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HANDBOOK OF SOVIET ADHESIVES

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HANDBOOK OF SOVIET ADHESIVES

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PREFACE

This handbook presents designations, compositions, and properties of adhesives available in the Soviet Union. The designation and property data are presented in handbook form to facilitate utilization. The adhesives are organized by broad category into thermoplastic, elastomeric, and thermosetting.

The Soviet standard or trademark for each adhesive is included, wherever available, in the tabular data. The tabular data contain general applications of adhesives. Most of these general applications, and the technological status of each adhesive, are estimated and are conjectural.

This handbook presents the detailed property data of individual adhesives in a manner designed to support bench-level personnel in research and development laboratories. Descriptions of Soviet test methods and standards can be found in "Handbook of Soviet Reinforced Plastics," FSTC-CW-01-102-73.

The presentation of these data follows a plan suggested by the US Army Materiel Command Technical Working Group on Organic Materials.

Constructive criticisms, comments or suggested changes are encouraged, and should be forwarded to the Commander, Foreign Science and Technology Center, Charlottesville, VA 22901 (ATTN: AMXST-PO).

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SUMMARY

The Soviets produce a variety of thermoplastic adhesive materials that have probable applications in individual equipment, clothing, shoes, and components of CBR warfare protective and detection devices. Such adhesives are suitable for use in nonstructural bonding with a maximum service temperature range of 30° to 40°C. These thermoplastic adhesives include casein-latex, cellulose, poly(vinyl acetate), polystyrene- and vinyl chloride-type polymers and copolymers.

The Soviets also produce thermoplastic adhesives with possible applications for hardware items, such as vehicles, tanks, aircraft and ship components, mines, fuses, and medium-service electrical and electronic components. These thermoplastics include poly(vinyl butanal and formal), acrylates, and phenolic and ester polyamides.

The Soviets appear to have adequate production capability in elastomeric adhesives to use these adhesives in nonstructural to limited-load bonded end-items, such as combat personnel equipment, clothing, and CBR warfare protective and detection devices. These adhesives, which are receiving supportive research and development endeavors, include styrene-butadiene, butyl, polyisobutylene, chlorinated, and reclaimed and natural elastomers.

Soviet elastomerics also have potential use in aircraft, aerospace and missile components that require low- to moderately high-temperature low-load bonding performance, artillery components, and electronic and electro-optical equipment. Use in ship-component bonding for suppression of vibration effects is also possible. These elastomerics include butadiene-acrylonitrile, polysulphides, polysiloxane, and polyurethane elastomers.

The bulk of Soviet efforts in adhesives is devoted to thermosets. These materials are used where high-load performance is required at temperatures near 200°C. Applications in military items include tank armor, automotive components, structural plastics for aircraft and naval vessels, electrical equipment, optical devices, and cryogenic apparatus. Thermosets of this type, claimed to be in the Soviet inventory and receiving active research and development efforts, include isocyanates, phenol formaldehydes, and furanes. Those claimed to be in production and under extensive research and development are the polyesters, including acrylates and glycidyl esters.

Certain high-performance thermoset adhesives are used in military systems that require retention of high-strength bonds under severe thermal and oxidative exposure for long periods at 200° to 350°C, and to 500°C for short-term use. Appropriate hardware bonded by adhesives include sophisticated aircraft, space vehicles, missiles, satellites, and rocket

or engine systems. Thermosets of this type claimed by the Soviets include epoxies, epoxy-polyamides, epoxy-polysulphides, epoxy modified triazine polyesters, phenolics, silicones, polyimides, polybenzimidazoles, polybenzothiazoles, polyphenylenes, polysiloxanes, and polyphosphazenes.

Section I.

INTRODUCTION

1. Soviet Capabilities in Adhesive Science and Technology

a. The Soviets have spent an estimated 50 million rubles over the last 5 years in their effort in adhesive science and technology. Although the Soviets have disclosed only an estimated 20% to 30% of their adhesives R&D, it is believed that they are about 2 to 3 years behind the United States in application aspects, with a production capability of about one-fourth of that of the United States. The Soviets believe that they can achieve production parity with the United States in about 12 to 16 years.

b. The Soviets are carefully monitoring Western adhesive technology, with particular interest in high-temperature adhesives. They have devoted substantial efforts to developing and modifying high-performance adhesive materials related to current and projected defense requirements. The Soviets have been establishing the technical, industrial, and economic foundations to compete effectively with Western nations in marketing adhesives and related production technology.*

2. Thermoplastic, Elastomeric and Thermoset Adhesives.

a. Soviet R&D and production efforts are in various stages of development for several categories of thermoplastic adhesives. These categories are shown in Table I. It would appear that the linear polyamides, acrylates, and hot-melt adhesives show the greatest level of R&D activity, with production levels adequate to meet Soviet needs.

b. Current Soviet production and R&D activity in elastomeric adhesives are shown in Table II. It appears that polychloroprene, silicones, and polyurethanes show the highest level of R&D activity, with adequate production levels.

c. The bulk of Soviet efforts in adhesives is devoted to thermosetting adhesives. It would appear, as indicated in Table III, that the silicones, polyesters, and epoxies exhibit the greatest R&D activity, with production adequate for Soviet needs. This class of materials is used where high-load performance is required at temperatures near 200°C.

*New York Times, November 12, 1973, p53.

Applications in military items include tank armor; automotive components near engine heat; honeycomb, sandwich or glass-reinforced or glass-structured plastics for walls, compartments, floors, and support structures in aircraft and naval vessels; electrical assemblies requiring high insulation and dielectric properties; low-temperature and cryogenic apparatus; light and heavy weapon launchers; missile and aerospace structures; optical devices and systems; and engine mounts. Thermosets of this type being developed or produced by the Soviets include isocyanates for increased adhesion in substrates (such as tire cord) and phenol-formaldehydes and furanes for binders in ablative materials. The polyester class of thermosets, claimed to be in Soviet production and receiving extensive R&D effort, includes acrylates and glycidyl esters, which are used in general-purpose laminates and optical devices.

d. Certain high-performance thermosets such as epoxies, phenolics, silicones, and polyaromatics are used in military systems that require retention of high-strength bonds under severe thermal and oxidative exposure (200° to 350°C for long-term use and to 500°C for short-term use). Appropriate bonded hardware includes sophisticated aircraft, space vehicles, missiles, satellites, and rocket or engine systems. The Soviets claim the following capabilities in epoxies: (1) amine-hardened epoxies that are versatile bonding agents for honeycomb sandwich construction, fuel tanks, body assemblies, and printed circuit laminates, (2) epoxy-polyamides used for bonding metals in spot welding, with service range from -70°C to +200°C, (3) epoxy-polysulphides for resilient bonds, with service from -100°C to +80°C, and (4) epoxy-modified triazine polyesters.

e. Significant Soviet phenolics include phenolic-nitrile for vibration-resistant bonds and phenolic-epoxy appropriate for honeycombs and low- to high-temperature structural bonds (-60°C to +220°C).

f. Soviet silicone adhesives include epoxy-silicones and silicone resins. These thermosets can be used for high-temperature bonding (to 250°C) in laminates and electronic equipment.

g. Soviet polyaromatic thermosets include polyimides (SP-1 adhesive), polybenzimidazoles, polybenzothiazoles, and polyphenylenes; it is claimed that all have been used in temperatures over 250°C as advanced-structural adhesives.

h. The Soviets are conducting basic research to improve the high-temperature performance of some of their thermosets by modifying these thermosets with moieties that confer added thermostability and

heat-resistance. Examples are phosphorus and silicon-incorporated polymethacrylates, ferrocene stabilized silicones, polyorganoboronsiloxane modified phenolic (Soviet VK-10 adhesive that has a claimed short-time use capability of 1000°C to 1200°C), and polyorganotitaniumsiloxane-modified phenolic. The Soviets are also researching polysilylphosphazenes (silicon modified phosphonitrilics), polysilazanes, and poly(amide-imides) as advanced adhesive thermosets.

Table I. Production and R&D Status of Soviet Thermoplastic Adhesives

Adhesive Type	R&D				Production		
	Production Supportive	Minimal	Active	Very Active	None	Limited	Adequate
Polyvinylidene Chloride		x				x	
Polyvinyl chloride-Vinylidene Chloride Variants		x				x	
Polyvinyl/Alkyl/Ether Phenoxy	x					x	
Dimethylvinylethynyl-Carbinol		x				x	
Protein-Albumin Derived		x					x
Cellulose Acetate		x					x
Cellulose Acetate Butyrate		x					x
Cellulose Nitrate		x					x
Ethyl Cellulose		x					x
Polyethylene		x					x
Polyvinyl Acetate and Alcohol		x					x
Polyvinyl Chloride, Chlorinated		x					x
Polyvinyl Chloride-Polyvinyl Acetate		x					x
Polystyrene		x					x
Vinyl Acetate-Ethylene Copolymers			x				x
Polyvinyl Formal			x				x
Cyanoacrylates			x				x
Polyamide (Nylon Types)			x				x
Linear Polyamide (Methylol, Phenolic and Ester Variants)				x			x
Poly(Methyl Methacrylate) and Other Acrylates				x			x
Hot Melt Adhesives				x			x

Table II. Production and R&D Status of
Soviet Elastomeric Adhesives

Adhesive Type	R&D				Production		
	Production Supportive	Minimal	Active	Very Active	None	Limited	Adequate
Butadiene-Acrylonitrile	x						x
Butadiene-Styrene	x						x
Chlorinated Rubber	x						x
Natural Rubber		x					x
Reclaimed Rubber		x					x
Butyl Rubber, Polyisobutylene	x						x
Polysulphides			x				x
Polychloroprene				x			x
Silicones				x		x	
Polyurethanes				x		x	

Table III. Production and R&D Status of Soviet Thermosetting Adhesives

Adhesive Type	R&D				Production		
	Production Supportive	Minimal	Active	Very Active	None	Limited	Adequate
Epoxy Silicone			x			x	
Epoxy Polyurethane			x			x	
Melamine Formaldehyde		x					x
Urea Formaldehyde		x					x
Phenolic Nylon			x				x
Phenolic Polyamide			x				x
Epoxy Nylon			x				x
Epoxy Polyamide			x				x
Epoxy Polysulphide			x				x
Furan			x				x
Isocyanate			x				x
Phenol-Formaldehyde			x				x
Resorcinol-Formaldehyde			x				x
Phenolic Epoxy			x			x	
Phenolic Neoprene			x			x	
Phenolic Nitrile			x			x	
Phenolic Polyvinylbutanal			x			x	
Silicones				x			x
Polyesters				x			x
Epoxies				x			x

Section II.

THERMOPLASTIC ADHESIVES

Designation

Trademark -----	BVA-1, BVA-2, BVA-4
Generic type -----	Vinyl acetate-butyl acrylate copolymer (solvent type)

Description

The vinyl acetate-butyl acrylate (VA/BA) copolymers are translucent, viscous tacky products soluble in most organic solvents (esters, ketones, alcohol, benzene, toluene, dimethylformamide, acetic and formic acids, etc.). Precipitants for them are water, aliphatic hydrocarbons, glycol and glycerin. The viscosity of 40% solutions of the copolymers in ethyl acetate is 20,000-30,000 cP (centipoise; units dyne-second/cm²).* The light transmission of the copolymers and of solutions of them is not below 99%. In film form, they have high elongation at break (up to 1000%) and low strength (5 to 8 kgf/cm²). With increasing butyl acrylate content in the copolymer, the extensibility increases, and the tensile strength falls.

Application

These materials are used for bonding films and fabrics to various substrates.

Technological Status

Research -----	1963 (est)
Development -----	1965 (est)
Engineering -----	1966-67 (est)
Production -----	1968 (est)

Properties

Data on the adhesion of the copolymers (the resistance to separation of combined films) to various polymeric materials are given.

*See Glossary, Page 273.

Adhesion of the VA/BA Copolymers to Various Materials

Material	Adhesion of the copolymers, in gf/cm, with L.V.N.*				
	0-5	0-6	0-7	0-8	0-9
PE	0.028	0.021	0.028	0.019	0.022
Polypropylene	0.067	0.081	0.053	0.060	0.060
PTFE	0.020	0.018	0.018	0.017	0.023
PVC	0.191	0.179	0.163	0.110	0.183
Polyamide-6	0.181	0.182	0.180	0.180	0.165
Lavsan	0.157	1.500**	1.500**	1.500**	0.147
Cellophane	0.300	0.250	1.350**	0.240	0.270

*L.V.N.-Limiting Viscosity Number (relative measure of molecular weight)

**Cohesion failure

In adhering the VA/BA adhesives to Kapron nylon fabric, there is a linear increase in bond strength with L.V.N. increase from 0.5 to 0.9. Above this there is no increase in bonding strengths.

