0.0229	11.2
Fluoroplastic 26	0.0452	5.67
Fluoroplastic 2M	0.112	2.28
" 23	0.182	1.41
" 2	0.195	1.31
Pentaplast	0.225	1.14
Epoxyphenol glass plastic	0.256	1.0
35Kh4G2 steel	0.0231	11.1
25L "	0.080	3.2

Table 49  
Resistance to hydroabrasive wear in the water-gravel medium

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Material	Wear, cm <sup>3</sup> , after 2 h of tests	Wear resistance coefficient
Fluoroplastic 2	0.45	3.3
" 23	0.48	3.1
" 26	0.60	2.5
" 2M	0.62	2.4
NO-68 rubber	0.70	2.1
Epoxyphenol glass plastic	1.50	1
35Kh4G2 steel	0.23	6.6
25L "	0.35	4.3
Note. Fluoroplastics and NO-68 rubber applied on the surface of glass plastic specimens		

on a typical elastomer having a marked specific elongation and low mechanical strength. As expected, the wear resistance of fiber glass plastics with a rubber coating is highest of all polymeric materials in the water-sand medium and lowest in the water-gravel medium.

Cavitation resistance. The propeller blades of high-speed vessels, turbines and pumps and other parts of hydraulic equipment are subject to cavitation erosion. At the present time, it is widely held<sup>16</sup> that cavitation erosion is due to the effect exerted on the surface by shock waves arising from the contraction of cavitation cavities. Two groups of erosion damage may be distinguished according to the mechanism of their formation - under conditions of steady and unsteady flow. In the first case, the boundaries of a cavitation cavity are fully defined. When the velocity of the incident flow is sufficiently high, the closing of individual bubbles results in erosion damage of comparatively low intensity. In the case of unsteady flow with a variable velocity or direction of the flow, the damage is much more pronounced, and the erosion develops faster.

Steady cavitation is practically nonexistent in pure form. Similar to it is damage observed on the blades of hydraulic turbines and also on rudders if they are not located in the propeller backwash. /102

Unsteady cavitation is characteristic of propellers and hull parts operating in the propeller backwash.

Tables 50-53 present data on the cavitation resistance of fiber glass plastics with different coatings.

The quantity used to describe the cavitation resistance of a coating is the volume loss during a given time interval:

$$\Delta V = \frac{G_1 - G_2}{\rho}, \quad (16)$$

where  $G_1$ ,  $G_2$  is the mass of the specimen before and after testing, g;  
 $\rho$  is the density of the coating material, g/cm<sup>3</sup>.

Table 50  
Cavitation resistance of polymeric materials in 6-h magnetostriction bench tests

Material	Weight loss, mg	Volume loss, cm <sup>3</sup>	Cavitation resistance coefficient
Polyvinyl butyral	6.6	0.0055	25.0
Polyethylene	8.5	0.0091	15.3
Polycarbonate	6.6	0.0055	25.0
Pentaplast	13	0.0093	15.1
Epoxyphenol glass plastic	28	0.014	1.0
LMtsZh-55-3-1 brass	20	0.0024	58.4

Table 51  
Cavitation resistance of polymeric materials in hydrodynamic bench tests

Material	Weight loss, mg		Volume loss, cm <sup>3</sup>		Cavitation resistance coefficient (based on data from 12-h tests)
	After 3 h	After 12 h	After 3 h	After 12 h	
Epoxyphenol glass plastic	136	350	0.068	0.175	1
Fluoroplastic 2 *	32	-	0.016	-	-
" 23 *	6	164	0.003	0.082	2.14
" 26 *	6	109	0.003	0.054	3.26
Pentaplast *	35	-	0.025	-	-
LMtsZh-55-3-1 brass	-	123	-	0.015	11.6

\*Note. These materials were applied on the surface of fiber glass plastic specimens by cladding.

Table 52  
Cavitation resistance of polymeric materials in impact erosion bench tests

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Material	Weight loss, mg		Volume loss, cm <sup>3</sup>		Cavitation resistance coefficient (based on data from 12-h tests)
	After 3 h	After 12 h	After 3 h	After 12 h	
Epoxyphenol glass plastic	435.6	-	0.218	-	1
Fluoroplastic 26*	50.0	95.0	0.025	0.047	3.75
" 2*	79.2	-	0.039	-	5.6
" SKF-26*	12.2	32.4	0.006	0.016	36.4

\*See the note in Table 51.

Table 53  
Cavitation resistance of polymeric materials in tests on a Venturi-tube type increased-capacity apparatus

Material	State of Surface			
	After 10 h	After 20 h	After 30 h	After 50 h
Epoxyphenol glass plastic	Surface attacked to a depth of 0.25 mm	Surface attacked to a depth of 0.5 mm	Surface attacked to a depth of 0.75 mm	-
Fluoroplastic 26*	No change	No change	No change	Surface attacked to a depth of 0.05 mm
" 2*	Same	Same	Same	Surface attacked to a depth of 0.75 mm

\* See the note in Table 51.

The cavitation resistance coefficient used is the ratio of the volume loss of the coating material to the standard fiber glass plastic without a coating.

A general pattern is observed in tests of polymeric materials: cavitation resistance increases with elasticity. Materials with a specific elongation up to 50%, such as fluoroplastic 2 and pentaplast, are inferior to elastomers in cavitation resistance, and after a long incubation period, a marked breakdown of the coatings begins and a large number of cracks are formed.

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However, if the cavitation resistance of polymers is compared to that of metals, the nature of the behavior changes according to the testing method. The

highest cavitation resistance is exhibited by fiber glass plastics with coatings tested on Venturi-tube type apparatus, where a relatively low pulse frequency is observed.

However, in tests at high pulse frequency (magnetostriction and hydrodynamic benches), the cavitation resistance of the polymers is much lower than that of metals. This phenomenon is due to the relaxation character of the hyperelastic deformation of polymers and relatively high values of relaxation time and specific elongation. A material which is elastic at low frequency is rigid at high frequency, since hyperelastic deformation cannot develop at high frequencies. If the time between two successive voltage pulses is shorter than the relaxation time of the material, brittle fractures are formed. If the time necessary for one cycle is longer (lower frequency) than the relaxation time, the fracture energy transmitted to the material is partly liberated and partly dissipated. Despite these losses part of the energy accumulates in the material. At a certain level of energy accumulation, the material of the coating begins to break down considerably.

13. Preparation of Binder and Impregnation of Glass Fabric

As was stated previously, glass fabrics preimpregnated with a binder on an impregnating machine are used as press materials in the fabrication of fiber glass plastic articles. Solutions of binder components in suitable solvents are used for the impregnation. Usually, the solvents used are alcohol-acetone or alcohol-toluene mixtures with a 1:1 ratio of alcohol to acetone (or toluene). Acetone and toluene are solvents for epoxy resins, and most of the curing agents used dissolve in alcohol.

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In the preparation of the impregnating lacquer, considerable attention must be given to the lacquer concentration, since by changing it, one can control the resin content of the impregnated glass fabric. At a certain impregnation rate, there is a linear relation between the lacquer concentration and the resin content, and this relation is different for fabrics of different weave types because of their varying densities. Figure 35 shows such a relation for satin and cord-braid glass fabrics.

The impregnating lacquer is prepared in a special heated container with a stirrer. A solvent is added to the epoxy resin heated to 60-70°C. The mixture is vigorously stirred until the epoxy resin dissolves completely, then a solution of curing agent is added.

Table 54 shows the compositions of certain impregnating lacquers used in ship machine building.

To prevent escape of the solvent, the impregnating lacquer should be stored in a sealed container at a temperature not above 20°C. The stability of lacquer viscosity is determined by the reactivity of the epoxy resins and curing agents. The greatest stability of viscosity (over 90 days) at 20°C is exhibited by lacquers based on halogenated epoxy resins with halogenated aromatic polyamines. The lowest stability (10 days at 20°C) characterizes lacquers based on epoxyresorcinol resins with aromatic polyamines.

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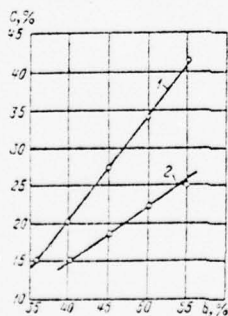


Fig. 35. Binder content C of impregnated glass fabric vs lacquer concentration b: 1 - satin glass fabric; 2 - cord-braid glass fabric.

Table 54  
Compositions of impregnating lacquers

Component	Content, parts by weight					
ED-13 epoxy resin	45.0	-	-	34.8	34.8	45.0
ETsD-13 epoxy compound	-	45.0	-	-	-	-
EKhd epoxy resin	-	-	45.0	-	-	-
Triethanolamine titanate	4.5	4.5	4.5	-	-	4.5
Bakelite lacquer	-	-	-	29.9	29.9	-
Dicyanodiamide	-	-	-	0.35	0.35	-
Ethanol	26.5	26.5	26.5	9.85	9.85	25.0
Acetone	25.0	25.0	25.0	25.1	23.18	24.58
DG-100 carbon black	-	-	-	-	1.75	1.75
Thiuram	-	-	-	-	0.17	0.17

Note. Lacquers whose composition includes DG-100 carbon black and thiuram are used for impregnating facing layers.

The impregnation of glass fabric with a binder is carried out in special impregnating machines equipped with drying chambers with an adjustable temperature. These machines are of two types: vertical and horizontal. Vertical machines are more popular, since this design prevents sagging of the cloth in the shaft and disrupting the orientation of the fiber. The main components of the machine are a bath for the binder, the feed drum, squeezing roll, driving shafts, guiding rolls, drying shaft, and takeup drum. Before the machine is charged, the glass fabric is rewound on a calender or rewinding machine into rolls of specified mass. The rewinding should be done under tension. The impregnation rate and temperature in the drying zones are determined by the viscosity and composition of the binder, type of solvent, specified content of the binder, its soluble part, and volatile substances in the impregnated glass fabric. For the epoxy binders described, the drying temperature is 80-100°C, and the impregnation rate ranges from 2 to 8 m/min depending on the height and construction of the drying shaft. /107

Table 55  
Physicomechanical characteristics vs content of soluble part of binder for epoxyphenol glass plastic

Content of soluble part of binder, %	Strength, kgf/mm <sup>2</sup>				Impact Strength, kgf m/cm <sup>2</sup>
	Tensile	Bending	Compressive	Shearing	
100	64.0	69.0	43.2	6.9	4.35
90	60.0	69.0	37.0	6.9	4.1
50	52.0	57.0	32.0	5.5	3.2
40	40.0	35.0	28.0	4.8	3.0

Table 56  
Change in the content of soluble part of binder with storage time and temperature for glass fabric impregnated with epoxyphenol binder

Storage time, days	Content of soluble part of binder, %, at temperature, °C			
	25-30	20	15	In refrigerator, ±5
1	100	100	100	100
5	80	100	100	100
7	65	83	100	100
10	49	70	90	100
15	40	51	80	100
20	35	45	72	100
30	26	38	59	100
60	26	31	51	92

The impregnated glass fabric designed for articles used in ship machine building should be plastic and easy to shape into articles of intricate configuration. The quality of the impregnated glass fabric is characterized by the content of binder, soluble part, and volatile substances. The content of the soluble part of the binder and volatile substances in the impregnated glass fabric is adjusted by changing the impregnation rate or temperature of the drying shaft. The content of the soluble part of the binder in the impregnated glass fabric changes with time and depends on the storage temperature. To increase the storage time, the impregnated glass fabric should be stored in a refrigerator at a temperature from 0 to 5°C; its storage time is 10 to 90 days, depending on the reactivity of the components.

As an example, Tables 55 and 56 show the physicochemical properties of an epoxyphenol glass plastic as a function of the content of the soluble part of the binder and data on the effect of the conditions of storage of the impregnated glass fabric.

#### 14. Effect of Binder Content on the Physicochemical Properties of Fiber Glass Plastics

As already stated, the required binder content of the fiber glass plastic is set during the preparation of the lacquer and impregnation of glass fabrics. This quantity has a decisive influence on the strength and elastic properties of the material.

The dependence of the tensile strength and modulus of tension of a fiber glass plastic on the binder content is expressed by the following analytical formulas:

$$\sigma = \sigma_{cl} \left[ j_{cl} + (1-j) \frac{E_{lac}}{E_{cl}} \right]; \quad (17)$$

$$E = E_{cl} \left[ j_{cl} + (1-j) \frac{E_{lac}}{E_{cl}} \right]. \quad (18)$$

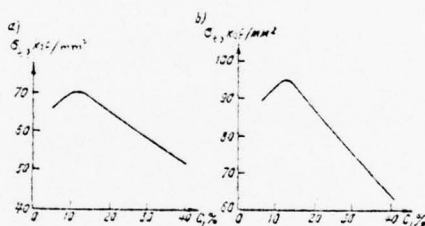
where  $\sigma$ ,  $\sigma_{g1}$  is the tensile strength of the fiber glass plastic and glass fiber,  $\text{kgf/mm}^2$ ;

$f_{g1}$  is the glass content of the fiber glass plastic in parts by volume;

$E$ ,  $E_{g1}$  are the moduli of tension of the fiber glass plastic and glass fiber,  $\text{kgf/mm}^2$ ;

$E_{bm}$  is the modulus of tension of the binder,  $\text{kgf/mm}^2$ ;

It is obvious from formulas (17) and (18) that the tensile strength and modulus of tension of a fiber glass plastic increase linearly with the glass content. However, even in structures operating in tension (Figs. 36 and 37), the binder content must not be reduced indefinitely. For each type of fiber glass plastic, there exists a limit of the binder content below which a continuous resin film is no longer formed, and the adequate bonding of the glass fibers is disrupted.



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Fig. 36. Tensile strength  $\sigma_t$  of fiber glass plastic vs binder content  $C$  for glass fabrics of brands: a - TS-8/3-250; b - T-25.

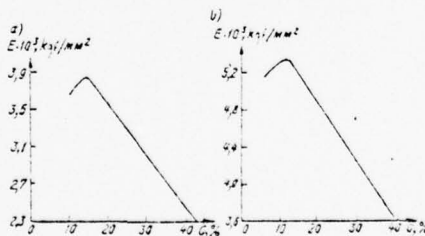


Fig. 37. Modulus of tension  $E$  vs binder content  $C$  for glass fabrics of brands: a - TS-8/3-250; b - T-25.



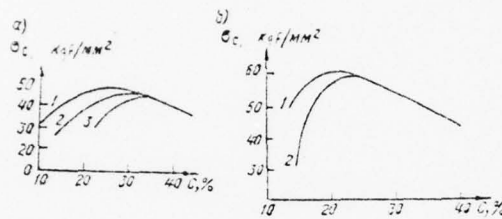
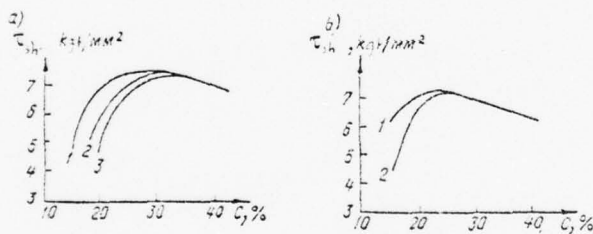


Fig. 38. Compressive strength  $\sigma_c$  vs binder content C for glass fabrics of brands: a - TS-8/3-250; b - T-25.  
 1 - pressure, 150 kgf/cm<sup>2</sup>; 2 - pressure, 50 kgf/cm<sup>2</sup>; 3 - pressure, 10 kgf/cm<sup>2</sup>.



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Fig. 39. Interlaminar shearing strength  $\tau_h$  of fiber glass plastic vs binder content C for glass fabrics of brands: a - TS-8/3-250; b - T-25.  
 1 - pressure, 150 kgf/cm<sup>2</sup>; 2 - pressure, 50 kgf/cm<sup>2</sup>; 3 - pressure, 10 kgf/cm<sup>2</sup>.

This is confirmed by the well-defined maxima on the curves of compressive and shearing strengths as functions of the binder content (Figs. 38 and 39).

It is also evident from the figures that the optimum binder content of fiber glass plastics is determined by the type of reinforcing material and molding pressure. On passing from untwisted to twisted threads and reducing the molding pressure, the binder content should be increased. This relationship is due to the diverse character of the binder distribution in fiber glass plastics.

On the basis of the binder distribution types employed, one can calculate the approximate binder content necessary for bonding the fibers in different kinds of fiber glass plastics. Two assumptions are made to simplify the calculation:

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- (a) the glass monofilaments in the thread have a circular cross section;  
 (b) at the maximum packing density, the binder distribution between the fibers is triangular (this hypothesis has been experimentally confirmed with models).

A diagram of the resin distribution in an untwisted primary thread is shown in Fig. 40. The percentage binder content in this case is

$$n = \left(1 - \frac{\pi}{2\sqrt{3}}\right) \cdot 100 = 9.2\% \quad (19)$$

During the manufacture of cord-braid fabrics from such thread and during the molding of fiber glass plastics, a flattening of the weft and warp threads takes place until their distribution becomes "rectangular" (Fig. 41).

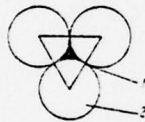
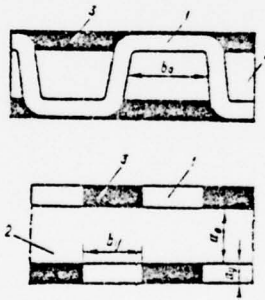


Fig. 40. Distribution of binder in untwisted thread.

1 - binder; 2 - glass fiber.



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Fig. 41. Distribution of binder in fiber glass laminate based on braid fabric under high molding pressure.

1 - weft; 2 - warp; 3 - binder;  $a_0, b_0$  - cross-sectional dimensions of warp thread, cm;  $a_y, b_y$  - same, weft thread.

The binder content of a fiber glass plastic based on a cord-braid fabric may be determined from the following formulas:

$$n = \frac{\delta \cdot \beta + \Delta \cdot \pi}{\delta} \cdot 100 \quad (20)$$

where

$$\beta = \left(1 - \frac{\pi}{4\sqrt{3}}\right) \cdot 100 = 54.7\% \quad (21)$$

$$\alpha = \left(1 - \frac{\pi}{2\sqrt{3}}\right) \cdot 100 = 9.2\% \quad (22)$$

$$\delta_w = \frac{K_w}{\gamma \eta_{gl} N_w} \quad (23)$$

$$\Delta_0 = \frac{2K_{wa}}{\gamma \eta_{gl} N_{wa}} \quad (24)$$

where  $n$  is the calculated binder content, %;

$\delta_w$  is the thickness of the cord fabric layer, cm;

$\Delta_0$  is the thickness of the cord fabric warp layer, cm;

$\delta$  is the thickness of the cord fabric, cm;

$a$  is the binder content of the cord fabric warp layer, %;

$\beta$  is the binder content of the cord fabric weft layer, %;

$K_{wa}$ ,  $K_w$  are the densities of the warp and weft threads in the fabric, threads/cm;

$N_{wa}$ ,  $N_w$  are the metric numbers of the warp and weft thread, cm;

$\gamma$  is the glass density, g/cm<sup>3</sup>;

$\eta_{gl}$  is the glass content of the thread, % ( $\eta_{gl} = 90.8\%$ ).

Calculations using the formulas showed that in fiber glass plastic based on cord-braid fabric, the binder content should be no lower than 16%.

In fiber glass plastics based on fabrics of twisted threads with a large number of ends, the binder content should be increased as compared to fiber glass plastics based on cord-braid fabrics. The binder content is increased primarily in the twisted thread itself as compared to the untwisted thread. A diagram of the binder distribution in such a thread is shown in Fig. 42.

The binder content is

$$n = \left(1 - \frac{\pi^2}{12}\right) \cdot 100 = 17.8\% \quad (25)$$

In addition, twisted threads are flattened less during weaving and molding than untwisted thread. At moderate molding pressures, the cross section of the threads may be assumed elliptical, whereas in the ideal case, at the maximum packing density, the binder distribution is schematically represented as shown in Fig. 43. Each glass thread shown in the figure already contains 17.8% of binder and 82.2% of glass. The remainder of the binder occupies the free space between the glass fibers. The binder content in such a fiber glass plastic is

$$n = \left(1 - \frac{\pi}{4} \eta_{gl}\right) \cdot 100 = 35\% \quad (26)$$

where  $\eta_{gl}$  is the glass content of the thread, % ( $\eta_{gl} = 82.2\%$ ).

The use of high molding pressures causes the threads to be flattened further and their cross section to change from elliptical to oval. The resin distribution pattern in this case is shown in Fig. 44.

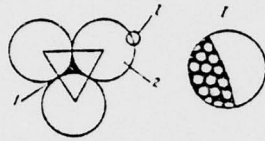


Fig. 42. Distribution of binder in twisted thread with a large number of ends.

1 - binder; 2 - glass thread.

The binder content is

$$\pi = \left[ 1 - \frac{K}{\gamma N a} \right] \cdot 100, \quad (27)$$

where

$$a = \frac{\frac{1}{K} - \sqrt{\left(\frac{1}{K}\right)^2 - \frac{4\left(1 - \frac{\pi}{4}\right)}{\gamma \eta_s N}}}{2\left(1 - \frac{\pi}{4}\right)}. \quad (28)$$

Here  $a$  and  $b$  are the geometric dimensions of the cross section of the thread, cm;  $\gamma$  is the glass density, g/cm<sup>3</sup>;  $N$  is the metric number of the thread, cm;  $K$  is the density of the threads in the fabric, threads/cm.

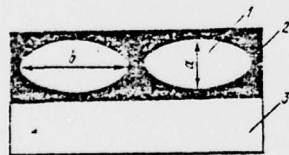


Fig. 43. Distribution of binder in fiber glass plastic based on fabric of twisted threads at low molding pressure.

1 - weft; 2 - binder; 3 - warp;  
 $a, b$  - cross sectional dimensions of thread, cm.

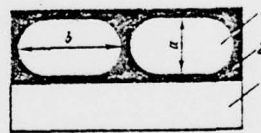


Fig. 44. Distribution of binder in fiber glass plastic based on fabric of twisted threads at high molding pressure.

1 - weft; 2 - binder; 3 - warp.

Calculations using formulas (27) and (28) have shown that in the fiber glass plastic based on satin fabric of brand TS-8/3-250, the binder content should be no lower than 26%. /113

The experimentally obtained optimum binder contents of fiber glass plastics confirm the validity of such calculations. Naturally, an ideal distribution of the binder cannot be obtained in fiber glass plastics, and therefore, the experimental optimum values usually are somewhat higher than the calculated ones. Table 57 gives the optimum (experimental) values of the binder content for fiber glass plastics based on satin and cord-braid fabrics at different specific molding pressures.

Table 57  
Optimum values of binder content for fiber glass plastics

Reinforcing material	Specific molding pressure, kgf/cm <sup>2</sup>	Optimum binder content, %
Satin-weave glass fabric of twisted threads	10	28-30
	50	24-26
	150	22-24
Cord-weave glass fabric of untwisted threads	50	20-22
	150	17-19

#### 15. Molding

Molding of fiber glass plastic articles is a complex process whose main parameters are temperature and time, heating and cooling rate, and specific pressure. The first three factors determine the chemical aspect of formation of the strength of the polymeric binder and are practically independent of the structure of the part. The magnitudes of specific molding pressure and cooling rate are determined to a large extent by the structure and dimensions of the parts.

During molding, the pressure overcomes the elasticity of the gases and water vapor evolved during the heating and curing of the binder, prevents delamination of the fiber glass plastic, provides for contact between the layers and penetration of the binder between the fibers of the filler, and promotes the distribution of the molding material over the volume of the mold.

The first stage of molding involves compaction of the entire mass of the fiber glass plastic; in the second stage, under the influence of elevated pressures, the binder penetrates into the gaps between the fibers of the threads, whereupon the contact area between the binder and glass increases. The third stage, which takes place at very high molding pressures (700-900 kgf/cm<sup>2</sup>), involves elastic deformation of the glass fiber and forcing of the fibers into one another. In the first two stages, the strength of the fiber glass plastic increases, and in the third stage, decreases.

Raising the specific molding pressures from 1 to 25 kgf/cm<sup>2</sup> is associated with a pronounced increase in the specific contact area between the glass and binder, an increase in the adhesive bond between them, a decrease in the porosity of the fiber glass plastic, and a regular increase in its strength and water resistance (Fig. 45). Thus, for example, the bending strength of epoxyphenolic glass plastic pressed at a pressure of 2.5 kgf/cm<sup>2</sup> is 33.3 kgf/mm<sup>2</sup>, and at a pressure of 25 kgf/cm<sup>2</sup>, 71.6 kgf/mm<sup>2</sup>. Even greater is the effect of pressure on the decrease in strength

after prolonged exposure to water. The presence of cavities between the glass fibers, appearing when the impregnation of the fiber glass reinforcing material during molding at low specific pressures is insufficient, promotes the penetration of water molecules and a weakening of the adhesion between the glass fiber and binder. After 180 days, the strength of specimens pressed at  $2.5 \text{ kgf/cm}^2$  drops by 40%, and that of specimens pressed at  $25 \text{ kgf/cm}^2$ , by 16%.

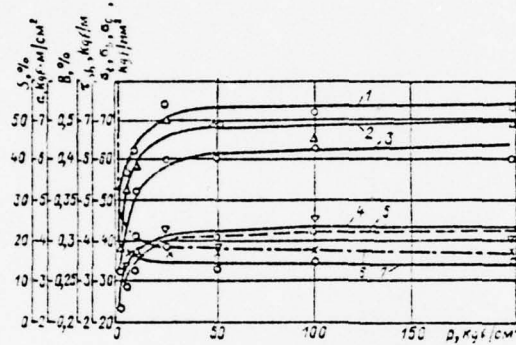


Fig. 43. Effect of specific molding pressure  $p$  on the physicochemical properties and water resistance of epoxyphenolic fiber glass plastic.

1 - for shear strength  $\tau_{sh}$ ; 2 - for bending strength  $\sigma_b$ ; 3 - for tensile strength  $\sigma_t$ ; 4 - for compressive strength  $\sigma_c$ ; 5 - for impact strength  $a$ ; 6 - for water absorption  $B$  of fiber glass plastic after 180 days' exposure to water; 7 - for decreasing the compressive strength  $S$  after 180 days' exposure to water.

Further increase of pressure in the range from 25 to  $200 \text{ kgf/cm}^2$  is associated /115 with only a slight further compaction of the fiber glass plastic, manifested chiefly in an increase of the stability of dielectric properties in water (Fig. 46). Pressures of  $300\text{--}600 \text{ kgf/cm}^2$  have practically the same effect and do not change the properties of the fiber glass plastic. Beyond  $700 \text{ kgf/cm}^2$ , an appreciable decline of the mechanical properties is observed, due to the breakdown of the glass fiber.

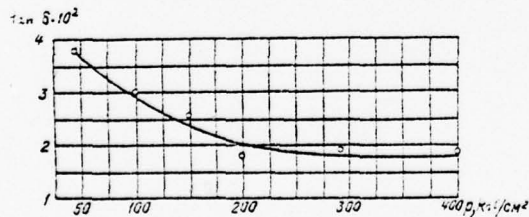


Fig. 46. Dielectric loss tangent  $\tan \delta$  of epoxyphenolic fiber glass plastic vs specific molding pressure  $p$  (the dielectric loss tangent was determined on the specimens after boiling in water for 6 h).

In selecting the specific molding pressure of articles, it is necessary to consider the complexity of their configuration. On passing from articles of simple shape such as plates to articles of complex geometric shape such as propellers, cones, etc., the specific pressure should be increased to 50-100 kgf/cm<sup>2</sup> because of the shaping losses.

The construction of the article also determines the choice of the cooling rate during molding. A properly selected cooling rate is a prerequisite for obtaining articles with minimum internal stresses. It is well known that the curing of thermosetting binders is associated with a decrease in volume, i. e., so-called "chemical shrinkage" of the binder. For hot-cured epoxy binders, the shrinkage is comparatively small, 0.5-1%; the internal stresses caused by chemical shrinkage amount to only 5-30 kgf/cm<sup>2</sup> (smaller values of shrinkage and stresses are observed in binders based on bifunctional epoxydiane resins, and higher values are observed in binders based on EKHD and EPOF polyfunctional epoxy resins).

A much greater role is played by the thermal shrinkage of the binder and thermal stresses caused by different linear expansion coefficients of the binder and glass (the linear expansion coefficient of aluminoborosilicate glass is  $2.0 \times 10^{-5}$  1/°C, and that of epoxy binder,  $(60-65) \times 10^{-5}$  1/°C). Even on slow cooling (1-3°C/min) the internal stresses in the article are 130-190 kgf/cm<sup>2</sup>. At a cooling rate of over 3°C/min, the internal stresses increase by 30-40%. Slow cooling at a rate of 1-3°C/min is particularly important for fiber glass plastic articles based on more rigid polyfunctional epoxy resins. Figures 47 and 48 show curves of internal stresses as a function of cooling rate and chemical structure of the binder. /116

The molding temperature and time are determined by the curing kinetics of the binders and are interdependent factors. The molding temperatures and times are selected so as to obtain specified physicomechanical properties of the fiber glass plastics. The well-known relation between the degree of curing and physicomechanical properties of the binder and fiber glass plastic makes it possible to utilize the dependence of the degree of curing on the curing temperature and time when selecting the optimum values of these parameters.

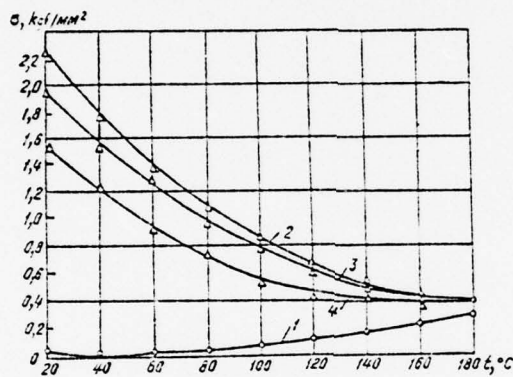
Kinetic curves of curing of epoxyphenolic and epoxyamine binders are shown in Figs. 49-54. The illustrated data were plotted on the basis of results obtained from a determination of the degree of curing by the methods of extraction in a Soxhlet apparatus and infrared spectroscopy ( $\tau$  being the curing time,  $n$  the amount of nonextractable substances present in the binder, and  $C$  the amount of reacted epoxy groups).

Extraction in a Soxhlet apparatus is based on the decrease in the solubility of a polymer during its curing. This method is carried out in a simple apparatus and may be applied to specimens of binder as well as fiber glass plastic. The infrared spectroscopy method makes it possible to follow the quantitative change in epoxy groups from the change in absorption intensity at a specified wavelength on films of the binder (Fig. 55). This method can be used only with quality specimens of binder without foreign inclusions (air, traces of moisture or solvent).

The data presented show a distinct correlation between the chemical structure of epoxy resins and their curing rate. The highest curing rate is characteristic of resorcinol polyfunctional resins. Compositions based on the trifunctional epoxycyanurate resin also have a high curing rate in comparison with epoxydiane resins.



The polyfunctional resin EKHD, a tetraglycidyl derivative of diaminodichlorodiphenylmethane, cures more slowly than epoxydiane resin. The reactivity of this epoxy resin depends on various factors having opposite effects. The increased functionality is inevitably associated with an increased reactivity. On the other hand, the presence of halogen atoms reduces the reactivity of the resin.



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Fig. 47. Residual stresses  $\sigma$  in films of cured epoxyamine binder based on epoxy-resorcinol resin EPOF vs cooling rate.

1 - heating of specimens at a rate of  $2^{\circ}\text{C}/\text{min}$  and holding at  $180^{\circ}\text{C}$ ; 2, 3, 4 - cooling of specimens at rates of 2, 10 and  $60^{\circ}\text{C}/\text{min}$ , respectively.