BAV-1 agents were tested under industrial conditions for the production of waterproof polyamide fabric. The VA/BA copolymers give high adhesion of the film-forming material to the fabric (4 to 5 on a scale of 5). High impermeability to water (900 to 1000 mm Hg before laundering and 500 to 700 mm Hg after wear) is shown.

By reduction of the molecular weight of the copolymers to L.V.N. = 0.2 to 0.3, modifications of the BAV designated as BAV-2 and BAV-4 are obtained. These have high bonding capacity to paper. The main properties of the BAV agents are shown.

Properties of the BAV Lacquars

Material	Content, % by wt., of		Viscosity of a 40% solution in ethyl acetate, cP
	VA in the co-polymer	Dry residue	
BAV-1	50	40	18,000 to 28,000
BAV-2	50	40	1,000 to 5,000
BAV-4	70	40	1,000 to 5,000

Designation

Trademark -----	Unknown
Generic type -----	Carboxylated lignin modified poly(vinyl alcohol)

Description

Films containing alkaline sulphate lignin dissolve instantaneously at 70°C. The use of carboxylated lignin confers water resistance on the poly(vinyl alcohol) (PVAL).

Application

Polyvinyl alcohol is widely used as a general-purpose light-duty adhesive. The lignin modifications give enhanced performance. Resistance to water is increased through the use of carboxylated lignin.

Technological Status

Research -----	1967 (est)
Development -----	1968 (est)
Engineering -----	1969 (est)
Production -----	1971 (est) (Production may be limited)

Properties

Mechanical Properties of Films Based on PVAL Cross-Linked With Lignin*

Property	Film of PVAL	Film of PVAL modified with,			
		alkaline sulphate lignin	carboxylated lignin, amount of COOH group, %		
			2.8	4.0	18.0
Tensile strength, kgf/cm ² :					
dry films	520	500	700	850	1000
wet films (after holding in water for 1 hr at 20°C)	125	100	250	250	350
Elongation at break, %:					
dry films	100	120	100	80	70
wet films (after holding in water for 1 hr at 20°C)	300	400	115	100	100
Vapor permeability in 24 hr g/cm ²	7.5	8.0	7.0	7.0	6.5
Solubility on water	Dissolves at 50°C	Dissolves at 70°C	Does not dissolve at 70°C		Does not dissolve upon boiling

*The amount of lignin and carboxylated derivatives of lignin in the modified films was 2% based on the PVAL.

Investigation of the strength properties of the films shows that the optimum amount of carboxylated lignin is 2% based on the PVAL.

Designation

Trademark ----- Unknown
 Generic Type ----- Mixed acetals of poly(vinyl alcohol),
 modified, cross-linkable

Description

Variations are effected through first-stage reaction with furfural. End products from syntheses are mixed acetals:

- polyvinylbutyralfurfural (abbreviated PVBF)
- polyvinylethanal-furfural (PVEF)
- polyvinylketal-furfural (PVKF)
- polyvinylfurfural (PVF)

With the condensation of poly(vinyl alcohol) with furfural, an acetal can be produced that has rings that are capable of further reaction to form three-dimensional polymers with improved heat resistance.

Application

After thermally induced cross-linking, the mixed acetals can be used as bonding agents and binder resins with improved heat resistance.

Technological Status

	<u>Vinyl Acetals</u>	<u>Furfural Variants</u>
Research -----	before 1900	1967 to 1968
Development -----		1969
Engineering -----		1969
Production -----	before 1900	1973

Properties

Condensation of PVAL with the furfural is effected in dilute hydrochloric acid as indicated.

Conditions of Synthesis of Mixed Acetals*

Acetals	Phase I		Phase II		Content of acetal units mol. %	
	Molar ratio aldehyde: units of PVAL	Temperature of reaction °C	Molar ratio aldehyde: units of PVAL	Temperature of reaction °C	furfural	second aldehyde
	Polyvinylbutyralfurfural (PVBF)	0.08-0.12	18-20	0.35	7-40	6.0-9.0
Polyvinylethanal-furfural (PVEF)	0.10-0.12	18-20	0.6	8-40	9.0-11.0	48-50
Polyvinylketal-furfural* (PVKF)	0.10-0.12	18-20	0.4-0.6	20	7.0-8.0	22-24
Polyvinylfurfural (PVF)	0.3	18-20			18-17	

Note: The concentration of hydrochloric acid in the reaction mixture was 3%, the duration of the first phase for all acetals 4 hr, of the second phase 8 hr.

*The ketal units are probably derived from cyclohexanone.

The addition of an unsaturated cyclic aldehyde increases the heat resistance of the polymers while maintaining the other mechanical properties unchanged. The shear strength of PVBF before and after heat treatment (150°C/2hr) is shown. Note that heating increases shear strength by a factor of almost three.

Mechanical Properties of Polyvinylacetals Based on Furfural

Property	PVF	PVBF	PVKF	PVEF	Polyvinyl- butyral (PVB)
Martens yield temperature, °C	90 to 94	58	84	96	48 to 55
Vicat softening temperature, °C	123	86	118	126	71 to 75
Impact strength, kgf/cm/cm ²	9 to 10	100 to 130	22 to 32	20 to 22	69 to 100
Flexural strength, kgf/cm ²	1000	1060	1545	1410	800 to 140
Shear strength, kgf/cm ²					
before heating	---	70	---	---	100
after heating	---	200	---	---	---
Brinell hardness, kgf/mm ²	18.7	12.4	15	17.3	11 to 12
Tensile strength, kgf/cm ²	400	450	515	470	450 to 600
Flexural modulus at 20°C kgf/cm ²	35,000	23,900	32,000	35,800	20,000 to 22,000
Elongation at break, %	5 to 7	4 to 15	6 to 19	4 to 3	15 to 29
Water absorption at 20°C, 24 hr, %	0.3	0.48	1.13	1.13	0.40

Designation

Trademark ----- CEVAc and its acetals (BEVAL, FEVAL, FOEVAL, EEVAL, KEVAL)
 Generic type ----- Copolymer of ethylene-vinylacetate; its acetals (butyral, furfural, formal, ethanal, ketal from cyclohexanone).

Description

The initial polymers used are copolymers of ethylene and vinyl acetate obtained by block copolymerization. Ethylene content varies from 10% to 50% by weight. Acetylation of the alcohol derived from CEVAc (called CEVAL) is initiated in a homogeneous medium. Solid poly(vinylacetal ethylene) is separated in a solid form. In general, CEVAL is dissolved in a mixture of ethyl cellosolve and water (cellosolve is 2-ethoxyethanol). An aldehyde or a ketone is added; the reaction is carried out at 10° to 20°C in the presence of hydrochloric acid as a catalyst. As substitution of the hydroxyl groups in the CEVAL proceeded, the acetal or ketal separated from the solution in the form of a fine-grain powder. This is repeatedly rinsed with water and dried at 50° to 60°C.

Application

The Soviets have not fully described how they use these agents. Ethylene-vinyl acetals may be used as fatigue-resistant adhesives in relatively low-load applications. These materials may be used as high performance hot-melt adhesives.

Technological Status

Research -----	1966 (est)
Development -----	1968 (est)
Engineering -----	1970 (est)
Production -----	1972 (est)

It is suspected that one or more of these acetals or ketals is being used as adhesives.

PropertiesConditions of Synthesis of Acetals and Ketals of Copolymers
of Ethylene and Vinyl Alcohol

Acetals*	Bath Ratio**	Concentration of HCl, %	Molar ratio of aldehyde to vinyl alcohol, units	Conditions of synthesis		Content of acetal groups, wt. %
				temp., °C	time, hours	
BEVAL	1:12.5	0.5	0.35	10 to 25	10	26.5
FEVAL	1:12	0.5	1.1	20	6	24.6
FOEVAL	1:15	1.0	0.7	60 to 90	6	16.8
EEVAL	1:12	0.5	0.6	10 to 40	8	25.2
FEVAL	1:12	0.5	1.0	20	6	15.5

*Designation of acetals of copolymers of ethylene with vinyl alcohol; BEVAL - butyral; FEVAL - furfural; FOEVAL - formal; EEVAL - ethanal; KEVAL - ketal based on cyclohexanone.

**Ratio of CEVAL to solvent.

Mechanical Properties of Acetals of Copolymer of Ethylene
With Vinyl Alcohol

Property	PVB	BEVAL	FEVAL	FOEVAL	EEVAL	KEVAL
Impact strength, kgf/cm/cm ²	60 to 100	120 to 175	15 to 20	20	20	
Brinell hardness, kgf/mm ²	10 to 11	5 to 7	10 to 15	10 to 15	15	15
Vicat softening point, °C	72	36	66	74	77	73 to 75
Strength, kgf/cm ²						
in static flexure	800	400 to 475	530 to 575	800	800 to 850	800
in tension	450 to 500	350 to 400	450 to 500	450 to 500	500	500
in Shear	120 to 150	110 to 130	85 to 100	120	100 to 110	90 to 95
Elongation at break, %	15 to 25	120 to 160	80 to 100	100	120	60
Water-absorption in 24 hr, %	0.4 to 1.0	0.2	0.1 to 0.2	1.1 to 1.2	1.1 to 1.3	0.6 to 0.7

A comparison of the properties of polyvinylbutyral (PVB) and BEVAL shows that the introduction of ethylene groups into the polymer chain causes a reduction in the strength and an increase in the elasticity of the polymer. The formation of crosslinks in heat-treatment of butyrals, the low content of crosslinks in the case of ketals, and the absence of crosslinks in CEVAL, are due to simultaneous participation of ethylene and acetal groups in crosslinking.

Crosslink Density of Derivatives of CEVAL After Heat Treatment

Acetals	Content of acetal group, %	Amount of fraction insoluble in ethyl alcohol after heating at 150°C, %			
		1 hr*	3 hr*	5 hr*	10 hr*
CEVAL	---	0	0	0	0
KEVAL	15.5	0	2.2	8.7	16.8
BEVAL	23.6	0	2.46	35.4	40.8
FEVAL	19.0	62.4	71.6	74.9	84.7

*Time of heat treatment; temperature unknown

Designation

Trademark ----- MP, MPT
 Generic type ----- Methylene chloride solutions of
 chlorinated poly(vinyl chloride).

Description

Dichloroethane bonding agents are used for bonding of articles made from LKF-2, (a composition based on polymethylmethacrylate, polyvinylchloride, and chlorinated PVC resin). Methylene chloride bonding agents MP and MPT have been suggested as alternatives since dichloroethane is toxic. MP bonding agent is composed of methylene chloride (80 to 90 parts by weight) and chlorinated PVC resin (10 to 20 parts by weight); MPT bonding agent contains methylene chloride (70 to 82 parts by weight), chlorinated PVC resin (10 to 20 parts by weight) and toluene (8 to 10 parts by weight).

Application

MP and MPT can be used for bonding all plastics soluble in methylene chloride (e.g., PMMA, chlorinated PVC, and others). The significance of the application is that a stronger bond results when the surfaces being joined dissolve in the bonding agent.

Technological Status

Research ----- 1966-67 (est)
 Development ----- 1967 (est)
 Engineering ----- 1968 (est)
 Production ----- 1968 (est)

Properties

The resistance to direct pull of bonded joints in LKF-2 plastic reaches 100 to 120 kgf/cm². The resistance to shear in compression of bonded joints under the same conditions exceeds 125 kg/cm². (At the loads indicated, there was no failure of the bonded joints.)

Testing of LKF-2 articles bonded with MP and MPT bonding agents to ascertain their resistance to the effect of vibration (vertical and horizontal vibration at a frequency of 40 Hz and amplitude 0.6 mm) revealed a high resistance to vibration (2.3 to 4.6X10⁶ cycles) both with full loading and without a load.

Maintaining the bonded specimens at room temperature for 18 months does not lead to any loss in strength. Compression shear tests conducted on specimens maintained under tropical climatic conditions for 9 months showed a strength increase to 224 kgf/cm² in the case of MP bonding agent, and to 215 kgf/cm² in the case of MPT.

Bond Strength* in LKF-2 Plastic

Bonding agent	Resistance to direct pull, kgf/cm ²		
	After 30 days storage under room conditions	After 30 days heat aging at 40°C	After 60 days aging in a weatherometer (40°C, 100% humidity, UV irradiation)
MP	119*	110	113
MPT	99	113	113

*Average of testing 10 specimens

Designation

Trademark ----- KA, KB, PFN-12, TPF-37
 Generic type ----- Poly(vinyl butyral) (PVB)

Description

Poly(vinyl butyral) (PVB) is widely used in the USSR. It has been used most commonly in the production of safety glass and for protective and decorative coatings.

PVB possesses good weather resistance and good resistance to abrasion but comparatively poor resistance to repeated flexure. It decomposes at temperatures above 160°C. PVB has good adhesion to carbon steel, aluminum, zinc, chromium, cadmium, nickel, stainless steel, oxidized aluminum and magnesium, glass, paper, wood, fabrics, and plastics.

Application

KA and KB are used in electrical engineering and in casting for the production of protective and decorative coatings. PVB slit film is used mainly in the production of safety glass.

Compositions PFN-12 and TPF-37 are used in vehicle repairing work, for spraying and smoothing weld seams.

Technological Status

Production ----- In use before 1955. No information available on status of research, development, and engineering.

Designation

Trademark ----- Unknown
 Generic type ----- Polyvinylketal (PVK)

Description

The PVK is applied to the glass as a 6 percent solution in alcohol-water (80:20 parts by weight). This is dried at room temperature. Bonding pressure is 2.4 kgf/cm² for 30 minutes.

Application

PVK adhesives are used for bonding glasses, ceramics, and metals. These adhesives can be blended with phenolics to give structural bonding agents.

Technological Status

Research ----- 1972 (est)
 Development ----- not known
 Engineering ----- not known
 Production ----- not known

Properties

The following figures show the adhesion strength of systems bonded with PVK, PVB, or PVF (formal), as a function of the various solvents:

<u>Solvent</u>	<u>PVK</u>	<u>PVB</u>	<u>PVF</u>
Alcohol-water (80:20) -----	10.8/6.3*	8.5	10.5
Dimethylformamide -----	8.0*	6.0	7.7
Alcohol-water (20:80) -----	7.0	---	---

*The adhesion strength of a system based on PVK containing 61% of ketal units.

Designation

Trademark ----- KS-609
 Generic type ----- Butyl methacrylate composition

Description

Type KS-609 adhesive is a solution of 40 weight parts polybutyl methacrylate in butyl methacrylate (60 weight parts) with the addition of quartz flour (50 weight parts).

The adhesive is cured without heating as a result of an oxidative-reduction system, benzoyl peroxide (contained in the polymer) plus dimethyl aniline. The shelf life of the adhesive is 4.0 to 4.5 hr from the moment the dimethyl aniline is introduced.

To prepare the adhesive, the polymer is dissolved in methacrylic acid butyl ester from which the stabilizer has been preliminarily removed; the transparent, colorless, viscous solution produced can be stored for 7 to 10 days. The filler and hardener are introduced before use.

Application

KS-609 is used for adhesive welded joints.

Technological Status

Research ----- 1956 (est)
 Development ----- 1957 (est)
 Engineering ----- 1958 (est)
 Production ----- 1960 to 1961 (est)

Properties

The strength of joints made with KS-609 adhesive increases with time. The maximum strength is reached in approximately 7 days; however, the shear strength reaches 40 kg/cm² in only 5 hours.

The adhesive is distinguished by its good water resistance; after exposure to sea water and fresh water for 30 days, the shear strength of adhesive joints is not reduced. At 60°C, the strength is half the strength at room temperature; however, the decrease in strength of joints with increasing temperature has no influence on the strength of adhesive welded joints. The strength of adhesive-welded joints made with KS-609 adhesive does not drop after aging at 80°C for 100 hours.

An important property of the adhesive, particularly for joints operating under fatigue loads, is its elasticity in the cured state; repeated bending of plates carrying layers of the adhesive does not cause cracking or peeling of the adhesive from the metal surface.

The adhesive is resistant to reagents used in the processes of chromic acid and sulfuric acid oxidation and phosphatizing, and it protects welded joints from electrolytes.

Tests in sea water with 1% hydrogen peroxide have established that joints and structures made by spot welding through KS-609 adhesive have good corrosion resistance.

The adhesive is not inclined to aging; 3 years after manufacture, the strength of joints had increased, and elasticity was retained.

The basic method of making adhesive-welded joints using KS-609 adhesive is by welding through the liquid adhesive. The adhesive is applied, before welding, to both surfaces to be joined in a layer 0.5 mm thick or to one of the surfaces in a layer up to 1 mm thick. In both cases, the adhesive fills the gaps evenly during welding and is partially pressed out from between the pieces joined, forming a lip about 3 mm wide.

The static shear strength of adhesive-welded joints is approximately 1.2 times higher than the strength of welded joints; the uneven separation strength of adhesive-welded and adhesive joints is virtually the same. The tensile and compressive strengths of adhesive-welded joints are approximately 1.5 times higher than those of welded joints. Butt and overlap specimens 2 mm wide, made of AMG-61 alloy, were used in the tests. The tests were performed on a resonant machine, using an asymmetrical loading cycle with an asymmetry factor of 0.1 and a frequency of repeated loadings of 200 to 2,800 oscillations per minute; the test base was 2×10^6 cycles.

Designation

Trademark ----- Tsiakrin
 Generic type ----- Methyl α -cyanoacrylate and
 bifunctional variants

Description

The increase in strength of a Tsiakrin adhesive joint at 20°C is completed 48 hours after bonding.

The heat resistance can be increased and water absorption reduced by introducing bifunctional compounds to adhesive compositions based on linear esters of cyanoacrylic acid. Introduction of cyclopentadiene and glycidyl methacrylate increases water resistance; addition of diallyl phthalate reduces thermal stability.

Adhesive joints made with Tsiakrin adhesive are resistant to the effects of gasoline, transformer oil, and mineral fuel. Exposure to water reduces the strength of adhesive seams.

Technological Status

Research ----- 1958 (est)
 Development ----- 1959 (est)
 Engineering ----- 1961 (est)
 Production ----- 1963 to 1964 (est) for basic
 methyl type

Properties

Strength of Adhesive Joints in Metals
 Made With Tsiakrin Adhesive
 Shear Strength Kg/cm²

Metal-Bonded	at -60°C	at 20°C	at 100°C
Duralumin (surface brushed)	107	125	78
30 KhGSA Steel	91	147	91
OT-4 Titanium Alloy	72	185	128

Strength of Adhesive Joints in Duralumin
Made with Tsiakrin Adhesive

Indicators	at -60°C	at 20°C	at 100°C
Shear Strength kg/cm ²	101	154	113
Even Separation Strength kg/cm ²	220	220	226
Uneven Separation Strength kg/cm ²	3	10	7

Designation

Trademark ----- Tsiakrin (M-1, M-3, MK-2)
 Generic type ----- Ethyl α -cyanoacrylate

Description

The ability of alkyl α -cyanoacrylates to cure under the action of alcohol and water enables these materials to be used as rapidly polymerizing adhesives.

Application

The stated use of adhesives based on α -cyanoacrylates is for bonding metals, natural and synthetic rubbers, glass, wood, and plastics. Cyanoacrylates are being used as tissue adhesives in living organisms. The advantages of these materials are their nontoxicity, high strength, and rapid curing.

Technological Status

Research ----- 1962 to 1964 (est)
 Development ----- 1965 (est)
 Engineering ----- 1965 (est)
 Production ----- 1966 to 1968 (est)

Properties

Composition and Some Properties of the
 Cyanoacrylate Adhesives

Adhesive	Composition based on	Viscosity cp	n_D^{20}
A*	Methyl α -cyanoacrylate	50	1.4450
B*	do	20	1.5130
Tsiakrin M-1	Ethyl α -cyanoacrylate	1.7	1.441
Tsiakrin M-3	do	2.3	1.441
MK-2		25	1.4420

*Non-Soviet

The adhesives Tsiakrin M-1 and M-3 contain 0.08 to 0.10% of sulphur dioxide as an inhibitor. Compositions based on cyanoacrylates consisting of the monomers and plasticisers have low viscosity. To increase the viscosity polymers that are soluble in the alkyl α -cyanoacrylates are added. These include poly(alkyl cyanoacrylates), polyacrylates, poly-methacrylates and cellulose esters. The Soviet Tsiakrin M-3 contains poly(ethyl cyanoacrylate) (3%) as a thickening agent. The addition of 3% of poly(ethyl cyanoacrylate) slightly increases the viscosity (2.3 cP) of the composition. The viscosity of Tsiakrin M-1 adhesive, which does contain poly(ethyl cyanoacrylate), is 1.7 cP.

With the addition of poly(ethyl cyanoacrylate), the stability of the adhesive in storage and its strength properties are somewhat reduced. MK-2 adhesive contains polyvinylacetate (MW 15,000 to 20,000) as a thickening agent.

The effect of humidity on the strength of bonds attained with these agents is shown below.

Influence of humidity of Ambient Medium on the Strength of an Adhesive Joint of Catgut Specimens

Adhesive	Shear strength, kgf/cm ² , with humidity of ambient medium, %			
	31	43	76	Variable humidity (room conditions)
A	56	56	39	32
Tsiakrin monomer	--	78	36	--
MK-2	128	124	67	65

Changes in the strength properties of joints based on MK-2 in storage at 3° to 5°C (catgut specimens bonded with a relative humidity of the ambient medium of 50%) are shown:

Time of aging of specimens, months	(Original)	----	1	2	3	4	5	6
Shear strength, kgf/cm ²	(100)	-----	93	98	92	-	104	95

Designation

Trademark ----- Tsiakrin
 Generic type ----- Higher Alkyl α -cyanoacrylates

Description

These cyanoacrylates can cure instantaneously on a surface that is to be bonded. The properties of adhesive compositions based on these cyanoacrylates can be varied within wide limits by modification of their structure.

A number of requirements are imposed on adhesive compositions, according to the field of application. Elasticity of an adhesive film can be important. Cyanoacrylate adhesive compositions having elasticity in the hardened state may be produced by using higher esters of α -cyanoacrylic acid, by adding plasticizers to the composition, or by blending the cyanoacrylates with other monomers.

Application

These cyanoacrylate adhesives find use where production speedup is required (e.g., small parts, metal-to-metal or plastics-to-metal). Their use as structural adhesives is very questionable since they have drawbacks (e.g., surface passivity impedes curing; curing in thick sections is unpredictable; and the agent is sensitive to moisture and alkalinity). The Soviets have pioneered the use of Tsiakrin types in joining human skin and tissues. Overall, a very limited volume is probably produced and used.

Technological Status

Research -----	1958 (est)
Development -----	1960 to 1962 (est)
Engineering -----	1962 to 1966 (est)
Production -----	1968 (est) for newer variants. Production is probably limited.

Properties

Increasing the number of carbon atoms in the radical in the ester group of the cyanoacrylate of a given homologous series reduces the elastic modulus, (i.e., the elasticity of the polymer increases). The lowest elastic modulus occurs with poly(β -butoxyethyl α -cyanoacrylate).

Adding various plasticizers to ethyl α -cyanoacrylate also leads to a change in the elastic modulus of the hardened compositions.

Dependence of the Mechanical Properties of Hardened Adhesive Composition on the Structure of the Cyanoacrylates

Composition	Elastic modulus**, kgf/cm ²	Shear strength*, kgf/cm ²	
		Initial	After 10 days in water
Ethyl α -cyanoacrylate (ECA)	15,700	180	85
n-Propyl α -cyanoacrylate (EPCA)	10,000	130	--
n-Butyl α -cyanoacrylate (BCA)	7,500	110	70
n-Amyl α -cyanoacrylate (AMCA)	5,000	80	80
Allyl α -cyanoacrylate	7,500	130	100
β -butoxyethyl α -cyanoacrylate	3,500	90	--
ECA + 25% PCA	9,300	160	--
ECA + 25% AMCA	7,300	120	--

*Strength of adhesive joint determined on duralumin specimens 60x20x2 mm.