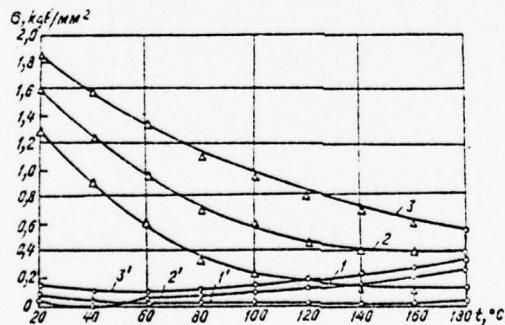


Fig. 48. Residual stresses  $\sigma$  in films of cured epoxyamine binders vs epoxy resin employed.

1', 2', 3' - heating of specimens at a rate of  $2^{\circ}\text{C}/\text{min}$ ; 1, 2, 3 - cooling of specimens at a rate of  $2^{\circ}\text{C}/\text{min}$ ; 1, 1' - ED-13 resin; 2, 2' - EPOF resin; 3, 3' - EKHD resin.

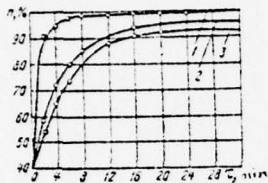
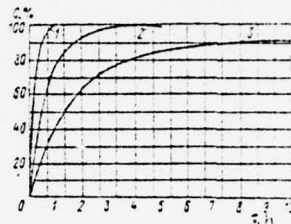


Fig. 49. Kinetics of curing of epoxy resins with phenolic resin at 160°C (based on extraction data).  
1 - UP-53 resin; 2 - ETsD-13 resin;  
3 - ED-13 resin.



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Fig. 50. Kinetics of curing of epoxy resins with triethanolamine titanate at 160°C (based on infrared spectroscopy data).  
1 - EPOF resin; 2 - ED-13 resin;  
3 - EKHD resin.

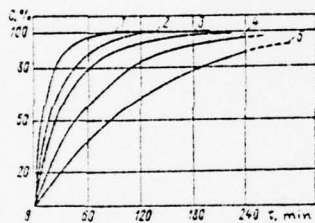


Fig. 51. Kinetics of curing of ED-13 epoxy resin with triethanolamine titanate (based on infrared spectroscopy data).  
1 - 180°C; 2 - 160°C; 3 - 140°C;  
4 - 120°C; 5 - 100°C.

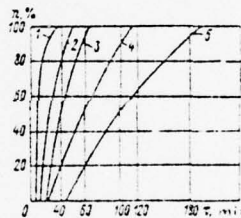


Fig. 52. Kinetics of curing of ED-13 epoxy resin with triethanolamine titanate (based on extraction data).  
1 - 180°C; 2 - 160°C; 3 - 140°C;  
4 - 120°C; 5 - 100°C.

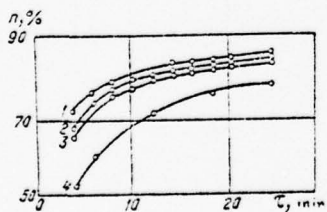


Fig. 53. Kinetics of curing of epoxy-phenol binder based on ED-13 epoxydiane resin (based on extraction data).  
1 - 200°C; 2 - 180°C; 3 - 160°C;  
4 - 140°C.

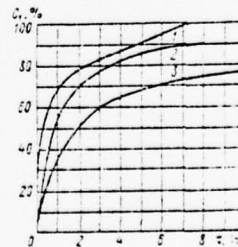


Fig. 54. Kinetics of curing of EKHD epoxy resin with triethanolamine titanate (based on infrared spectroscopy data).  
1 - 180°C; 2 - 160°C; 3 - 140°C.

With increasing molding temperature, the rate and degree of curing increase. For instance, in resorcinol and epoxydiane resins in the course of curing with triethanolamine titanate at 140-180°C, the epoxy groups disappear completely, whereas at 100-120°C, even during prolonged curing lasting 24 h, from 2 to 5% of epoxy groups remain unreacted.

In the EKhd resin, the epoxy groups disappear at temperatures of 180-200°C. In the course of curing at 140°C and 160°C, the spectral changes cease after 8-10 h, and the band characteristic of epoxy groups, 4500  $\text{cm}^{-1}$ , does not disappear completely, attesting to the presence of unreacted epoxy groups in the composition of the cured products (Fig. 55).

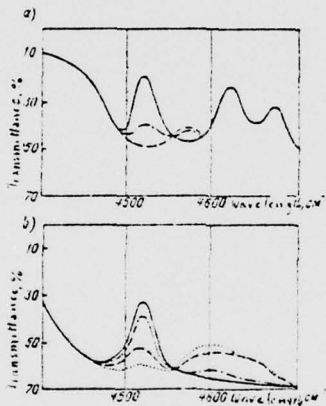


Fig. 55. Spectra of epoxy resins during curing with triethanolamine titanate: a - ED-13 resin; b - EKhd resin.

— immediately before heating;  
 - - - after the temperature is raised to 160°C;  
 - · - · after 2 h at 160°C;  
 ····· after 8 h at 160°C.

The curing of phenol-formaldehyde resin is a complex process involving several reactions simultaneously, and therefore, it is practically impossible to calculate the curing rate constant. In curing with triethanolamine titanate, for all the epoxy binders studied at a constant temperature of 100-180°C, the same fraction of epoxy groups react during the same time interval, as can be graphically expressed by the following linear relation (Fig. 56):

$$\ln \frac{C_0}{C} = K\tau, \quad (29)$$

where  $C_0$  is the amount of epoxy groups before curing, % ( $C_0 = 100\%$ );  
 $C$  is the amount of free epoxy groups at a given instant, %;

$\tau$  is the curing time, min;  
 $K$  is the reaction rate constant,  $\text{min}^{-1}$ .

The linear relation between reaction rate and epoxy group concentration indicates that the curing reaction of the epoxy resins studied may be assumed to be first order,<sup>63</sup> which makes it possible to calculate the curing time at any given temperature in the 100-180°C range. The curing time of different binders determined from these kinetic curves is given in Table 53. /120

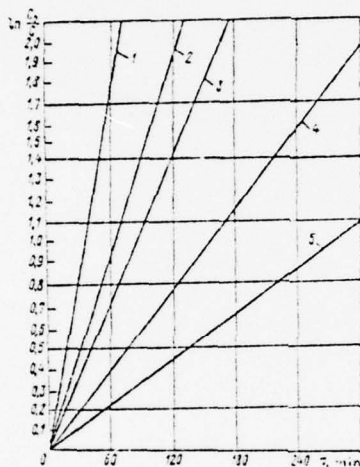


Fig. 56. Semilogarithmic plot of curing of ED-13 epoxy resin with triethanolamine titanate based on data of spectral analysis.

1 - 180°C; 2 - 160°C; 3 - 140°C; 4 - 120°C;  
 5 - 100°C.

As was stated above, for epoxyamine binders, the curing time is determined from spectral analysis data; for epoxyphenolic binders, it is determined from extraction data (because of the difficulties involved in preparing specimens), and the curing time used is the solubility loss time plus 30%, allowing for the error of the extraction method.

In calculations of the curing rate and time for epoxyamine binders at different temperatures, use may be made of the Arrhenius equation (Fig. 57):

$$K = K_0 e^{-\frac{E}{RT}}, \quad (30)$$

where  $K$  is the rate constant;  
 $K_0$  is the preexponential factor;  
 $E$  is the activation energy;

R is the gas constant;  
T is the curing temperature.

In estimating the kinetics of curing involving a simultaneous change in temperature and curing time, it is of interest to use the method of mathematical planning of the experiment. An experiment-planning scheme is illustrated with the example of epoxyamine binder based on ED-13 resin.

The equation obtained is

$$R = 83,3 + 12,8x_1 + 4,96x_2 - 2,9x_1^2 + 0,8x_2^2 - x_1x_2. \quad (31)$$

where  $x_1, x_2$  are, respectively, the curing time and temperature in arbitrary units; /121

R is the degree of curing, %.

Equation (31) applies in the temperature range from 100° to 180°C.

The final choice of the molding conditions must be made on the basis of results obtained from the determination of the physicomechanical properties of the binders and fiber glass plastics.

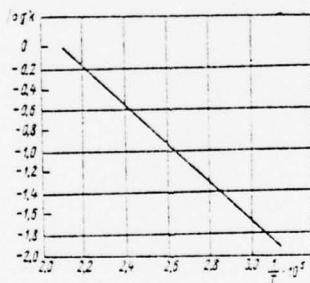


Fig. 57. Reaction rate constant K of curing of ED-13 epoxy resin with triethanolamine titanate as a function of temperature in Arrhenius coordinates.

Results of tests of the physicomechanical properties of epoxy binders and fiber glass plastics fabricated under different conditions are shown in Tables 59-64. Analysis of the results shows that in contrast to the degree of curing, the mechanical properties are determined not only by the molding temperature and time, but also by the heating rate up to the molding temperature.

Table 58  
Conditions for molding ship machine building articles from fiber glass plastics based on various binders

Binder	Resin	Curing Agent	Molding temperature, °C	Specific molding pressure, kgf/cm <sup>2</sup>	Holding time at molding temperature, min	Heating rate, °C/min
Epoxyphenolic	ED-13	Resorcinol type phenol-formaldehyde resin	160	25-100	60	1
Same	UP-63	Same	160	25-100	30	0.5
	ETsD-13	"	160	25-100	50	1
Epoxyamine	ED-13	Triethanolamine titanate	160	15-50	90	1
	ETsD-13	Same	160	15-50	80	1
	UP-63	"	160	15-50	60	0.5
	EPOF	"	160	15-50	40	0.5
	EKhD	"	180	15-50	150	0.5
	ED-13	Diamino-diphenyl-dichloromethane	180	15-50	120	1
Epoxy-resorcinol	EKhD	Same	180	15-50	180	0.5
	EKhD	Resorcinol	160	25-100	90	0.5

Table 59  
Physicomechanical properties of epoxyphenolic binder vs curing temperature and heating rate

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Property	Curing temperature, 200°C			Curing temperature, 160°C
	Heating (6-8 h) at 100°C at a rate of 20°C/min to 200°C	Heating rate 20°C/min	Heating rate 3°C/min	Heating rate 3°C/min
Adhesion, kgf/mm <sup>2</sup>	0.75	1.25	1.70	2.40
Strength, kgf/mm <sup>2</sup> :				
tensile	1.5	3.1	7.0	6.7
bending	Slip out of clamps	4.7	10.0	9.9
compressive	-	-	18.2	17.0
Impact strength, kgf m/cm <sup>2</sup>	Slip out of clamps	0.03	0.081	0.08

Note. Adhesion of epoxyphenolic binders was determined by A. F. Nikolayev's method.<sup>31</sup> Curing time was 30 min.

Table 50  
Effect of heating rate on the physicommechanical properties of epoxy-glass plastics

Heating rate, °C/min	Strength, kgf/mm <sup>2</sup>					
	Bending		Compressive		Interlaminar Shear	
	Epoxy-phenolic	Epoxy-amine	Epoxy-phenolic	Epoxy-amine	Epoxy-phenolic	Epoxy-amine
1	69.0	80.5	46.0	56.0	6.9	7.0
3	66.0	80.0	45.0	56.0	6.8	7.0
5	64.0	80.0	42.0	55.3	6.4	6.9
8	62.5	78.0	41.0	54.0	6.0	6.7
16	60.0	71.0	35.0	51.5	5.5	6.0
20	58.0	66.0	33.0	49.3	4.4	5.8

Remarks. 1. ED-13 epoxy resin.  
2. Curing temperature, 160°C.

Table 61  
Effect of curing temperature on the physicommechanical properties of epoxyamine binders

Resin	Curing temperature, °C	Strength, kgf/mm <sup>2</sup>			Adhesive strength, kgf/mm <sup>2</sup>	Specific elongation, %	Impact strength, kgf m/cm <sup>2</sup>	Glass transition temperature, °C	Microhardness, kg/mm <sup>2</sup>	Dielectric constant
		Tensile	Compressive	Bending						
ED-13	120	5.3	16	9	2.9	2.9	0.3	94	15.7	3.4
	140	5.9	19	11	3.7	2.9	0.36	93.1	16.5	3.3
	160	5.3	18	10.5	3.0	2.9	0.35	98.5	16.5	3.2
	180	7.1	18	11	1.8	1.8	0.15	113.7	17.8	3.2
EKhd	120	7.4	23	11	4.1	2.4	0.19	100.3	20.5	3.5
	140	9.0	27	13	4.7	2.3	0.17	111.0	25.3	3.4
	160	9.0	25.8	12.1	4.6	2.3	0.16	111.2	30.0	3.4
	180	9.9	27	13.9	3.7	1.4	0.07	127.0	32.9	3.4
EPOF	120	7.4	20.5	10.4	3.3	2.0	0.07	120	20.1	4.3
	140	8.2	22	12.5	3.7	1.8	0.06	127	24.1	4.2
	160	9.0	21	11.4	3.5	1.3	0.06	129	23.8	4.1
	180	8.6	22	13.2	2.7	1.3	0.03	138	26.7	4.1

Note. Heating rate, 0.5°C/min.

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Table 62  
Effect of molding temperature on the physicommechanical properties of epoxy-glass plastics

Glass Plastic		Pressing temperature, °C	Strength, kgf/mm <sup>2</sup>				Impact Strength, kgf m/cm <sup>2</sup>
Resin	Curing Agent		Tensile	Compressive	Bending	Inter-laminar Shear	
ED-13	Triethanolamine titanate	140	80.5	54.0	32.0	7.3	4.6
		160	80.0	55.0	32.0	7.2	4.7
		180	82.0	56.0	34.0	6.5	4.3
		200	82.5	55.0	33.0	5.7	4.0
EKhd	Triethanolamine titanate	140	86.5	69.0	98.0	9.8	4.8
		160	85.0	70.0	100.0	9.8	4.9
		180	86.0	70.0	100.0	9.0	4.5
		200	86.0	69.5	99.0	8.0	3.9
ED-13	Phenol-formaldehyde resin	160	64.0	46.2	69.0	6.9	4.3
		200	64.0	44.7	69.1	6.2	3.6

Note. Heating rate, 0.5°C/min.

Table 63  
Effect of holding time on the physicommechanical properties of epoxyamine binders 124

Resin	Holding time, h	Strength, kgf/mm <sup>2</sup>			Impact Strength, kgf m/cm <sup>2</sup>	Glass Transition temperature, °C	Adhesive strength, kgf/mm <sup>2</sup>	Dielectric constant	Micro-hardness, kgf/mm <sup>2</sup>
		Tensile	Compressive	Bending					
ED-13	2	6.8	18.0	10.5	0.35	98.5	3.0	3.2	16.5
	15	7.1	19.7	11.2	0.24	117.1	2.8	3.2	17.0
EKhd	2	8.0	25.8	12.1	0.16	111.2	4.6	3.4	30.0
	15	9.5	27.2	13.7	0.12	158.6	3.7	3.4	33.0

Note. Curing temperature, 160°C.

For epoxyphenolic binders, both excessively rapid heating (15-20°C/min) to 160-200°C and protracting of heating stages at 60-100°C are dangerous. Obviously, the proportions required between the rates of the main and side reactions are disrupted in both cases. On rapid curing, the polymer obtained is brittle and inhomogeneous in composition. The tensile, bending and impact strengths of the binder cured by rapid heating to 200°C are 2-2.5 times lower than on heating at a rate of 1-3°C/min. The cohesive strength of the binder whose heating stage was protracted at 60-100°C was 4-4.4 times lower, and the adhesive strength, 3 times lower than those of the binder cured under optimum conditions.



Table 64  
Effect of holding time on the physicomechanical properties of epoxyamine glass  
plastics

Resin	Holding time, h	Strength, kgf/mm <sup>2</sup>				Impact Strength, kgf m/cm <sup>2</sup>
		Tensile	Compressive	Bending	Interlaminar shear	
ED-13	2	80.0	55.0	82.0	7.2	4.7
	15	81.5	56.0	82.3	7.3	4.6
EKhd	2	85.0	70.0	100.0	9.8	4.9
	15	86.4	69.8	100.4	9.6	4.8

Note. Curing temperature, 160°C.

Epoxy resins cured with triethanolamine titanate are less sensitive to heating rate, but fast heating to 160°C is also undesirable in this case. Obviously, on brief heating to high temperatures, the initiation rate increases: 40-50% of epoxy groups are used up during the first few minutes, but at the same time, the collision frequency of intermediate polymerization products increases, and the number of chain breaks becomes more frequent. At the same time, the end products of curing consist of a multitude of short polymer chains and have low cohesive strength.

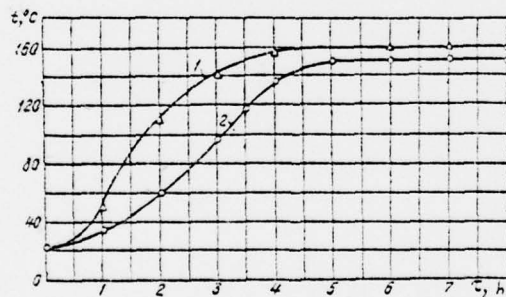


Fig. 58. Temperature difference as a function of heating time.  
1 - in mold; 2 - in article.

The heating rate has a stronger effect on the strength of articles than on the strength of specimens. At a high heating rate, a considerable delay in the heating of the middle layers (Fig. 58) is observed in an article because of the low thermal conductivity of the fiber glass plastic, causing the curing to occur

at different times and resulting in internal stresses. Thus, for a blade of a propeller 1.5 m in diameter, when the mold is heated at a rate of 0.8-1.2°C/min, the temperature lag in a cross section with a maximum thickness of 60 mm is 50-20°C. At a heating rate of 5-8°C/min, the temperature lag of the inner layers for the same blade amounts to 90-50°C and is unacceptable.

In the molding of fiber glass plastic articles for ship machine building, heating rates from 0.5 to 3°C/min have been established. A heating rate of 0.5°C/min is used in the fabrication of large-sized fiber glass plastic articles based on epoxydiane resins, when the mass of the mold exceeds 2 tons, and for all other fiber glass plastic articles (irrespective of size) based on polyfunctional epoxy resins.

Table 59 presents test results for binder specimens prepared at various temperatures. Specimens cured at 120°C have low cohesive and adhesive strength and microhardness, this being due to incomplete curing and the presence of unreacted epoxy groups in the structure of the cured binder. /126

As the curing temperature is raised above 160°C, the main adhesion centers, i. e., hydroxyls, disappear, and thermal-oxidative degradation of the binders takes place, causing a regular decrease in adhesive strength and a sharp increase in the brittleness of the cured binder. As the curing temperature of the binder is raised from 160 to 200°C, the residual stresses at the glass-polymer interface increase 1.5-fold (Fig. 59). The decrease in the adhesive strength of the binders inevitably leads to a sharp decrease in the strength of fiber glass plastics, particularly in interlaminar shear. As the molding temperature is raised to 200°C, the fatigue strength of fiber glass plastics under alternating and repeated static loads also decreases.

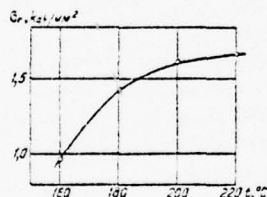


Fig. 59. Residual stresses  $\sigma_r$  in films of cured epoxyamine binder based on EPOF epoxyresorcinol resin vs curing temperature  $t$ .

In view of the fact that the durability of a fiber glass plastic and its delamination resistance are extremely important properties, a molding temperature of 140-160°C is recommended for ship machine building articles. The load-carrying capacity of propellers molded at this temperature is 20-30% higher than that of propellers molded at 200°C.

Tables 63 and 64 give the results of tests of binders and fiber glass plastics molded for 2 and 15 h at 160°C. The tests show that as the holding time is extended to 15 h, the cohesive strength and microhardness of the binders increases, and the glass transition temperature rises. At the same time, the adhesive strength and elasticity of the binders decrease. The strength of fiber glass plastic specimens at room temperature remains practically unchanged with increasing holding time. Increasing the holding time during the molding of fiber glass plastic articles causes an appreciable increase in heat resistance.

## 16. Fiber Glass Plastics with Protective Coatings

With the expanding scope of application of polymeric materials in ship machine building, it becomes necessary to develop materials combining a high structural strength with excellent erosion properties under different service conditions.

The principal structural polymer - fiber glass plastic - does not possess the /127 required erosion resistance in many cases. Fiber glass plastic, for example, is characterized by the erosion of the resin film under the influence of solar radiation and low cavitation resistance and resistance to hydroabrasive and abrasive wear. These disadvantages of fiber glass plastics limit their use for many articles in ship machine building where their application would be highly promising, for example as hydrofoil propellers and pump impellers operating in corrosive media.

The problem of increasing the erosion resistance of fiber glass plastics is solved by creating a surface layer made up of various polymeric materials or metals. The material is chosen in each specific case on the basis of the service conditions and technological characteristics.

The materials used most extensively as surface layers in ship machine building are thermoplasts, rubbers, polyurethanes and organic coatings.

The application of surface layers may be carried out by jointly molding the material of the coating and the main molding material, or applying on the finished fiber glass plastic. When the coating is applied on the finished plastic, the surface of the latter is subjected to shot blasting and degreased.

Thermoplast-base coatings. The thermoplasts used for coating fiber glass plastics are mainly polyethylene and various brands of fluoroplastics. The choice of a given thermoplast is made on the basis of its processing and mechanical properties. Thus, polyethylene, which has a high chemical stability, erosion resistance and water resistance, is recommended as a coating for plastic blades, rotors and housings of pumps handling corrosive fluids, operating in abrasive media, etc. Fluoroplastic 4, which has valuable antifriction properties, may be successfully used in friction components.

The application of a surface layer of thermoplasts is achieved in several ways:

- (a) using a lacquer of thermoplasts;
- (b) gluing or joint molding of fiber glass plastic with a film of thermoplasts;
- (c) cladding.

In the first method, the thermoplast lacquer is prepared by dissolving the polymer in a suitable solvent or solvent mixture. Depending on the brand of the polymer and its viscosity, lacquers of different concentrations are prepared.

The coating is applied in layers with a brush or paint sprayer on the cured fiber glass plastic. The application conditions are chosen as a function of the required coating thickness, brand of polymer and solvent. Only soluble thermoplasts - fluoroplastics of brands 42, 23, 2, and 26 - may be used for applying the coatings. /128

The optimum coating thickness is 100-150  $\mu\text{m}$ . When a coating over 150  $\mu\text{m}$  thick is obtained in this manner, its adhesion to the fiber glass plastic declines considerably, so that fiber glass plastics with such coatings are suitable only for service under atmospheric conditions, and their use for protection against cavitation and abrasives is ineffective.

This method is best suited for renewing the surface layer of articles, since it is technologically simple and may be carried out directly on ships.

It is well known that because of their chemical inertness, all thermoplasts have low adhesive strength. To improve the adhesive properties, the film is first activated; this consists in treating it with a solution of metallic sodium in a mixture of naphthalene and tetrahydrofuran for 15 min, then washing with acetone and water to remove the organic substances and salts. After the activation, the surface of the film is coated with an adhesive layer. The adhesive layer used may consist of epoxy adhesives, for example of the following composition: ED-5 resin - 100 pts. wt. and L-19 low-molecular polyamide - 80 pts. wt. Bonding of the activated film to the adhesive layer is carried out at a pressure of 25-50  $\text{kgf/cm}^2$  and may also be done on the finished fiber glass plastic as well as during the molding process.

Despite the activation of the film, this method does not provide for a dependable service of the fiber glass plastic under complex conditions. At the same time, the method of bonding the film during molding, which requires no additional operations and does not prolong the technological fabrication cycle, is a very promising one.

The most effective method of increasing the adhesion of film coatings is the introduction of epoxy compositions into the thermoplasts. The composition of the thermosetting film is chosen so as to obtain its high adhesion while preserving all the attractive properties of the thermoplast. One such material that has been developed is an epoxyfluoroplastic film based on fluoroplastics and an epoxy composition in the proportion of 80:20 to 92:8. Fluoroplastics of brands 42, 26 and 23 are used in the newly developed film.

To preserve the specified proportion of the components and ensure the joint curing of the molding material and surface layer, the melting temperature of the surface layer material should correspond to the curing temperature of the binder and amount to 150-130°C (depending on the type of binder employed).

When the melting temperature of the surface layer material is below the curing temperature of the binder, the molding involves mixing of the components of the surface layer and binder, leading to a disruption of the specified proportions and a decline in the properties of the surface layer. When a thermosetting film is used having a melting temperature above the curing temperature of the molding material, joint curing of the laminate is not achieved, and the adhesion declines sharply.

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To make the film convenient to handle and prevent its stickiness, it is necessary to use solid components of an epoxy composition, for example, solid epoxydiane resins with a molecular weight of 800-1200, which are compatible with fluoroplastics. To obtain a long storage period of the film, the curing agent should have a low activity at room temperatures. Therefore, aromatic polyamines may be used as the curing agent, with a melting temperature not below 100°C, for

example, 3,3',5,5'-tetrachloro-4,4'-diaminodiphenylmethane, 3,3'-dichloro-4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl sulfone.

The cladding method is based on the penetrability of a molten thermoplast. In cladding, adhesive strength is achieved by mechanical bonding of the thermoplast to the cells of the glass fabric.<sup>44</sup>

Cladding consists of the following operations. The thermoplast powder is applied on the shaping blanks of nonimpregnated glass fabric and melted in a closed mold under pressure. Because of the high viscosity of the melt, the thermoplast penetrates only partially into the thickness of the glass fiber, and the other side of the latter remains free of the thermoplast. The clad blank is coated with a solution of binder on the unprotected side and dried until the solvent is driven off. The blank obtained, one side of which is coated with the thermoplast melt, and the other side with the binder, is molded along with the main stack of blanks under the schedule usually employed for the given type of fiber glass plastic.

In selecting the brand of thermoplast, it is necessary to consider the following conditions:

(a) the thermoplast must have a high viscosity of the melt to ensure only a partial penetration of the thermoplast into the cells of the glass fabric;

(b) the melting temperature of the thermoplast should be higher than that of the viscofluid state of the binder to avoid mixing the binder and material of the surface layer in the course of the molding.

Rubber-base coatings. Rubber, which has highly elastic properties, withstands abrasive, hydroabrasive and cavitation wear better than other materials. Because of their high elasticity, rubber coatings absorb most of the kinetic energy expended in reversible deformations.

The highest wear resistance is exhibited by rubbers based on Nairit and polyurethane rubbers.

Rubberizing may be accomplished in two ways: bonding calibrated uncured rubber to cured fiber glass plastic, followed by heat treatment in molds at a specific pressure of 100-150 kgf/cm<sup>2</sup>, and suitable temperatures and rubber vulcanization times, and

joint molding of impregnated glass fabric with vulcanized calibrated rubber under conditions selected for molding the given type of fiber glass plastic.

In both cases, use is made of adhesive sublayers, the best of which is leuconate adhesive (MRTU 6-14-235-69). Leuconate is a 19-21% solution of paratriphenylmethane triisocyanate in dichloroethane. In the first method, to increase the adhesion, the surface of the fiber glass plastic is subjected to shot blasting and degreasing, and the adhesive sublayer is applied on it. In the second method, the adhesive sublayer is applied on the surface of rubber preactivated with concentrated sulfuric acid.

Rubber coatings are easily damaged in service because of the low cohesive strength of rubber.

Polyurethane-base coatings. In their properties, polyurethanes are analogous to rubber coatings, but excel them in wear resistance. The technology of application of polyurethane coatings on fiber glass plastic articles is similar to that of application of polyurethanes on metal articles and is described in detail in Chapter 10.

## 17. Metallization of Fiber Glass Plastics

Metal coatings impart special properties to fiber glass plastics and improve their erosion resistance.

Valuable properties of the coatings are manifested when their thickness is less than 1  $\mu\text{m}$ . In most cases, the metal is held on the fiber glass plastic by the physical bonds between the molecules of the metal and macromolecules of the binder. When metallized articles are used at fluctuating temperatures, it is necessary to consider the existing significant difference between the linear expansion coefficients of the metal and fiber glass plastic (a 2 to 10-fold difference), which gives rise to internal stresses.

A substantial number of methods of metallizing fiber glass plastics are known; vacuum evaporation, cathode sputtering, reduction of the metal from gaseous compounds, chemical and electroplating, and metal spraying. In practice, the latter three methods have become the most popular ones.

The method of obtaining metal coatings by chemical reduction of metals from salts or complex compounds consists in carrying out oxidation-reduction reactions based on electron exchange. The rate of the reaction, i. e., reduction of the metal, depends on the type of reductant, hydrogen ion concentration (pH), temperature, and presence of a catalyst. Metal ions bound into complex compounds are most easily reduced. The adhesive strength of a metal coating obtained in this manner is determined by the adhesion between the surfaces of the metal and fiber glass plastic and is a function of the wettability and roughness of the fiber glass plastic surface. /131

The chemical metallization method produces smooth, brilliant and matte surfaces. Disadvantages of this method include a complex preparation of the surface, the difficulty of metallizing large-sized and shaped articles, considerable labor intensity, and high losses of metal due to its deposition on the tub walls. A new chemical metallization method - the sorption method - has been developed in the last few years.

Electroplating metallization is based on the deposition of metals from aqueous solutions or salts by electrolysis. The quality of the coatings depends on the electrolysis conditions, concentration of the salt of the deposited metal in the electrolyte, temperature, current density and shape of the article.

In many cases, to increase the adhesion of the electrodeposit, carbon black or graphite, which under suitable conditions becomes exposed, is introduced into the binder of the fiber glass plastics. The best adhesion of electrodeposits is achieved by means of special etching, for example in concentrated sulfuric acid or a mixture of sulfuric and chromic acids. Etching of the surface leads to the formation of microchannels and microcavities which are filled with chemically reduced copper, silver, or palladium. The current-conducting layer obtained is subjected to copper, nickel, or chromium plating. An electrodeposit 30  $\mu\text{m}$  thick has a high wear and corrosion resistance.

The chief disadvantages of electroplating are the high cost, complexity, and difficulty of the process.

One of the cheapest and most universal metallization methods is spraying. This is a thermomechanical process, in which the molten metal is pulverized into fine particles by an air jet and deposited on the surface of the article. The spraying method may be used to obtain a coating thickness up to several millimeters. Metals or their alloys with fairly low melting points are used for spraying.

The technological process of spraying involves three consecutive operations: preparation of the surface, deposition of the coating, and treatment of the coating.

Preparation of the surface consists in degreasing it and making it rough by means of shot blasting treatment. The spray coating is then carried out in a special metallization chamber.

Depending on the initial state of the sprayed metals and method of their fusion, the spraying is carried out by using different types of equipment:

- wire gas type;
- wire electric-arc type;
- powder type;
- operating on liquid metal.

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In the metallization of fiber glass plastics, the articles cannot be heated above 100°C.

The best spraying results are obtained with a normal direction of motion of the metal particles. If the particles are incident on the surface being sprayed at an angle smaller than 60°, they are reflected from it. The distance from the nozzle of the metallization device to the workpiece should be 10-15 cm. If this distance is greater, the diameter of the metal-air jet increases, the velocity of the sprayed particles decreases, and oxidation and the porosity of the coating increase. Thus, for example, when the distance from workpiece to the nozzle is 30 cm, the oxide content of the coating is 40%, its wear resistance decreases by a factor of 5-10 and its hardness by a factor of two.

For each type of sprayed metal, there is an upper limit of coating thickness above which the metal peels off and cracks. Thus, for zinc this value is 0.15-0.20 mm, and for aluminum, 0.3-0.4 mm.

A coating obtained by spraying has no metallic luster, is quite porous (up to 60% by volume) and has a rough surface. To give the surface the necessary finish and reduce the porosity, the coating is polished after spraying.

Metallization markedly increases the heat resistance of fiber glass plastics, this being due to the high reflectivity and thermal conductivity of the metal. Metal coatings reflect up to 92% of luminous and thermal radiation. The coatings increase the chemical resistance and dimensional stability of articles used at elevated temperatures. The working temperatures of articles after metallization are raised by 50-100°C.