**Specimens of diameter 3 mm, depth 4.5 mm.

Influence of the Plasticizer on the Mechanical Properties of
Hardened Cyanoacrylate Adhesive Compositions

Composition*	Elastic modulus, kgf/cm ²	Shear strength, kgf/cm ²
ECA	15,700	180
ECA+5% DBP	10,500	150
ECA+10% DBP	8,000	170
ECA+20% DBP	4,000	130
ECA+30% DBP	2,000	80
ECA+10% DHP	8,700	140
ECA+5% DBS	11,700	160
ECA+10% DBS	3,700	120
ECA+5% ethyl cyanoacetate (ECAT)	3,500	130
ECA+10% ECAT	3,000	130
ECA+10% ECAT	750	70

*DBP - dibutyl phthalate, DHP - dihexyl phthalate;
DBS - dibutyl sebacate
ECA - ethyl cyanoacrylate

Thickening agents (polymers) can increase elasticity. The elastic modulus of an adhesive composition is reduced to half with the addition of 5% of poly(ethyl cyanoacrylate) to ethyl α -cyanoacrylate. The same effect is observed with a composition with 5% of a copolymer of vinyl acetate and vinyl-n-butyl ether. Polyacrylates (PMA and PBA), and also poly(butyl methacrylate) (PBMA), were found to be very effective flexibilizers.

The intensity of the plasticizing depends on the chemical nature of the polymer. Best results are obtained with the additions of 20% ethyl α -cyanoacrylate. It is possible that copolymerization occurs or else the change in the modulus is determined by the presence of unreacted monomer.

Designation

Trademark ----- Fenilon S1 and S4; Terlon S
 Generic type ----- Aromatic polyamides

Description

Aromatic polyamides combine high-yield temperature and heat resistance with adequate electrical and strength properties. Aromatic polyamides can be produced in film form. To produce these films, polyamides synthesized by emulsion and low-temperature polycondensation in solution are used. The films are "dry-formed" from solution in amide solvents (dimethylformamide and dimethylacetamide).

Application

Films based on aromatic polyamides are recommended for use in the electrochemical industry. Lacquers of aromatic polyamides can be used in the cable industry for coating of leads. Estimated continuous use temperature is 240° to 250°C. (Higher values may be attainable through compounding.) Stabilized variants may reach the 300° to 350°C range for short-time exposure.

Technological Status

Research ----- 1965 to 1966 (est)
 Development ----- 1967 (est)
 Engineering ----- 1969 (est)
 Production ----- 1969 (est) for original Fenilon or
 Terlon types; 1970 to 1971 (est)
 for sulphone and newer variants
 (production probably limited).

Properties

Some properties of the arylamides are given below.

Physicomechanical Properties of Films Based on Aromatic Polyamides

Type of polymer		Specific viscosity of 0.5% solution	Softening temperature, °C	Elongation at break, %	Tensile strength kgf/cm ²
1	Fenilon S1	1.2	290	10	1000
2	Fenilon S4	1.4	290	10 to 50	1000 to 1500
3	Terlon S	2.0	280	40 to 60	2000
4	Based on 2,7-diamino-diphenyl sulphone and isophthaloyl chloride	2.3	420	45	1800
5*	Based on 2,7-diamino-diphenyl sulphone and isophthaloyl and terephthaloyl chlorides	3.6	500	2-5	1400
6*	Based on 2,7-diamino-diphenyl sulphone and terephthaloyl chloride	2.5	548	2-5	2000
7*	Based on 2,7-diamino-diphenyl sulphone and the chloride of diphenyl oxide dicarboxylic acid	1.35	---	24	1300
8*	Based on 4,4-diamino-diphenyl sulphone and the chloride of naphthalene dicarboxylic acid	1.6	380	13	1000
9	Based on <i>m</i> -phenylenediamine and hexamethylenediamine (55:45) with isophthaloyl chloride	1.15	220	10	1000
10	Based on <i>m</i> -phenylenediamine and the chlorides of isophthalic and naphthalene dicarboxylic acids (50:50)	0.75	290	12	1100
11	Based on <i>m</i> -phenylenediamine and the chlorides of terephthalic and naphthalene dicarboxylic acids (50:50)	2.0	300	13	600

*The sulfone designations may or may not be correct. Note that unusually high softening temperatures are stated for these variants.

Aromatic polyamides (as films) show high heat resistance and effective strength properties. It is assumed that the macromolecules have high rigidity, but many of the films have considerable elongation at break. Films based on Fenilon (poly[m-phenyleneisophthalamide]) can be prepared with elongation at break of 100% at 20°C.

Films of aromatic polyamides do not act as high-frequency dielectrics; nevertheless, insulating properties are quite high and change little with change in temperature. The heat stability of the aromatic polyamides is very satisfactory. All the dielectric properties of Fenilon S1 remain unchanged after holding at 250°C for 5000 hours. The comparatively high permittivity of the aromatic polyamides makes them possibly useful for increasing the capacity of condensers.

Designation

Trademark ----- PFE-2/10; MPF-1
 Generic type ----- Methylolpolyamides

Description

The PFE-2/10 adhesive consists of a 25% to 30% solution of methylolpolyamide in a mixture of alcohol and water. The viscosity of the adhesive is 20 to 60 cP. The adhesive has satisfactory adhesion to silicate and organic glass, metals, ceramics, leather, concrete, paper, plastics, and other materials; it is cured in the presence of catalysts at room temperature and elevated temperatures.

Type MPF-1 adhesive is more heat resistant than PFE-2/10 adhesive and provides higher strength of adhesive joints in metals. It is a methylolpolyamide, modified with phenol-formaldehyde polymer of resol type. The adhesive is used both in liquid form and as an adhesive film.

Application

Type MPF-1 adhesive is designed for bonding of metals (duralumin, steel, and magnesium alloys) to each other and to plastic foam, textolite, and other materials in products for use in the $\pm 60^{\circ}\text{C}$ temperature interval. It is prepared by mixing solutions of methylolpolyamide and phenol-formaldehyde resins.

Technological Status

Research -----	1950 to 1952 (est)
Development -----	1952 (est)
Engineering -----	1953 (est)
Production -----	1955 to 1956 (est)

Properties

The adhesive joints are resistant to the effects of oils, fats, gasoline, and kerosene and has limited resistance to long-term exposure of the water.

Strength of Adhesive Joints in Various Materials
Made With PFE-2/10 Adhesive

Material Bonded	Bonding Temperature °C	Strength of Adhesive Joint kg/cm ² *
Aluminum	20	20 to 25
Silicate Glass	150	200 to 250
Heat-Resistant Organic Glass	100	175 to 200
Oak	---	90 to 100
Textolite	---	30 to 45
Getinax	---	20 to 30
Aminoplast	---	20 to 25
Polystyrene Foam	---	4 to 45
Leather	---	5 to 6

*The type of loading, shape and size of specimens and bonding conditions of materials were not indicated.

The technology of bonding with MPF-1 adhesive consists of applying the liquid adhesive to the surfaces to be bonded and drying the adhesive coat, after which an adhesive film is placed between the surfaces to be bonded and held under a pressure of 1.0 to 5.0 kg/cm² at 155 ±5°C for 1 hour.

One feature of MPF-1 adhesive is the high strength of adhesive joints that it produces in uneven separation. This is of great significance, because of the use of this adhesive to produce bonded-metal load-bearing structures.

Strength of MPF-1 Adhesive Joints in Duralumin

Test Temperature °C	Shear Strength, kg/cm ²	Uneven Separation Strength kg/cm ²	Even Separation Strength kg/cm ²
-60	131	36	482
20	175	65	318
60	94	42	137

The adhesive joints have high dynamic strength and are resistant to vibration; with a load of 55 kg/cm², an overlap joint can withstand 1.9×10^6 cycles before rupture. When tested for long-term strength (load 120 kg/cm²), adhesive joints do not rupture for 160 hours.

Section III.

ELASTOMERIC ADHESIVES

Designation

Trademark ----- KR-5-18, KR-5-18 p, KR-6-18, VKR-7
 Generic type ----- Butadiene-acrylonitrile

Description and Properties

Adhesives Based on Butadiene-Acrylonitrile Rubber

Adhesive Type	Materials Bonded	Bonding Mode			Type of Test	Indicators	Notes
		Pressure kg/cm ²	Temperature, °C	Time, Hr			
KR-5-18	Type 203B rubber + steel	15	At least 15	48	Even separation strength after vulcanization at 143 °C, kg/cm ²	at least 48	Adhesive joints resistant to oils and fuels
KR-5-18 p	Type 203B rubber	15	At least 15	48	Peeling strength after holding for 48 hours at 20°C, kg/cm	6 (strip width 2.5 cm)	---
KR-6-18	Nonvulcanized type 3826 or 181 rubber	Contact	At least 20	8	Peeling strength, kg/cm--20 minutes after bonding; after hot vulcanization; after exposure to fuel for 24 hours at 20°C	2.5 } (strip width 5 cm) 6 5	Adhesive joints function at temperatures from -60 to +200°C
VKR-7	Type 203B rubber vulcanized	Rolled	20	At least 24	Peeling strength, kg/cm--20 min after bonding; 5 days after bonding	0.6 2.2	Adhesive joints function at temperatures up to 200°C

Technological Status

Research ----- 1955 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1957 to 1958 (est)

Designation

Trademark ----- Types 88, 88N, 88NP, 4NB-UV
 Generic type ----- Polychloroprene

Description

The sevanite (type 88) and nairit (type 88N) adhesives are solutions of a rubber mixture and butyl phenol-formaldehyde resin type 101, in a mixer of ethyl acetate and gasoline (2:1). This mixture can also be used to dilute the adhesive in case the mixture thickens. Only type 88N is being produced.

88NP adhesive contains nairit as its basic component; at normal temperatures, this component is in the crystallized state. Bonding using this adhesive must be performed at a temperature of at least 18°C (relative humidity 65% to 75%). The viscosity of the adhesive does not change when the adhesive is stored for a period up to 9 months.

The adhesive is designed for bonding of rubber to metals without heating. The technology of application of the adhesive does not differ from the technology of application of 88N adhesive.

Type 4NB-UV adhesive is a composition based on nairit rubber, soluble in a mixture of ethyl acetate and gasoline (1:1). The dry residue is 23% to 27%; storage life is 3 months.

Application

The adhesive is used to bond vulcanized rubber and rubber-fabric materials based on nairit, natural, sodium-butadiene, and nitrile raw rubber without vulcanization, and to bond nonvulcanized rubber and rubber-fabric materials based on nairit, nitrile (SKN-18 and SKN-26), as well as mixture of nairit and nitrile rubber, with subsequent vulcanization.

Technological Status

Research ----- 1950 (est) early types
 Development ----- ?
 Engineering ----- ?
 Production ----- 1955 to 1963 (est)

Strength of Adhesive Joints of Vulcanized Rubber With Duralumin and Steel Made With Polychloroprene Adhesives

Adhesive Type	Bonding Mode			Strength		
	Pressure, kg/cm ²	Temperature, °C	Time, hr	Even separation, kg/cm ² at least		Peeling, kg/cm
				After 24 hours holding	After 48 hours holding	
88NP	0.2	18 to 30	24	11	13	2.0
88N	0.2	At least 12	24	11	13	2.0
4NB-Chv	Rolling	At least 18	20-25 min	Bonding strength of R-29 sponge rubber, 20 min after bonding: 1.4 kg/cm.		

Designation

Trademark ----- PU-2, PU-2M, PU-2B; VK-5, VK-11
 Generic type ----- Leykonat Polyurethanes

Description and Application

PU-2 adhesive consists of a composition based on the product of condensation of an aliphatic dicarboxylic acid with polyhydric alcohols (product 24), isocyanate (product 102-T), and a filler (cement). The recipe for the adhesive (weight/parts) is:

Product 24 -----	200
Product 102-T -----	100
Cement (Portland 400) -----	25

When the components are mixed, the reaction causes a gradual increase in viscosity of the mixture, which is first converted to a pasty state, then to a solid product. The time required for this conversion to the pasty state is usually 15 to 90 minutes. The adhesive is used in the paste state. The shelf-life of the finished adhesive is at least 2 hours. At room temperature, the strength of the adhesive joint decreases very slightly; the strength at 60°C decreases by 5% to 10%. The holding time of adhesive joints in duralumin at $105 \pm 5^\circ\text{C}$, pressure 3 kg/cm², should be 4 hours.

Bonding with PU-2 adhesive can also be performed at room temperature. In this case, the strength of the adhesive joint and maximum shear strength (170 to 180 kg/cm²) are increased with the passage of time up to 20 to 30 days. After 1 day, the strength is 25 kg/cm²; after 3 days, 120 kg/cm². Adhesive joints made with PU-2 adhesive have low thermal stability. At 20°C, the shear strength of adhesive joints in duralumin is about 200 kg/cm²; at 100°C, 70 kg/cm². Type PU-2 adhesive is used for bonding of organic glass and attachment of capron and lavsan fabric to the glass.