Metal coatings decrease the water absorption of articles made of fiber glass plastics and increase their resistance to corrosive media. The erosion resistance to abrasive and hydroabrasive wear of the articles is markedly improved. For example, the abrasive wear resistance of fiber glass plastic articles with a steel coating is five times greater than the erosion resistance of the same articles without a coating.<sup>45</sup>

At the present time, the plastics metallization technology is being steadily improved, and the industrial application of metallized polymers is rapidly increasing. Thus, while in 1965 the consumption of metallized ABC copolymer in U.S. shipbuilding was 300 tons, in 1970 it rose to 2,000 tons.

In the metallization of plastic articles, it is necessary to consider that the assortment of polymers suitable for metallization is very limited. Three main groups of plastics are distinguished according to the magnitude of adhesion between the polymer and metal coating.

The first group includes polymers providing for high tear resistance (3-5 kg) /133 and an adhesion strength stable with time, such as special grades of ABC copolymers, polypropylene and polysulfone. The second group includes polyester resins and certain copolymers of styrene, for example with acrylonitrile or butadiene. Metallization of such polymers is most desirable when they are used for the fabrication of comparatively small articles of spherical and round shapes, since adhesion in such cases is achieved only as a result of the so-called enveloping effect.

The third group of plastics, which lends itself least to metallization, includes polyvinyl chloride, polyamides, epoxy, phenol-formaldehyde and urea-formaldehyde resins, polycarbonates, and polyformaldehyde. Some of these plastics can be successfully metallized by spraying. However, metal coatings on articles made of such plastics usually exhibit poor resistance to mechanical and thermal stresses.

Of great importance is a proper selection of articles suitable for metallization. In each case, the selection of the article is determined by economic, technological and service considerations, which are taken into account in the selection of the metallization method and brand of plastic. The shape and design of the article must meet the requirements of the technological metallization process, since they determine the adhesive strength of the metal coating.

The characteristics of each metallization method must be considered; for example, in electroplating metallization - the nonuniformity of the metal coating on the surface of the article: the metal deposits faster on faces and projections than in depressions, recesses, cavities and covered areas.



Chapter 5. BASIC PRINCIPLES OF DESIGN OF SHIP MACHINE BUILDING ARTICLES MADE OF FIBER GLASS PLASTICS AND EQUIPMENT FOR THEIR MOLDING

13. Basic Principles of Design of Articles

As was noted previously, epoxy glass plastics are used in ship machine building for making ship propellers, fan and pump impellers, various types of fairings, etc. In view of the relatively limited experience in the fabrication of such articles from fiber glass plastics, there are no special methods of their structural design, and as a rule, the design of such articles is carried out at the present time by using methods adopted for the corresponding metal articles. However, all designs used for metals cannot be mechanically transferred to the design of articles made of fiber glass plastics. It is necessary to consider such characteristics of fiber glass plastics as anisotropy of physicomachanical properties, brittleness of glass fiber, less elastic properties, relatively low fatigue strength, etc. /134

In the design of articles made of fiber glass plastics, it is necessary to avoid abrupt changes in thickness and discontinuous junctions, since this is associated with sharp bends and breaks of the glass fiber which inevitably result in considerable loss of strength. To obtain equivalent strength and rigidity margins of metal and plastic articles, their cross sections must sometimes be made thicker. In each individual case, the size of the thickening is determined by the relationship between the ultimate strength and elastic modulus of the plastic and metal. When shaping the cross sections, it is necessary to keep in mind that thin sharp edges of fiber glass plastics are insufficiently strong; the smallest allowable radius of curvature of the edges is 0.75-1.5 mm, depending on the size of the articles. /135

When threaded joints are made, it is necessary to use metallic reinforcement. The latter should be made of steel, since its coefficient of linear expansion is the closest to that of fiber glass plastic. The reinforcing material in the article should be oriented so that the maximum number of fibers coincide in direction with the trajectory of the principal normal stresses arising in the article during service. The remaining fibers should be oriented according to the direction of action and the relationship of other stresses in the article.<sup>57</sup>

In addition, when designing articles it is necessary to consider the technological feasibility, related to the limited dimensions of the hydraulic presses and the difficulties involved in fabricating the equipment.

The design of ship machine building articles made of fiber glass plastics is discussed in greatest detail by using the example of ship propellers (Fig. 60).

Ship propellers are made in either all-plastic or composite form. Advantages of the all-plastic version include a smaller mass of the propeller, low labor intensity of fabrication, and absence of a metal boss and bracing parts.

However, in selecting the version to be constructed, it is necessary to consider the following:

- impossibility of molding all-plastic propellers larger than 1.2-1.5 m in diameter because of the limited dimensions and power of the molding equipment; /136
- impossibility of molding all-plastic propellers having overlapping blades (in normal projection);

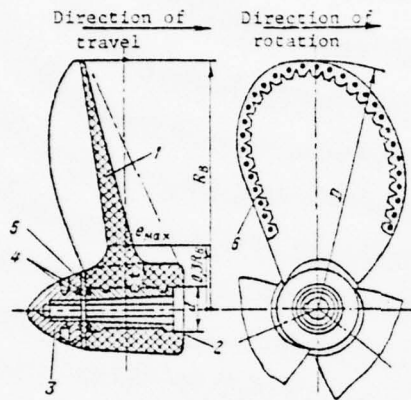


Fig. 60. All-plastic propeller.

1 - fiber glass plastic blade; 2 - reinforcing hub; 3 - firing nut; 4 - packing rings; 5 - lock washer; 6 - edging.

reduction in the strength of all-plastic propellers in the region where the blade meets the boss, due to the bending of the glass fiber unavoidable in this region.

Most popular are propellers of composite design, which consist of plastic blades, metal bosses and metal bracing parts. The joint between the blades and boss is made rigid for fixed pitch propellers (FPP). The bosses and bracing parts of propellers are made from the same brands of metals as metal propellers.

The blade cross sections of all-plastic propellers are made 40-50% thicker than metal ones, and in addition, the allowed stresses are reduced by 25-30%.

To reduce the effect of bending of the glass fiber on the strength of the blades, the radius of the fillets is taken to be equal to  $(0.04-0.05)D$ , where  $D$  is the propeller diameter.

The boss of all-plastic propellers is in the shape of a truncated cone with a larger diameter on the forward end of the boss. The conicity of the lateral surface of the boss is taken to be equal to 1:5 and 1:6. Likewise, the use of a barrel-shaped boss which also has a larger diameter on the forward end is allowed. The boss diameter should be no greater than 0.2-0.25 of the propeller diameter.

The joint between the all-plastic propeller and the shaft may be both a key joint and a splined joint (Fig. 61). In a key joint, the conical opening is re-

inforced with a metal hub. If the propeller has threaded openings, reinforced metal elements are provided for them. To improve the bond between the reinforcing hub and the fiber glass plastic, knurling in the form of radial and axial grooves is made on the outer surface of the hub. In the case of a splined joint between the propeller and shaft, the use of a reinforcing hub may be omitted.

To provide for the necessary strength, the thickness  $t$  of the fiber glass plastic layer around the reinforcing hub is

$$0,3d < t < b_{max}, \quad (32)$$

where  $d$  is the diameter of the reinforcing hub;

$b_{max}$  is the maximum blade thickness in the root section.

Because of the lower shearing strength of fiber glass plastic in comparison with metal, all the locking elements (clearance lugs of lock washers, screws, etc.) are placed in the reinforced metal hubs. To protect the end of the shaft from penetration of water from the rear and forward ends, the boss is sealed with gaskets or cord made of rubber and foam plastic. The fairing nuts are made as in metal propellers. /137

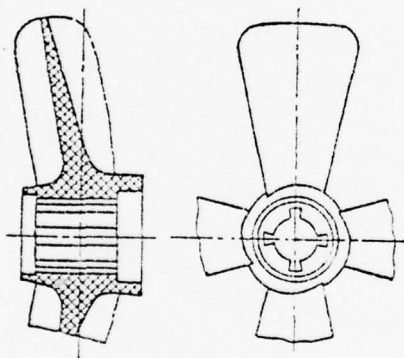


Fig. 61. Splined joint between all-plastic propeller and shaft.

In designing propellers in the composite version (Fig. 62) particular attention should be given to the choice of the type of joint between the blades and boss, since this component carries the highest load and is difficult to build. The use of a design for mounting plastic blades which duplicate the mounting of metal blades (the blades had a joining flange and were mounted on the boss by means of mounting pins) has led to negative results, i. e., breakage of the blades. The blades broke along the flange. An analysis of the causes of the failure showed that in this design, it is impossible to obtain a blade with the appropriate strength, since the glass fibers in the junction area between the blade and the flange are inevitably subjected to bending that leads to a marked decrease in local strength.

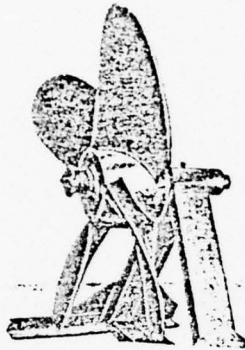


Fig. 62. Composite propeller with plastic blades.

From the standpoint of maximum utilization of glass fiber strength, the best mounting design is the wedge-shaped type, i. e., the so-called dovetail, in which the blade root is a natural extension of the blade with a very slight change in thickness. Wedge-shaped mounting is reliable in service and requires the smallest boss dimensions. When mounted in this manner, the blade has a root in the shape of a truncated wedge with a small angle at the apex. A wedge-shaped slot of suitable dimensions is made on the boss, then the blade is inserted into this slot and rigidly mounted.<sup>57</sup>

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#### 19. Technological Molding Equipment

The chief type of technological equipment used for making ship machine building articles from hot-pressed epoxy glass plastic are press molds. Press molds must meet stringent requirements for accuracy and finish of the shaping surfaces, since their quality determines the accuracy and surface finish of fiber glass plastic articles.

Depending on the dimensions of the molded article, both loose and fixed type press molds may be employed. Press molds with a mass no greater than 25 kg may be made loose, and as an exception, loose press molds of greater mass (up to 100 kg) may be allowed for making experimental specimens. As a rule, fixed press molds, which considerably facilitate the molder's work, are used for molding articles used in ship machine building.

Structurally, press molds may be of open or closed type. The latter are most convenient to handle and produce articles of the best quality. The seam obtained with closed type molds is practically insignificant and does not affect the dimensions of the article. However, fabrication of such molds for intricate-shaped articles is very costly, and therefore their use is justified only for articles of simple configuration.<sup>58</sup>

Open-type molds with a horizontal splitting plane without charging chamber are used for fabricating articles of complex configuration such as ship propeller blades, turbine impellers, etc.

Open-type molds are easier to fabricate and their design is simple and convenient in placing the parisons of molding material and unmolding the article. In the course of molding in such molds, a seam that must be removed is formed in the junction between the die and the force. In steel press molds, the die should have a shearing lock for pressure trimming of the seam.

The parts of press molds may be divided into two groups: those participating directly in the shaping of the article (die, force, linings, cores, inserts, rings, pushers), and those performing auxiliary operations in joining the parts of the press mold and opening, heating and cooling it, etc. (force holders, bands, heating platens, heating elements, upper and lower platens, supporting platens guiding the columns and inserts, mounting parts). /139

Press mold parts of the first group operate at high loads with prolonged heating at 160-170°C. For this reason, materials used for these press mold parts should be machinable and have minimum deformations during heat treatment and high hardness, wear resistance, heat resistance and mechanical strength.

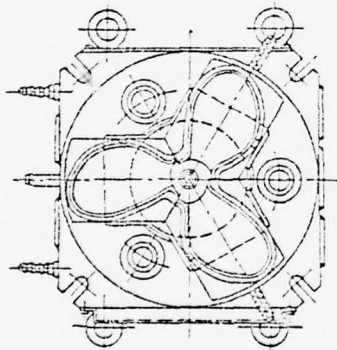


Fig. 63. Mold for all-plastic propeller.

These requirements are met by tool and alloy steels. When the production volume does not exceed a few hundred articles, use may be made of cheaper and machinable carbon and structural alloy steels.

When the production volume does not exceed 100 pieces, aluminum alloys such as silumins may be used for press mold parts of the first group. Silumins (alloys based on the aluminum-silicon system) have the necessary casting properties combined with satisfactory mechanical properties. Silumin press molds are 1.5-2 times less expensive than steel ones.

An appreciable reduction in the cost and labor intensity of fabrication of press molds for ship machine building articles is achieved by using metal-cement press molds. Such molds are 5 to 8 times cheaper than steel molds, and the

duration of their fabrication is reduced by a factor of 3 to 4. They are recommended for molding a small number of articles (not more than 20 because of their low wear resistance).

Metal-cement press molds (Fig. 63) consist of the following main parts: welded bodies of the dies and punches of shaping shells, filler, support plates, and parts for unmolding. Of these parts, those subjected to the most wear are movable cores, guiding columns and bushings, and therefore in order to raise the resistance, they are subjected to heat treatment and chromizing.

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Press mold parts of the second group are made of carbon steels in all cases.

In determining the position of an article in a press mold, the following steps are taken:

- (a) one-piece propellers are placed with the plane of the disk perpendicular to the direction of pressing, and with the suction surface facing the die;
- (b) individual blades are placed with the plane of the largest projection perpendicular to the direction of pressing;
- (c) fairings are placed with their axes in the direction of pressing.

With these positions of the articles in the press mold, the best molding conditions are achieved, the possibility of slipping of the parisons upon application of the pressure is eliminated, the design of the press mold is simplified, and its height dimensions are decreased.

In making unions of press mold parts, fixed joints of the shaping cores with the force and die, on the one hand, and joints of guiding columns with bushings are achieved by means of tunking or force fit. Movable joints of shaping cores and pushers with the force and die are made by use of running fit, and movable joints of guiding columns with bushings - by use of running fit  $X_3$ .

The quality of the articles is determined to a large degree by the finish of the shaping surfaces of the press molds, which should be 1-2 classes higher than the required surface finish of the articles. Thus, the shaping surfaces of the press mold die and force should have a finish of at least class 8-10.

The surface finish of articles which do not directly participate in the shaping of an article (lateral surfaces of forces and dies) and the finish of the mating surfaces of the guiding elements and parts (guiding columns and bushings) should not be below class 8.

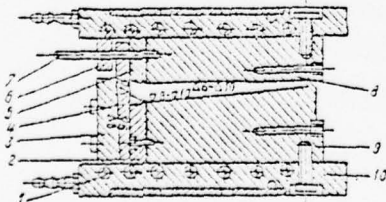


Fig. 64. Press mold for individual blade.

1 - electric heater; 2 - die insert; 3 - die holder; 4 - shaping insert; 5 - force insert; 6 - force holder; 7 - pin; 8 - force; 9 - die; 10 - heating platen.

Press molds for molding ship machine building articles from hot-pressed epoxy-glass plastics must be heated to 160-170°C. The shaping surfaces must have a uniform temperature field with deviations no greater than ±5°C. The appreciable inhomogeneity of the force and die thicknesses during molding of intricate-shaped articles leads to major difficulties in providing for a uniform temperature field. A more uniform field can be obtained by removing heat carriers from the shaping surfaces and reducing the total amount of heat supplied. However, all these steps increase the press mold heating time, i. e., prolong the molding cycle.

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In practice, steam and electric heating of press molds are the two principal methods used. Steam heating is less expensive and can be closely controlled. However, it can be used only by plants with the necessary boiler equipment. The heating lines through which the steam is circulated are usually made in the heating platens, and sometimes in the force or die base itself. The total length and number of the lines are determined by calculation according to the steam parameters.

The chief type of electric heating used for press molds is ohmic heating with tubular elements.

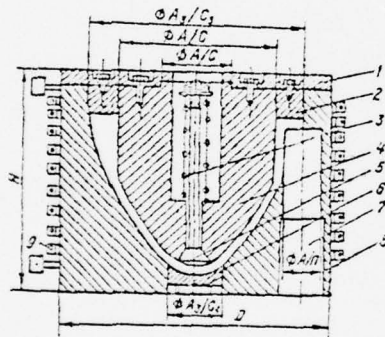


Fig. 65. Press mold for propeller fairing.

- 1 - force holder; 2 - ring;
- 3 - spring; 4 - force head;
- 5 - ejector; 6 - die insert;
- 7 - cylindrical core; 8 - die;
- 9 - induction coil.

In the construction of press molds with a high relative height ( $H/D = 2-4$ , where  $H$  is the height and  $D$  is the outside diameter of the press mold), for example press molds for propeller fairings, heating with tubular elements is inefficient and does not provide for the required temperature uniformity. In such cases, induction heating with industrial frequency current is used for steel press molds. The induction coils are made in the form of spiral cylinders of copper tubing. The calculation of induction heating amounts to determining the power and dimensions of the induction coil.

As an example, Figs. 63-65 show press molds for all-plastic propellers, blades and propeller fairings.

Chapter 6. TECHNOLOGY OF FABRICATION OF FIBER GLASS PLASTIC ARTICLES FOR SHIP MACHINE BUILDING

Ship propellers, parts of airfoil fans, pump impellers and blades of compressors made of fiber glass plastics have much in common in their fabrication technology. These articles are usually made with a metal edging that increases their shock resistance and operational reliability. /142

The process of fabrication of such articles from fiber glass plastics includes the following operations: cutting of the molding material and preparation of the edging, placing of the molding materials in the mold and preforming, placing the edging on the preform, holding at temperature under pressure and cooling, and finally, unmolding followed by machining.

In the molding of intricate-shaped fiber glass plastic articles, the operations involving preparation and placement of the molding material are of particular importance, since the correct placement assures the necessary geometry and external appearance of the article. This is due to the fact that a fiber glass plastic laminate is characterized by a low flowability of the molding material, so that its ability to be redistributed over the cavity of the press mold under the influence of pressure is extremely limited. As an example, the technology of fabrication of all-plastic and composite ship propellers is discussed in detail below.

20. Ship Propellers

The shape and dimensions of composite propeller blades required by the drawing are achieved by using a packet of blanks of impregnated glass fabric, cut in accordance with the drawing of the articles.

Cutting of blanks out of impregnated glass fabric is carried out according to the drawings, which are made as follows.<sup>56</sup> The cross sections of the developed contour of the blade are cut every 2-4 mm by planes parallel to the chord of the section. The contours of the templates are drawn by using the points obtained. A graphical version of a cut-out article is shown in Fig. 66. /143

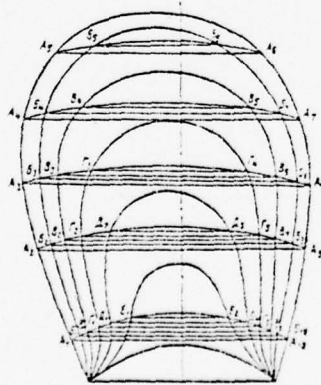


Fig. 66. Diagram of templates for cutting the molding material for a propeller blade.



The required number of blanks is calculated from the following formulas:  
number of main blanks per blade

$$n_m = \frac{t_{\max}}{\Delta t} \delta; \quad (33)$$

number of blanks shaping the blade root,

$$n_r = \frac{t_r - t_{\max}}{\Delta t} \delta, \quad (34)$$

where  $t_{\max}$  is the blade thickness in the root section, mm;  
 $\Delta t$  is the thickness of one sheet of impregnated glass fabric, mm;  
 $t_r$  is the maximum thickness of the blade root, mm;  
 $\delta$  is the pressing coefficient of the material.

The pressing coefficient is determined from experimental data obtained by molding a test specimen:

$$\delta = \frac{\Delta t}{t} n, \quad (35)$$

where  $t$  is the thickness of the molded specimen, mm;  
 $n$  is the number of blanks.

In preliminary calculations, the pressing coefficient of glass fabrics impregnated with epoxy binders may be taken as 1.25-1.35.

The number of blanks, determined by calculation, is controlled according to the mass. Theoretical cutting is refined by experimental controlled placement of the charge of molding material in a cold press mold; by selecting the position of the numbers of sections, one achieves a smooth transition of the blade into the root and the proper shaping of the blade surface and contour. The charge of blade molding material is also more accurately determined experimentally on the basis of two to three experimental moldings. /144

The material is usually cut into blanks manually, using cutters of U8A tool steel (GOST 1435-64). The molding material to be cut is first marked with templates. The latter are made of polyvinyl chloride plastic Getinaks, aluminum, or other sheet material. When marking the material, it is necessary to follow strictly a specified orientation scheme. A mass-corrected set of blanks is dismantled strictly by sections and stored in a refrigerator at  $0 \pm 5^\circ\text{C}$ .

The edging is made of stainless brass or steel sheet (Fig. 67).

The final adjustment of the edging is made on a model of the blade before complete adhesion to the model is obtained. The points of the edging sheet are set so that the distance between them is not less than twice the thickness of the blade edge, and bent at a  $90^\circ$  angle.

The inner surface of the edging is etched, washed with water, dried, and coated with a layer of BF-4 Butvar-phenol adhesive (GOST 12172-66). The Butvar-phenol adhesive increases the adhesive strength between the surface of the edgings and the blade material.

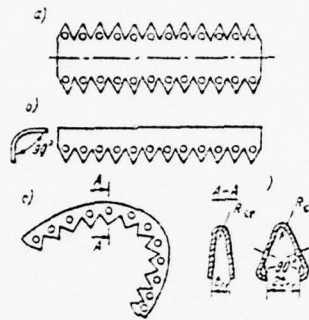


Fig. 67. Diagram of preparation of edging: a - spreading out of the edging after the cutting of teeth and drilling of holes; b - edging after preliminary bending; c - edging after bending to radius and model; d - edging after setting and bending of teeth.

The material is placed in a press mold preheated to 40-50°C. A separating layer is first applied on the working surface of the force and die. A K-21 (MRTU 6-02-457-63) organosilicon fluid of 10% concentration is most frequently used as the separating layer. Application of this fluid requires heat treatment for 2 h at 210-230°C. The organosilicon separating layer withstands 10 to 20 moldings.

The lower half of the stack of blanks is placed in the die in order of increasing numbers, and the upper symmetric half of the stack is placed in reverse order. During the placement, all the main blanks are interlaid with additional blanks of the root. If necessary, periodic pre moldings of the material are performed in order to compact it at a specific pressure of 0.5  $p_{eff}$ .

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After all the blanks have been placed, preforming is carried out at the full effective molding pressure for 3-5 min at 40-60°C.

The shaped preform is cut along its contour by 5-8 mm (depending on the size of the blade), then the edging is placed on the blade. The edging is reduced with a press for 3-5 min at a specific pressure of 0.2-0.3  $p_{eff}$ . The carefully placed edging should be uniformly compressed over the entire contour of the blade with a maximum clearance of 3 mm, no marks of "biting" of the edging or unbending of the teeth being permitted.

The press mold is closed, and the molding is carried out according to the schedule worked out for the given type of fiber glass plastic.

The molded blade is machined. The machining is performed on: the blade edges, in order to remove the seams and provide for the radius of

curvature required by the drawing and for an edge finish not below 76;  
the lateral faces of the root of a detachable blade for placing the blade  
in the slot of the hub by sliding fit with the required space.

The removal of the seam along the contour and the finishing of the edges are  
done with a hand tool (metal hack saws, files, emery paper) or a pneumatic hand  
tool. Depending on the thickness of the seam and blade edges, use may be made  
of RT-2 trimmers, PN-1 and PN-5 pneumatic hack saws, TsDM and TsDM-30 disk saws,  
ShP-2 and ShR-06 pneumatic grinders, and DM-175 trimmers.

The lateral faces of the blade root are worked with a cutting tool used for  
metal working, but with a special geometry of the cutting part, the blade being  
clamped in a special device.

Acceptance of the blades is based on the results of their external inspection,  
determination of the blade mass, pitch and radius, and a strength check.  
The radius and pitch are determined by means of a portable pitch gauge mounted  
directly on the propeller hub. A preliminary check of the blade pitch is made  
because the adopted designs and method of bonding the plastic blade to the metal  
hub make it possible when necessary to correct the blade pitch and reduce the  
difference in pitch between the blades by rotating the root in the slot of the hub.  
Adjustment of the propeller pitch is used within  $\pm 10\%$  of the nominal pitch, and  
this has practically no effect on the propulsive qualities of the propeller.

During the assembly of the propeller, the contact surfaces of the parts to be /146  
joined are degreased and coated with a thin layer of K-153 epoxy compound. The  
blade is mounted in the slots of the hub and press-fitted with wedges. After  
pressing, the ends of the wedges are cut off flush with the ends of the hub.  
Machining of the wedges is not recommended, since this operation involves a  
crumpling of the root that may weaken the joint between the blade and the hub.  
During the pressing of the wedges, the blade root is subjected to compression and  
therefore, the length of the compressed part of the wedge is first calculated to  
provide for the required tension. The elements of fit of the edges are calculated  
by a special method.<sup>57</sup> Measurements of deformations have shown that the compression  
stresses in the root during pressing with wedges reach 100 kgf/cm<sup>2</sup>, which amounts  
to 2-3% of the compression strength of the fiber glass plastics and is safe.

The assembled propeller is subjected to static balancing on equipment used  
for balancing metal propellers.

The technology of the molding of all-plastic propellers is identical to that  
of molding of blades of composite propellers. Some changes are introduced only  
into the cutting and placement of the molding material. The blanks are usually  
cut for each blade separately, since the warp of the glass fabric must be exactly  
parallel along the axis of the blade, and the blades are at an angle in the pro-  
peller (Fig. 68). The root part of each blade blank must end in a ring forming  
the hub.

The total number of blanks per propeller is determined from the formula

$$n_p = \frac{L_h \cdot \delta}{\Delta t} \quad (36)$$

where  $L_h$  is the hub length, mm;

$\delta$  is the pressing coefficient;

$\Delta t$  is the thickness of one sheet of impregnated glass fabric, mm.

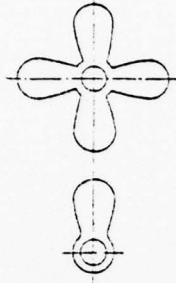


Fig. 68. Templates for cutting molding material into all-plastic propeller.

The number of main blanks per blade is

$$n_{ma} = \frac{t_{max} \delta}{\Delta t}, \quad (37)$$

where  $t_{max}$  is the thickness of the blade in the root section, mm.

The number of additional ring blanks necessary for shaping the hub is

$$n_r = n_p - n_{ma}. \quad (38)$$

Blanks of molding material are placed in a predetermined pattern; the main ones must adhere closely to the central core. Ring blanks are placed at regular intervals between the main blanks. The upper part of the hub is shaped only with ring blanks. During the placement of the blanks, they are additionally pressed at a specific pressure of  $0.5 p_{eff}$  if necessary. Ring blanks are pressed in the upper part of the hub by means of special inserts at a specific pressure of 2-3 kgf/cm<sup>2</sup>.

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After molding, the following parts are subjected to machining:  
 blade edges, to remove the seam and obtain the required radius of curvature and an edge finish not below 76;  
 end surfaces of the propeller hub, to achieve the required dimensions along the height of the hub and perpendicularity of the support planes to the propeller axis;  
 splined opening in the propeller hub, to obtain the required precision of the opening for mounting on the shaft.

All-plastic propellers are controlled with respect to mass and geometric dimensions. The unbalance of the propellers is eliminated by drilling holes in the hub and filling it with lead.

## 21. Compressor Blades

Compressor blades of ship gas-turbine installations operate in a moving unsteady flow of gases whose temperature is 200-300°C. During their operation, the

compressor blades are subjected to the combined action of centrifugal and inertial forces of a cyclic character. Moreover, the gas flow contains inclusions of various solid and liquid particles which collide with the blades at speeds of 100-300 m/sec, causing their erosion wear and corrosive damage.

At the present time, compressor blades are made chiefly out of stainless steels, for example, Kh17N2. The manufacture of intricate-shaped blades from stainless steel is a laborious process consisting of 20-25 operations.

The use of plastics for compressor blades makes it possible to reduce the labor intensity of their manufacture by a factor of 10-15, to decrease the mass of the gas-turbine installation significantly, to raise its efficiency, and to eliminate corrosive attack of the blades.<sup>15, 19</sup>

Because of increased requirements for the strength and erosion resistance of the material of compressor blades made of polymers, the most suitable material are fiber glass plastics with a special protective coating. Thus, Rolls Royce and Westinghouse Electric make compressor blades out of fiber glass plastics containing phenolic and polyimide binders, which are characterized by high heat resistance. Research is being conducted on the application of carbon-filled plastics.

Favorable experience in the operation of low-pressure straightener compressor /148 blades of ship gas-turbine installations operating at 80-100°C has been accumulated in the Soviet Union. These blades are made by hot molding in closed-type press molds of oriented fiber glass plastic with a phenol binder (brand AG-4S). Special antierosion coatings, i. e., polyurethane, metal, and others, are used to increase the erosion resistance of such blades. The technology of manufacture of compressor blades is analogous to that of ship propeller blades.

Extensive use of plastic materials for compressor blades is limited by their comparatively low heat and erosion resistance. Most economical at the present time is the use of plastics for compressors of experimental turbines, permitting a considerable reduction of the labor intensity, cost and period of manufacture of turbines.<sup>20</sup>

## 22. Vessels for Storing Gases and Liquids

The shape of the vessels for storing liquid and gaseous products is most frequently cylindrical or spherical, or a combination of these shapes. Most convenient from the standpoint of economy of the material and uniform stress distribution is the spherical shape. The use of reinforced plastics considerably simplifies the technology of manufacture of the vessels and reduces their mass.

The chief method of manufacture of the vessels is winding, whereby the reinforcing material impregnated with a binder is wound onto a mandrel under tension. The heat treatment is carried out on the mandrel in a heating chamber. Depending on the strength requirements of the vessels, different combinations and versions of designs for placing the reinforcing material on the mandrel during the winding are used in specified directions. In the production of cylindrical vessels operating under pressure, the glass fibers are arranged so that the strength of the vessels in the annular direction is twice as high as the strength in the longitudinal direction.

The choice of equipment for the winding is determined by the structure of the article and type of winding. The winding technology and equipment are discussed in detail in the literature.<sup>5\*</sup>

Vessels made by winding without the use of an inner sealing coating may be used at effective pressures up to 4-6 kgf/cm<sup>2</sup>. At elevated pressure, such containers fail because of leaks. To improve the gas tightness, coatings of rubber and thermoplastic materials are employed.

### 23. Propeller Cones

In modern shipbuilding, carbon and stainless steels and nonferrous alloys (bronze and brass) are the chief materials used in the production of propeller cones. The use of fiber glass plastics makes it possible to reduce the cost of cones severalfold as a result of the reduction (by a factor of 2-4) in the labor intensity of manufacture and savings of scarce metals, and also to decrease their mass by a factor of 3-4 in comparison with metal cones, and to eliminate electrochemical corrosion. Positive experience has now been accumulated (in the course of five-six years) in the operation of plastic cones of fixed and variable pitch propellers 0.3-2.9 m in diameter for various types of ships. /149

In most cases, plastic cones are mounted on a standard portion of a metal cone without a change in the joint. In their design, the basis used is the structure of the corresponding metal cones, the following requirements being considered:

the surfaces parallel to the direction of pressing are made with technological gradients of not less than 2%;

undercuts and surfaces with reversed gradient relative to the direction of junction are not allowed;

fitting sites are made with a gap of third grade of fit; all tunking (interference) type fits are reinforced with metal, since fluctuations in the fit of the molding material make it impossible to obtain a grade of fit above three, and interference fits are gradually weakened by the creep of fiber glass plastics;

stiffeners are provided to increase the rigidity of the body in cones over 500 mm in diameter.

According to the operating conditions, cones and their structural elements may be divided into two groups: those designed only to function as a stream lined structure and those additionally performing the functions of sealing the hub of a variable-pitch propeller. The first group includes standard type fixed-pitch propeller (FPP) cones and variable pitch propeller (VPP) cones with an insulated hydraulic or mechanical blade-setting system (Fig. 69). Such cones are subjected to a hydrostatic pressure determined by the depth of submersion of the propeller and to the action of the water thrown by the propeller. Because of the small magnitude of these loads, cones of the first group usually are not designed for strength, and the main geometric dimensions are chosen on the basis of the following empirical relations: wall thickness  $t \geq 5 + 0.0125 D$ ; number of holding-down bolts  $z \geq \frac{0.4}{d}$ ; diameter of holding-down bolts  $d \geq 5 \pm 0.025D$ ; thickness of flange under holding-down bolts  $b \geq 1.5d$ . Here  $t$  is the thickness of the cone wall, measured perpendicularly to the tangent of the outer contour;  $D$  is the largest diameter of the cone, mm. /150

Cones of the second group include structural ones used in certain VPP designs with hydraulic drives and performing the additional function of sealing the propeller hub. Two practical design variants of such cones have been developed: one in which the body of the cone receives the structural load directly from oil, and one with an additional partition (rear wall) isolating the cavities of the hub and cone (Fig. 70).

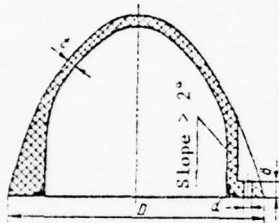


Fig. 69. Plastic cone of FPP.

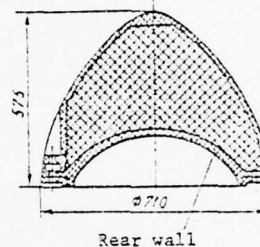


Fig. 70. Plastic cone with strength bulkhead of VPP.

Cones with a loaded body are used only for propellers up to 1.5 m in diameter because of the danger that the system will spring a leak if the cone body is damaged.

When the cone body is damaged, depressurization of the hydraulic system does not occur in structures with an additional partition (rear wall). In this case, the cone body is not loaded, and is constructed according to the empirical formulas cited. The structural load is carried only by the rear wall, which is made in a simple shape permitting a more complete utilization of the strength of the oriented fiber glass plastic. A decrease in stress concentration is achieved by means of a smooth transition from the spherical part of the rear wall to the flange and by using special shaped washers under the holding-down bolts. The rear wall at the site of the seal (contact with the hub) is reinforced with a metal bushing.

The thickness of the rear wall of the cone is determined by calculation on the basis of the following assumptions:

- the cone material is plane-isotropic and satisfies the continuity condition;
- the calculated regime is quasi-stationary, corresponding to the maximum load  $P$  with an action time  $\tau$  equal to the operating time of the cone at this load.

The assumptions used being taken into account, the stress on the critical section of the cone in the calculated regime is determined from a formula employed in boiler construction for designing elliptical metal bottoms loaded with a uniform internal pressure:

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$$\sigma_{\theta} = \left( \frac{\rho D_{in}^2}{2H} + p \right) \cdot \frac{1}{400} \quad (39)$$

where  $p$  is the effective pressure,  $\text{kgf/cm}^2$ ;  
 $D_{in}$  is the inside diameter of the cone,  $\text{cm}$ ;  
 $t$  is the wall thickness,  $\text{cm}$ ;  
 $H$  is the cone height,  $\text{cm}$ .

The material for the cones is chosen as a function of the operating conditions and magnitude of the load. Hot-molded epoxy-glass plastics are used for loaded (structural) cones.

Table 65.  
 Mechanical properties of epoxy-glass plastics as a function of the angle between the direction of acting force and the direction of glass fabric warp

Characteristic	Angle between directions of acting force and glass fabric warp, °							
	0		90		45		30	
	Epoxy- nolic	Epoxy- amine	Epoxy- nolic	Epoxy- amine	Epoxy- nolic	Epoxy- amine	Epoxy- nolic	Epoxy- amine
Strength, $\text{kgf/mm}^2$ :								
tensile	64.0	73.0	47.0	62.4	23.2	33.0	30.8	39.0
compressive	46.0	56.0	37.0	45.0	19.0	24.1	25.0	27.5
bending	69.0	80.5	55.0	67.0	30.6	32.0	34.0	41.2
Tensile elongation, %	1.8	2.0	1.3	1.9	5.6	5.7	5.0	5.0
Modulus of tension, $10^3$ $\text{kgf/mm}^2$	3.0	3.1	2.5	2.6	1.5	1.6	1.7	1.7

In a parallel arrangement of glass fabric layers, the fiber glass laminate is an orthotropic material with the highest tensile and bending strength indices only in the principal directions of reinforcement, i. e., at  $0^\circ$  and  $90^\circ$  angles between the direction of the glass fabric warp and the load application axis (Table 65). Under the influence of hydrostatic pressure, the cone walls are in a plane-stressed state, the principal stresses in all the radial directions being equal. Consequently, a fiber glass plastic with a transversally isotropic (plane-isotropic) structure should be used in the manufacture of loaded cones. Such a structure is exhibited by a fiber glass plastic in which the direction of the warp is shifted by a specified angle  $\alpha$  in each blank (Fig. 71). For manufacturing loaded cones, a reinforcement scheme is recommended in which the direction of the warp is shifted by angle  $\alpha = 30^\circ$  in each blank. /152



According to the existing technology, during the placement of the molding material blank, the press molds are subjected to volume drawing on the top force in diagonal directions (at a  $45^\circ$  angle to the glass fabric warp). To give elasticity to the molding material, the blanks are heated to  $40-50^\circ\text{C}$  before being charged. At  $40-50^\circ\text{C}$ , as a result of softening of the binder, the deformability of the molding material increases, and its curing does not occur.

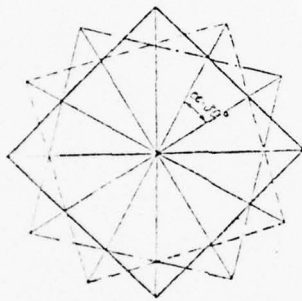


Fig. 71. Diagram of rotation of molding material blanks through pitch angle of reinforcement  $\alpha$  during placement.

The diagonal direction of drawing is determined on the basis of experimental studies of the deformation of impregnated glass fabric at different angles of load application relative to the glass fabric warp. A diagram of the deformability of satin weave glass fabric in color coordinates is shown in Fig. 72. In placing the material, it is desirable to use a blank contour corresponding to the curve shown in the diagram, but with warp and weft maxima. After being drawn in the diagonal directions, owing to the relative displacement of the glass fiber filaments, such a blank assumes the shape of the cone without rupture of the glass fiber (Fig. 73), overlaps of the layers, butts, creases, or ridges.

During placement, the ends of the blanks are clamped in a special device provided in the design of the press mold and ensuring additional tension of the reinforcing material.

To determine the dimensions and number of blanks, the cone is divided into equidistant sections every 5-10 mm. The number of blanks in each section is determined from formula (33).

The cones are molded according to the schedule adopted for the given type of molding material.

The material for fabricating nonloaded cones can be less strong. Cutoffs of molding materials obtained from the cutting of blanks for structural parts and propellers are used for this purpose. In order to increase the flow of the material so as to fill up the mold better, the cutoffs are ground up.

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Materials obtained from molded cutoffs possess adequate strength and water resistance and are no different in strength from a molding material as popular as

AG-4V. The water absorption and decrease of strength in water for specimens made of molded cutoffs are somewhat greater than for oriented fiber glass plastics, but are still within the acceptable range (water absorption after 120 days, 0.3%; attendant decrease in strength, 15-20%).

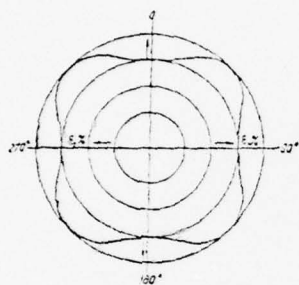


Fig. 72. Polar diagram of deformation of impregnated glass fabric.

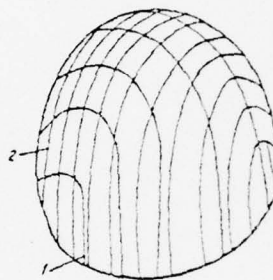


Fig. 73. Blank of impregnated glass fabric after volume drawing.

1 - warp; 2 - weft.

#### 24. Technical and Economic Advantages of Fiber Glass Plastics

The chief purpose of the use of fiber glass plastics in lieu of metals for articles used in ship machine building is to economize scarce metals, reduce the labor intensity of fabrication and cost of the articles, and improve their service properties.

The blades of propellers, turbines, compressors, and centrifugal pumps have a complex configuration, and their fabrication must meet strict precision and surface finish requirements. Fabrication of such articles from metals requires the use of expensive specialized equipment, large capital investments in the organization of production and large production facilities, and a considerable investment of manual labor that does not lend itself very well to mechanization. For example, according to technical standards, the machining of a propeller casting 3.0 m in diameter requires 2225 h, including 1740 h of manual work; the machining of a propeller casting 0.8 m in diameter requires 202 h, including 132 h of manual work. The machining of compressor blades consists of 27 operations.

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The use of fiber glass plastics makes it possible to dispense with machining almost completely and reduce the fabrication labor intensity by a factor of 8-10 in the case of all-plastic construction and a factor of 3-5 in the case of composite construction; and to reduce the requirements for industrial facilities and capital investments by a factor of 2-3. The mechanization level is higher, the number of employees is reduced, and the need for special machines is eliminated.

Of major national economic importance is the economy of scarce metals, since 40% of all the articles are made from nonferrous alloys and stainless and alloy

steels. It should also be considered that the metal utilization factor is very low, 0.4-0.6. The replacement of one ton of metal propellers with plastic ones saves 550-600 kg of copper, 350-400 kg of zinc (in the case of brass propellers), 140-200 kg of chromium, and 10-100 kg of nickel (in the case of stainless steel propellers).

In each individual case, the cost reduction depends on the batch production, design, and size of the article. The greatest cost reduction (by a factor of 3-4) is observed in the production of all-plastic articles which previously had been made of stainless steels and brass. A further reduction of the cost of plastic articles may be achieved by reducing the cost of the equipment and initial components of the fiber glass plastic (glass reinforcing material, epoxy resins and curing agents). Another way of cutting costs is to raise the level of standardization in design and production.

In addition to the economic advantages of using plastics instead of metals, there are a number of performance advantages.

All plastic articles used in ship machine building are characterized by a considerable mass reduction due to the lower density of fiber glass plastic. Thus, fiber glass plastic propellers are three to four times lighter than all-steel propellers and 1.5-2 times lighter than composite ones. The lower mass of plastic propellers simplifies their assembly on the ship while substantially reducing the labor intensity of the work involved.

The advantage of fiber glass plastic propellers also pertains to the vibration problem. Studies performed directly on ships have shown that the source of increased axial vibration in the propeller-shaft-engine system is the nonuniformity of the torque and axial thrust per complete revolution of the propeller. Axial vibration has an adverse effect on the machinery of the ship, causing increased wear and an accelerated breakdown of its parts, particularly gearing. Many ship building companies (in the USA, England, FRG, etc.) recommend the use of propellers with an increased number of blades, from four-five to five-six, as an effective measure against axial vibration. As the number of blades increases, the peak of resonance vibrations shifts to higher rotational frequencies, causing a decrease of vibration amplitude in the nominal operation of the machinery. However, increasing the number of blades inevitably results in a reduction of propeller efficiency. Operating experience shows that the use of plastic propellers makes it possible to obtain the same effect with respect to torsional oscillations and vibrations without increasing the number of blades. /155

The use of plastic propellers also permits a considerable reduction in the vibration of the body and acoustic noise. While operating at the rated speed, a steel propeller set up a vibration up to 98 dB in the 500-1000 Hz range in the afterpeak. When the propeller was replaced by a plastic one, the vibration level at the same points decreased by 10-13 dB. The noise level on the open deck decreased by 3-7 dB over the entire frequency range during the operation of the plastic propeller.

The decrease in vibration and torsional oscillations due to the use of plastic propellers is probably a result of their smaller weight and consequent reduction in the moment of gyration and higher damping properties of fiber glass plastics in comparison with structural metals. As a result, the energy of the high-frequency oscillations arising in the operating propeller is "killed" by plastic blades to a considerable degree through conversion into heat and dissipa-

tion into the surrounding medium. At the same time, the fraction of energy transmitted by the propeller to the mechanisms coupled to them decreases appreciably.

The use of plastic propellers decreases the dynamic and thermal loads on the parts of the engine and shaft line and improves their operating conditions. Tests of fiber glass plastic propellers on medium-sized fishing trawlers and "Raketa" motor boats have shown that for the same power load on the engines, a 3-10°C average decrease in the temperature of the gases in the cylinders is observed. The reduction (by 20-40%) in the dynamic and thermal loads and resonance stresses also has a favorable effect in reducing the wear of friction pairs and increasing their durability.

In seawater, a metal propeller coupled with a hull forms a galvanic couple (due to the difference in materials), causing a strong attack of the hull. This is prevented by use of protective shielding. Being a dielectric, fiber glass plastic does not form a galvanic couple.

Metal alloys from which ship propellers are made have low corrosion resistance. Experience shows that after 6-7 months of service, considerable corrosion damage appears on carbon steel propellers which causes an appreciable reduction in propulsive performance; after 1.5-2 years, the propellers break down completely.

Brass propellers are also attacked in water as a result of dezincing of the alloy. Dezincing is caused by electrochemical corrosion. The action of seawater gives rise to local currents based on a potential difference. The zinc is "washed out", and the surface of the propellers is attacked, reducing their propulsive characteristics. In contrast to metals, fiber glass plastics have high corrosion resistance, and therefore, fiber glass plastic propellers undergo practically no electrochemical corrosion in seawater. /156

Thanks to the high corrosion resistance of ship propellers made of fiber glass plastic, their use in lieu of carbon steel propellers on ships of the fishing fleet increases the service life of propellers by a factor of 3-4, and eliminates expenditures due to additional docking of the ships and losses due to their idling for the purpose of replacing damaged propellers.

The speed of ships with carbon steel propellers is reduced by the roughness of the propeller surface, caused by corrosion. Therefore, the use of fiber glass plastic propellers makes it possible to increase the ship's speed (by an average of 0.5 knot) and correspondingly increase the fish catch per ship. The total savings realized by replacing a carbon steel propeller by a fiber glass plastic propeller ranges from 10 to 35,000 rubles per year per ship.

Chapter 7. QUALITY CONTROL OF ENGINE COMPONENTS AND FINISHED PRODUCTS MADE OF FIBER GLASS PLASTICS

The technology of manufacture of epoxy-glass plastic products used in ship machine building consists of several operations: preparation of binder solution, mechanized impregnation of glass fabric, molding and assembly. Careful step-by-step control and control of the initial materials are required to obtain quality products. The necessity of strict step-by-step control is also due to the fact that there are as yet no sufficiently reliable methods for detecting defects in finished fiber glass plastic products. /157

25. Quality Control of Initial Components

Quality control of epoxy resin. The main characteristics of resin are the epoxy group content and gelation period.

The epoxy group content (epoxy number) determines the curing agent quality required for complete curing. The method of determination of the epoxy number (GOST 10587-72) is based on the reaction of epoxy groups with hydrochloric acid forming the corresponding chlorohydrin.

Usually, resins with a gelation period of 1.0-2.5 h are used for hot-pressed epoxy-glass plastics. The dependence of physicomechanical properties of epoxyphenolic fiber glass plastics on the reactivity of epoxy resin is shown in Table 66.

Table 66  
Physicomechanical properties of epoxyphenolic fiber glass plastics vs reactivity of epoxy resin /158

Property	Gelation period of epoxy resin, h		
	1-2.5	4-5	8-10
Strength, kgf/mm <sup>2</sup> :			
tensile	64.0	55.0	49.5
compressive	43.2	35.8	29.0
interlaminar shear	6.9	6.5	5.6
Water absorption, %:			
after 220 days in water	0.30	0.65	1.1
after 1 h of boiling	0.23	0.31	0.46
Bending strength after 220 days in water	$\frac{55.3}{80}$	$\frac{45.1}{71}$	$\frac{26.5}{50}$

Remarks. 1. Bakelite lacquer with a polymerization rate of 85 sec was used in the preparation of the binder.  
2. Numerator indicates absolute values of strength in kgf/mm<sup>2</sup>, and denominator indicates percentages of initial values.

Quality control of curing agents. Triethanolamine titanate and resol-type phenol-formaldehyde resin (bakelite lacquer) are the curing agents most commonly used for hot-curing fiber glass plastics.

Triethanolamine titanate is a thick transparent liquid with a brown to grayish brown color. The main controllable indices are the titanium content (in terms of titanium dioxide) and relative viscosity. The titanium dioxide content is determined by oxidizing a weighed amount of triethanolamine titanate with nitric acid, then calcining in a muffle furnace for 2 h at 600-700°C until the organic matter is completely driven off. After calcination, the residue consists of titanium dioxide. The amount of titanium dioxide should range from 20 to 22%.

The relative viscosity is determined with a standard falling-sphere viscometer. The relative viscosity used is the time required by a steel sphere 7.88-7.97 mm in diameter and a mass of 2.046-2.054 g to travel a distance of 100 mm between two marks on a glass cylinder 18-19 cm long and 21-22 mm in diameter, filled with triethanolamine titanate. The test is carried out at 50°C. The relative viscosity must not exceed 60 sec.

The main verifiable indices of bakelite lacquer are the polymerization rate and dry residue.

The polymerization rate is determined on a polymerization plate heated to 155 ± 5°C (GOST 901-71). The polymerization rate used is the time elapsed from the instant when the resin was applied on the plate until the formation of breaking threads. The use of bakelite lacquer with a polymerization rate of 80-115 sec is recommended for the preparation of epoxyphenolic fiber glass plastics. A reduction of the polymerization rate to 50-60 sec indicates partial polycondensation of the resol resin, due to a decrease of its reactivity. The use of bakelite lacquer of reduced reactivity leads to incomplete curing and a decline in the physicommechanical properties of the fiber glass plastic (Table 67).

Table 67  
Physicommechanical properties of epoxyphenolic fiber glass plastics vs reactivity of bakelite lacquer

Property	Polymerization rate of bakelite lacquer, sec	
	80-100	50-60
Strength, kgf/mm <sup>2</sup> :		
tensile	64.0	52.4
compressive	69.0	57.5
bending	43.2	30.2
Water absorption after 220 days in water, %	0.30	0.88
Bending strength after 220 days in water	$\frac{55.3}{30}$	$\frac{33.4}{58}$
Remarks. 1. Epoxy resin with a gelation period of 2 h was used in the preparation of the binder.		
2. Numerator indicates absolute values of strength in kgf/mm <sup>2</sup> ; denominator indicates percentages of initial values.		

The dry residue or lacquer concentration is obtained by drying a weighed amount of lacquer to constant mass in a thermostat at  $100 \pm 5^\circ\text{C}$ . The lacquer concentration increases in prolonged storage because of volatilization of the alcohol solvent, and therefore, if this characteristic is not controlled, the proportions of the components are upset.

Quality control of glass fabrics. Glass fabrics are checked by means of the indices of breaking strength, moisture content, and sizing agent content.

The breaking strength of a fabric is determined by testing specimens measuring  $100 \times 25$  mm on a tensile tester. Fabrics of reduced strength are not acceptable for the fabrication of products used in ship machine building.

The moisture content of a glass fabric is determined from the mass loss of the specimen after the latter is dried to constant mass in a thermostat at  $110^\circ\text{C}$ . Prior to impregnation, a fabric with a high moisture content must be dried.

The moisture content of a glass fabric may also be determined by means of a special instrument, the IVS-4 fiber glass plastic moisture meter designed by L. L. Novitskiy.<sup>45</sup> This instrument operates on the principle of coulometric determination of the moisture content of a predried gas which is passed through a chamber containing the glass fabric specimen to be checked, where the latter is moistened.

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The sizing agent content of the glass fabric is determined by calcining a weighed amount in a muffle furnace at  $400-600^\circ\text{C}$ .

#### 26. Quality Control of Impregnating Lacquer and Impregnated Glass Fabric

In the preparation of impregnating lacquer, the concentration, polymerization rate and density are controlled, whereas in the preparation of epoxyphenolic lacquer, the ratio of the main components (epoxy and phenolic resins) is controlled.

The lacquer concentration determines the deposition of resin on the fabric during impregnation, and hence, the resin content of the article. The density of epoxy lacquers is obtained by means of a type IIIa glass densimeter (GOST 1300-57).

The proportion of the components is checked by means of the number of epoxy groups in the epoxyphenolic lacquer (epoxy resin content) by titrating a weighed amount of lacquer (0.7-0.8 g) with a solution of hydrochloric acid in acetone. A  $70 \pm 3\%$  epoxy resin content of the lacquer is allowed.

The polymerization rate of impregnating lacquer is determined by means of the procedure described above for bakelite lacquer. Usually, the polymerization rate for epoxyphenolic lacquer is 100-150 sec. This index permits a correct determination of the molding conditions of the articles.

The principal indices of impregnating lacquers providing for the required quality of impregnated glass fabrics are given in Table 68.

The quality of the impregnated glass fabric is checked by means of the chemical composition and strength of specimens molded from it. The chemical composition indices are the content of volatiles, resin, and its soluble part (Table 69).

The resin content  $C_{res}$  is determined by igniting a weighed sample of molding material to constant mass in a muffle furnace. The calculation is made by means of the formula

$$C_{res} = \frac{a-b}{a} \cdot 100 - C_v - C_s \quad (40)$$

where  $C_v$  is the content of volatiles, %;

$C_s$  is the content of sizing agent, %;

a, b is the mass of the sample before and after ignition, g.

Table 68  
Properties of impregnating lacquers

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Property	Curing Agent			
	Triethanolamine Titanate			Phenol-formaldehyde resin
	ED-13	ETsD-12	UP-63	ED-13
Content of dry residue, %	52 ± 2	52 ± 2	52 ± 2	50 ± 2
Polymerization rate of lacquer at 160 ± 2°C, min	12-13	8-9	5-6	1.7-2.5
Viscosity of lacquer according to VZ-4 viscometer at 20°C, sec	12-14	12-14	12-14	12-14
Density according to densimeter at 20°C, g/cm <sup>3</sup>	0.94-0.98	0.95-0.98	0.95-0.98	0.94-0.96
Color and appearance	Transparent solution, yellow to light brown, containing no foreign inclusions or undissolved resin particles			

Table 69  
Properties of impregnated glass fabrics

Property	Curing Agent				
	Triethanolamine Titanate				ED-13 phenol-formaldehyde resin
	ED-13	ETsD-13	UP-63	EKhD	
Binder content, %	30 ± 3	30 ± 3	30 ± 3	30 ± 3	30 ± 3
Content of volatiles, %	0.4±0.2	0.4±0.2	0.4±0.2	0.4±0.2	1.2±0.2
Content of soluble part of binder, %, not less than	90	90	90	90	97



When the impregnation conditions or storage conditions of the impregnated material are disrupted, a partial curing of the resin takes place. This process is checked by determining the amount of resin capable of dissolving (soluble part of the resin). The specimen of impregnated glass fabric (100 x 100 mm) is placed for 15 min in acetone. The soluble part of the resin is

$$C_{\text{sol}} = \frac{a-b}{\frac{C_0 \cdot a}{100}} \cdot 100, \quad (41)$$

where  $C_{\text{sol}}$  is the content of soluble part of the resin, %;

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a, b is the mass of the weighed sample before and after dissolution, g.

Molding material with a 100% content of the soluble part ensures the flowability necessary for obtaining quality articles of intricate shape. For articles of simple shape, material of somewhat reduced flowability with an 80-90% content of the soluble part may be employed.

Completeness of removal of the solvent from impregnated glass fabric is checked by means of the content of volatiles, which are determined by drying a weighed sample of the material in a thermostat at  $105 \pm 5^\circ\text{C}$  for 30 min. Excess solvent (above 1-2%) causes an increase in the porosity of the fiber glass plastic and hence, a decline in the quality of the articles.

The principal controllable characteristics of the mechanical properties of specimens molded from impregnated glass fabric are the tensile, compressive, bending and interlaminar shear strengths. Their determination is made according to suitable standards on specimens cut out of molded plates.

#### 27. Quality Control of Fiber Glass Plastic Articles

Fiber glass plastic articles may contain isolated defects due to the existing level of manufacturing technology of the materials and their processing into articles. The most common defects in hot-molded fiber glass plastic articles and their causes are listed in Table 70.

The principal methods of quality control of fiber glass plastic articles are:  
visual control;  
control of internal structure;  
control of strength by random destructive testing of one or more articles in a batch.<sup>33</sup>

Visual control is the simplest and permits a preliminary rejection of articles. This method is based on the fact that the appearance of the article indirectly reflects its quality. For example, the presence of different shades on the surface of the articles may serve as an indication of reduced strength owing to the fact that no uniform temperature field has been provided for. The presence of creases, resinous areas, or local bleached areas indicates an inappropriate choice of pressure and departure from cutting patterns.

It should be noted, however, that the relationship between the state of the surface of an article and its quality is not clear-cut, since the appearance of the article may be affected by many secondary factors such as the color of the fabric

and resin, the quality of the lubricant, etc. Another disadvantage of the visual method is its subjective nature, and it is therefore used only as an additional method in conjunction with others. /163

Table 70  
Defects in fiber glass plastic articles

Defect	Possible Causes
Pits, cracks and delaminations inside the article	Improper charge; falling between layers of material during molding of oily substances
Blisters on the surface	High content of volatiles, disruption of technological molding conditions (unmolding of article without cooling)
Formation of creases on the surface of article	Inaccurate cutting of molding material blanks, displacement of blanks during closing of press molds; local deficiency or excess of molding material
Incomplete molding of edges	Inaccurate cutting of molding material blanks
Local or overall whitening of surface	Molding pressure above permissible range
Visible disruptions in fabric texture	
Change in color of article as compared to standard specimen	Disruption of temperature conditions of molding

Of the second group of methods for checking internal structure, the most common is ultrasonic flaw detection. It essentially consists in the fact that during their passage through a body, ultrasonic waves tend to change their velocity and direction of propagation when traversing the interface between media of different density and elasticity, and to be differently absorbed by media of different density. Ultrasound can be used to determine the density of a material, foreign inclusions, delaminations, cavities, etc.

On the basis of the physical principles underlying the control methods and equipment, one can distinguish the pulse-echo, shadow, impedance, pulse and other methods.<sup>17</sup>

The pulse-echo method is based on the detection of defects by means of ultrasonic pulses reflected from the defects. The DUK-12 ultrasonic pulse-echo flaw detector is best suited to the control of articles made of fiber glass plastics.

The instrument is designed for the control of fiber glass plastic articles up to 30 mm thick and detects flaws with an area of 20 mm<sup>2</sup> or larger. The accuracy of determination of the depth of occurrence is 3-5%. A disadvantage of the instrument is the fact that it can only be used to approximate the area of the defect. The instrument is simple and convenient to operate.

The shadow method is based on the detection of the shadow effect due to a flaw. There are several versions of this method, involving differences in the electronic part or in the design of the scanning part. The shadow method is used in the DUK-17 ultrasonic flaw detector, designed for semiautomatic control of plastic propellers and other articles made of fiber glass plastics. Shadow flaw detectors do not permit the determination of the depth of the flaw; this is a disadvantage, and therefore when this depth is to be measured, it is also necessary to use the DUK-12 pulse-echo flaw detector. A drawback of the instrument is its cumbersome nature. An advantage is its simplicity and convenience of electronic adjustment, presence of automatic features, and the ability to obtain a very clear flaw detection diagram that is an objective document of control. /164

The impedance acoustic method is the basis of the IAD-2 and DIK-1 flaw detectors. Particularly effective is the method used for checking bonded and laminar structures with a maximum thickness of 5-8 mm for detecting delaminations. In plastic shipbuilding, they are successfully used for the control of molding and thin-walled structures. Advantages of the method are the simplicity of the equipment, its portability, and the absence of an immersion medium. Equipment based on the impedance method complements the pulse-echo method, in which there is a "dead" zone of 1-5 mm; this zone is checked with impedance instruments.

The free oscillation method (UIKP-2 and DVS-1 flaw detectors) is based on the study of the spectrum of free oscillations of the structural portion being checked. Each structural element has its characteristic portion of the spectrum. Having selected a portion of the spectrum on a quality portion of the material, one can easily detect a marked change in amplitude on the indicator when the gauges are mounted on the portion of material with delaminations. The instruments should be used for checking articles from 2 to 15 mm thick with a surface finish not below 74.

All the above-described methods of nondestructive control make it possible to find certain flaws of an article, but do not give any idea of its strength. For this reason, the industry also uses the pulse method for checking the physico-mechanical properties of the material of an article (the UKS-1, UKB-1m, DUK-20 and UZIS-7 instruments). The method consists in measuring the time taken by an ultrasonic pulse to cover a known distance (base) in the material and the pulse attenuation time, and calculating the pulse propagation velocity. The elastic and strength characteristics and the porosity of the material of the article are calculated from the propagation velocity and attenuation rate.

The UKS-1 instrument is transistorized, and the UKB-1m and DUK-20 instruments have electron tubes; the instruments make it possible to perform measurements of ultrasound velocity over a wide frequency range, from 5 to 800 kHz, with base dimensions from 50 to 500 mm. A common disadvantage of these instruments is the lack of gauges for exciting transverse waves in the material.

The UZIS-7 instrument is characterized by the fact that it is designed for laboratory measurements of longitudinal and transverse ultrasound velocities at frequencies of 1.67-5 MHz on small specimens measuring 5-50 mm. The precision of this instrument is higher than that of UKS-1, UKB-1m and DUK-20 instruments.

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To determine the porosity and mechanical properties of the material of the articles, in addition to the propagation velocities of ultrasonic waves in fiber glass plastic, it is necessary to know the binder content of the article. This parameter may be determined with the aid of the IKS instrument.

Control of blade quality<sup>19</sup> includes:  
visual inspection;  
determination of mass;  
detection of delaminations and air inclusions;  
determination of elastic and strength characteristics and density of the blade material;  
determination of binder content;  
calculation of the porosity of the material;  
tests for strength to fracture.

External inspection of blades involves checking for the presence of visible crease defects, swellings and local squeezing out of binder, incomplete molding, and "biting" of the edging.

The mass of each blade is checked, after removing the seam, by weighing on a technical balance with a maximum error of 0.5%.

Delaminations and air inclusions are detected with a DUK-17 ultrasonic flaw detector.

In determining the elastic and strength characteristics and density of a material by the ultrasonic method, the propagation velocity of longitudinal waves is measured from the direction of the driving surface of the blade in three directions along the warp, weft and at a 45° angle in the plane of the fabric sheet. Piezoelectric transducers with a frequency of 80 KHz are used for the measurement.

Fracture tests of blades aimed at determining their load-carrying capacity are performed by bending through an angle; this method most closely approximates the service conditions and corresponds to the commonly employed Taylor calculation scheme. During the tests, the time of the start of blade fracture (indicated by the first audible crack), the time of blade fracture (indicated by the maximum reading of the dynamometer of the tester) and the deflection at the end of the blade (from zero load to complete fracture of the blade) are recorded.

The test results are used to calculate the stresses and plot graphs of stresses and deflection at the end of the blade as functions of the load, and the reserve factor is calculated.

23. Polyamides

Polyamides are high-molecular linear compounds whose macromolecules consist of flexible methylene chains and polar amide groups  $-C(=O)-NH-$  regularly arranged along the chains. The presence of amide groups capable of forming hydrogen bonds between neighboring macromolecules determines the physicomechanical properties common to all polyamides.<sup>34</sup> /166

Depending on the location of the amide groups, polyamides exhibit different crystallizing capacities. As the degree of crystallinity increases, so do the strength, hardness and wear resistance of the articles, and their deformability decreases. With increasing number of amide groups in the macromolecule, the melting point rises and the hardness and rigidity of the polymer increase.

In external appearance, these are solid products ranging from white to light yellow in color. They exhibit appreciable mechanical strength, particularly in the oriented state, high wear resistance properties, a low coefficient of friction, a high damping capacity, resistance to impact loads, and elasticity.

The starting material for polyamides are amino acids or their lactams, diamines and dicarboxylic acids.

Depending on the raw material employed, polyamides are divided into aliphatic and aromatic ones. Thus far, aliphatic polyamides have been used most extensively in industry. In the 1960's, in order to increase the heat resistance, aromatic polyamides were synthesized. Among aliphatic polyamides, those of brands 6, 66, 68 and 12 are being produced in the USSR on an industrial scale. /167

A number system is widely used for designating the chemical composition of polyamides. A polyamide obtained from an amino acid is denoted by a single number corresponding to the number of carbon atoms in the initial amino acid (for example, polyamide 11 is a polymer of aminoundecanoic acid).