Type PU-2M adhesive is a modification of type PU-2 adhesive; alcohol is added to the composition of the adhesive. The adhesive is distinguished by longer shelf life and somewhat lower toxicity. This adhesive is used primarily for bonding of decorative facing materials, various glass and cotton-based fabric coverings, perchlorovinyl film materials, porolon, cotton fabric, etc.

Type PU-2B adhesive is a modification of type PU-2, designed for bonding of organic glass and attachment of capron fabric to the glass. In order to eliminate the danger of "silvering" of the organic glass, gasoline is introduced to the composition of the adhesive as a nonpolar solvent. Adhesive joints can be used in the temperature interval from -60° to $+130^{\circ}\text{C}$.

Type VK-5 adhesive is designed for bonding of metals (aluminum and titanium alloys, 30 KhGSA steel) and nonmetallic materials (textolites and foam plastics) in products operating for extended periods of time at $\pm 60^{\circ}\text{C}$. Type VK-5 adhesive is vibration resistant, fungus resistant, resistant to the effects of fuels and oils and variable temperatures ($\pm 60^{\circ}\text{C}$), and does not cause corrosion of metals. The data presented on changes in strength, following artificial aging of adhesive joints in D-16AT aluminum alloy clad at 60°C for 1000 hours and at 100°C for 500 hours, indicate significant increase in strength of VK-5 adhesive during thermal aging.

VK-11 adhesive is a polyurethane composition modified with perchloro-vinyl resin. The adhesive is prepared by mixing of the initial components just before use. The shelf life of the adhesive is 6 to 8 hours. The viscosity, according to the VZ-1, is 20 to 25 seconds. The adhesive consumption rate is 150 to 200 g/m^2 . During bonding, open-holding for 30 to 40 minutes is recommended after application of the first coat and 10 to 15 minutes after application of the second coat. The pressure is created by a roller. A 24-hour holding period is recommended before beginning installation work. The adhesive is used to attach decorative facing materials (various pavinols based on glass and cotton fabric, porolon to plywood and primed or painted magnesium alloys). The adhesive has high resistance to the effects of atmospheric conditions. The strength of adhesive joints does not drop following thermal aging at 60°C for 500 hours.

The adhesive Leykonat is a solution of p,p',p''-triphenylmethane triisocyanate in dichloroethane. A concentration of the triisocyanate is 19% to 21%. The adhesive can be diluted with dichloroethane if it thickens. The storage life at 0° to 20°C in sealed containers is 1.5 years. Leykonat is used for bonding of nonvulcanized rubber made of nitrile, chloroprene, or natural raw rubber to duralumin, steel, or brass, with subsequent vulcanization.

Technological Status

Research ----- 1955 to 1956 for earlier types;
 1964 for later types (est)
 Development ----- ---
 Engineering ----- ---
 Production ----- 1959 (for PU types); 1964 (Leykonat);
 1965 to 1966 (for VK-5 and VK-11) (est)

Properties

Strength of Adhesive Joints in Metals Made With PU-2 Adhesive

Test Temperature °C	Duralumin		EYalt Steel	
	Long-Term Shear Strength	Endurance in Shear kg/cm ² *	Long-Term Shear Strength	Endurance in Shear kg/cm ²
20	115(1500) hr	40	160(1500) hr	79
60	65(300) hr	15	110(300) hr	55
80	15(300) hr	12	80(300) hr	40
100	5(100) hr	10	40(100) hr	30
120	---	--	20(100) hr	--

*Test base 6.10 cycles

Strength of Adhesive Joints Made With VK-11 Adhesive

Materials Bonded	Peeling Strength, kg/cm		
	At -60°C	At 20°C	At 60°C
Pavinol + plywood	120 to 130	100 to 110	60 to 75
Pavinol + duralumin, anodized with protective coating	30 to 120	60 to 110	30 to 60

Strength of VK-5 Adhesive Joints

Materials Bonded	Shear Strength kg/cm ²	
	At 20°C	At 60°C
D-16 anodized aluminum alloy	90	25
30KhGSA steel	155	25
VT-4 titanium alloy	135	40
911-1 textolite	90*	50*
D-16 clad alloy + textolite	103	24
D-16 anodized alloy + FK plastic foam	13*	6*
D-16 anodized alloy + PU plastic foam	3*	2*

*Rupture through textolite and plastic foam

Shear Strength of Adhesive Joints Made With VK-5 Adhesive in Duralumin as a Function of Aging Time

Aging Time, hr	Aging Temperature °C	Shear Strength kg/cm ²	
		At 20°C	At 60°C
Initial data	---	120	47
300	60	174	103
1000	60	178	111
500	100	196	110

Bonding Mode and Properties of Polyurethane Adhesives Types VK-11, PU-2M, and PU-2B

Adhesive Type	Form of Adhesive	Materials Bonded	Bonding Mode		Consumption Adhesive g/m ²	Shelf Life	Strength of Adhesive Joints			
			Pressure kg/cm ²	Temperature °C			Time, hr	At -60°C	At 20°C	At 60°C
VK-11	Liquid	Pavinol (a leather substitute) + plywood	Rolled on	20	24	6 to 8 hr	Peeling Strength, kg/m	120 to 130	100 to 110	60 to 75*
PU-2M	Fluid Mass	Pavinol + plywood	Contact	20 to 25	24	1 day	20	70	50**	
PU-2B	Pasty Mass	Organic glass ST-1 Organic glass ST-1 + capron	1.5 to 2.0	20	24	1 day	Shear Strength, kg/cm ²	150	230	185***
						---	130	120	90***	

*The strength of the adhesive joint does not drop when heated to 60°C for 500 hours
 **After heating to 60°C for 500 hours, peeling strength of plywood and pavinol at least 50 kg/m in water for 30 days
 ***Strength of adhesive joints does not drop after heating to 80°C for 500 hours and holding in water for 30 days

Designation

Trademark ----- UK-B-2 (based on UK-1 or SKU-8)
 Generic type ----- Polyurethane (PUR)

Description

PUR elastomers UK-1 and SKU-8, with hydroxyl end groups, are used to prepare UK-B-2. For crosslinking Leykonat (a 20% solution in dichloroethane of p,p¹,p¹¹-triphenylmethane triisocyanate (TPTI)), and also a less toxic product, the adduct of trimethylolpropane with 2,4-toluene diisocyanate (TPTDI) are used.

Application

Polyurethane (PUR) bonding agents are used for bonding various non-metallic materials in articles functioning under dynamic loading. PUR's are also a base for bonding compositions in shoe production as well. There is a trend to replace polychloroprene, poly(vinyl chloride) and other types of bonding agent for attaching soling materials by PUR types.

Technological Status

Research -----	1968 (est)
Development -----	1970 (est)
Engineering -----	1970 (est)
Production -----	1971 (est)

Designation

Trademark -----	PUR, modified
Generic type -----	Polyurethanes containing phenoxy groups

Description

The diisocyanates used are 2,4-toluene diisocyanate (TDI) or 1,6-hexamethylene diisocyanate (HMDI).

Application

It is expected that the Soviets are using moderate amounts of these phenoxy-containing polyurethanes in bonding metals, rubbers, certain plastics, glasses, and ceramics. Anticipated maximum service temperature is 100° to 120°C. Weathering characteristics are estimated to be satisfactory.

Technological Status

Research -----	1967 (est)
Development -----	1968 to 1969 (est)
Engineering -----	1970 (est)
Production -----	1971 (est)

Properties

The tables show that with increase in the content of phenoxy groups there is a marked improvement in the tensile strength, σ , and the elongation at break, ϵ , a raising of the glass transition temperature, and an increase in the adhesion strength of PUR + metal or PUR + rubber systems.

Physicomechanical Properties of Polyurethanes Based on a Mixture of Polyethers (T+F-3) and TDI

T/F-3 ratio	Content, %		Strength, kgf/cm ²				Elongation at break, %	Glass transition temperature °C
	phenoxy groups	soluble fraction	tensile	uniform direction pull	peeling*			
100/0	0	1.4	6.4	6	---	35	-45	
80/20	10.7	1.9	9 to 10	10 to 11	-/0.95	35	-34	
60/40	21.5	2.43	12 to 15	15	2.15/2.5	55	-22	
50/50	26.9	2.78	15 to 16	15 to 17	2.45/2.55	85	-17	
40/60	32.2	2.99	25	21 to 22	4.0/3.0	100	-11	
30/70	37.6	3.35	29	35	4.5/3.9	155	-8	
20/80	43	---	50	50	8/4.75	---	---	

*Figures before the stroke, from steel; after, from rubber

Physicomechanical and Adhesion Properties of Polyurethanes
Based on a Mixture of Polyethers + TDI

Weight ratio of the polyethers	Distance between crosslinks	Content, %		Strength, kgf/cm ²		Elongation at break, %	Glass transition temperature, °C
		of phenoxy groups	of soluble fraction	tensile	uniform direct pull of polyether urethane + steel		
T+F-2 Polyether Mixture							
100/0	1250	0	1.06	7.7	7.2	30	-43
80/20	1450	8.9	1.56	10.0	10.0	40	-29
40/60	2420	26.8	4.67	16.6	14	205	-9
30/70	3080	31.3	6.0	34 to 41	20 to 21	390	-3
D+F-3 Polyether Mixture							
60/40	2710	18.9	10.7	9 to 11	10	270 to 300	-23
40/60	1880	28.8	3.66	34.40	17	260 to 270	-4
20/80	1470	37.8	4.15	120 to 140	50	210 to 220	+12

Section IV.

THERMOSETTING ADHESIVES

Designation

Trademark ----- FL-2, F-8, FL-1, F-10
 Generic type ----- Furyl resins (mastic form)

Description

To protect against corrosion or retention of toxic materials, equipment and wall surfaces can be covered with tiles or sheet materials. To attach such materials, adhesives or mastics with chemical resistance and impermeability to toxic materials are required.

Oligomers based on furyl alcohol are useful as anticorrosion materials. Compositions based on furyl resins are resistant not only to acidic media but also to alkalis.

Mastics based on FL-2 furyl resin and on blended furyl products (F-8, FL-1, F-10) are discussed. Fillers used include quartz powder, basalt powder, graphite powders, and other materials.

Application

Mastics based on unmixed FL-2 resin and its variants have been used for the bonding of chemically resistant and mercury-impermeable materials and for sealing joints. Mastics based on FL-2 resin were used in sealing joints of coverings of acid-resistant ceramic tiles.

Technological Status

Research -----	1960 (est)
Development -----	1962 (est)
Engineering -----	1963 (est)
Production -----	1964 to 1968 (est) (It is expected that sufficient production capacity exists to allow export of such materials to other countries.)

Properties

Hardeners used were p-chlorobenzene sulphonic acid, p-chlorosulphonyl-phenylurethane, p-chlorobenzene sulphonyl chloride and others. The best results are obtained with FL-2 resin with the hardener p-chlorobenzene sulphonic acid (6% to 10% of the weight of resin).

Resistant¹ of Mastics Based on Various Furyl Resins
and Lacquers to Acids, Alkalis and Salts

Medium	Resistance of mastics based on		
	FL-2 ²	F-8 ²	F-10 ³
Sulphuric acid			
5%	C/C	C/C	O
30%	C/C	C/C	O
40%	C/-	-	-
60%	C/-	-	-
80%	H/-	-	-
Hydrochloric acid			
5%	C/H	C/C	C
20%	C/H	C/C	C
Nitric acid			
5%	C/H	O/-	O
10%	C/H	O/-	O
20%	H/H	H/-	H
Phosphoric acid			
10%	C/-	-	-
40%	C/-	-	-
60%	C/-	-	-
Water	C/-	O/-	-
Caustic soda solution			
5%	C/-	C/C	C
30%	C/-	C/C	C
Hydrofluoric acid			
5%	C/C	-	-
40%	C/H	-	-
Ammonium bifluoride solution			
5%	C/C	-	-
20%	C/H	-	-

¹C - resistant (no failure of the mastic);

O - relatively resistant (the mastic may be used to protect structures under the regular action of the media in question);

H - nonresistant (the mastic fails and its use is not permissible).

²Before the stroke, at room temperature; after, at 90-100°C.

³At room temperature

Adhesion of Mastics Based on Furyl Resins and
Lacquers to Various Materials

Materials being bonded	Bond strength (kgf/cm ²) of materials bonded with mastics based on			
	FL-2	F-10	FL-1	FL-4
Concrete/plasticised PVC	25.0	---	27.0	4.8
Concrete/PVC linoleum (sic)	26.4	---	47.0	10.3
Concrete/Relin	12.4	14.0	6.8	4.2
Concrete/Viniplast	28.0	30.0	29.0	5.7
Concrete/PS tile	33.0	21.0	25.0	9.2
Concrete/Fenolit tile	53.5	43.5	28.5	17.0
Concrete/Metlakh (ceramic tile)	13.0	43.4	13.0	22.0
Concrete/asbestos-ebonite tile	37.0	26.5	24.3	11.5
Concrete/concrete	34.5	38.5	46.5	12.0

FL-2 mastic resists chlorobenzene, solvent R-4 (kerosene type), dichloroethane, carbon tetrachloride and benzene; it is not resistant to ketones. Additional data on FL-2 follows:

Density, g/cm³ ----- 1.57
 Water permeability (at 3 atmospheres
 in 1 hour) ----- Impermeable
 Heat resistance after 25 cycles of change
 in temperature (20° to 100°C cycle) ----- No change
 Low-temperature resistance after 25 cycles
 of change in temperature (-20° to 20°C cycle) - No change
 Sparking ----- Does not spark
 Volume resistivity, ohm-cm ----- 6.5x10⁹
 Permeability to mercury after 6 months ----- Impermeable
 Sorption of mercury vapor ----- Medium
 Desorption of mercury vapor ----- Low
 Atmospheric resistance (weatherometer) ----- Specimens turned
 somewhat dull
 Shrinkage (using an optical apparatus),% ----- 1.9
 Vicat softening point, °C ----- 84

Designation

Trademark ----- FAB
 Generic type ----- Furfural-acetone/epoxy copolymers

Description

Furan compositions may be used for the production of materials with relatively high chemical resistance. Various furan compounds blend well with epoxy resins, which have considerable strength of adhesion to glass fiber. FAB resins are products of modification of compounds of furfural and acetone with an epoxy resin.

The FAB epoxy-furan resins are produced by the reaction of furfural, acetone, and ED-5 epoxy resin in the presence of caustic soda.

The degrees of hardening of the resin are determined by extraction of the solubles with acetone.

The following FAB epoxy-furan resins exist:

	FAB-1	FAB-1.5	FAB-2
Initial components, mol			
furfural -----	1	1	1
acetone -----	1	1	1
ED-5 resin -----	1	1.5	2
Epoxy group content, % -----	13.5	19.3	22.2

The FAB resins are hardened in the presence of various amines or anhydrides, in particular triethanolamine titanate (TEAT) in amounts of 18% to 24%, on the weight of the resin at relatively high temperatures.

Application

The FAB agents are claimed to have high chemical resistance. Maximum service temperature may be in the range of 140° to 180°C. FAB's may have use as cheap general-purpose adhesives. They undoubtedly have utilization in binding glass laminate structures.

Technological Status

Research ----- 1963 (est)
 Development ----- 1965 (est)
 Engineering ----- 1966 (est)
 Production ----- 1968 (est)

Properties

The following conditions of hardening FAB resins are optimum:

	FAB-1	FAB-1.5	FAB-2
Hardening schedule, °C -----	120 to 180	120 to 150	120 to 150
Amount of TEAT,% by weight ---	12	18	24
(Note: Hardening is gradual, and total duration is 16 hours.)			

Some of the properties of TEAT-hardened FAB resins are given below:

	FAB-1	FAB-1.5	FAB-2
Density, g/cm ³ -----	1.2 to 1.3	1.2 to 1.3	1.2 to 1.3
Degree of hardening, % -----	82.8	94.4	99.5
Flexural strength, kgf/cm ² ---	868	895	859
Brinell hardness, kgf-cm/cm ² -	22.3	---	---
Impact strength, kgf/cm ² -----	7.5	13.7	8.1
Weight loss in liquid media at 20-25°C, % in 24 h:			
distilled water -----	0.05	0.03	0.02
3% Na ₂ CO ₃ solution -----	0.06	0.05	0.04
solar oil -----	0.05	0.07	0.08
6% H ₂ SO ₄ solution* -----	0.09	0.09	0.11

*(in 144 hours)

FAB-1.5 resin has properties of the highest strength. Increasing the epoxy group content beyond this point leads to a reduction in these properties. The chemical resistance of hardened binder resins based on FAB resins is high (and is virtually independent of the epoxy group content).

Glass fiber laminates based on FAB resins are produced by pressing under the following conditions:

Pressure, kgf/cm ² -----	3 to 4
Temperature of pressing, °C --	150
Residence, minutes -----	10

The main properties of glass fiber laminates based on FAB resins hardened with TEAT are:

	FAB-1	FAB-1.5	FAB-2
Amount of TEAT, % by weight ---	12/12	18/18	-/24
Number of plies -----	6/3	6/3	-/3
Temperature of hardening for 16h, °C -----	120 to 180	120 to 150	120 to 150
Flexural strength, kgf/cm ² ----	1731/3188	3580/3222	-/2618
Impact strength, kgf-cm/cm ² ---	68.7/115.6	-/320.0	-/94.6

Note: Figures before the stroke, ASTT(b)-S₂-0 glass; after stroke, MTBS glass.

Designation

Trademark ----- FM-2
 Generic type ----- Furfural phenol-formaldehyde

Description

With phenol-furfural resins, useful properties may be obtained by using some other aldehyde (e.g., formaldehyde) in addition to furfural, and also by carrying out the reaction in two stages. The use of FM-2 thermosetting furfural-PF resin as a binder for the inner layers of a paper laminate plastic confirms these conclusions.

The resin specimens are synthesized by a two-stage procedure with modifications. FM-2 resin is a thick liquid with a high content of free monomers.

Content of free monomers, %:

furfural -----	10.4/3.5*
phenol -----	3.8/1.7
formaldehyde -----	1.3/0.6
Molecular weight -----	400 to 500/650 to 800
Moisture content, % -----	2.3/2.1
Drop point, °C -----	-/100 to 102
Gelling time at 150°C, sec ---	100/140

*Figures before the stroke, before precipitation; after the stroke, after precipitation. The yield of powdery resin is 85% to 87% of the weight of the liquid resin used in the precipitation.

Application

It is expected that FM-2 resins are used to replace phenolformaldehyde binders or adhesives where some flexibility is desired.

Technological Status

Research -----	1964 (est)
Development -----	1965 to 1966 (est)
Engineering -----	1967 (est)
Production -----	1967 to 1968 (est)

Properties

Study of the dependence of the gelling time of FM-2 resin and of grade A bakelite lacquer shows that at high temperatures (180° to 200°C) both resins gel at approximately the same rate. The difference in the gelling time of FM-2 resin and the bakelite lacquer at 200°C is 8 sec. This difference increases with lowering of the temperature. This is evidence that at lower temperatures FM-2 remains in the viscous flow state for a longer time than does the grade A A-stage resin.

Gelling Time of FM-2 Resin in the Presence of Various Hardeners

Hardener	Gelling time*, sec					
	Amount of hardener, %					
	0.1	0.5	1.0	2.0	3.0	5.0
Benzene sulphonic acid	$\frac{128}{300}$	$\frac{80}{165}$	$\frac{58}{105}$	$\frac{17}{26}$	---	---
Zinc chloride	$\frac{130}{305}$	$\frac{60}{140}$	$\frac{47}{90}$	---	$\frac{24}{42}$	$\frac{15}{30}$
Maleic anhydride	$\frac{136}{330}$	$\frac{97}{195}$	$\frac{84}{140}$	---	$\frac{43}{101}$	$\frac{40}{33}$
Phthalic anhydride	$\frac{140}{380}$	$\frac{123}{332}$	$\frac{114}{310}$	---	$\frac{92}{255}$	$\frac{80}{215}$
Benzoyl peroxide	---	---	$\frac{108}{350}$	$\frac{102}{334}$	$\frac{97}{304}$	$\frac{92}{290}$

*Numerator, at 150°C; denominator, at 130°C

Raising the temperature of heat treatment to 120° or 140°C increases the yield of the insoluble part of the resin to 90% or 96%. Further raising of the temperature of heat treatment to 180°, 200°, and 200°C sharply raises the rate of hardening. Heat treatment for 10 to 30 min at these temperatures leads to complete hardening of the resin.

The relatively long gel time of FL-2 resin (250 sec at 250°C) is associated with the comparatively low crosslink density of hardening products and with loss of solubility and fusibility; this determines the elastic properties of the hardening products.

Hardening of FL resin can be represented as follows: at a temperature as low as 60°C interaction of the methylol groups with the α -hydrogen of the furan ring commences. The hardening process is more rapid at 160°C, and occurs very rapidly at 180°C. At 180°C the spectrum takes a form typical of hardened resins. Hardening of the resins occurs not only as a result of the reaction of methylol groups and reactive positions of phenol and furan rings but also as a result of additional crosslinking at the double bond in the furan ring.

Designation

Trademark -----	VIAM B-3, KB-3, VIAM F-9, KR-4, TSNII MOD-1, TSNIIPS-1, TSNIIPS-2, others
Generic type -----	Unmodified phenol-formaldehydes, cold-cured

Description

These adhesives are produced basically from unmodified phenol-formaldehyde resins of resol type, cured at normal temperatures using acid catalysts. To accelerate the curing process, the temperature may be increased to 50° to 60°C. Sulfonaphthenic acids (G. S. Petrov reagent) and sulfuric acid are most frequently used as acid catalysts. Solvents (acetone, ethyl alcohol) are introduced to certain adhesive compositions.

One common shortcoming of adhesives of this type is the fact that they hydrolyze cellulose; another drawback is that they are toxic, because they contain free phenol and formaldehyde.

Application

The primary use of adhesives based on unmodified phenol-formaldehyde resins is the bonding of wood, plywood, wood-based plastics, wood-chip board, food containers, plastic foam, and other porous materials. The adhesives are water resistant.

Technological Status

Research -----	1945 or earlier for basic types (est)
Development -----	-
Engineering -----	-
Production -----	1945 to 1947 (est)

Composition of Adhesives Based on Unmodified Phenol-Formaldehyde Resins

Type of Adhesive	Resin			Catalyst			Solvent	
	Type	Viscosity cp	Free phenol content, % not over	Free formaldehyde content, % not over	Name	Quantity, weight parts per 100 weight resin	Name	Quantity, weight parts per 100 weight resin
VIAM B-3	VIAM B	500 to 1000	21.1	---	Grade 1 kerosene catalyst	$\frac{1400}{a^*}$	Acetone or alcohol	10
KR-3	B	150 to 300	5.0	4.0	do	$\frac{1600-2100^{**}}{a^*}$	acetone***	7 to 10
VIAM F-9	VIAM F-9	500 to 1000	2.5	3.5	do	$\frac{1400}{a^*}$	alcohol	10
KR-4	R	---	3.0	2.0	Grade 1 or grade 2 kerosene catalyst	$\frac{4500}{a^*}$	alcohol or acetone***	6 to 9
TsNIIMOD-1	TsNIIMOD	---	3.0	2.0	do	$\frac{3290}{a^*}$	---	---
TsNIIPS-1	TsNIIPS-1	not over 600	25.0	4.0	Mixture 2.25 weight parts kerosene and 10 weight parts formaldehyde	93	---	---
TsNIIPS-2****	TsNIIPS-2	not over 100	12.0	---	sulfuric acid (d = 1.80) Kerosene catalyst (acid no 65-75)	1 20	---	---

*a is the acid number of the kerosene catalyst

**depending on bonding temperature between 60° and 15°C

***the solvent is a component part of the adhesive

****the adhesive includes 10 weight parts glycerine and 5 weight parts tricesylphosphate

Properties of Adhesives and Adhesive Compounds Based On
Unmodified Cold-Cured Phenol-Formaldehyde Resins

Type of Adhesive	Properties of Adhesive			Bonding Mode				Shear Strength of Adhesive joint on wood at 20°C, kg/cm ²	
	Viability hours	Viscosity according to VZ-1, sec	Adhesive consumption g/m ²	Open Holding		Holding Under Pressure			
				Temp °C	Time, hr	Temp °C	Time, hr		Pressure, kg/cm ²
VIAM B-3	2 to 4	20 to 120	150 to 350	20	5 to 15	20	3 to 16	0.5 to 5.0	130
KB-3	2.5 to 4.0	20 to 90	180 to 250	20	5 to 15	20	5 to 25	0.3 to 5.0	180
VIAM F-9	2.0 to 3.5	18 to 80	150 to 200	20	10 to 15	18 to 23	At least 18	2.5 to 5.0	130
VZ1-F9	3.5 to 5.0	30 to 160	150 to 200* 700 to 800**	20 to 25	5 to 10	At least 20	At least 10	1 to 3	140 (at -60°C) 100***

*Bonding of organic glass

**Bonding of organic glass to synthetic fabric

***Strength of adhesive joint of organic glass at temperatures of -60° to +60°C

Designation

Trademark ----- S-1, S-35, SBS-1, SKS-1, SP-1, SBT,
 others
 Generic type ----- Unmodified phenol-formaldehydes,
 hot-cured

Description

Phenol-formaldehyde adhesives which are cured hot are widely used. Hot-cured adhesive resins are water-soluble. The bonding temperature of adhesive materials with phenol-formaldehyde hot-curing adhesives is 140° to 150°C.