A combination of two numbers indicates that the polyamide was obtained from a diamine and a dicarboxylic acid. Separate numbers indicate the content of carbon atoms in the chains of the diamine and dicarboxylic acid (for example, polyamide 66 is a polymer based on hexamethylenediamine  $NH_2(CH_2)_6NH_2$  and adipic acid  $HOOC(CH_2)_4COOH$ ).

Polyamide 6 is produced in the largest volume in the USSR; its raw material is  $\epsilon$ -caprolactam. In practice, hydrolytic and anionic polymerization of  $\epsilon$ -caprolactam is employed. In the first case, the catalyst is  $\epsilon$ -aminocaproic acid, formed by the hydrolysis of a lactam, or AG salt - the reaction product of equimolar amounts of adipic acid and hexamethylenediamine. The polymer obtained is called capron and is processed by pressure casting or extrusion.

Anionic polymerization involves the use of a catalytic system consisting of  $\epsilon$ -caprolactam sodium salt and cocatalysts (N-acetylcaprolactam or toluylene diisocyanate). The anionic polymerization reaction goes to completion in 1.5 h. The

polymer is obtained directly in the molds and does not require washing or drying. The polymer obtained by anionic polymerization is called caprolon.

Polyamides 66 and 68 are obtained from diamines and dicarboxylic acids. Their synthesis takes place in two steps:

- (a) preparation of AG salts from hexamethylenediamine and adipic acid (polyamide 66) and SG salts from hexamethylenediamine and sebacic acid (polyamide 68);
- (b) polycondensation of the salts obtained at 270-280°C.

Polyamide 12 was synthesized by hydrolytic polymerization of  $\epsilon$ -dodecalactam. Two brands of polyamide 12 are produced in the Soviet Union: cast brand 12L and extrusion brand 12E. In its properties, polyamide 12 is analogous to the French polyamide 11 (riisan) and differs favorably from other polyamides in its higher moisture resistance.

The principal physicomechanical and dielectric properties of polyamides of the enumerated brands are given in Table 71. As is evident from the table, all the polyamides have similar mechanical properties in the initial state. The highest impact strength and elongation are exhibited by polyamide 6. All polyamides are characterized by so-called cold flow or creep. Under identical testing conditions, polyamide 6 has the greatest creep.

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Table 71  
Physicomechanical properties of polyamides

Property	Polyamide				
	6	11	66	12	68
Density, g/cm <sup>3</sup>	1.14	1.04	1.14	1.02	1.10-1.11
Strength, kgf/mm <sup>2</sup> :					
tensile	7.0	7.0	10.0	7.0	5.0
compressive	-	-	10.0	6.5	12.0
bending	9.0	10.0	11.0	6.0	9.0
Modulus of elasticity, 10 <sup>2</sup> kgf/mm <sup>2</sup>	1-2	2	16	16	100
Impact strength, kgf m/cm <sup>2</sup>	1.3	-	1.4	1.0	1.2
Elongation, %	350	300	100	250	100
Brinell hardness, kgf/mm <sup>2</sup>	8	5	10	-	25
Heat resistance, °C:					
Martens	55	55	65	45	60
Wick	160	160	230	140	195
Brittle temperature, °C	-25	-55	-25	-	-
Equilibrium water absorption, %	8-12	0.5-1.5	7-8	1.7	3.2
Thermal conductivity coefficient, W/(m K)	0.25	-	0.25	0.25	-
Specific heat capacity, kJ/(kg K)	2.1	2.3	2.0	2.5	-
Volume resistivity, Ohm cm	10 <sup>14</sup>	10 <sup>14</sup>	10 <sup>14</sup>	10 <sup>15</sup>	3 x 10 <sup>14</sup>
Dielectric constant at 10 <sup>6</sup> Hz	4.2	3.7	4.0	3.5	4.0
Dielectric loss tangent at 10 <sup>6</sup> Hz	0.03	0.03	0.02	0.02	0.025
Breakdown voltage, kV/mm	16	25	25	30	23

Experimental data show that the greatest increase in deformation takes place in the first few tens of hours of testing, the subsequent increase in deformation being slight. At stresses close to the proportionality limit, 100-hr deformations increase considerably, but do not reach the limiting value. At low stresses, the 100-hr deformations are close to limiting ones. For example, for polyamide 6 at stresses up to 90 kgf/mm<sup>2</sup>, deformations after 110 h amount to 99.9% of limiting ones.

At stresses greater than the proportionality limit, there is observed a qualitative jump in the behavior of the material, leading to a pronounced flow of the material followed by fracture.

In the design of articles made of polyamides, creep being taken into consideration, the allowed stresses must not exceed 0.1 of the tensile strength at normal temperature. The yield point of polyamides depends substantially on the working temperature. For example, the yield point of polyamide 68 in the temperature range from 20 to 110°C drops from 4.00 to 1.50 kgf/mm<sup>2</sup>. /169

The long-time and fatigue strengths of polyamides are determined to a considerable extent by the loading conditions, this being related to the phenomena of self-heating, which are characteristic primarily of alternating loads. Interruptions in the course of fatigue testing substantially affect the fracture time of the specimens and sharply increase their fatigue limit. The regularity of this increase makes it possible to conclude that during the interruption, the ability of the material to resist loads is partially recovered. The strength may be recovered completely, and in some cases even in excess of the initial value.

A valuable quality of polyamides is their exceptionally high damping capacity, which considerably surpasses that of steel and even rubber. The logarithmic damping decrement for U8 steel is 0.22, for vacuum rubber 0.14, and for polyamides 0.38. Particularly advantageous in the use of polyamides as a material for bearings is the fact that in the temperature range from 50 to 80°C, the decrement reaches a maximum (0.56). Barium sulfate, molybdenum disulfide and graphite are used as antifriction additives to polyamides. The highest wear resistance characterizes specimens with a 20-25% addition of barium sulfate or 4-6% addition of graphite. Polyamide compositions with molybdenum disulfide and graphite also possess rapid breaking-in characteristics.

The presence in the structure of polyamides of polar amide groups which form hydrogen bonds with water molecules accounts for their high hygroscopicity. The rate of diffusion of moisture and degree of water absorption depend on the content of polar amide groups and on the structure of the polymer. The lower the concentration of amide groups, the lower the water absorption.

In the series of aliphatic polyamides described, the greatest water absorption is exhibited by polyamide 6 (8-12%), and the greatest water resistance, by polyamide 12 (1.7%). Moisture has a plasticizing effect on polyamides, increases elasticity, and simultaneously reduces mechanical strength, modulus of elasticity and hardness. During the storage of polyamides in air at 20°C and 65% relative humidity, the moisture content becomes completely stabilized. Under these conditions, the water absorption of polyamide is 2-3%.

Completely dehydrated polyamides lose their elasticity and become more brittle not only because of removal of the plasticizer, i. e., water, but also because of partial washing-out of the low-molecular fractions. In designing articles, it is necessary to consider the change in the dimensions of the parts as the water absorption process takes place. Parts made of polyamides should contain a constant amount of moisture at different humidities of the ambient medium in order to achieve constant dimensions of the parts.

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From the standpoint of stability of the dimensions of the parts and mechanical properties at high humidity, polyamide 12 is best. Its bending strength after maximum saturation decreases by 15-18%, and after saturation in a medium of 65% relative humidity, by 8-9%. Under the same conditions, the decrease in strength of polyamide 68 is 40 and 28%, and that of polyamide 6, 72 and 57%, respectively.

The dimensional stability and mechanical properties of polyamide parts are also determined by the operating temperature. With rising temperature, polyamides become more elastic and their strength and modulus of elasticity decrease. During long-term service, even at small loads, they can operate only at a temperature no higher than 100°C. Thus, after polyamide parts are kept for 42 days at 130°C, they lose 86% of their strength. At loads on the order of 18.5 kgf/cm<sup>2</sup>, the operating temperature must not exceed 50°C. The lowest heat capacity is that of polyamide 6.

When exposed to high temperatures for long periods, polyamide articles become brittle and wear out rapidly.

The deterioration of operating conditions of polyamide parts at elevated temperatures is also increased by their low thermal conductivity. The thermal conductivity coefficient of polyamides is 0.2-0.3 W/(m K). The removal of the heat produced by friction during the operation of the parts is poor, resulting in the risk of local overheating. The thermal conductivity is improved by introducing antifriction additives.

Polyamides are characterized by a high coefficient of linear expansion: it is ten times greater than that of steel.

The lower limit of working temperatures is determined by the brittle temperature; it is -60°C for polyamide 12. As they are cooled below 0°C, polyamide parts partially lose their elasticity. Under load, such parts can operate at -10°C.

Polyamides are made into articles by different methods: die casting, extrusion, or centrifugal casting. Because of the absence of the plastic deformation zone and low viscosity of the melt, polyamides are not worked by molding.

In die casting of polyamide parts, it is necessary to consider the characteristics of these materials: a narrow melting range, low viscosity of the melt, hydrophilic nature, and appreciable influence of processing conditions on their structure and strength. The casting temperature depends on the melting temperature of the material being processed, and should be 20°C higher than the melting temperature of the material. In each specific case, the temperature is determined more accurately by experimental means as a function of the size and shape of the cast article. Because of the ready oxidizability of polyamides in the molten state,



the casting process must be carried out so as to keep the material from remaining in the molten state for any appreciable length of time. Of major importance are the casting rate, arrangement of the pouring gates and proper design of the mold. /171

Polyamides have a low melt viscosity,  $(2-4) \times 10^3$  P. The mobility of the melt is an advantage in charging of the mold and makes it possible to obtain thin-walled articles of complex shape. However, such a melt may leak out of the nozzle even without the application of pressure, and therefore, all the mating members of a casting machine are closely fitted and have self-closing nozzles.

Polyamides are hydrophilic products which sometimes contain significant amounts of moisture. Processing of moist polymers causes their degradation, swelling of the mass, formation of surface microcracks, and decline of the strength of the articles. Therefore, prior to fabrication of the articles, polyamides are usually dried at 80-85°C in a layer 3-4 cm thick in a vacuum for 1-24 h until the moisture content of the mass is no higher than 0.1%.

The structure of polyamides in the finished article is chiefly determined by the processing conditions. Articles with a crystalline structure are obtained if the melt is injected into a mold heated to 40-60°C and the mold is slowly cooled. It is well known that a crystalline structure increases the tensile strength, rigidity and hardness, and articles with such a structure have a better wear and friction resistance.

Casting in a cold mold and rapid cooling gives articles in which the amorphous phase predominates, marked by a high elasticity and impact strength. However, casting of polyamides in cold molds is possible only in the fabrication of thin-walled articles. The casting of large-sized, thick-walled articles involves the danger of formation of shrinkage cavities. This is due to poor thermal conductivity; the polyamide layers located near the walls of the cold mold solidify, the supply of melt is cut off, and the interior of the article still contains a liquid mass, which on solidification produces shrinkage.

In the case of large-sized articles, the low thermal conductivity of polyamides also causes (even in heated mold casting) an inhomogeneous coarse-spherulite crystalline structure with the presence of a surface amorphous layer. To obtain parts with a homogeneous fine-spherulite structure, additional heat treatment at 240-220°C is recommended. The duration of the heat treatment depends on the thickness of the articles and ranges from 1 to 8 h. The articles are heat-treated in castor oil and in a melt of sodium nitrate, sodium nitrite, and potassium nitrate in the proportion of 1:1:2.

As previously noted, the properties of polyamides are frequently improved by using various fillers such as talc, graphite, molybdenum disulfide, or barium sulfate. The introduction of fillers increases the hardness and strength of the polymer and improves its heat resistance, antifriction properties and water resistance. However, the impact strength decreases in inverse proportion to the amount of filler introduced. /172

It is most advantageous to introduce the fillers directly during the synthesis of polyamides, since inert fillers do not disturb the rate of formation of polyamides.

The optimum amount of filler is determined by the function of the material. Accumulated experience has shown that polyamides with 5-10% filler provide for reliable operation of such parts as bushings, liners, and bearings.

Fenilon. Among aromatic polyamides, the Soviet industry produces fenilon - poly-m-phenylenisophthalamide, which is the polycondensation product of an aromatic diamine (m-phenylenediamine) and derivatives of aromatic dicarboxylic acids (isophthalic acid).<sup>34, 62</sup>

Aromatic diamines of low reactivity do not react with dicarboxylic acids, and therefore, instead of a dicarboxylic acid, use is made of its more reactive derivatives, dichlorides, and the reaction is carried out at low temperatures in solution or at the interface.

Like other aromatic polyamides, fenilon is characterized by high compressive strength, excellent antifriction properties and high chemical stability; its glass transition temperature (270°C) and melting point (430°C) permit long-term use of the articles at high temperatures. The molecular mass of fenilon suitable for processing into articles is 20,000-70,000. The physicomaterial properties of fenilon are given below.

Density, g/cm <sup>3</sup> .....	1.33-1.36
Tensile strength, kgf/mm <sup>2</sup> .....	12.0
Compressive strength, kgf/mm <sup>2</sup> .....	30.0
Impact strength, kgf m/cm <sup>2</sup> .....	2.0
Modulus of compression, kgf/mm <sup>2</sup> .....	4.4 x 10 <sup>2</sup>
Brinell hardness, kgf/mm <sup>2</sup> .....	34
Wick temperature, °C.....	270
Frost resistance, °C .....	-70

Fenilon-base molding materials are used in ship machine building. They are finely divided white and pink powders (bulk density, 0.12-0.35 g/cm<sup>3</sup>).

Parts made of fenilon are fabricated by hot molding at 320°C and a specific pressure of 1000-1500 kgf/cm<sup>2</sup>; holding time under pressure is 5-15 min, and the articles must be cooled under pressure to 230°C. The polymer in the press mold is heated to the molding temperature without pressure.

Fenilon has strength characteristics similar to those of aliphatic polyamides. The elastic modulus of fenilon is considerably higher than those of aliphatic polyamides. The chief advantage of fenilon is the possibility of using the articles over a wide temperature range, from -60°C to +250°C. Fenilon is also marked by high atmospheric resistance. It is similar in water resistance to aliphatic polyamide 6. The maximum water absorption of fenilon is 9-10%. It is a good dielectric whose properties undergo comparatively little change after exposure to atmospheric conditions and practically no change in the temperature range from 20 to 220°C.

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Fenilon has attractive antifriction properties, stable over a wide temperature range. Thanks to a high heat resistance, it withstands higher friction loads than aliphatic polyamides. In dry friction against steel, its friction coefficient is 0.42. The wear resistance of fenilon at room temperature is 1/4-1/3 that of polyamide 6. Filling of fenilon with graphite and molybdenum disulfide (up to 8.5%) substantially improves its antifriction properties.

Caprolon. In recent years, a widely applied method in the USSR and abroad involves the preparation of articles used in ship machine building from polyamides by anionic (low-temperature, block) polymerization directly in the molds. Use of this method makes it possible to process the polymer without resorting to expensive casting machines and molds, and to obtain large-sized castings with minimum equipment costs. The anionic polymerization method is particularly effective in the production of shipbuilding articles frequently encountered in shipbuilding and produced in small batches, such as stern bearings, rudder stock bearings on ships, cutters and rescue boats, valve bonnets, filtering cartridges, and other parts.<sup>58, 60</sup>

At the present time, the starting material most commonly used in the production of articles by this method is  $\epsilon$ -caprolactam, the material based thereon being known as caprolon or caprolite. The polymerization of  $\epsilon$ -caprolactam is carried out in the presence of alkali catalysts and activators (cocatalysts) in an inert gas atmosphere at normal pressure directly in the molds at 170-180°C.

In comparison with polyamide 6 (capron), which is analogous in chemical structure but is prepared by hydrolytic polymerization, caprolon has better mechanical properties (Table 72).

The basic patterns of change in the mechanical properties of caprolon acted upon by water, atmospheric conditions and elevated temperatures are analogous to those described previously for polyamides.

The maximum water absorption of caprolon at 20°C is 6-7%. Five to eight years are required to achieve the maximum water absorption of bushing-type articles when the wall thickness is 15-20 mm. The dimensions of the articles increase simultaneously with water absorption. At the maximum water absorption, the diameter of the articles obtained (disks, rings and bushings) increases by an average of 2%. /174

Table 72  
Physicomechanical properties of capron and caprolon

Property	Capron	Caprolon
Density, g/cm <sup>3</sup>	1.14	1.16
Strength, kgf/mm <sup>2</sup> :		
tensile	5.5-7	9-9.5
compressive	8.5-10	12-12.5
bending	9-10	12-15
Modulus of tension, 10 <sup>2</sup> kgf/cm <sup>2</sup>	0.8-1	2.06-2.31
Impact strength, kgf m/cm <sup>2</sup>	1.0-1.3	1.0-1.6
Tensile elongation, %	100-350	120-130
Brinell hardness, kgf/mm <sup>2</sup>	8-12	20-25
Melting temperature, °C	210-215	220
Heat resistance, °C:		
Wick	160	220-230
Martens	55	-
Thermal conductivity coefficient, W/(m K)	0.25	0.25

In its antifriction properties, caprolon has very high indices in a friction pair with metals at sliding speeds from 3 to 5 m/sec and specific pressures up to 25 kgf/cm<sup>2</sup>.<sup>3</sup> The wear resistance of caprolon under certain conditions surpasses that of other materials (guaiac, textolite, rubber, wood laminate) used in the manufacture of stern bearings. Thus, within the range of sliding speeds of 0.5-10 m/sec and specific pressures up to 10 kgf/cm<sup>2</sup>, the rate of wear of caprolon does not exceed 0.1-0.15 μm/h, whereas it is 0.19 μm/h for guaiac, rubber and textolite, and 0.22 μm/h for wood laminates.

The most important factor determining the properties of the polymer obtained is the choice of catalyst and cocatalyst (activator). The catalyst used is metallic sodium, and the activators are mono-, bi- and trifunctional compounds, for example acetylcaprolactam, N-N'-acetylbis lactam, N-, N', N''-trimesinoyl-tercaprolactam, toluylene diisocyanate, and hexamethylene diisocyanate.

The structure of the polymer and its properties vary according to the functionality of the activator. Monofunctional activators provide for growth of polymer chains in only one direction. To obtain a branched polymer of high molecular mass, it is desirable to use bi- and trifunctional activators, which cause the caprolon molecule to grow in two and three directions.

It has been found that polyamides obtained in the presence of mono-, bi- and trifunctional activators have a crystalline structure; the degree of crystallinity decreases with increasing functionality of the activator, leading in particular to a decrease in the hardness of the polymers.

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The use of new polyfunctional activators opens the possibility of varying the properties of caprolon, thus extending the scope of its application.

To obtain a polymer of maximum molecular mass, the catalyst, activator and caprolactam in the reaction system should be present in strictly equimolar amounts.

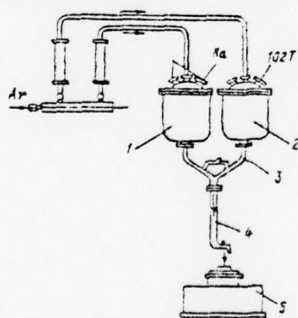
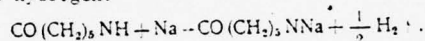


Fig. 74. Flow diagram of assembly for block polymerization of caprolactam

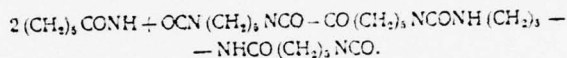
Of major importance for carrying out the process of anionic polymerization is the adherence to the temperature conditions (temperature of the mold, drying, polymerization and cooling of the articles). Departure from the temperature conditions leads to either a decrease in polymerization rate and increased content of low-molecular products at below-optimum temperature, or to an intensification of the degradation process and formation of defects (pores, cavities, etc.).

A flow diagram of the apparatus for block polymerization of caprolactam is shown in Fig. 74. The process takes place as follows. Caprolactam is charged into reactors 1 and 2, where it melts at 70-100°C, then the molten caprolactam is heated to 125±5°C in a stream of inert gas (nitrogen or argon) and is dried for 1.5 h to a moisture content of 0.02%. An inert medium is a necessary requirement for carrying out anionic polymerization, since the slightest amount of oxygen (over 0.05%) promotes oxidation of caprolactam.

In reactors 1 and 2 at 138-140°C in a stream of inert gas, caprolactam is mixed with a catalyst (metallic sodium), and the reaction takes place vigorously with the liberation of hydrogen:



An activator (toluylene diisocyanate) is charged into reactor 2:



Then the melts from the two reactors are fed through mixer 3 down tube 4 into mold 5 preheated to 170°C, where the polymerization takes place. /176

To obtain articles with a high dimensional accuracy and a guaranteed constancy of physicomechanical properties, it is necessary to maintain a given mold temperature to within ±5°C. The cooling rate varies with the thickness of the castings, and on average, the rate of decrease of the temperature of the article should not exceed 6-10°C per hour (to reduce the internal stresses in the article).

In some cases, cracking and premature fracture of parts is observed in caprolon castings during their service and storage. These phenomena are caused by a nonuniform supermolecular structure of the polymer, which accounts for the inadequate stability of mechanical properties and considerable fluctuations of shrinkage. The problem of directed control of the supermolecular structure of caprolon during its synthesis is one of high current interest.<sup>53</sup>

There exist a number of methods permitting the control of polymer structures for the purpose of obtaining materials with optimum mechanical properties. The most acceptable methods of control of the supermolecular structure and properties of caprolon are optimization of the temperature conditions of synthesis and introduction of artificial cross-linking nuclei (ACN).

The introduction of ACN into polymers has been dealt with in many studies. ACN are usually introduced into the solution or melt of the final polymers and take part only in the crystallization of the product, without affecting the polymerization process. In the case of anionic polymerization, ACN must be introduced into the monomer melt simultaneously with the catalytic system, and the entire process of polymerization followed by crystallization of the polymer should be carried out in their presence. Therefore, ACN additions should be inert with respect to the catalytic system. The cross-linking agents used may be finely divided solids - oxides of aluminum (Al<sub>2</sub>O<sub>3</sub>), lead (PbO), titanium (TiO<sub>2</sub>) as well as carbon black and graphite. A disadvantage of such solid cross-linking agents is the nonuniformity of their distribution over the entire mass of the substance introduced.

Much more promising is the use of cross-linking agents soluble in the caprolactam melt, such as the dyes caprosol red C and active phthalocyanine blue. The introduction of dyes into the reaction mixture improves the mechanical properties of caprolon.<sup>63</sup>

Studies of the supermolecular structure of caprolon modified with dyes have shown that the homogeneity and size of the spherulites change with changing concentration of the dye introduced. Thus, the average diameter of spherulites of unmodified caprolon and caprolon obtained with 0.005% phthalocyanine blue is 30-35  $\mu\text{m}$ , the diameter of spherulites of caprolon obtained with 0.01% of the dye is 20-25  $\mu\text{m}$ , and with 0.05%, about 15  $\mu\text{m}$ . Thus, as the concentration of phthalocyanine blue increases to 0.05%, the size of the spherulites decreases by a factor of two, and the homogeneity of the macrostructure increases.<sup>63</sup> /177

In addition, the introduction of dyes creates the conditions for a uniform distribution of crystallization centers throughout the polymer, leading to a simultaneous crystallization of the polymer formed in the entire volume of the casting, a decrease in the volume of shrinkage cavities, more stable values of shrinkage in height, and a more uniform distribution of density over the cross section (Table 73).

Table 73  
Density,  $\text{g}/\text{cm}^3$ , of caprolon castings with a cross-linking agent<sup>72</sup>

Distance from center of cylindrical castings 70 mm in diameter and 120 mm high	Unmodified Caprolon	Caprolon + 0.01% of caprosol red C
2	1.145	1.154
11	1.149	1.156
22	1.155	1.158
31	1.157	1.158

## 29. Polycarbonates

Polycarbonates are polycondensation products of carbonic acid and polyatomic alcohols, which may be aliphatic and aromatic alcohols. Of greatest industrial importance at the present time is polycarbonate based on diphenylolpropane.

In the USSR, polycarbonate is produced under the name diflon. The industrial method of preparation of polycarbonate consists in the direct phosgenization of diphenylolpropane. Quality polycarbonate can be obtained only by using diphenylolpropane of a high degree of purity that has been repeatedly recrystallized. Of major importance is the degree of washing of the polymer obtained to remove the excess alkali and sodium bicarbonate. Traces of alkali and salts in the polymer sharply reduce its resistance to steam and boiling water.

The physicomechanical properties of polycarbonate depend on the molecular mass and polydispersity of the product obtained. For articles used in ship machine

building and other structural articles obtained by die casting, it is desirable to use polycarbonate with an average molecular mass of 30,000-35,000. A further increase of the molecular mass of polycarbonate complicates the technology of its processing because of increased viscosity of the melt. /178

Of no less importance than the average molecular mass is the polydispersity of the product. The presence of low-molecular fractions in the polymer composition increases its water resistance and strength.

The polycarbonate structure contains an amorphous and a crystalline phase. The volume fraction of the crystalline phase in the articles can be as high as 40%.

The supermolecular structure of polycarbonate consists of regions in the form of fibrils and spherulites of radial, mixed and radial-annular type. The spherulites are up to 8-10  $\mu\text{m}$  in size. The structure of polycarbonate determines its physico-mechanical properties. The highest strength characteristics are exhibited by polycarbonate with a homogeneous fine-spherulite structure.<sup>22</sup>

Articles used in ship machine building are usually made from polycarbonate by die casting on machines with screw conveyer plasticization. Because of the high viscosity of the melt, the die casting of polycarbonate is carried out at pressures of 900-2000  $\text{kgf/cm}^2$  at 260-300°C. The diameter of the pouring channel should be no smaller than 1.2 mm.

The supermolecular structure and mechanical properties of polycarbonate are determined by the specific pressure, casting temperature, shape and rate of cooling of the articles and the mold (Tables 74-77).

Studies have shown<sup>57</sup> that the optimum casting temperature of polycarbonate is 300°C. The viscosity of polycarbonate melt at 300°C is 4000-6000 P. The optimum mold temperature during casting is 100°C. A fine homogeneous spherulitic structure is obtained at this temperature.

Slow cooling creates the most favorable conditions for an ordered structure.

Table 74  
Effect of die-casting temperature on the mechanical properties of polycarbonate

Die-casting temperature, °C	Strength, $\text{kgf/mm}^2$		Tensile elongation, %
	Tensile	Bending	
260	6.53	10.14	43.6
280	6.58	10.17	37.6
300	6.75	10.17	28.0
320	6.31	9.96	25.0

The mechanical properties and supermolecular structure of polycarbonate can be improved by subsequent heat treatment and introduction of small amounts of cross-linking agents into the polycarbonate composition. Heat treatment of the /179

articles is carried out in silicone oil at 135°C for 80 min, followed by slow cooling in the mold at a rate of 16-25°C/h. The cross-linking agents used for polycarbonate are finely divided high-melting oxides of metals, i. e., titanium, germanium and zirconium. The introduction of cross-linking agents, for example titanium dioxide, in amounts up to 0.2% makes it possible to increase the modulus of normal elasticity by 25-30%.

Table 75  
Effect of mold temperature on the mechanical properties of polycarbonate

Mold temperature, °C	Strength, kgf/mm <sup>2</sup>		Tensile elongation, %
	Tensile	Bending	
40	6.43	9.96	22.6
60	6.56	10.11	17.4
80	6.63	10.13	15.0
100	6.75	10.17	14.0
120	6.88	10.20	10.8

Table 76  
Effect of specific casting pressure on the mechanical properties of polycarbonate

Specific pressure, kgf/cm <sup>2</sup>	Strength, kgf/mm <sup>2</sup>		Tensile elongation, %
	Tensile	Bending	
750	6.14	9.95	18.4
880	6.36	10.17	25.2
1070	6.41	10.27	27.2

Table 77  
Effect of holding time during cooling on the mechanical properties of polycarbonate

Holding time, min	Strength, kgf/mm <sup>2</sup>		Tensile elongation, %
	Tensile	Bending	
30	6.23	10.20	14.6
60	6.37	10.20	20.0
90	6.36	10.20	25.2
120	6.40	10.36	27.0

The extensive and rapidly increasing use of polycarbonate is explained by its excellent mechanical properties. In ship machine building, of particular importance are such properties of polycarbonate as relatively high strength and impact resistance (higher than in all thermoplasts), dimensional stability over a wide temperature range, low creep (for thermoplasts), water- and atmospheric resistance, attractive antifriction properties, and self-extinction (Table 78).

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Table 78  
Physicomechanical properties of polycarbonates

Characteristic	Makrolon	Leksan	Diflon
Density, g/cm <sup>3</sup>	1.2	-	1.2
Impact strength, kgf m/cm <sup>2</sup>	-	-	1.20
Strength, kgf/mm <sup>2</sup> :			
tensile	6.25-6.50	5.60-8.40	6.00-7.00
compressive	8.40	7.70	8.00-9.00
bending	10.00	-	10.80-10.50
Elongation, %	60-100	-	50-100
Hardness, kgf/mm <sup>2</sup>	12.3	-	15-16
Elastic modulus, kgf/mm <sup>2</sup> :			
tensile	(2.2-2.5)x10 <sup>2</sup>	2.2 x 10 <sup>2</sup>	(2.2-2.4)x10 <sup>2</sup>
compressive	2.5	1.68	-
Poisson's ratio	-	-	0.36
Linear expansion coefficient,	60	-	60
10 <sup>6</sup> °C <sup>-1</sup>			
Water absorption after 24 h,	-	-	0.3
%			
Martens yield temperature, °C	135-137	-	135-140
Glass transition temperature,	140	143	140
°C			
Degradation temperature, °C	310-340	-	320-340
Melting range of crystalline	222-230	-	-
phase, °C			
Cold resistance, °C		Below -100°C	

Under service loads and at high temperature, the creep of polycarbonate is accompanied by a peculiar form of brittle fracture of polymers, i. e., the formation of "silver" cracks. Silver cracks constitute a region of the same material but with a different refractive index. Thus, the creep of polycarbonate is accompanied by partial separation of the material into layers.

The impact resistance of polycarbonate remains almost unchanged in the temperature range from -120 to 120°C.

During aging at temperatures up to 70-80°C, the strength and elastic properties of polycarbonate undergo practically no change, and only the elongation decreases. At 90 and 120°C, the initial period of thermal aging of polycarbonate is even characterized by a strengthening and increase in rigidity, which are explained by a general ordering of the structure under the influence of heat treatment with stress relaxation. /181

In the course of further aging, thermal degradation of polycarbonate begins, and its strength gradually decreases. Stabilization of these competing processes takes place comparatively rapidly, and practically no change in properties is observed even after 3000 h. The glass transition temperature of polycarbonate is 135-140°C. At these temperatures, the strength and elastic characteristics of the material decline sharply.

To increase the service life of polycarbonate articles and extend the service temperature range, the polymer is filled with finely chopped glass fiber.

High-molecular polycarbonate is a relatively water-resistant material at room temperature. At 20 and 50°C, equilibrium is established rapidly, and equilibrium water absorption does not exceed 0.2-0.3%. The mechanical properties of polycarbonate under brief loads remain almost unchanged after exposure to water. However, on specimens located in water at 20°C, after prolonged loading, "silver" cracks are formed after only 300 h, analogous to the cracks due to thermal aging for 50-100 h at 90°C. The formation of cracks causes a decrease in the durability of articles operating under constant loads in water in comparison with articles used in air. The adsorbed moisture can be removed by treating the specimens with 70% sulfuric acid, whereupon the defects disappear and the mechanical properties are completely restored. Thus, at 20-50°C only a physical interaction of water with polycarbonate takes place which reduces the durability of the articles, and no hydrolysis occurs.

During exposure to water at 70-90°C, the aging mechanism of polycarbonate changes. A chemical reaction of polycarbonate with water, i. e., hydrolysis of the polymer, takes place. One can postulate that the water causes rupture of the bonds at the carbonyl bridge with hydrolysis of the end groups. The hydrolysis products are not washed out of the polymer and occupy a greater volume than the initial molecules. This gives rise to nonuniform internal stresses causing rupture of the intermolecular bonds and formation of cracks. The formation of cracks always begins at a depth of 0.1-0.3 mm from the surface of the specimen, confirming the difference between the properties of the material of the outer and inner layers. Such cracks do not disappear after treatment with 70% sulfuric acid, as in the case of service in water at 20°C, and reduce the durability of the articles much more substantially.