Application

Adhesive resins of this type are used for bonding plywood, various types of plywood slabs, plywood pipes, shuttle materials (S-1 adhesive resin), water-resistant plywood (S-35 adhesive resin), layered wood plastics (adhesive resins SBS-1, SKS-1, SP-1), and food containers (SBT resin).

Phenol-formaldehyde low-viscosity resins type S-1, S-35, and SBT (20 to 30 sec on the VZ-4 viscosimeter) are used for the production of wood-chip plates.

Technological Status

Research ----- 1945 or earlier for basic types (est)
 Development ----- -
 Engineering ----- -
 Production ----- 1945 to 1947 (est)

Properties

Properties of Hot-Cured Phenol-Formaldehyde Adhesive Resins

Indicators	S-1	S-35	SBS-1	SKS-1	SP-1	SBT*
Concentration %	45 to 50	5±2	50 to 55	50 to 55	45 to 50	40 to 45
Content of free phenol, %	2.5	2.0	14	16	---	0.25
Viscosity, °E	100 to 300	150 to 300	15 to 40 and 40 to 100	15 to 40 and 40 to 100	15 to 45	30 to 100 and 150 to 300
Alkalinity, %	--3.5	4.5	---	---	2.5	2.5
Storage life, days	20 to 30	15 to 30	180	180	20 to 30	20 to 30
Peeling strength of plywood, kg/cm ²						
In dry state	20	15	---	---	20	15
After boiling water for 1 hr	18	10	30	30	18	10

*Content of free formaldehyde in resin not over 0.35%

- Notes:
1. S-1 resin is based on crystalline phenol.
 2. S-35 resin can be made with MLK phenol.
 3. SBS-1 resin (phenol) and SKS-1 resin (tricresol) are alcohol-soluble products.
 4. SBT resin is a water-soluble product of condensation of phenol and urea with formaldehyde in an alkaline medium with the addition of resorcinol.

Composition (weight parts) of Phenol-Formaldehyde
Hot-Cured Adhesive Resins

Initial Components	S-1	S-35	SBS-1	SKS-1	SP-1***	SBT
Phenol	100	100*	100	---	100	100
Phenol fraction	---	---	100**	---	---	---
Tricresol	---	---	---	100	---	---
Formalin (37%)	127	129.72	100	100	115	169
Caustic soda (40%)	25	25	---	---	18.75	25
Ammonia (25%)	---	---	6	3	---	---
Urea	---	---	---	---	---	---
Resorcinol	---	---	---	---	---	75
Ethanol	---	---	---	---	8	8.5
Water	63	165.28	---	---	31.25	131

*The free phenol fraction or tricresol can be used instead of phenol.

**The free phenol fraction used in place of phenol.

***The formula for the resin includes 4 weight parts Petrov reagent.

Designation

Trademark ----- Rezol-300
 Generic type ----- A-stage phenol-formaldehyde (PF)
 (used in making VK-4)

Description

An important component of VK-4 is the PF resin Rezol-300, which has a long gelling time. The quality of bonds made with VK-4 adhesive depends on the properties of different batches of this A-stage resin. VK-4 has been described as a phenolic-methylolpolyamide resin modified with SKN-40 acrylonitrile rubber.

Application

VK-4, derived from a modified phenolic (Rezol-300) and SKN-40 rubber, is widely used by the Soviets for joining metals and bonding honeycomb structures. Service temperature up to 275°C is claimed.

Technological Status

Research ----- 1964 to 1965 (est)
 Development ----- 1966 to 1967 (est)
 Engineering ----- 1966 to 1967 (est)
 Production ----- 1968 (est)

Properties

With increase in the gelling time, the bond strength of the honeycomb structure at room temperature and at 275°C increases. This may be explained by the fact that a PF resin, like all high-molecular compounds, is polydispersed and contains many fractions differing in their gelling time and MW.

Influence of Gelling Time of Rezol-300 Resin
on the Strength of Honeycomb Structure Bonded Joints

Resin batch	Gelling time, sec	Resistance to direct pull, kgf/cm ²	
		20°C	275°C
A	326	25.8	10.8
B	368	22.9	9.9
C	398	25.3	12.0
D	410	31.2	14.4
E	615	31.5	16.2

Main Physico-Chemical Characteristics of Rezol-300 Resin

Form of Resin	Batch A		Batch B		Batch C		Batch D				
	Gelling time, sec	MW*	Gelling time, sec	MW*	Gelling time, sec	Viscosity, cS	Gelling time, sec	Viscosity, cS	Content of hydroxyl groups, %	Viscosity, cS	MW*
Initial	368	235	362	265	398	---	250	410	---	---	---
Re-precipitated fraction	307	300	304	320	342	167	375	334	17.3	591	290
1	Does not melt	800	Does not melt	870	Does not melt	---	750	Does not melt	16.4	---	770
2	do	490	do	580	do	1130	520	do	16.8	1409	600
3	339	310	292	350	377	163	350	282	16.8	238.3	430
4	714	215	1175	190	1115	25.5	220	1048	19.1	24.5	210

*Molecular weight

Dependence of the Strength of the Bonded Joints
(VK-4 Bonding Agent) on the Polymerization Time
of Rezol-300

Polymeri- zation time, sec	Shear Strength, kgf/cm ²		Shear strength, kg/cm ² , after ageing at 300°C		Peeling strength at 20°C, kgf/cm	Color of the film of the bonding agent
	20°C	300°C	20°C	300°C		
277	185	22	86	37	18	Grey (brittle)
343	192	30	137	36	21	Blackish-grey (brittle)
372	203	33	129	75	36	Blackish-grey (elastic)
448	237	36	120	90	33	Black (elastic)
582	206	40	90	77	37	do
603	190	57	118	55	32	do

Note: According to the TU specification the shear strength (σ_{sh}) at 20°C is greater than 150 kgf/cm², at 300°C, $\sigma_{sh} > 30$ kgf/cm², while the peeling strength at 20°C is 28 kgf/cm.

Raising free phenol by 12% to 20% gives no marked change in joining strength; 20 percent phenol does not corrode VK-4 joints of 30 KhGSA steel or aluminum.

Strength Characteristics of Joints Between 30KhGSA Steel,
Made With VK-4 Adhesive Obtained From Different Fractions of
the PF Resin

Form of Resin	Appearances of Adhesive Film	Shear strength, kgf/cm ²		Peeling strength, kgf/cm
		20°C	300°C	20°C
Initial	Black, elastic	178 to 226	52 to 69	28 to 44
Re-precipitated	Black, less elastic	161 to 193	43 to 70	23 to 30
Fraction				
1	Grey, brittle	76 to 160	26 to 54	13 to 21
2	Black with grey deposit	152 to 169	49 to 57	18 to 23
3	Black, glossy elastic	153 to 179	39 to 62	25 to 27
4	Black, glossy elastic	218 to 286	35 to 50	38 to 46
Norm	Black, elastic	150	30	23

Strength Characteristics of Joints in a Honeycomb Structure Made
With VK-4 Resin Obtained From Different Fractions of the PF Resin

Form of Resin	Strength			
	direct pull, kgf/cm ²		peeling, kgf/cm	
	20°C	275°C	20°C	275°C
Initial	22.0 to 31.2	11.6 to 14.4	11.6 to 14.4	7.5
Re-precipitated	21.7 to 30.8	13.4 to 15.0	8.0 to 14.0	4.3
Fraction				
1	16.3 to 27.3	9.5 to 11.1	6.8 to 10.0	4.3
2	17.2 to 31.8	11.9 to 15.8	7.5 to 11.8	5.8
3	28.0 to 32.8	14.0 to 16.7	10.7 to 13.7	9.5
4	29.8 to 36.5	15.7 to 19.6	13.1 to 19.0	11.0
Norm	26	13	---	---

Fractions 3 and 4 (which have the lowest molecular weight) have a molecular weight of 190 to 220 and a gelling time of 714 to 1175 sec. They are readily soluble in alcohol and can be used to produce a black, highly elastic film (particularly fraction 4). The strength characteristics of the bonded joints in the honeycomb structure obtained with VK-4 adhesive are higher at all test temperatures than those of the joints obtained using the initial resin.

The best quality of films is obtained with Rezol-300 (cure time: 378 sec) dissolved in the absolute alcohol. The peeling strength of joints based on these films is higher (liquid bonding agent: 43 kgf/cm; film-form: 47 kgf/cm) than it is when the resin is dissolved in high purity water-containing alcohol (liquid bonding agent: 23 kgf/cm; film: 28 kgf/cm).

The following table shows the dependence of strength of the joints (and also of the quality of the resin) and the bonding agent films on the storage time of the Rezol-300. The cure time of the dry resin and the shear strength of the joints change only slightly over 6 months' storage (and correspond to the TU specification for the bonding agent).

Dependence of the Strength of Bonded Joints (Using VK-4)
on the Storage Time of Dry Rezol-300

Resin	Storage time, months	Polymerization time, sec	Color of film of bonding agent	Shear strength kgf/cm ²			Peeling strength at 20°C, kgf/cm
				20°C	275°C	300°C	
Dry	0	412	Black	207	75	44	31
	3	---	do	218	63	42	25
	6	389	do	208	80	55	26
Solution in ethyl alcohol (60%)	0	390	do	165	91	31	23
	1	375	do	163	74	40	--
	3	305	Black with grey tinge	205	119	61	23
	6	270	Grey	184	83	57	8

Rezol-300 was first produced by a process involving a three-fold washing of the resin in the last stage of polycondensation. The resin is initially washed with cold water and then with water heated to 50° to 60°C. The resin is dried at 25° to 40°C to a moisture content of no higher than 3%. An improved process has been developed that eliminates the washing stages. Here the resin is dried in vacuo at 60° to 80°C, giving a translucent melt. At the end of this drying period, the resin is collected in the dry form.

Designation

Trademark -----	FF-40
Generic type -----	Phenol-phenolphthalein-formaldehyde modified with epichlorohydrin (called polyglycidyl ethers)

Description

Polyglycidyl ethers are produced by the reaction of PF oligomers of novolak, or A stage resin type, with excess of epichlorohydrin, in the presence of an alkali. Various substituted derivatives of phenol used in the production of the initial PF oligomers make it possible to vary the properties of the final products within wide limits. For instance, polyepoxy oligomers synthesized from alkylated phenols have good solubility in several organic solvents. Polyepoxy resins obtained from novolak oligomers (based on phenol) have improved heat resistance after being hardened with amines or with anhydrides.

Application

Glycidyl ethers may be used as adhesives for substrates with high structural and high heat (225° to 250°C) performance.

Technological Status

Research -----	1966 (est)
Development -----	1967 (est)
Engineering -----	1969 (est)
Production -----	1972 (est) (Production may be limited)

Properties

Polyglycidyl ethers are obtained either as liquids or solids. They are soluble in acetone, methyl alcohol, and other solvents. The most heat-resistant polymers are obtained on the basis of an A stage resin oligomer with high content of methylol groups. The glycidyl ethers of these oligomers contain many functional groups which are capable, by reaction with amines or anhydrides of dicarboxylic acids, of giving branched three-dimensional polymers resistant to high temperatures.