A distinctive characteristic of polycarbonate is the stability of its dielectric properties over a wide range of frequencies and temperatures. For example, the volume resistivity of polycarbonate at -30°C is  $10^{17}$  Ohm cm, at 100°C,  $2.1 \times 10^{15}$  Ohm cm, and at 150°C,  $2.5 \times 10^{13}$  Ohm cm. The dielectric characteristics of polycarbonate remain unchanged in the range of current frequencies from 10 to  $10^8$  Hz.

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Important advantages of polycarbonate are its attractive antifriction properties (Table 79) and high wear resistance.

Table 79  
Antifriction properties of polymers

Polymer	Density, g/cm <sup>3</sup>	Hardness, kgf/mm <sup>2</sup>	Friction Coefficient
Polyamide 6	1.13	5-12	0.4
Polycarbonate	1.2	15-16	0.26
Polyformaldehyde	1.4	20-25	0.24
Fenilon	1.42	21-30	0.24

### 30. Polyacetal Resins

In their molecular structure, polyacetals are simple polyethers of the general formula  $(CH_2O)_n$ . Polyacetals obtained from formaldehyde include polyformaldehyde and its copolymers.

The excellent mechanical, dielectric and antifriction characteristics of polyacetals combined with water resistance, dimensional stability and usability over a wide temperature range make these materials very promising for ship machine building. The volume of production of polyacetals is increasing rapidly. In 1960, 7,000 tons of acetal resins were produced throughout the world, and by 1970, the production was already 100,000 tons.

The industry produces polyformaldehyde - a homopolymer containing acetal end groups and copolymers of trioxane and ethylene oxide, trioxane and dioxolane, formaldehyde and dioxolane, etc. A typical representative of the homopolymer is Delrin, made by the Dupont Co., and a typical copolymer is Hostaform C, made by Celanese Corp. (USA) and Hoechst (FRG).<sup>25</sup>

Copolymers based on SFD formaldehyde and STD trioxane are produced in the Soviet Union.

The homopolymer has a high degree of crystallinity, rigidity and hardness. Copolymers have a slightly lower crystallinity, rigidity and hardness, but have the advantage of high thermal stability. The future belongs to copolymers, since the low thermal stability of polyformaldehyde considerably interferes with its processing into articles.<sup>25</sup>

The raw material for the production of polyformaldehyde and copolymers based thereon is high-purity (99.9%) formaldehyde containing no more than 0.05% moisture and up to 0.03% formic acid. Formaldehyde is chemically unstable, which considerably complicates its production technology. /183

In addition to formaldehyde, trioxane is also used for preparing polyacetals. Trioxane, a cyclic trimer of formaldehyde, is polymerized by a cationic mechanism with opening of the ring. The polymer formed has the same chemical structure as polyformaldehyde.<sup>25</sup>

The introduction into the molecular chain of polyoxymethylene (polyformaldehyde) of units of a different structure which prevent chain depolymerization makes it possible to increase the thermal stability of polyformaldehyde considerably. The complexity of the problem lies in the fact that the copolymers should contain the minimum possible amount of copolymer (less than 2-5 mole percent), uniformly distributed over the molecular chain, and the end groups of the macromolecules must include units of the copolymer.

With increasing copolymer fraction, the stabilizing effect increases, but at the same time there is a decline in the most valuable properties of the polymer, i. e., crystallinity, rigidity and hardness. Ethylene oxide and dioxolane are the copolymers most commonly employed.

Polyacetals are processed by die casting and extrusion. Articles used in ship machine building are usually made by die casting with the aid of casting

machines and a preplasticizer, equipped with exhaust ventilation. Processing with such machines gives a homogeneous casting mass, and the material may be heated to a lower temperature.

In processing polyformaldehyde, it is necessary to consider the low thermal stability of the melt. The maximum temperature of the melt must not exceed 220°C, and the minimum, 190°C. With increasing casting temperature, polyformaldehyde decomposes with the evolution of monomeric formaldehyde, causing further autocatalytic decomposition of the polymer.

The optimum processing temperature in the 190-220°C range is selected empirically for each type of machines. The material cylinder of the casting machine should be equipped with heaters with close temperature control ( $\pm 0.5^\circ\text{C}$ ). In addition to selecting the acceptable casting temperature, in the case of processing of homopolymers, it is necessary to determine the residence time  $\tau$  of the polymer melt in the cylinder of the casting machine and to make it comparable to the acceptable stability time of the melt at the given temperature. This value is usually calculated from the formula

$$\tau = \frac{mV_c}{g}$$

where  $m$  is the volume of the material in the cylinder,  $\text{cm}^3$ ;  
 $g$  is the volume of injected material,  $\text{cm}^3$ ;  
 $\tau_c$  is the duration of one casting cycle, min.

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To prevent the material from decomposing, it is necessary to match the size of the articles (volume of the injection) to the volume of the casting machine cylinder, and the ratio  $g/m$  should be kept optimal (1:6 or 1:10). The limitations related to the duration of heating of the copolymers consist in the fact that at 200°C, the polymer must not remain in the cylinder of the machine for more than 1 h, and at 220°C, more than 30 min.

Polyacetals as well as polyamides are characterized by low viscosity of the melt under the processing conditions. For this reason, various shutoff devices preventing the melt from leaking out during the return of the plunger are used during the casting of polyformaldehyde. The pressure during the casting is varied from 500 to 1000  $\text{kgf/cm}^2$  and is selected more or less precisely depending on the intricacy of the mold and wall thickness of the article.

The crystallization rate of polyacetals is very high, and crystallization can take place when the mold is incompletely filled. Therefore, the casting is done in molds heated to 70-140°C. In this case, a slower cooling rate and hence, a more uniform polymer structure is obtained.

The relatively high crystallinity of acetal resins causes an appreciable shrinkage of the polymer (from 1.5 to 3.5%) during its hardening in the mold. If the mold is heated above 85°C, an additional 0.2-0.3% shrinkage may take place after the casting is removed. To stabilize the dimensions of such articles and obtain a more homogeneous microstructure, the articles are heat-treated in oil at about 150°C.

Polyacetals are among the stiffest and strongest thermoplasts. Their strength characteristics are at the level of the corresponding characteristics of polyamides and polycarbonate. The normal elasticity modulus of polyacetals is higher

than that of the remaining structural thermoplasts. In resistance to impact loads (specific impact strength, 1.20-1.30 kgf m/cm<sup>2</sup>), polyacetals are similar to polyamides, but much more brittle than polycarbonate. Among thermoplasts, polyacetals have the highest fatigue strength values and considerably surpass polycarbonate in their resistance to multiple impact loads.

Drawbacks of polyacetals include a sharp decrease in specific impact strength during testing of specimens with an Izod notch. The impact strength of notched specimens is 0.07-0.09 kgf m/cm<sup>2</sup>, and therefore, when constructing parts exposed to impact loads, it is necessary to avoid stress concentration as much as possible.

The physicommechanical properties of polyformaldehyde are given below.

Density, g/cm <sup>2</sup> .....	1.4	/185
Strength, kgf/mm <sup>2</sup> :		
tensile .....	6.50-7.00	
compressive .....	13.00	
bending .....	8.00-11.00	
Elastic modulus, 10 <sup>2</sup> kgf/mm <sup>2</sup> :		
tensile .....	4.2	
bending .....	3.5	
Poisson's ratio .....	0.35	
Impact strength, kgf m/cm <sup>2</sup> .....	1.20-1.30	
Brinell hardness, kgf/mm <sup>2</sup> .....	20-25	
Coefficient of friction .....	0.35	
Wick temperature, °C .....	160-170	
Dielectric loss tangent at 10 <sup>4</sup> Hz .....	4 x 10 <sup>-3</sup>	
Dielectric constant at 10 <sup>5</sup> Hz .....	3.3	

In wear resistance, polyacetals are inferior only to polyamides, surpassing them in dimensional stability and moisture resistance. The mechanical properties of the specimens decline only slightly after they are kept for 365 days in water at room temperature. The creep of specimens immersed in water increases slightly (by 8-10%) in comparison with that of specimens kept in air. During service in boiling water, the strength of the specimens decreases sharply as a result of irreversible breakdown, i. e., hydrolysis.

In dielectric properties, polyacetals are similar to polyamides.

The dielectric properties of polyformaldehyde remain practically unchanged from 10<sup>2</sup> to 10<sup>5</sup> Hz, and decline only slightly during service at 100% relative humidity.

In contrast to polyamides, whose brittleness already manifests itself at temperatures below 0°C, articles made of polyacetals can be used at temperatures down to -60°C (Table 80). The melting range of polyformaldehyde is 164-167°C, and the deformation temperature (at a load of 13.5 kgf/cm<sup>2</sup>) is 110-130°C. On heating

Table 80  
Thermal properties of acetal resins

Property	Homopolymer (Delrin)	Copolymer (Hostaform C)
Melting range of crystalline phase, °C	175-180	164-167
Glass transition temperature, °C	-60	-60
Wick temperature, °C	167	154
Thermal conductivity coefficient at 20°C, kcal/(m h °C)	0.27	0.27
Specific heat capacity at 20°C, cal/g °C	0.35	0.35
Linear expansion coefficient, °C <sup>-1</sup>	4.5 x 10 <sup>-5</sup>	1.3 x 10 <sup>-4</sup>
Temperature of start of thermal oxidative degradation, °C	150	145
Temperature of start of thermal degradation, °C	250	270

to 100-120°C, polyacetal articles are still fairly rigid, but they cannot withstand service under these conditions. The upper limit of working temperatures for parts under load is 85°C. The higher heat resistance and water resistance of polyformaldehyde are responsible for the fact that under heavy duty conditions at high relative humidity, 60-80°C and appreciable loads, polyformaldehyde articles perform less reliably than articles made of other thermoplasts.

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A disadvantage of polyacetals is their low light resistance and their combustibility. Ultraviolet light accelerates the reaction of oxidative degradation of the polymer; the mechanical properties decline sharply, and the brittleness of the polymer increases. The introduction of photostabilizers and inhibitors into polyacetals slows down aging to some extent.

Polyacetals are combustible, burn practically without a residue, and their combustion rate is similar to that of polyethylene and polystyrene.

### 31. Polyimides

Polyimides are a new class of high-molecular-weight compounds. The first polymers with imide rings in the chain were obtained as long ago as the beginning of the 20th century. However, only after the development of a two-step synthesis by the Dupont Co. (USA) in the late 1950's did polyimides come to be widely studied and applied. At the present time they are being successfully adopted in the USSR, Japan, England, FRG and other countries.<sup>37, 52</sup>

Thanks to a valuable combination of excellent mechanical properties and exceptional heat resistance and thermal stability, polyimides are very promising materials. In chemical structure, they are heterochain polymers whose linear chains consist of aromatic and imide rings.

The starting materials for the synthesis of polyimides are derivatives of aromatic tetracarboxylic acids, aromatic and aliphatic diamines, di- and tetraesters, diimides, acid chlorides, and diisocyanates.

According to their method of preparation, polyimides may be divided into two major groups:

- with aliphatic units in the main chain;
- with aromatic units in the main chain.

Comparing the physicochemical properties of aromatic polyimides with the chemical structure of a monomer unit, the polyimides studied may be divided into four major groups.

Polyimides of the first group contain only aromatic rings joined to each other directly by imide rings. They are rigid nonsoftening polymers which at 20°C have an elastic modulus of  $10^3$  kgf/mm<sup>2</sup> and at 400°C, over  $3 \times 10^2$  kgf/mm<sup>2</sup>, i. e., higher than the majority of carbon chain polymers at 20°C. /187

Polyimides of the second group include polymers with heteroatoms in the dianhydride component which join benzene rings, rigidly linked by imide rings to the aryl radical of the diamine component. Polyimides of this group do not melt or soften either, and their elasticity is low.

Polyimides of the third group contain heteroatoms only in the diamine component. These polymers form rigid, strong and elastic films. Their elongation at rupture is 40-50% even at -195°C. The elastic modulus increases with the length of exposure to high temperature. Thus, on rapid heating to 400°C, the elastic modulus during the first few seconds is on the order of 1.0 kgf/mm<sup>2</sup>, then rapidly increases to 100 kgf/mm<sup>2</sup>.

Polyimides of the fourth and last group have heteroatoms in both the dianhydride and diamine component. These polymers are elastic and are marked by the lowest density.

The production of articles from polyimides involves major technological difficulties. The latter are primarily due to the necessity of removing large amounts of solvent (solutions of polyamido acids contain no more than 20-30% of dry substance) and water evolved during imidization.

As in the case of epoxy resins, direct conversion of concentrated solution of polyamido acid into a polyimide block has, for all practical purposes, not been used to date. To obtain plastics from polyimides, the polyimido acid is usually separated from the solution in the form of films, powders, or coatings on a glass tape; partial or complete imidization by chemical or thermal means is carried out, then the material is processed into articles by molding or sintering.

A whole series of polyimide-base binders have been developed for fiber glass plastics. Polyimide binders first provided for a stable structural strength of fiber glass plastic at temperatures above 300°C, whereas for a fiber glass plastic based on the traditional phenolic binder, the service life even at 260°C is only 150 h. The physicochemical properties of fiber glass plastics based on polyimide binders are listed in Table 81.

Interesting results have been obtained by using DFO polyimide as binder.<sup>52</sup> DFO polyimide softens at 270°C and in the 300-400°C range is in the viscofluid state, i. e., is a thermoplast. Molding material based on it is obtained by impregnating under pressure a washed and calcined glass tape with a 15% solution of polyamido acid, then drying and heat-treating in a vacuum while gradually raising

the temperature to 300°C. Compression molding is carried out at 370-390°C at pressures from 500 to 2000 kgf/cm<sup>2</sup> and is followed by cooling under pressure.

Table 81  
Physicomechanical properties of fiber glass plastics based on polyimide binders

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Brand of polyimide binder	Binder content of fiber glass plastic %	Bending strength, kgf/mm <sup>2</sup>							Mass loss, %
		In initial state		After thermal aging at 300°C					
		at 20°C	at 300°C	100 h	500 h	1000 h	1500 h	2000 h	
STP-1	25-30	55-70	28-33	32-35	30-36	26-30	15-23	10-13	0.75
STP-2	25-30	22	23	14	14	-	14	14	2.0
Stp-3	25-30	36-44	23-25	23-27	23-32	28-29	12-19	-	1.0
STP-5	23-25	65-67	30-36	32-46	32-45	-	35-37	30-31	0.5
STP-6	35-40	32-37	-	31	29	26	-	-	-

Note. The tests were performed on specimens measuring 55 x 6 x 4 mm.

The fiber glass plastic obtained has the following physicomechanical properties (at 40% glass fabric content):

Density, g/cm <sup>3</sup> .....	1.90
Elastic modulus at 20°C, kgf/mm <sup>2</sup> .....	10 <sup>3</sup>
Bending strength at 20°C, kgf/mm <sup>2</sup> .....	32.0
Impact strength, kgf m/cm <sup>2</sup> .....	1.6-2.4

Thanks to its comparatively low viscosity (about 10<sup>4</sup> P at 380°C), DFO polyimide can be processed not only by molding but also die casting. Testing of DFO polyimide specimens have shown that this polyimide has a better combination of physicomechanical properties than all existing thermoplasts. Its Wick temperature is 80°C higher than that of the most heat-resistant of modern thermoplasts - polyphenylene oxide. DFO polyimide retains high strength and rigidity at temperatures above 200°C, where other thermoplasts cannot withstand minimum mechanical loads; it is extremely resistant to ultraviolet radiation. On irradiation with a mercury lamp for 200 h, the properties of the DFO film remained unchanged, whereas simultaneously tested films of polyethylene, lavsan and capron cracked and completely lost their elasticity.

The Dupont Co.<sup>52</sup> is producing in experimental quantities the plastic Vespel, nonfilled (SP-1) and filled with 15% graphite (SP-2) in the form of blocks, from which parts are made mechanically. The properties of SP-1 plastic are listed below. /189

Density, g/cm <sup>3</sup> .....	1.42
Strength, kgf/mm <sup>2</sup> :	
tensile at 20°C .....	8.75
tensile at 250°C .....	5.00



Elastic modulus, $10^4$ kgf/mm <sup>2</sup> :	
at 20°C .....	3.3
at 250°C .....	1.34
Strength, kgf/mm <sup>2</sup> :	
compressive at 20°C .....	15.50

SP plastics have low water absorption and acid resistance, are insoluble in organic solvents, but are decomposed by strong alkalis and superheated steam.

SP-2 plastic is used in the manufacture of fuel line parts, compressor piston rings, etc. Tests of the parts have proven this material to be very promising.

Highly promising is the use of polyimides as solid antifriction materials requiring no lubrication. The use of polyimides makes it possible to raise considerably the upper limit of working temperatures and the permissible maximum loads and speeds. Because of their high wear resistance, low friction coefficient (0.10-0.17 without a lubricant) and high mechanical strength, polyimides are used for self-lubricating sliding bearings designed for long service at high temperatures. In their wearing characteristics, polyimides considerably surpass teflon-base materials. The best antifriction properties are exhibited by polyamide filled with fibrous copper.

### 32. Thermoplasts Reinforced with Glass Fiber

In recent years, interest in reinforced thermoplasts has been steadily increasing. The positive economic aspects of their die casting permit their use for the fabrication of stronger parts. Industrial production of glass-filled thermoplasts was first started in 1958; two brands of glass-filled polyamides were fabricated. In recent years, the assortment of filled thermoplasts has expanded so much that over 1000 different brands are now in existence. At the present time, almost all thermoplasts can be filled with glass fiber. By 1970, the production of reinforced thermoplasts in the USA had increased sevenfold over 1966.

The introduction of a glass fiber filler into thermoplasts has considerably extended their scope of application. The presence of excellent physicomechanical properties at normal as well as elevated and particularly subzero temperatures, high dimensional stability, rigidity, low density and small shrinkage all permit the use of these materials in diverse areas of technology.<sup>5</sup> /190

In reinforcing thermoplasts, it is necessary to consider all the factors affecting the properties of the material, chemical nature of the polymer and filler, phase state of the polymer, adhesion of the polymer and filler, conditions of formation of the filled polymer from solution or melt, nature of treatment of the filler surface, nature of its distribution in the polymer mass, etc.

Reinforcing with glass fiber doubles and in some cases triples the breaking strength of most polymers.

The dimensional stability during service improves, shrinkage decreases, water absorption drops by 25-50%, and the coefficient of thermal expansion decreases by 15-20% as compared to nonreinforced thermoplasts. The properties of glass-fiber-

reinforced thermoplasts depend to a considerable degree on the length of the glass fiber and type of sizing agents employed. The strength of a material is greater, the longer the individual glass fiber threads. However, homogeneous cast parts cannot be made when the glass fibers are long. In the last few years, a short glass fiber 0.7 mm long has been proposed for reinforcing thermoplasts. Materials reinforced with this type of fiber are more easily plasticized, so that lower pressures and temperatures may be used in the manufacture of parts.

The optimum amount of glass fiber in polyamides is 30-33%. In the presence of this glass fiber content, a fairly high strengthening of the material takes place, and the capacity of the material to be processed by die casting is preserved. Glass-filled polyamides of brands 68VS, 68VSM and KVS in the form of granules are produced by the Soviet industry.

At a comparatively low density ( $1.35 \text{ g/cm}^3$ ), glass-filled polyamides differ advantageously from unfilled ones in a wide operating temperature range: from  $-60$  to  $150-170^\circ\text{C}$  under load and from  $-200$  to  $200^\circ\text{C}$  without load. Glass-filled polyamides are characterized by high strength properties and a low coefficient of linear expansion  $(1.5-3.0) \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ , so that they can be used for a comparatively easy fabrication of parts with complex ferrous metal fittings.

The manufacture of semifinished products in the form of granules makes it easy to process them by the usual methods: die casting and extrusion at  $250-270^\circ\text{C}$  and a specific pressure of  $1000-1400 \text{ kgf/cm}^2$ . Glass-filled polyamides may be successfully used for intricate-shaped parts instead of such widely used fiber glass materials as AG-4V and 27-63V; at the same time, the labor intensity of the fabrication is reduced by a factor of 6-10.

Glass fiber 5 mm long is introduced into polycarbonate in amounts up to 30%. This improves its mechanical properties, raises the upper limit of working temperatures by  $15-20^\circ\text{C}$ , and lowers its sale price by 25% (Table 82). In the presence of a higher glass fiber content, the rigidity and hardness of the polymer increase, impact strength decreases, density increases substantially, and processing becomes more difficult. Glass-filled polycarbonate is processed by die casting. /191

Table 82  
Physicomechanical properties of glass-filled polycarbonate

Property	Unfilled polycarbonate	Polycarbonate containing 30% glass fiber
Strength, $\text{kgf/mm}^2$ :		
tensile	6.5	9.0
bending	10.0	14.5
Tensile elongation, %	80	3.0
Modulus of tension, $10^2 \text{ kgf/mm}^2$	2.2	5.5
Impact strength, $\text{kgf m/cm}^2$	1.5	0.45
Poisson's ratio	0.36	0.27
Fatigue strength, $\text{kgf/mm}^2$ (based on $10^7$ cycles)	2.0	2.5
Coefficient of linear expansion, $^\circ\text{C}^{-1}$	$60 \times 10^{-6}$	$27 \times 10^{-6}$

Table 83  
Mechanical properties of glass-filled polyformaldehyde of brand Dyurakon GR-29

Property	Filled poly-formaldehyde	Unfilled poly-formaldehyde
Tensile strength, kgf/mm <sup>2</sup> :		
at 23°C	7.7	6.2
at 71°C	4.7	3.5
Bending strength, kgf/mm <sup>2</sup>	11.0	9.0
Elongation at 23°C, %	2	60
Modulus of tension, 10 <sup>2</sup> kgf/mm <sup>2</sup> :		
at 23°C	7	2.88
at 71°C	4.99	1.5

The introduction of a glass filler into polyformaldehyde permits a substantial improvement of the strength indices, heat resistance, and particularly dimensional stability of the parts. Usually, 20% of glass filler is introduced, this amount of filler being sufficient to raise the maximum service temperature by 20-30% and the modulus of bending by a factor of over 2 (Table 83).

Table 84  
Properties of glass-filled polypropylene

Property	Content of glass filler, %	
	20	40
Strength, kgf/mm <sup>2</sup> :		
tensile	4.9	6.3
bending	4.9	7.7
compressive	4.2	4.9
Elongation, %	3	2
Heat resistance at load of 18.5 kgf/cm <sup>2</sup> , °C	140	150

Glass fiber filler can be introduced into polypropylene in amounts of 20-40%. In comparison with other glass-filled thermoplasts, polypropylene has the advantage that it can be used to make articles of intricate shape such as propellers for boats with outboard motors. Glass-filled polypropylene can be processed with worm gear type casting machines under the following conditions: cylinder temperature, 220-240°C; mold temperature, 60-80°C; specific pressure, 700-800 kgf/cm<sup>2</sup>. The properties of glass-filled polypropylene are listed in Table 84.

## 33. Stern Bearings

The reliable operation of stern bearings is determined in most cases by the properties of the antifriction materials used in the "propeller - bearing bush" friction pair. It is well known that the material used for propeller shafts is steel, lined with bronze or stainless steel in the region of the working necks. A wide assortment of materials are used for stern bushings. /193

Studies have shown<sup>53, 66</sup> that one of the promising materials is caprolon. Stern bearings made of caprolon are successfully used on tugs, icebreakers, fishing trawlers, and crew boats. Caprolon ensures a reliable operation of propeller shaft bearings with linings of OTs10-2 bronze and stainless steel.

Use of caprolon stern bearings reduces the mass of bearings by a factor of 2-3, the fabrication labor intensity by 40-50%, and the cost of bearings by 50-60%.

According to their design characteristics, caprolon sliding bearings may be divided into the following types:

type I - bearings in the form of a smooth bush pressed into a stern bushing or bracket (for shafts 30-130 mm in diameter);

type II - bearings in the form of a bush with a flange pressed into a stern tube or bracket (for shafts 30-500 mm in diameter);

type III - bearings in the form of a smooth bush pressed into a metal bushing (for shafts 260-500 mm in diameter);

type IV - bearings in the form of several smooth bushes pressed into an intermediate bushing (for shafts 260-500 mm in diameter); /194

type V - bearings with a set of bushes made of caprolon plates (for shafts 200-500 mm in diameter).

Caprolon sliding bearings are prepared by free casting followed by mechanical treatment. The articles are cast in open and closed type molds. The selection of the type of casting mold is determined by the batch production of the cast parts and the volume of mechanical treatment of the castings. In single-unit or small-batch production, the casting is made in open molds of simplified design. In the manufacture of large series of bushings, it is desirable to cast them by centrifugal casting. The casting molds should be made of a material that is chemically resistant to the action of the alkaline caprolactam solution, thermally stable at temperatures up to 250°C, and sufficiently resistant to the loads arising in the course of shrinkage of the material and during unmolding.

Parts of the mold, i. e., internal cores and flanges subjected to loads during unmolding, are made of stainless steel; parts shaping the outer surface of the casting are made of aluminum alloys to reduce the mass of the molds. In designing the molds, it is necessary to consider the shrinkage of the material in the course of polymerization, crystallization and cooling.

The shrinkage of finished articles is as follows:

in open-mold casting - 3.5-4.5% along the outside diameter, 2-2.5% along the inside diameter, and 5-7% along the height;

in closed-mold casting - 2-2.5% along the outside and inside diameters and 5% along the height.<sup>53</sup>

Caprolon castings obtained by the free-casting method are subjected to mechanical working and assembled. Mechanical working is done with standard metal-cutting equipment. Caprolon is satisfactorily worked with all types of metal-working tools.

The technology of mechanical working is determined by the structural type of the bearing. For example, the working of type I and II bearings includes pre-treatment of the blank along the outside and inside diameters and ends, finishing of the opening and ends, as well as finishing of outside fitting diameter.

Type III bearings are worked by pressing caprolon bearings into an intermediate metal bush, then the fitting points of the intermediate bush and side pockets are finished. The opening is finished according to the drawing only when the bearing has already been mounted in the stern tube.

Fitting of a caprolon stern bearing consists in pressing caprolon bushes into an intermediate (metal) bush. The pressing may be carried out with hydraulic and manual presses as well as clamping devices.

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The mounting of caprolon stern bearings set up in the intermediate metal bush and caprolon bearings - bushes pressed directly into the stern tube - is done according to the process flow diagram used for mounting rubber-metal bushes and other materials by means of special devices. When caprolon bushes are pressed directly into the stern tube (without an intermediate metal bush), it is necessary to take all steps to protect the surfaces of the bushes from mechanical damage.

In caprolon bearings, the mounting clearance decreases after the ship is launched because the material swells. During the first month, the swelling takes place fairly rapidly, and during the subsequent months and years, slowly. Swelling of the bearings compensates their wear during the first three to five years of operation. At the same time, swelling of the bearing appreciably decreases the mounting clearance when the ship is afloat and should be taken into account when drilling the inside diameter of the bearing prior to launching. For example, for a nominal bearing diameter of 40 mm, the bearing is drilled to a size of  $40.3 \pm 0.5$ , which provides for a sufficient clearance in the first period of the most intense swelling of the bearing and for its preservation during subsequent years of service.

Quality control of caprolon castings is accomplished by ultrasonic and x-ray methods. The ultrasonic method, which is most promising for large-sized castings, involves the use of the same instruments as in quality control of fiber glass plastics: DUK-17, DUK-66, etc. The x-ray method is used mainly for control of castings up to 200 mm thick by means of RUT-60-20-1 units using BPV-60 x-ray tubes. These control methods make it possible to detect such defects as cavities, cracks and pits.

#### 34. Ship Piping

The chief cause of premature failure of metal piping is the action of seawater, which is very corrosive, on their inner surface. The use of polymers of high corrosion resistance for the main components of piping, i. e., tubes and fittings, is of definite interest, since it permits an increase in their durability.

At the present time, in addition to the use of steel tubes with protective coatings, polyethylene tubes, which have a high corrosion resistance and a small mass, have found use in individual shipbuilding systems.

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In foreign shipbuilding, tubes made of polyvinyl chloride, polyethylene and polypropylene are used for cooling systems of storage batteries, washing off radioactive deposits, and for cold and hot water supply systems at whaling bases.

The Soviet industry has mastered the manufacture of extruded tubes of low and high density polyethylene. The tubes are produced in three series. They are designed for long-term service at an internal pressure of 6.0 and 10 kgf/cm<sup>2</sup>.<sup>55</sup> Tubes of polymer materials combine a high corrosion resistance with an adequate erosion resistance in a medium of high-speed seawater. For this reason, the permissible velocity of water in tubes made of plastics or metal tubes lined with plastics is 5.0 m/sec versus 1.2 m/sec for copper tubes and 3.0 m/sec for steel ones. Hence, when tubes of polymeric materials are used, the overall dimensions of the systems may be substantially reduced.

A successful combination of the mechanical strength of the metal shell and high corrosion resistance of the polymer can be achieved by using metal tubes lined with polyethylene tubes on the inside. The metal tubes are lined by combined mandrel-free drawing of the metal and plastic tube (for small-diameter tubes) or by reducing the lining insert.

The lined tubes are bent and flanged for joints by means of standard equipment used in a copper tube plant. The components of branches are made in the form of shaped parts whose metal housings are lined with polymers by die casting. The tubes are designed for long-term service in sea and fresh water at pressures up to 10 kgf/cm<sup>2</sup> and temperatures up to 65°C. Piping made of lined tubes is used at the "Vostok" fishing base and other ships of the fishing fleet.

Chapter 10. POLYMERIC COATINGS USED IN SHIP MACHINE BUILDING

35. Coating Materials

Polyethylene is a typical thermoplast; its industrial production was first set up in 1938 in England and in 1939 in Germany.

Three types of polyethylene, low, high and medium pressure, found technical application (Table 85). For coatings, it is best to use high pressure polyethylene (HPPE), which forms coatings by the particle fusion method more easily than the other types. In addition, HPPE has the highest resistance to thermal oxidative degradation and light aging. Polyethylene coatings protect articles from the action of corrosive media and have attractive physicomechanical and electrical insulation properties.<sup>71</sup>

The high chemical stability and water resistance of polyethylene are due to its high crystallinity and close packing of macromolecules in regions of crystalline formations.

The introduction of fillers (glass fiber, titanium oxide, aluminosilicate) into polyethylene substantially improves its strength characteristics. The highest strength is exhibited by compositions with glass fiber 5 mm long at up to 30% content. The water absorption of the coating increases when the filler content is above 30%, indicating a loosening effect of the filler on the packing of macrochains at the phase boundary.

In hardness and decorative appearance, polyethylene coatings are inferior to many other polymeric coatings. Their chief disadvantage is a pronounced cracking tendency during service.

Table 85  
Properties of polyethylenes

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Property	High pressure polyethylene	Low pressure polyethylene
Density, g/cm <sup>3</sup>	0.92-0.94	0.94-0.96
Molecular mass	10,000-45,000	70,000-400,000
Degree of crystallinity, %	53-67	80-90
Temperature limits of application, °C:		
upper	85	110
lower	-70	-65
Tensile strength, kgf/cm <sup>2</sup>	120-150	220-280
Elongation at rupture, %	150-600	200-800
Modulus of tension, kgf/cm <sup>2</sup>	1,500-2,500	8,000-10,000
Dielectric loss tangent at 10 <sup>6</sup> Hz	(2-5) x 10 <sup>-4</sup>	(2-4) x 10 <sup>-4</sup>

In ship building, polyethylene is used for protecting piping, drinking water tanks and other equipment.

Polyvinyl butyral (Butvar) is a polyvinyl acetal - a derivative of polyvinyl alcohol. It is obtained by condensing polyvinyl alcohol with butyraldehyde in the presence of hydrochloric acid. Polyvinyl butyral is an amorphous white powder con-

taining 78% butyral and and 2-3% acetate groups. It is produced in plasticized and unplasticized form. Flexible (plasticized) polyvinyl butyral contains 16-18% plasticizer (dibutyl phthalate, dibutyl sebacate, etc.), whose introduction makes the film highly flexible and cold resistant.

The properties of rigid and plasticized polyvinyl butyral are listed in Table 86.

Polyvinyl butyral-base coatings are characterized by high atmospheric resistance, stability to ozone, and good wear resistance. The coatings are gas and oil resistant: after being kept in mineral oil for 7 years, the samples retain their original properties.

In shipbuilding, polyvinyl butyral-base coatings are used for parts to give the latter protective and decorative or insulating properties.

The coatings work well in dry and moist air, sea fog, oil and fuel media at temperatures up to 60°C.

Polyvinyl butyral may be used to obtain coatings of different colors. The pigments used for polyvinyl butyral are zinc oxide, titanium dioxide, ochre, ultramarine, gas black, etc.

Table 86  
Physicomechanical and electrical properties of polyvinyl butyrals

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Property	Polyvinyl butyral	
	Rigid	Plasticized
Density, g/cm <sup>3</sup>	1.07-1.1	1.05
Tensile strength, kgf/cm <sup>2</sup>	280-500	140
Elongation, %	5-15	150-400
Elastic modulus, 10 <sup>5</sup> kgf/cm <sup>2</sup>	0.20-0.24	-
Martens temperature, °C	48-54	-
Coefficient of linear expansion, °C <sup>-1</sup>	8 x 10 <sup>-5</sup>	-
Water absorption, %	1.0-3.0	1.0-2.0
Dielectric constant at 10 <sup>6</sup> Hz	2.8-3.3	3.92
Dielectric loss tangent at 10 <sup>6</sup> Hz	0.0065	0.06
Volume resistivity, ohm cm		

The best coating quality is given by "slit" polyvinyl butyral, whose melt spreads well over surfaces thanks to a lower viscosity.<sup>50</sup>

The coatings are applied by gas-flame, jet and vibrovortex spraying, spraying in an electrostatic field, and other methods.

Pentaplast is a thermoplastic crystalline polymer. Its high chlorine content (45.5%) and very dense crystal structure provide for an exceptional chemical inertness and resistance to solvents. The chloromethyl groups of the polymer are linked



to those carbon atoms of the main chain where there are no hydrogen atoms near nearby. On heating, this precludes the detachment of hydrogen chloride, which usually accelerates further thermal degradation and gives pentaplast a high thermal stability.

Pentaplast is marked by high water resistance, strength, hardness, and low coefficient of friction. The water absorption of pentaplast after 360 days is 0.1%, and the mechanical properties and dimensions of the articles remain constant after exposure to water for a long time. It has high chemical stability, wear resistance and excellent dielectric properties.

The physicommechanical and electrical properties of pentaplast are given below.

Density, g/cm <sup>3</sup> .....	1.4	
Strength, kgf/cm <sup>2</sup> :		
tensile .....	400	
compressive .....	750-900	
static bending .....	680-700	
Elongation at rupture, % .....	30-50	
Specific impact strength, kgf cm/cm <sup>2</sup> .....	40-80	/200
Martens temperature, °C .....	45	
Elastic modulus, kgf/cm <sup>2</sup> :		
at -60°C .....	52,000	
at 20°C .....	10,000	
at 80°C .....	5,000	
Brinell hardness, kgf/mm <sup>2</sup> .....	13	
Water absorption, % .....	0.01	
Coefficient of linear thermal expansion, °C <sup>-1</sup> .....	(8-11.5) x 10 <sup>-6</sup>	
Volume electrical resistivity, ohm cm .....	1 x 10 <sup>15</sup>	
Surface electrical resistivity, ohm .....	5 x 10 <sup>14</sup>	
Dielectric permeability:		
at 50 Hz .....	3.1	
at 10 <sup>6</sup> Hz .....	2.8	

The formation of pentaplast coatings is complicated by the crystallization process, which affects many properties of the films, the magnitude of internal stresses, and the adhesion of the coating to the metal surface. Pentaplast in coatings is usually in the crystalline state. By changing the conditions of their formation, one can control the crystallization rate and degree of crystallinity of the polymer, and hence, change its mechanical properties and create conditions for the formation of high-quality coatings.

Studies<sup>27</sup> have established that by changing the conditions of cooling of the coating (cooling in air, rapid cooling in water, slow cooling in air), one can obtain a polymer with a degree of crystallinity from 0 to 28%. Sudden cooling of the polymer heated above the melting point of the crystalline phase stabilizes a considerable content of the amorphous phase and is called quenching.

Quenching in water followed by slow crystallization at 20-25°C to 16% crystallinity permits one to obtain coatings with no internal stresses, no shrinkage after removal from substrate and high adhesion to the metal surface.

On air cooling to the same degree of crystallinity, the internal stresses formed decrease the adhesion; on slow cooling in air, the increase in internal stresses is so appreciable that the adhesion practically drops to zero.

Thus, the optimum conditions of formation of coatings include obligatory quenching with a temperature difference from 200 to 20°C followed by slow crystallization of the polymer. During the crystallization of the polymer, carried out by keeping the latter for at least 24 h at 20-25°C, relaxation of internal stresses takes place without weakening the adhesion of the film to the substrate.

Pentaplast, a rigid crystalline polymer, has high heat resistance but insufficient elasticity and cold resistance. The glass transition temperature of amorphous segments of pentaplast ranges from -5 to 7.5°C.

In the temperature range from 0 to 20°C, a marked change takes place in the deformational and strength properties of pentaplast: the impact strength of the specimens at 0° is 10 kgf cm/cm<sup>2</sup>, versus 140 kgf cm/cm<sup>2</sup> at 20°C. /201

The introduction of liquid plasticizers (dodecyl phthalate, dibutyl sebacate) into pentaplast leads to a certain improvement in impact load resistance and lowering of the brittle point.

Pentaplast is used for coating various parts used in ship machine building.

To protect articles used under tropical conditions, practical application of pentaplast is possible only if the stabilization problem is solved, since in the unstabilized polymer, elevated temperatures or ultraviolet irradiation in air give rise to extensive changes which impair the initial physicomechanical properties of pentaplast.

Polyamides are heterochain polymers containing amide repeating groups -C-NH- in the main chain of the macromolecule.

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In hardness, mechanical strength, heat resistance and adhesion to surfaces, polyamide coatings surpass polyethylene ones. However, because of insufficient moisture resistance, they are not used as anticorrosive and weatherproof coatings, but primarily as wear-resistant ones.

Polyamide coatings<sup>41</sup> should be used between -40 and 100°C. Prolonged exposure to atmospheric oxygen above 100°C leads to a marked decrease in the mechanical strength and adhesion of the coatings. When the parts are used in oil, a temperature of 130-140°C is permissible. At room temperature, coatings 320-340 μm thick provide protection for 60 days in distilled water and seawater. At higher temperatures, polyamide coatings swell considerably, lose their adhesion and peel off.

The properties of polyamides are considerably improved by the introduction of various fillers - graphite, talc, molybdenum disulfide, glass fiber, etc. The filler is introduced in amounts up to 10% by mixing manually or in ball mills.

Polyamide coatings are applied by spraying, i. e., flame, electrostatic, vibro-vortex spray coating and other methods. Of fundamental importance in the technology of production of polyamide coatings are the cooling conditions. Depending on the purpose of the coatings, various cooling conditions may be chosen. If high wear resistance is required, the coating should be heat-treated in an organosilicon liquid or mineral oil prior to the cooling. Such treatment promotes crystalliza-

tion of the polymer, increases hardness and decreases the coefficient of sliding friction and moisture absorption of the film. To obtain elastic and flexible coatings of improved adhesion, rapid cooling of the article is required (quenching in cold or mineral oil). /202

Epoxy compositions have been included among powder coatings comparatively recently and have already found application. This is explained by the following advantages of epoxy-base coatings over other powder compositions and materials:

- the films are formed at lower temperatures (100-200°C);
- the properties of the coatings may vary with the chemical composition of the materials (brand of epoxy resin and curing agent);
- the coatings are characterized by stronger adhesion;
- attractive protective properties are obtained with a small thickness of the coating.

Epoxy coatings are obtained by using powder compositions based on resins of brands E-40, E-05, E-41, E-33, etc.<sup>50</sup>

Epoxy resins in powder systems are cured primarily by using the following curing agents: cyanamides, complex compounds of boron trifluoride with amines, aromatic amines, anhydrides of polybasic organic acids, etc.

The composition of epoxy materials include modifiers, fillers, and pigments. Among modifiers, the one used most extensively is polyvinyl butyral, introduced in the amount of 5%.

The fillers and pigments introduced into powder systems should be stable to heat and inert to curing agents, and be capable of becoming highly dispersed during the preparation of powders. Thixotropic agents, which control the viscosity and spreading of the melts, must be introduced into powder compositions to ensure the quality of the coatings.

Epoxy coatings are characterized by high adhesion, mechanical strength, distinctive electrical insulation properties, and chemical stability. They are stable to water, oils, and fuel.<sup>13</sup>

Powdered epoxy compositions can be applied in different ways, but the vortex and electrostatic methods are most commonly employed. They adhere to vertical walls practically without running even when subjected to considerable overheating and present in large thickness, and undergo practically no oxidative degradation.

Powdered epoxy coatings with fillers (titanium oxide, aluminum powder) are commonly employed for protecting equipment and piping used in seawater.

Recently, extensive studies have been conducted for the purpose of increasing the elasticity of epoxy resins through modification with polyamides, rubbers, and fluoroplastics, for example, the epoxy-Novolac block copolymer (ENBC).

To increase the elasticity of films and coatings based on epoxy-Novolac resins, use is made of various oligomer and polymer materials as modifiers: polyethers, rubbers, polyvinyl butyrals, and fluorinated hydrocarbons.<sup>64</sup> /203

The reaction of the epoxy groups of ENBC with the carboxyl groups of rubber involves the formation of a ternary epoxy-Novolac-rubber block copolymer. It has

been found that as the amount of rubber increases, the elastic properties of the films improve, while their strength properties decline. The optimum combination of elasticity, strength and content of the insoluble component are exhibited by films containing 50-100% rubber.

Coatings based on these compositions have a nice appearance, high values of physicochemical properties (elasticity, shock resistance, adhesion) and attractive dielectric properties, and retain these indices when used in seawater.

Combining the block copolymer and 42V fluoroplastic in the presence of the catalyst triethanolamine formed FEN lacquers in which the ratio of the initial components ENBC and 42V fluoroplastic is 1:2 and 1:2.5.

Coatings and films based on FEN lacquers are elastic, weatherproof, water and heat resistant, and possess excellent physicochemical and insulating properties (Table 87).

Table 87  
Properties of films and coatings based on the epoxy-Novolac block copolymer and compositions based thereon

Property	ENBC	KEN-50	KEN-100	FEN-42V
Film density, g/cm <sup>3</sup>	1.4	1.2	1.25-1.3	-
Tensile strength, kgf/cm <sup>2</sup>	1200	250-330	190-220	350-370
Elongation, %	1-2	15-20	85-95	60-65
Impact resistance measured with U-1 instrument, kgf cm/cm <sup>2</sup>	Not resistance	50	50	50
Flexibility measured with ShG-1 instrument, mm	Same	1	1	1
Relative hardness	0.95	0.7	0.46	0.6
Water absorption after 30 days, %	0.4	-	1.0-1.2	0.5-0.6
Volume electrical resistivity, ohm cm	10 <sup>15</sup>	4 x 10 <sup>13</sup>	2.5 x 10 <sup>13</sup>	3 x 10 <sup>14</sup>

Epoxyfluoroplastic coatings combine the high mechanical and adhesive strength of epoxy resins with the elasticity of F-42 fluoroplastic. They harden at elevated and room temperatures and adhere strongly to metals. The properties of epoxy-fluoroplastic films and coatings are listed below.

Tensile strength, kgf/cm <sup>2</sup> .....	400-450	/204
Elongation, % .....	200	
Water absorption after 30 days, % .....	0.6	
Impact resistance measured with U-1 instrument, kgf cm/cm <sup>2</sup> .....	50	
Flexibility measured with ShG-1 instrument, mm .	1	
Volume electrical resistivity, ohm cm .....	6 x 10 <sup>13</sup>	

Among polymeric materials used as protective coatings, polyurethanes hold a special position because of their exclusively high elasticity. This results in an exceptionally high resistance of coatings based on them to abrasive and hydro-abrasive erosion and also to cavitational forces.

Such coatings are better able than others to withstand multiple alternating deformations, heavy vibrational loads, and sharp temperature fluctuations. Also of major interest are their sound-absorbing, damping and ablative properties.

A. L. Labutin<sup>36</sup> has developed a whole series of liquid rubber-coating compositions (SKU-7, SKU-8, etc.) based on polyesters, but the best combination of properties is exhibited by compositions based on SKU-PFL rubber. SKU-PFL mixed with the vulcanizing agent 3,3'-dichloro-4,4'-diaminodiphenylmethane (Diamer X) and catalyst oleic acid yields elastic coatings which surpass any other polymeric materials in wear resistance.

The preparation of working compositions consists in mixing the components before the formation of the coatings. To provide for the required adhesion and water resistance of the coatings, the rubber-coating compositions are applied on a priming layer providing an additional barrier to moisture, which diffuses through the polyurethane coating film.

The physicochemical properties of films and coatings based on SKU-PFL rubber are listed in Table 88. The chemical stability of films prepared from SKU-PFL is low, but they resist the action of many dilute acids, alkalis, and mineral salts.

Liquid nairits are low-molecular rubbers. They are obtained by chemical degradation of chloroprene rubbers.

A mass-produced rubber is nairit A. To increase the solubility, the required amount of sulfur is introduced in the form of a solution in mineral oil or as an aqueous dispersion. Oil and disperse nairits, respectively, are thus obtained, which undergo degradation more readily than other types of nairit in the course of rolling in the presence of tetraethylthiuram disulfide (thiuram E) with the formation of low-molecular products. Soluble low-molecular elastomers suitable for use as film-forming substances are thus obtained. Vulcanized coatings based on them possess excellent physicochemical properties and retain the oil resistance characteristic of chloroprene rubbers.

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Crystallizing nairit of brand NT is the product of polymerization of chloroprene under special conditions. Nairit of brand NT decomposes to form low-molecular, readily soluble products used as base for rubber-coating compositions. These products retain their ability to crystallize at room temperature; coatings based on them may be used in vulcanized as well as unvulcanized form, so that their scope of application is naturally expanded.

The solubility of liquid nairits is so high that 65-67% solutions of rubber mixtures based on them have the consistency of ordinary oil paint and can be applied with a brush.

Coatings based on liquid nairits do not have the necessary adhesion to metal and are applied on primers, the most useful of which is chlorinated nairit primer. The primer may be applied on the surface with a brush, by spraying, dipping, and

pouring. It provides for strong adhesion of nairit coatings to both ferrous and nonferrous metals.

Adhesion of nairit coatings to metals is also provided by adhesives - leuconate and 88-N. However, leuconate quickly reacts with moisture and can therefore be used only when the humidity does not exceed 65%. Moreover, it does not create an additional barrier to the penetration of water and electrolyte solutions to the metal. 88-N adhesive is free of these disadvantages, but its application is limited by its short working life.

Table 88  
Physicomechanical properties of films and coatings based on SKU-PFL polyurethane

Property	Vulcanization	
	at 20°C	at 120°C
Film density, g/cm <sup>3</sup>	1.1	1.1
Breaking strength, kgf/cm <sup>2</sup>	150-250	200-350
Elongation, %	350-450	400-450
Residual elongation, %	2-8	5-210
Shore hardness, kgf/cm <sup>2</sup>	81-86	88-91
Brittle point, °C	-70	-70
Flexibility measured with ShG-1 instrument, mm	1	1
Impact resistance measured with U-1 instrument, kgf cm/cm <sup>2</sup>	50	50
Water absorption after 30 days at 20°C, %	2	1
Gas and oil resistance at 20°C	Satisfactory	
Dielectric properties at 50 Hz:		
dielectric loss tangent	0.036	-
dielectric constant	4.2	-
Volume resistivity, ohm cm	10 <sup>14</sup>	-
Breakdown voltage, kV/mm	22	-

Cold-dried unvulcanized coatings with liquid NT nairit base are devoid of /206 elastic properties and have a comparatively narrow range of working temperatures, from -25 to 50°C. At temperatures above 50°C, unvulcanized coatings undergo creep when simultaneously subjected to a load.

Vulcanized coatings with a liquid NT nairit base are 8 to 10 times more wear-resistant than coatings of oil and dispersed nairits and are similar in this respect to polyurethane elastomers, which are extremely wear-resistant (Table 89).<sup>36</sup> NT nairit-base coatings are characterized by water resistance.

Liquid neoprene,<sup>36</sup> produced abroad in large quantities, is used in the form of rubber coatings on a chlorinated rubber primer (neoprecal, primer 107) for protecting articles used in chemical machine building and shipbuilding from corrosive media and abrasive and erosive wear.

Table 89  
Physicomechanical properties of nairit-base films and coatings

Property	Disperse nairit, vulcanization for 21 h at 100°C	NT nairit	
		Unvulcanized	Vulcanized at 120°C
Density, g/cm <sup>3</sup>	1.3-1.5	1.5	1.5
Breaking strength, kgf/cm <sup>2</sup>	85-90	50-60	30-90
Elongation, %	200-220	250	180
Flexibility measured with ShG-1 instrument, mm	1	1	1
Impact resistance measured with U-1 instrument, kgf cm/cm <sup>2</sup>	50	50	50
Brittle point, °C	-30	-40	-30
Adhesion to St. 3 steel on chlorinated nairit primer, kgf/cm <sup>2</sup>	35-45	-	30
Water absorption after 30 days at 20°C, %	8-10	3-5	2-3
Oil resistance	Good		
Dielectric properties	Unsatisfactory		

Nairit is used in shipbuilding for coating instruments and devices used in service maintenance of tankers and other tank ships transporting highly inflammable products.

Fluoroplastics are crystalline polymers in which fluorine has been substituted for hydrogen atoms. The fluorine is bonded very strongly to carbon, also reinforcing the main carbon chain of the polymer molecule.

The domestic industry is producing a large number of fluoroplastic brands which are individual and modified polymers of fluoroolefins and their copolymers: fluoroplastics 4, 3, 4M, 3M, 2, 2M, 30, 42L, 32, 40, 1, 3B, 26, 26. /207

Fluoroplastic coatings possess highly protective properties: stability to corrosive media, good insulating properties, low friction coefficient, resistance to impact, and heat and cold resistance (Table 90).

For friction components operating at low temperatures, fluoroplastics of brands 4D and 42L are used as antifriction coatings.<sup>50</sup>

Coatings based on fluoroplastics 3 and 3M have high strength, electrical resistance and hardness. The diffusion coefficient of fluoroplastic 3 is 1/100 that of fluoroplastic 4; this makes it possible to use it as a protective coating, although it is inferior to fluoroplastic 4 in dielectric properties.

Fluoroplastics 1, 2 and 2M are the hardest and strongest of all fluoropolymers: they exhibit practically no flow in the cold state, are highly weatherproof, wear-resistant and dimensionally stable.

Table 90  
Physicomechanical and electrical properties of fluoroplastics

Property	Fluoroplastic			
	1	3	2	2M
Density, g/cm <sup>3</sup>	1.35-1.40	2.1	1.7-1.8	1.7-1.8
Tensile strength, kgf/cm <sup>2</sup>	500-600	350-400	500-600	450-550
Elongation, %	70-140	70-200	10-250	300-400
Modulus of flexure, 10 kgf/cm <sup>2</sup>	10-14	11.6-14.5	16.2	-
Fusion temperature, °C	180-190	210	170-180	155-165
Application temperature, °C	-80- +150	-195- +150	-60- +150	-60- +150
Brinell hardness, kgf/mm <sup>2</sup>	10-12	10	13-15	7-9
Water absorption after 24 h, %	0.0	0.0	0.015	0.01
Volume electrical resistivity at 10 <sup>6</sup> Hz, ohm cm	10 <sup>13</sup>	1.5 x 10 <sup>13</sup>	7 x 10 <sup>12</sup>	10 <sup>11</sup> -10 <sup>12</sup>
Dielectric loss tangent at 10 <sup>6</sup> Hz	0.02	0.01	0.136	-

Fluoroplastics are used for coating parts of compressors, valves, coupling sleeves, fastenings, etc.

The strength and wear resistance of fluoroplastic coatings may be varied over wide limits by introducing reinforcing fillers and solid lubricants into their composition. The fillers are various metals and glass; the solid lubricants are boron nitride, molybdenum disulfide, graphite, etc. /208

The use of various glass fibers and filamentary crystals (mullite) as the filler reduces the internal stresses and increases the adhesion to metals. Fluoroplastics are applied by spraying methods: flame, high-voltage electric-field and slurry spraying.

To improve the mechanical strength and adhesion characteristics, certain fluoroplastic coatings are quenched in cold water.

An increase in adhesion and decrease in internal stresses<sup>10</sup> is achieved by priming the metal surface with sealants prepared from fluoroplastic rubbers and used in the form of solutions. Use of these primers increases adhesion by a factor of 5-15.

Production of brands of modified powdered fluoroplastics designed for the preparation of coatings (30, 30P, 40, 40DP, etc.) has been started recently. Depending on the function of the protective coating, these powdered polymers may be used to create compositions that make it applicable to specified service conditions. This is accomplished by increasing the bulk density and selecting the particle size distribution and shape of the powder particles. It has been found<sup>11</sup> that as the bulk density increases, the protective property of the film



improves, as does its density, since the more uniform the packing and smaller the number of loose-packed regions in the layer of the polymer powder particles, the smaller the number of pores obtained after the polymer has been partially fused.

The compacting operation consists in heat-treating the polymer powder at elevated temperatures. The optimum heat treatment temperatures for powders of brand 30 are 200°C, with a treatment time of 60 min; for brand 40, 240°C, 50-70 min; for 4M, 220°C, 40-50 min. In films of compacted fluoroplastics 30 and 40, internal stresses decrease considerably, and specific elongation markedly increases.

Copolymers of hexafluoropropylene with tetrafluoroethylene and vinylidene fluoride - viton, teflon - 100X, KYeL-F, and polyvinyl fluorides<sup>7+</sup> are widely employed in foreign technology at the present time.

#### 36. Properties of Coatings

Adhesion. Adhesive strength depends on the nature of the polymer and composition of the adhesive. A nonpolar adhesive wets the metal surface well, and therefore, even in the absence of active functional groups, a certain adhesive strength is achieved. A much stronger bond between the polymer and metal is achieved when the polymer has functional groups that interact with the metal surface.<sup>10</sup>

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It is important that the adhesive not merely contain a certain number of polar groups, but rather that these groups be capable of strongly interacting with the surface groups of the metal.

The presence of 0.5% of carboxyl groups in the polymer provides for strong adhesion (up to 360 kgf/cm<sup>2</sup>); polymers containing hydroxyl groups in the molecule also possess high adhesive strength.

Of major interest for adhesion systems is the mechanism of interaction of polymeric adhesives with the oxide film formed on practically any metal surface. As a result, ionic bonds may be formed at the polymer-metal boundary in many cases. This type of bond occurs most frequently in the contact of metals with carboxyl- and hydroxyl-containing polymers.

Considering the variety of factors affecting adhesive strength, one should expect that by modifying not only the binder but also the metal surface, one could achieve a significant increase in adhesive strength. The chief method of obtaining such a modification is to create additional chemical bonds acting at the adhesive-metal interface.

The stability of the adhesive bond may be increased by pretreating the metal surface with substances tending to form at least a sparse network of chemical adhesive bonds between the metal and polymer. A chemisorbed monolayer is formed on the metal surface.

The increase in initial adhesion and stabilization of properties in the presence of an adhesion-active sublayer is due to the formation of covalent adhesive bonds in the system. The molecules of the sublayer are initially chemisorbed on the

metal surface. The formation of chemical bonds between the macromolecules of the polymer and the surface compounds on the metal is highly probable during the formation of the polymer coating.<sup>49</sup>

The adhesion-active substances used are toluylene diisocyanate,  $\gamma$ -amino-propyloxysilane and oleic acid. Of these, the most active is toluylene diisocyanate, obtained by reacting phosgene with toluylenediamine.

The extent of the adhesive contact is largely dependent on the chemical nature of the metal and the microrelief of its surface. The most extensive and chemically active surface under the coating is obtained by shotblasting the metal with split shot, the sharp edges of which produce the required roughness on metal surfaces. With increasing height of microirregularities (sanding, sandblasting), the adhesive strength of the coatings increases. At the same time, with increasing height of the microirregularities, the internal stresses increase, causing a decrease in adhesive strength. /210

The maximum adhesive strength is achieved when the height of the projections is 20-24  $\mu\text{m}$ . When the projections increase from 24 to 200  $\mu\text{m}$ , the internal stresses increase and the strength of the adhesion bond decreases. With increasing height of the microirregularities, the growth of internal stresses causes cracking of the protective film.

Tables 91 and 92 present data showing the effect of the degree of surface treatment and brand of metal on the adhesion of coatings.<sup>21</sup>

Table 91  
Adhesive strength vs brand of metal

Metal	Adhesion, kgf/cm <sup>2</sup>		
	Capron	Polyvinyl butyral	Pentaplast
Steel St. 3	310	340	220
Steel St. 45	350	400	-
Brass L-62	230	260	135
Aluminum	400	420	240
Bronze	-	200	110

Note. Adhesion determined by the "mushroom" method; metal surface treated with sand.

The properties of a coating and the strength of adhesion to the metal are largely dependent on the film thickness: the thinner the film, the stronger its adhesion to the metal. This increase in adhesion<sup>10</sup> with decreasing thickness may be explained by the orienting influence of the solid surface, which is stronger for thin films. A significant role is also played by the scale factor, since the probability of existence of defects in the adhesive layer increases with its thickness.

Table 92  
Adhesive strength, kgf/cm<sup>2</sup>, vs method of preparation and microrelief of St. 3 steel surface

Method of Surface Preparation	Grade of finish	Coating			
		Capron	P-68	Polyvinyl butyral	Pentaplast
Grinding	6	310	200	250	200
Sandblasting	4	360	260	340	220
Sandblasting and phosphatizing	4-3	420	-	380	280
Shotblasting	3	300	240	320	260

Note. Adhesion determined by normal detachment.

The anticorrosive and insulating properties of thin coatings are not nearly as good, and they wear out faster. /211

The optimum thickness of polyvinyl butyral, polyamide and pentaplast coatings is 0.25-0.3 mm; as the coating thickness increases from 0.2 to 0.6 mm, the adhesive strength between the coating and metal drops sharply (the adhesion of capron to St. 3 steel decreases by a factor of 1.3-1.5).

One of the chief factors determining the properties of adhesion bonds is the molecular and structural mobility of the polymer.

A reduction in molecular and structural mobility usually leads to an increase in adhesive strength. The introduction of fillers and artificial cross-linking nuclei is the best way of altering the structural state of a polymer. In this case, the character of the change in adhesive and cohesive properties is similar.

The adhesive strength in a polymer-metal system as a function of the content of fillers in the adhesives is frequently described by a characteristic curve with a maximum. Obviously, the role of free functional groups in the adhesive is manifested here as well.

Internal stresses. The mechanism of formation of internal stresses in films formed on a solid substrate consists in the fact that as the solvent volatilizes, the film can contract only in thickness; as a result, stresses parallel to the surface of the film arise in the latter.

Stresses may also arise during other processes associated with a decrease in volume. Since the process of film formation frequently takes place at high temperatures, cooling of the system causes an increase in stresses as a result of different coefficients of linear expansion of the coating and substrate, as well as crystallization shrinkage.

Rapid cooling increases internal stresses because of insufficient relaxation; slow cooling promotes more complete relaxation processes due to orientation of the structural elements, which decreases the stresses in the coating.

On rapid cooling, the degree of crystalline order in polyethylene type polymers decreases. It would seem that a decrease in crystallinity, i. e., a certain amorphization of the coatings on rapid cooling, should improve the cracking resistance, but despite the specific elongation values and impact strength, which are thereby increased, quenched coatings break down faster. This phenomenon is due to the more active effect of nonrelaxed internal stresses, which are greater than in slow cooling, and the breaking strength is lower.

Table 93  
Effect of cooling rate and heat treatment on the mechanical properties of low-pressure polyethylene coatings

Conditions of Preparation of Coating	Degree of crystallinity, %	Internal stresses, kgf/cm <sup>2</sup>	Breaking strength, kgf/cm <sup>2</sup>	Elongation, %
Cooling conditions:				
rapid (quenching)	75	62	150	6.8
slow	77.5	58	183	3.2
Heat treatment for 4 h:				
at 180°C	75	32	180	4.8
at 200°C	76	30	160	7.6

To remove the internal stresses and increase cracking resistance, the coating /212 should be heat-treated at elevated temperatures. As a result of prolonged action of heat, the internal stresses in the coatings are reduced by almost one-half, while adhesion increases.

Coatings based on certain fluoropolymers, polyvinyl butyral and pentaplast should be quickly cooled in water during their formation; the internal stresses thus formed are small, and with time decrease to an insignificant value.

This may be explained by the dissimilar structure of the material and coating, formed under different conditions. On slow cooling, the coating has a more crystalline structure<sup>27</sup> and compact packing, its volume is smaller, and hence, the internal stresses are higher in this case. On rapid cooling, an amorphous structure predominates in the coatings. The degree of order of the macromolecules is lower, and the internal stresses are also small.

The internal stresses, which increase in the course of aging of polymeric coatings, reach values comparable to the strength of the films, and in many cases cause cracking of the films or their spontaneous peeling. Of particular interest therefore are ways of controlling the stresses in polymeric coatings. In particular, by changing the temperature of film formation, moisture content of the medium, proportions of the components, amount of plasticizers and pigment, one can actively affect the magnitude of internal stresses and their buildup kinetics.

By altering the nature of the support and using elastic primers for polymeric coatings, one can alter the adhesive strength and thereby control the internal stresses and hence, the useful life of the coating.

As a result of the damping influence of primers, the impact resistance and elasticity of the coatings are appreciably increased.

Fillers have a substantial influence on the internal stresses of coatings. On the one hand, internal stresses are decreased by the introduction of fillers because the coefficient of thermal expansion of the film material decreases, and on the other hand, they increase, since the relaxation processes are inhibited (the elastic modulus increases) and the glass transition temperature rises. The resultant of these processes is usually positive in the case of amorphous polymers and negative in the case of crystalline ones.

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Internal stresses in polymeric coatings are determined by the optical method and method of bending through an angle according to GOST 13036-67. The latter method is based on measurement of deflection from the initial position of the free end of a cantilevered elastic metal plate with a polymeric coating.

The internal stresses  $\sigma_i$  are calculated from the formula

$$\sigma_i = \frac{\Delta h E s^2}{3 l^2 \Delta s (s + \Delta s)}$$

where  $\Delta h$  is the deflection of the support from the initial position, cm;  
 $E$  is the elastic modulus of the support, kgf/cm<sup>2</sup>;  
 $s$  is the thickness of the support, cm;  
 $l$  is the working length of the support, cm;  
 $\Delta s$  is the thickness of the polymer film, cm.

Water resistance. The water resistance of a coating is determined by its porosity and swelling capacity. The very slight true porosity of high-molecular film-forming substances is due to the presence of a small amount of solvents or plasticizers. The formation of a three-dimensional reticular structure promotes a decrease in structural porosity.

The service life of a polymeric coating is represented by the rate of penetration of water molecules into the polymer mass, i. e., by the value of the diffusion coefficient. The technique for determining diffusion coefficients is described in Ch. III. Given below are the diffusion coefficients, in 10<sup>-6</sup> cm<sup>2</sup>/h, of various polymeric films, determined by the sorption method.

SKU-PFL (cold vulcanization) .....	6.1
KEN-50 .....	2.3
KEN-100 .....	4.1
SKU-PFL + 5% SKTN .....	11.0
Pentaplast .....	2.0
Fluoroplastic .....	3.6
Polyethylene .....	2.0
Epoxyfluoroplastic lacquer .....	1.0

The diffusion coefficient of the SKU-PFL urethane elastomer is somewhat different (6 x 10<sup>-5</sup> cm<sup>2</sup>/h) from the coefficients of polymeric materials; this correlates well with the higher water absorption of these elastomers. The introduction of fillers (5-15% of SKTN rubber) reduces the water resistance of polyurethanes and causes the diffusion coefficient to increase to 1.1 x 10<sup>-4</sup> cm<sup>2</sup>/h.

Some investigators<sup>41</sup> believe that the water absorption of films and their impermeability to water depend on the reticulation, which is associated with the formation of internal stresses; the latter may give rise to isolated cavities which promote better penetration of water vapor through the film and an increase in its water permeability.

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As a rule, the introduction of pigments promotes a decrease in the permeability of coatings, particularly if the particles are scale-shaped; however, when the critical volume content of the pigment is reached, the permeability of the film increases.

The best results (Fig. 75) for the water resistance of polymeric materials were obtained with films cured at high temperatures; the water absorption of pentaplast films is insignificant.

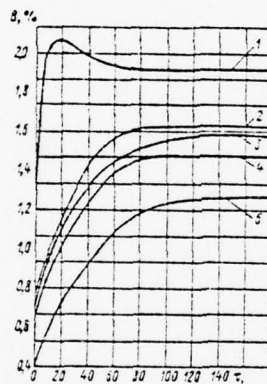


Fig. 75. Water absorption B, %, of coatings.

1 - SKU-PFL polyurethane (cold vulcanization);  
2 - KEN-50 composition; 3 - SKU-PFL polyurethane (hot vulcanization); 4 - KEN-100 composition; 5 - FEN-42V composition.

Capron, polyamide 68, low-pressure polyethylene and polyvinyl butyral have poor anticorrosive properties: coatings of capron and polyamide 68 peel off after 2-3 months of exposure to water, and those of polyvinyl butyral and polyethylene, after 4-5 months. Coatings based on fluoroplastic are water-resistant and can be used under high humidity and tropical climate conditions.

The protective capacity of the films also depends on the thickness and number of layers of the applied coating. With increasing number of layers, the protective capacity improves as a result of multiple overlap of the pores in the film and lengthening of the path of moisture diffusion toward the support. The more severe the service conditions, the greater the thickness which the coating should have:

in the presence of constant action of water, the thickness of the coating should be no less than 200  $\mu\text{m}$  or even 300  $\mu\text{m}$ .

The decrease in the adhesive and mechanical characteristics of coatings during long-term exposure to seawater is directly proportional to the water absorption of polymeric films (Fig. 76).

The long-term strength of pentaplast coatings is shown in Fig. 77 ( $\sigma$  being the effective stresses and  $\tau$ , the length of the tests). The combined action of the corrosive medium and loads significantly reduces the long-term strength of the coatings.<sup>41</sup>

Dielectric properties. The principal dielectric properties of thin-film polymeric coatings are given in Table 94.

Table 94  
Dielectric properties of thin-film plastic coatings

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Coating	Thickness of layer, $\mu\text{m}$	Dielectric loss tangent	Breakdown voltage, kV/mm	Electrical resistivity, ohm cm
Capron	450	-	33	$0.1 \times 10^{14}$
P-68 polyamide	300	-	43	$10^{15}$
Polyvinyl butyral	280	$2.0 \times 10^{-2}$	72	$0.8 \times 10^{16}$
Pentaplast	200	$1.6 \times 10^{-2}$	80-100	-
VD polyethylene	250	$4 \times 10^{-4}$	45-60	$2 \times 10^{14}$
Polyepoxides	200	$4 \times 10^{-3}$	60	$8 \times 10^{14}$
Polychlorotrifluoroethylene	250	$4 \times 10^{-4}$	150-200	$1.2 \times 10^{16}$

Coatings based on polyethylene and fluoroplastics have excellent electrical insulation properties over a wide temperature range. The low water absorption and high chemical resistance ensure the stability of the electrical insulation properties when the coating is used in corrosive media.

The electrical insulation properties of elastomer coatings change with the type of electric current, duration of action of the voltage, and relative humidity of the ambient medium. In the presence of direct current, even with a high voltage, the breakdown voltage of elastomer coatings is 2-2.5 times that of 50-Hz alternating current.

The appreciable drop in the breakdown voltage of elastomers under mechanical load is due to the partial polarizability of the material in extension, and to the accelerated oxidation of the elastomer, which is in a stressed state.

In studying polymeric materials used for protecting articles operating in corrosive media, the chief criterion for estimating the protective capacity of the coatings is the electrical resistivity of the film, preventing the migration of ions and reducing the corrosion current to an insignificant value.

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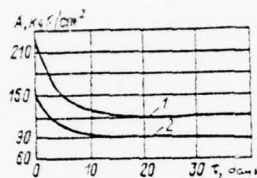


Fig. 76. Adhesive strength  $A$ ,  $\text{kgf/cm}^2$ , of pentaplast coatings with steel and brass vs time of exposure  $\tau$  to seawater (normal detachment method).

1 - St. 3 steel; 2 - L-62 brass

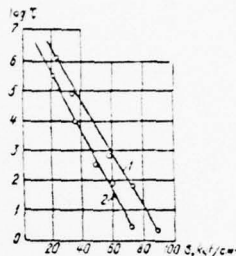


Fig. 77. Useful life of pentaplast-base coatings on steel vs stress.

1 - in air; 2 - in water.

The high resistance in the initial state and the ability to maintain it at this level during prolonged exposure to seawater indicate an insignificant permeability of the coating to ions of the electrolyte, and hence, excellent anticorrosive and electrical insulation properties of the coatings. The process of change in properties in water may be broken down into three periods:

- (a) a comparatively rapid decrease in resistance due to diffusion of corrosive agents and an increase in their quantity in the film;
- (b) a state of equilibrium, when further water absorption and drop in resistance cease;
- (c) intensive corrosion of metals under the film and breakdown of the coatings; further drop in resistance.

During the first few days of exposure to water, the resistance of most films drops by 2 to 3 orders of magnitude, which corresponds to the maximum water absorption by the films and an active diffusion process. After 60 days, a state of equilibrium is established in the majority of the coatings, and the water absorption and decrease in resistance cease. A certain increase in resistance after three days of exposure of pentaplast-base coatings to water may be explained by the formation of an oxide film on the surface of the specimen, and the resistance of the films subsequently undergoes a certain decrease.

When pentaplast-coated specimens whose edges are well-insulated are exposed to seawater, practically no drop in resistance occurs because of the slight water absorption.

The introduction of pigments into fluoroplastic-base coatings causes a certain decline in dielectric properties, although it slightly increases the stability of the films exposed to seawater. The most stable dielectric properties



are those of coatings based on KEN and FEN lacquers, which correlates with the water absorption kinetics of coatings based on these lacquers.

Erosion resistance. An adequate amount of information has been collected on the erosion resistance of metals, but in the case of the erosion resistance of plastics and synthetic materials, the data are scarce and in many cases contradictory. The highest cavitation resistance is exhibited by elastic synthetic materials, i. e., polyurethanes and rubber.<sup>76</sup>

Japanese scientists have conducted many studies to determine the cavitation resistance of chromium and nickel-base polyurethane, rubber and electroplated coatings. The highest resistance to cavitation erosion is exhibited by chromium, /217 and among polymeric coatings, rubber ones are only slightly inferior to chromium.

According to the Japanese researchers, the high cavitation resistance values obtained for rubber coatings are due to the ability of elastic materials to absorb pulsating impact loads. The tests enabled the Japanese researchers to recommend neoprene coatings along with chromium for protection of the propellers of fast ships.

Results of tests of coatings based on polyurethane compounds have shown good prospects for the application of the elaborated urethanes as protective coatings for abrasive and hydroabrasive erosion and cavitation.

In tests on a hydrodynamic stand, the erosion rate is so high that the start of destruction of the coating is difficult to record, and a complete detachment of the films takes place in just a few minutes.

Testing on devices reproducing the cavitation process with a high rate of action (of magnetostriction vibrator type) may appreciably distort the results obtained because of the difference between the cavitation processes in nature and in the testing chamber.

The study of the relative stability and determination of the mechanism of cavitation breakdown of a coating make it necessary to reproduce a cavitation process analogous to the natural process. Under laboratory conditions, this is accomplished by using cavitation-erosion stands equipped with a Venturi chamber. The method for testing the polymers and their resistance to erosion wear is given in Ch. 3.

The erosion resistance of coatings tested on a vibrator and in a Venturi chamber at flow velocities up to 55 m/sec is given in Table 95.

Materials having elastic characteristics and the ability to extinguish (damp) pulsating loads exhibit the highest resistance to erosion wear. In their resistance to erosion wear, coatings based on SKU-PFL polyurethane and nairit considerably surpass carbon steel and approach chromium-nickel steel. When the adhesive strength is unsatisfactory, a weakening of adhesive contact and peeling of the coating off the substrate may occur during the testing.

Materials of great hardness and rigidity (pentaplast) are the least stable to cavitation.

Weathering resistance. The weathering resistance of coatings is studied under field conditions and in artificial climate devices. Adhesive contact between the polymer and metal substantially affects the properties of the coatings, and therefore, the processes of aging and destruction of coatings under atmospheric conditions differ from the processes taking place in blocks and free films.

Table 95  
Cavitation-erosion resistance of polymeric coatings

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Coating	Thickness of coating, $\mu\text{m}$	Duration of tests, h	Nature of Breakdown
SKU-PFL vulcanized coating on LMsZh-55-3-1 brass	1.5	200	No breakdown
Same on St. 3 steel	2.5	400	Same
Vulcanized coating based on NT nairit on St. 3 steel (epoxy-nairit primer)	2.0	300	Start of cavitation erosion
Kh18N10T steel	-	400	No breakdown
St. 3 steel	-	15.0	Start of cavitation erosion
Pentaplast on AZhN-9-4-4 bronze	0.280	8.5	Breaking off of coating at the cavitation center
Fluoroplastic-1 on AZhN-9-4-4 bronze	0.160	20.5	Coating peels from the edge
5-4-71 paint on LMsZh-55-3-1 brass	0.300	80.0	-
FEN2-42V on brass	0.160	29.5	90% of coating peeled off
KEN-50 on brass	0.180	100	No breakdown

The state of the coatings during the studies is estimated from the change in chemical and optical properties, microhardness, impact hardness of the coating material, and retention of adhesive contact.

The study of the changes occurring in the chemical composition of a polymeric coating involve determination of the molecular mass of the material (viscometry method), crystallinity of the polymer (x-ray diffraction analysis), and changes in the crystal lattice (method of electron diffraction). The state of the surface of the coating is estimated from its reflectivity by measuring its brilliance.

In the course of natural atmospheric aging of polyethylene coatings,<sup>33</sup> it was noted that after only 6 months of exposure, a network of cracks appeared on the irradiated portion of the specimens. Tests of pentaplast coatings under tropical climate conditions showed that they undergo appreciable changes after 8-10 months of exposure to atmospheric conditions; the stability of the polymers is affected not so much by the intensity of the radiation as by its wavelength.

Absorption of ultraviolet light initiates the rupture of the molecular chains of polyethylene and promotes the formation of oxide (carbonyl) groups, which in

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turn are active centers of radiation absorption. The appearance of oxidized groups is demonstrated by the increase in the dielectric loss tangent, the value of which depends on the relaxation of the carbonyl groups in the coating material.

A considerable change in the composition and structure of pentaplast may be detected in the infrared absorption spectra of films aged under the same conditions as the coatings. /219

Analysis of the infrared spectra showed the presence of hydroperoxy groups; the spectrum contains an absorption band around  $3480\text{ cm}^{-1}$ , corresponding to O-H stretching vibrations of hydroperoxy groups, and the  $845\text{ cm}^{-1}$  absorption band of O-O vibrations of hydroperoxy groups.

These data make it possible to postulate a mechanism for the process of oxidative degradation of pentaplast.<sup>2,3</sup>

The initiation is accomplished by the detachment of hydrogen from a methylene group, which is the most vulnerable unit of the macromolecule. After the addition of oxygen with the formation of a peroxy radical, the chain propagation process proceeds via the formation of hydroperoxide, whose decomposition leads to the formation of aldehyde, ester and acid groups. The relative quantities of these groups are determined by the different probabilities of bond rupture in the peroxy radicals, which propagate the oxidation chain or recombine.

Thus, the oxidative degradation of pentaplast develops as a chain radical process, the inhibition of which requires the use of thermal and light stabilizers of the initial polymer.

Additional crystallization of the polymer occurs in the regions of rupture of strained bonds. This is manifested in an increase of the degree of crystallinity and microhardness of the coating material. At the same time, cracks along the boundaries of spherulitic formations and the appearance of fibrous structure in the spherulites of the polymer are visible in the field of an optical microscope.

Processes of cross-linking of the coating material take place along with degradation processes under the influence of ultraviolet irradiation. In cross-linking, hydrogen splits off from the hydrocarbon chain, and the free bond thus formed links up with the analogous free bond of a neighboring molecule, forming cross-links.

The degree of cross-linking of a polymer is characterized by the insoluble fraction formed, whose quantity increases with the exposure. Significant changes in the chemical structure of the coating are reflected in the mutual orientation of the chains, i. e., the characteristic regularity of the supermolecular structure is markedly disrupted. The optical picture of the spherulites disappears, and individual protuberances appear. Numerous cracks running along the boundaries of these protuberances are observed. The reflectivity of the coatings decreases appreciably.

When tested in an artificial weather device, the coatings undergo significant changes. After only 50 h of testing, the pentaplast coating darkens, the surface becomes rough, and a decrease in luster (Fig. 78) and increase in microhardness are observed. The increase in microhardness during the initial period of aging is due to additional crystallization causing an increase in rigidity and hardness.

Subsequently, the crystalline structure breaks down, microcracks develop in the material, amorphization of the coating takes place, and the microhardness decreases (Fig. 79). /220

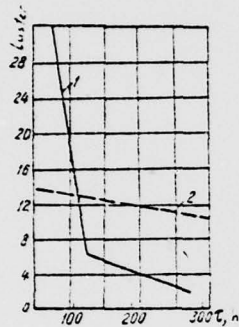


Fig. 78. Change in luster of pentaplast-base coatings during aging.  
1 - nonirradiated side; 2 - irradiated side.

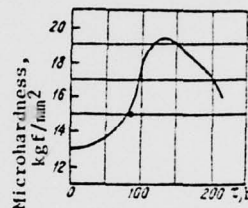


Fig. 79. Change in microhardness of pentaplast during aging.

After 500 h of testing in the artificial weather apparatus, the coating effectively loses its protective functions, cracks, and crumbles. The cracking and peeling are due to internal thermal stresses, which arise under thermal cycling conditions and are due to the marked difference between the coefficients of linear expansion of the material of the coating and substrate.

Testing of polyamide coatings established that ultraviolet radiation also causes degradation and oxidation of the material, a decrease in molecular mass, and a decrease in dielectric loss tangent. The changes taking place in the polymer lead to an increase in the degree of crystallinity. The supermolecular structure of a polycaproamide coating undergoes visible changes.

The introduction of fillers shielding polymers from the action of light increases the stability of polyamide compositions; the maximum increase in stability, up to two years, is achieved by adding graphite. On the whole, polycaproamide coatings are more stable to ultraviolet radiation than polyethylene ones and may be recommended for use in regions of dry tropical climate in components and parts protected from direct solar radiation.

In tests of coatings under light filters absorbing ultraviolet irradiation, their breakdown takes place much more slowly. After 12 months of exposure, only isolated local microcracks in the supermolecular structure of the material are observed, evidently due to overheating of local regions.

One of the methods of stabilizing polymers to light involves the use of compounds which intensely absorb ultraviolet light without undergoing photolysis.

Thermal oxidative degradation of pentaplast is inhibited by introducing inhibitors, i. e., antioxidants (phenols, aromatic amines, esters of phosphorous, propionic and lauric acids).<sup>33</sup> The best protection from light is provided by polymers which are derivatives of benzophenone, benzoic or salicylic acids and resorcinols, and which absorb the ultraviolet portion of the spectrum. The introduction of the photostabilizer 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (tinuvin P) in the amount of 0.25% of the mass of the polymer powder into the composition of the polymers increases the stability of polyethylene and polyamide coatings by a factor of two to three. /221

### 37. Methods of Preparation of Coatings

The methods of applying polymeric materials on the surface of articles are quite varied. This variety is determined by the type of materials employed, technology of their application and equipment used.

Discussed below are the most commonly employed methods of applying polymeric coatings and new progressive methods.

Vortex spray-coating. In vortex spray-coating (application in a fluidized bed), the preheated article is dipped in a bath with a powdered polymer contained in a fluidized bed. After removal from the bath and additional heating of the article, the adherent particles melt, and, spreading over the surface, form an even coating.

In most cases, powders are fluidized with compressed air. However, because of the thermal oxidative degradation of finely divided polymer powders, it is preferable to use an inert gas.

The fluidization rate affects the properties of the coatings, particularly adhesion and continuity, and one should therefore select a gas flow rate at which a uniform and quiet boiling of the powder is observed.

The film thickness, quality of the coating and its adhesion depend on the preheating temperature, residence time of the article in the bath, height of the fluidized bed, and duration of the fusion process. The optimum heating temperature of the parts during application of coatings based on epoxy resins in a fluidized bed ranges from 160 to 180°C. If the temperature conditions are disturbed, the properties of the coatings decline sharply, and for this reason, it is not recommended to change the thickness of the coating by changing the heating temperature.

The principal technological parameters of the process for obtaining coatings from various polymers in a fluidized bed are presented in Table 96. /222

Devices for applying coatings by this method are simple to build and operate. The coating may be applied both manually and on conveyer production lines.

Disadvantages of the vortex spray-coating method include the difficulty of coating articles of different thicknesses, cumbersomeness of the equipment for coating large-sized articles, and nonuniform coating of edges and corners.<sup>23, 71</sup>

Table 96  
 Technological parameters of preparation of coatings from powdered polymers in a fluidized bed

Polymer	Preheating temperature of part, °C	Residence time of part in bed, sec	Additional heating temperature of part, °C	Duration of additional heating of part, min
Low-pressure (stabilized) polyethylene	250-340	3-20	200-220	2-7
P-68 polyamide	230-300	1-15	220-250	2-3
Polyvinyl butyral	230-360	3-20	220-230	2-7
Pentaplast	280-330	5-25	230-240	3-20
3M fluoroplastic	260-280	6-10	210-270	240
Epoxy resin	140-160	4-10	150-180	120-180

Vibratory spray coating. The method essentially consists in bringing heated parts in contact with powdered polymers in a suspended state through vibration. Two types of vibratory apparatus have become most popular: in the first, the vibrations are executed by the entire vessel containing the powdered polymer, and in the second, only the elastic bottom vibrates, while the walls of the apparatus remain stationary.

The fluidization effect in these devices is achieved by subjecting the powdered material to forced oscillations of definite frequency and amplitude.

The vibratory method has some advantages over the vortex method: the preheating temperature of the parts may be somewhat lower, since there is no cooling of the polymeric material by the passing gas flow, and no powder particles are blown out; no compressed air or gas is required.

The construction of vibratory spray coating devices is fairly simple. The vibrators, which are the chief element of the apparatus, may be mechanical, pneumatic, electromagnetic, or electrodynamic.

The vibratory method also has several drawbacks which limit its application. /223 They include a small coefficient of volume increase during fluidization (up to about 1.15), higher requirements for the polymer (finely divided powder) and the necessity of a careful selection of the components with regard to mass and particle size to prevent demixing into fractions; nonuniformity of the fluidized bed with respect to the height and cross section of the apparatus, causing the coating of the article to be nonuniform with respect to height.

Vibratory vortex method. This method is practically free of the drawbacks inherent in fluidization by vibration. The simultaneous action of gas and vibration on the polymer particles creates a homogeneous structure of the fluidized bed and in addition, precludes separation of the powder. The role of vibration essentially amounts to separating the particles, thus decreasing the friction between them, and the ascending flow of gas (air) keeps the polymer particles in a suspended state.

The vibratory vortex method yields a uniform fluidized bed when various powders are used, including those that are difficult to fluidize by the usual vortex method.

Coatings prepared in laboratory vortex spraying apparatus have a uniform and much greater thickness than in other types of devices. It is no longer necessary to select a powdered polymer in narrow particle-size fractions, since there is no demixing of polydisperse mixtures during fluidization by simultaneously acting vibration and gas; this is particularly important when using a material with various types of additives (fillers, stabilizers, pigments, etc.).

Centrifugal method. The centrifugal method consists in applying a layer of polymeric material on a suitably prepared and heated surface of a rotating article. When it comes in contact with the heated surface, the polymer powder fuses and spreads under the influence of centrifugal forces. This yields a coating of uniform thickness.

This method is used to prepare thin-layer polymeric coatings on large-sized parts in the shape of bodies of rotation: inserts, bushings, connecting flanges, or stators of electric motors.

When this method is employed, the additional action of centrifugal forces on the fused polymer provides not only for a high quality of the coating but also for its stronger adhesion. The centrifugal method began to be used in the Soviet Union and abroad for coating the inner surfaces of metal tubes.

Electrostatic method. The method of application of polymeric coatings in an electrostatic field is one of the most promising ones. The coating is applied by using the corona discharge effect due to the action of a high-voltage current. The ions thus formed, which have the same charge as the corona electrode, are repelled from it and move in the direction of the oppositely charged electrode. A high-voltage electric field is produced in the space between the electrodes. If polymer particles are introduced into this space, the ions charge them on contact. The charged particle moves toward the electrode (part) of opposite charge and settles on its surface. /224

After deposition, the charged polymer particles can remain on the surface of the cold part for a long period of time, this being due to the property of dielectrics of retaining polarization even after the electric field is removed. This extends the applicability of the method, since it permits application of polymeric coatings on parts even without preheating.

Two types of processes have become common: pneumatic and electrostatic spraying of the polymer.

In the pneumatic spraying method, the powdered polymer at low pressure, 0.8-1.0 kgf/cm<sup>2</sup>, is fed into the space between two electrodes. The sprayed particles acquire a negative charge and deposit on the surface of the part being coated.

The application of a polymer powder by electrostatic sprayers is analogous to the process described above. The role of the sprayer in this case is played by the corona electrode.



Thin-layer polymer coatings may be obtained in an ionized fluidized bed. This method essentially consists in the fact that the cold part is immersed in a fluidized bed of powdered polymer acted upon by the corona discharge of a high-voltage electric field. The polymer particles are charged, and, acted upon by electrostatic forces, uniformly deposit on the part, which is moved to an oven for fusion.

This method may be used to apply almost all of the known polymeric materials withstanding the temperature necessary for fusing the powder. The coating obtained has not only a uniform but also a predetermined layer thickness.

The thickness of the deposited powder layer depends on the charge of the particles and residence time of the article in the high voltage field. The higher the applied voltage, the thicker the powder layer. By changing the magnitude of the electric field, one can vary the thickness of the coating over a wide range (from 20 to 800  $\mu\text{m}$ ). Practice has shown that the residence time of articles in an ionized fluidized bed is 2 to 10 sec.

Manual devices and automated mechanical lines are used for electrostatic spraying of polymeric materials.

A series of installations of mechanized and semiautomatic lines have been developed in the Soviet Union. One of the most advanced industrial installations for preparing polymeric coatings in an ionized fluidized bed is the "Raduga" type mechanized line, which makes it possible to obtain coatings on both cold and pre-heated articles. /225

Control of the lines involves automatic and manual operation, stepless variation of conveyer speed, and control of the high voltage supplied to the bath, residence time of the articles in the fluidized bed, and power of the fusing oven.

Flame spraying. In the flame spraying method, a stream of air containing suspended particles of powdered material is passed through the flame of a gas burner. The polymer particles heated in the flame soften, fall on a prepared surface, and fuse on it; on cooling, a continuous polymeric coating is formed.

The temperature of the gas flame is 650-700°C or higher, and the speed of travel of the polymer through the flame zone is 20-30 m/sec.

Polyolefins, polyamides, polyvinyl butyral, fluoroplastic 3, pentaplast, etc. may be used for spraying. Most suitable for spraying are powders of polymeric materials with a particle size of 0.10-0.25 mm. To obtain coatings of large thickness on large-sized articles, it is best to use a powder with a particle size of 0.15-0.25 mm; for thin coatings, the size of the powder particles should be 0.10 mm.

The preheating temperature of the surface to be coated is given below for certain polymers in °C:

Epoxy polymers .....	135
Polyethylene .....	200
Polyvinyl butyral .....	230
Polyamides .....	200-210
Fluoroplastic 3 .....	270

The flame spraying method is best suited for applying polymers on large-sized articles, and even coatings made of inert polymers, for example polyethylene, exhibit satisfactory adhesion. Flame spraying is performed with UPN-4 units and used mainly to seal off cavities, coat welds, and seal joints and parts. This method is used for coating storage battery containers, fans, pipes, parts of pumps, etc.

The powdered material and combustible air-acetylene mixture are fed to the sprayer burner by means of compressed air at 3-6 kgf/cm<sup>2</sup>.

The flame spraying method has not found wide application for the following reasons: partial decomposition of the polymer during spraying and decline of the physicomechanical properties of the coating; difficult sanitary working conditions; necessity of using equipment operating under pressure; low output; complex control of the technological process of application of the coating.

Preparation of coatings from suspensions. Suspensions are used to prepare coatings based on polymers with a high temperature of transition to the visco-fluid state, close to the degradation temperature. To eliminate coagulation, the suspensions are stabilized with surfactants. The thickness of the coating depends on the concentration and viscosity of the suspension. With increasing polymer viscosity, the thickness of the coating increases, but an excessive thickness of the layer promotes the formation of cracks. Suspensions prepared from fluoroplastics, synthetic rubbers, or pentaplast are used for the preparation of coatings. /226

The suspensions are deposited by dipping, pouring, or spraying. The air pressure during the spraying is 3-4 kgf/cm<sup>2</sup>, and the distance of the nozzle from the surface being coated, 30-40 mm.

Films obtained from a suspension based on pentaplast and fluoroplastics 3 and 3M, after the solvent is driven off in air, are fused at 200 ± 10 and 270 ± 5°C, respectively. After the last layer has melted, the coatings are quenched with water.

When the coated part is cooled slowly, the polymer crystallizes, and a tough solid coating is formed. Since the coefficient of thermal expansion of the coatings is 8-10 times greater than that of steel, stresses decreasing the adhesion to the metal are formed at the interface on slow cooling. Quenching removes the stresses formed at the interface; on rapid cooling, the polymer passes to an amorphous, rubberlike state and forms elastic films resistant to impact loads.

The amorphous coating crystallizes for 10-20 h at room temperature and is transformed from a soft material vulnerable to mechanical damage into a strong, tough material suited for service.

The formation of films of fluoroplastics 1 and 2M proceeds via the formation of a gel whose drying requires a temperature of 80-90°C. The first and last layer are fused at 250 ± 20°C.

Films of fluoroplastics 1 and 2M are characterized by high density and uniformity. Quenching promotes the formation of smooth lustrous films but is not an obligatory operation, since the internal stresses during the formation of the coatings are small.

Radiant heat method. The radiant heat method surpasses the flame method in all parameters, being more universal and highly productive. In this method, a jet of powdered polymer is directed into a powerful flux of radiant heat rays, where the particles of the material melt and are deposited at high speed on the surface being coated. The polymer thrown onto the surface bonds with it, forming a coating. Heating is carried out with NIK-200 quartz lamps.

A comparison of the efficiency of the radiant heat and flame methods in the case of deposition of a polyvinyl butyral-base coating on steel is given in Table 97.

Table 97  
Comparison of the efficiency of the radiant heat and flame methods

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Property	Method	
	Flame	Radiant heat
Adhesion, kgf/cm <sup>2</sup>	378	455
Consumption of material, kg/m <sup>2</sup>	1.04	0.76
Removal of powder (waste), %	36	-
Output, m <sup>2</sup> /h	1.5	3.8
Energy consumption, kcal/m <sup>2</sup>	20,800	5400

It is characteristic that flame spraying gives a very loose, inhomogeneous coating with a large quantity of microcracks and gas bubbles. Use of the radiant heat method precludes such defects, since a homogeneous structure is formed.

Thus, the radiant heat method ensures a 25-30% lower consumption of polymer powder; the efficiency of the method is 1.5-1.8 times greater than that of the flame method. Moreover, application of coatings by this method may be carried out in inert, explosive and inflammable media.

Rubber coating. Rubber coating is a method of protecting a metal or other surface from corrosion and other attack by means of rubber. This method can be used while simultaneously molding the rubber with metal fittings, gluing rubber sheets, or applying liquid rubber-coating compositions. The first method is most commonly used for articles where the rubber coating, in addition to providing protection from the working medium, also functions as an elastic element of the structure. The second method is widely used for protecting various reservoirs, tanks, and housings.

For rubber coating, use may be made of high molecular nairit rubbers, as well as special resin- and pastelike compositions based on nairits of low molecular mass and polyurethanes. Leuconate glue and a chlorinated nairit primer are used to increase the adhesion of liquid nairit-base coatings to the surface of metals and other structural materials.

Rubber-coating compositions based on nairits are applied with a brush, by dipping, or by spraying. Polyurethane compositions are applied by airless electrostatic spraying, since the use of air-type paint sprayers does not produce quality coatings.

Rubber-coating compositions applied at room temperature have optimum physico-mechanical properties 14 days after application. To reduce the vulcanization time, the coating may be heated for 2 h at 120°C after exposure to air. In anti-corrosion protection of small parts, coatings 0.8-1.2 mm thick are used. /228

The coating quality is checked on the basis of appearance, thickness, adhesion to metal, and continuity. The appearance is checked visually. This involves checking for the presence of cracks, depressions, irregularities, or blisters. The coating film should be smooth and of uniform color. The color match is checked by comparing with a standard.

The adhesive strength of the coating is checked on blank specimens coated simultaneously with the article. The adhesive strength is determined by means of the grid notching method in accordance with GOST 9754-61. When a millimeter grid is applied, the coating should not peel off.

The continuity of the coatings is checked by using instruments based on different principles and designs, i. e., electric spark and electrolytic flaw detectors. The thickness of the coating is determined with various measuring instruments, from simple micrometers to radioisotopic thickness gauges.

## CONCLUSION

At the present time, polymeric materials have become some of the basic structural materials used in many areas of science and technology. In ship machine building, polymeric materials began to be used comparatively recently - since 1959-60, so that the technical literature on this subject is limited.

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The present book makes an attempt to reflect the experience with the use of polymeric materials in Soviet ship machine building.

Most widely used are hot-pressed epoxy glass plastics, since they combine high strength and water resistance and permit fabrication of an article with a high dimensional accuracy and surface finish without additional mechanical treatment. Epoxy glass plastics are used in the production of ship propellers, fairings, fan blades and turbines. The authors present experimental data obtained from many years of studies on the water, atmosphere and erosion resistance, short-time and long-time strength of hot-molded epoxy-glass plastics.

Among thermoplastic materials, the most detailed description is given for caprolon, which is widely used for fabricating bearings and other parts.

A promising direction in ship machine building is the use of polymeric coatings, the most frequently used of which is pentaplast, which surpasses other polymers in water resistance and adhesion.

Extensive adoption of polymeric materials in ship building makes it necessary to conduct a number of studies aimed at mechanizing and automating the technological processes involved in the manufacture of the articles and at developing reliable nondestructive methods of control.

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The adoption of polymeric materials is determined by the progress made in the chemical industry, which in the near future should master the production of such promising materials as high-strength polyfunctional resins, polyimides, and epoxyfluoroplastic films and lacquers equivalent in quality to the best specimens of foreign polymeric materials.

The material pertaining to coatings was written on the basis of the results of studies and with the participation of V. F. Afonchenko.

M. A. Mirkin, L. S. Koretskaya and T. I. Tkachenko took part in the studies of atmospheric and water resistance.

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