Properties of the Hardened Polyglycidyl Ethers*

Batch of FF-40 resin	Molar ratio FF-40: ECH***	Content of fraction insoluble in acetone, %	Coke Number, %	Heat distortion temperature, ** °C	Temperature corresponding to 10% weight loss, °C	Weight loss, in %, in heating at 300°C for time, hours		
						1	3	6
1	45	98.1/98.5	51.1/47.2	305/220	290/265	25.3/32.3	34.2/39.7	40.1/52.2
	60	99.0/98.7	60.0/53.0	345/265	340/315	21.4/29.0	25.5/35.4	34.0/43.3
	90	96.6/97.2	64.4/58.1	360/250	370/330	17.8/27.5	21.9/28.0	29.7/31.1
2	60	97.7/98.2	46.7/42.8	300/215	280/250	27.7/40.0	37.1/54.6	44.5/60.2
	90	98.4/96.8	50.2/47.3	330/225	310/295	22.2/31.6	30.2/42.8	40.3/58.6
3	45	97.1/97.0	53.5/48.8	310/240	300/270	23.1/32.8	29.3/40.0	39.4/54.3
	60	99.3/98.7	61.0/55.4	360/280	350/320	17.8/27.5	21.9/28.0	32.7/40.2
	90	98.8/97.9	66.6/59.3	365/260	385/340	16.6/21.1	20.8/27.6	30.5/36.6

*Figures before the stroke, polyglycidyl ether hardened with trimellitic anhydride; after the stroke, hardened with m-phenylenediamine.

**Deformation of the specimen by 20% at the temperature indicated.

***Epichlorohydrin.

Designation

Trademark ----- Fenofmolits
 Generic type ----- Arylene-phenol-formaldehydes

Description

The process for making these resins is licensed by the LITSENZINTORG Company (Moscow V-420).

Fenofmolits are produced by condensation of eutectic mixtures of aromatic hydrocarbons of any reactivity and degree of polycyclic structure, with phenol and formaldehyde, in a weakly acidic medium. This method has the advantage over the previous two-stage methods as it is implemented in the presence of catalytic amounts of acids and does not require the employment of special acid-resistant apparatus or the recovery of considerable amounts of sulphuric acid.

Application

These arylene-phenol-formaldehyde resins can be used as binder resins in the production of glass reinforced plastics; they can be used as general adhesives for various substrates up to about 140°C. (Molding compounds can be made of filled resins for use in electrical and electronic end items.)

Technological Status

Research -----	-
Development -----	1966 (est)
Engineering -----	-
Production -----	1970

Properties

The Soviet development of these modified phenolics shows their desire to pursue programs that reduce the cost of primary high-usage resins. For the starting material for the production of the arylene-phenol-formaldehyde, resins waste from the "coke-chemical" industry is used. The cost of 1 ton of Fenofmolits is said to be reduced by 25%, compared with that of 1 ton of phenol-formaldehyde resin.

The employment of eutectic mixtures of hydrocarbons in Fenofmolits makes it possible to extend the range of hydrocarbons now employed by using those with high melting point. In addition to artificial eutectic mixtures of hydrocarbons, it is possible to use natural complex eutectics (e.g., crude anthracene).

The characteristics of resins based upon these "coal-tar" derivatives are shown below:

Characteristics	Resins based on		
	crude anthracene	eutectic mixture of fluoranthene and pyrene	eutectic mixture of caronene (sic) and pyrene
Time of gelling on a tile at 160°C, sec	60 to 18	80 to 90	60 to 70
Amount of extractibles in 1:1 alcohol-benzene mixture, %	2 to 3	2 to 3	2 to 3
Coke number, %	60 to 63	65 to 67	70 to 72
Ubbelohde drop point, °C	110 to 120	104 to 106	110 to 115
Weight loss at temperature, °C			
100	0	0	0
200	0	0	0
300	1.9	1.7	1.1
400	5.5	5.3	4.2
500	23.7	23.2	20.8

Designation

Trademark ----- VK-32-200, VK-32-250, VK-3, VK-4,
 VK-13, VK-13M, VK-32-2, others
 Generic type ----- (Phenol-formaldehyde)-(butadiene-
 acrylonitrile) copolymer variants

Description

V. A. Kargin and others have produced block copolymers of phenol-formaldehyde resins of novolak type with butadiene-acrylonitrile rubber. The combination of acrylonitrile rubber with small quantities of novolak resin forms block copolymers of high strength. Cresol, phenol-furfural, and resorcinol resins, in combination with acrylonitrile rubber, are most frequently used for the manufacture of adhesives. The introduction of cresol-formaldehyde resin lowers the resistance of the adhesive compounds to the effects of high temperatures. The best adhesive properties are those of compositions based on phenol-formaldehyde resin and acrylonitrile rubber (containing at least 40% acrylonitrile). In addition to acrylonitrile rubbers, phenol-rubber adhesives are made with polychloroprene (neoprene) in combination with polyamide (nylon). Adhesive compositions with polychloroprene rubber are less heat resistant than those with acrylonitrile rubber.

Application

VK-32-200, VK-3, VK-4, VK-13, and VK-13M structural adhesives are used for bonding of metals and as for glass-reinforced plastics and other materials. VK-32-200 adhesive is designed for bonding of glass-fiber heat-insulating materials to metals at room temperature. The adhesives consist of two components that are mixed before use.

Phenol-rubber adhesives are widely used for gluing of honeycomb structures of metals and glass-reinforced plastics. When honeycomb structures are bonded, special bonding modes are used. The adhesive joints of honeycomb structures characteristically show high strength indices. Structural phenol-rubber adhesives are also produced in the form of films.

Technological Status

Research ----- 1959 (est) for original types
 Development -----
 Engineering -----
 Production ----- 1960 (est) for original types
 Development work continues on new
 variants

Properties

At high temperatures, phenol-rubber structural adhesives retain satisfactory long term strength, as can be seen from the example of VK-32-200, VK-13, and VK-13M adhesives. As to the resistance to the effects of water and various climatic conditions, phenol-rubber adhesives are claimed to be the best of all known structural adhesives.

Long-Term Strength of Adhesive Joints With
Structural Phenol-Rubber Adhesives at 20°C

Adhesive Type	Shear Stress, kg/cm ²	Time to Rupture, hr
VK-32-200	140	500
VK-3	80	500
VK-1	130	500
VK-13	125	1000
VK-13M	90	500

Composition and Properties of Phenol-Rubber Structural Adhesives

Adhesive type	Components						Viscosity on VZ-1, sec
	Phenol resin		Rubber mixture		Viability of adhesive, hr	Storage life, months	
	Name	Storage life, months	Name	Storage life, months			
VK-32-200	IF Varnish	3	Product No. 3	3	At least 24	15-70	
VK-3	IF Varnish	3	Product No. 4	3	6-24	15-100	
VK-4	Resol 300	6	Product No. 5	3	24	Not over 350	
VK-13	Resol 300	6	Product No. 6	4	24	Not over 200	
VK-10M	Resol 300	6	Product No. 7	4	24	200	

Note: Product No. 3 is acrylonitrile rubber plus hardener; No. 4 is modified acrylonitrile rubber; No. 5 is acrylonitrile rubber with mineral filler; No. 6 is carboxyl-containing rubber; No. 7 is carboxyl-containing rubber with mineral filler.

Strength of VK-4 Glue Adhesive Bonds Between D16 Alloy Sheet and Honeycomb Filler of Foil 0.05 mm Thick (Cell Size: 5mm)

Filler Material	Test Conditions	Layer separation strength, kg/cm ²	Rupture through foil	Layer separation strength, kg/cm ²	Rupture through foil
		At 20°C		At 275°C	
AMg Aluminum alloy foil	Initial data	30.4	75	17.4	60
	After holding for 50 hr at 275°C	21.2	73	12.5	53
Foil of sintered aluminum powder	Initial data	29.7	40	18.2	Through adhesive
	After holding for 50 hr at 275°C	17.7	Through adhesive	13.6	Through adhesive

Shear Strength of Adhesive Joints of Liquid and Film Phenol-Rubber Glues

Type of Glue	Shear Strength, kg/cm ²				
	At -60°C	At 20°C	At 80°C	At 200°C	At 300°C
VK-32-200:					
liquid	180	170	---	70	35
film	230	160	---	60	22
VK-3:					
liquid	350	170	110	60	---
film	300	150	100	50	---
VK-4:					
liquid	280	150	---	70	30
film	240	125	---	60	35 (275°C)

Fatigue Shear Strength of Adhesive Joints in Duralumin Made
With Phenol-Rubber Structural Adhesives at 20°C

Adhesive type	Maximum Cycle Stress,* kg/cm ²			Adhesive type	Maximum Cycle Stress,* kg/cm ²		
	10 ⁵ cycles	10 ⁶ cycles	10 ⁷ cycles		10 ⁵ cycles	10 ⁶ cycles	10 ⁷ cycles
VK-32-200	75	55	37	VK-13	---	---	105
VK-3	90	82	75	VK-13M	---	---	85
VK-4	95	85	75				

*cycle asymmetry factor in tests $f = \sigma_{\min} / \sigma_{\max} = 0.1$.

Long Term Strength of Adhesive Joints of Metals Made With
VK-13 and VK-13M Adhesives at High Temperatures

Type of Adhesive	Metal Bonded	Test Temperature, °C	Shear Strength, kg/cm ²	Time to Rupture, hr
VK-13	30KhGSA Steel	250	46	1000
			30	1500
		300	27	80
			10	500
			5	1000
VK-13M	Duralumin	200	43	500

Uneven Tensile Strength of Adhesive Joints Based on Structural
Phenol-Rubber Adhesives

Adhesive type	Uneven Tensile Strength, kg/cm ²						
	At -60°C	At 20°C	At 80°C	At 150°C	At 200°C	At 250°C	At 300°C
VK-32-200	20	30	---	17	10 to 12	10	5
VK-3	38	65	50	28	16 to 20	---	---
VK-4	25	32	---	---	---	9.5*	6
VK-13	33	45	---	---	16	12	8
VK-13M	60	45	35	---	8	---	---

*At 275°C

Designation

Trademark ----- BF-2, BF-4, BF-6, FA-24, BFR-2,
 VS-10T, VS-350, FRAM-30
 Generic type ----- Phenolic-Poly(vinyl butyral)

Description

The BF adhesives are alcoholic solutions of phenolic resin and poly(vinyl butyral). BF-6 contains plasticizers and colophony. Poly(vinyl butyral) containing 43% to 48% butyral groups and not over 3% acetate groups is used to produce adhesives. The poly(vinyl butyral) is dissolved in 95% ethyl alcohol; the viscosity of a 10% to 13% solution is 30 to 60 sec using a Ford-Engler viscosimeter. The resol resin used to manufacture BF adhesives is produced by condensation of 5 moles phenol with 6 moles formaldehyde in the presence of 1.5% ammonia (a catalyst of the process). The resin should have a concentration of 50% to 65%; curing time at 150°C should not exceed 90 to 100 sec, content of free phenol -- not over 15%.

FA-24 adhesive is a composition based on phenol-formaldehyde resin and poly(vinyl formal) plus alkoxysilane. The adhesive has high shear strength when it is used to bond various materials and differs from BF adhesive in its higher thermal stability.

BFR-2 adhesive is a phenol-formaldehyde resin of resol type, modified with poly(vinyl butyral furfural). The viscosity of the adhesive, determined with the VZ-1 device, is 70-90 sec, dry residue 14% to 18%. The strength of an adhesive joint of duralumin at 20°C is about 200 kg/cm², at 200°C about 100 kg/cm². Adhesive joints using BFR-2 adhesive withstand heating to 200°C for 500 hours.

The basis of VS-10T and VS-350 adhesives is VS-10 composition, which is a mixture of poly(vinyl acetal) containing free hydroxyl groups and alkoxysilane. The components of this mixture do not react with each other at normal temperatures; when heated, the chains of the poly(vinyl acetal) are cross-linked by siloxane bridges at the points of location of the hydroxyl groups, forming a three-dimensional polymer. Bonding with VS-10 composition leads to the formation of strong adhesive joints of metals and nonmetallic materials; however, when the temperature increases, the shear strength of the adhesive joints using VS-10 decreases from 250 kg/cm² at 20°C to 15 kg/cm² at 100°C, which apparently results from the insufficient rigidity of the three-dimensional grid formed. Type VS-350 adhesive differs from VS-10T in that it contains phenol-formaldehyde-furfural resin. Adhesive joints made with VS-350 adhesive have shear

strength near the strength of VS-10T adhesive joints, but significantly higher strength for even separation and long-term strength at high temperatures. Type FRAM-30 adhesive consists of two components: the binder (resin) and accelerator. The shelf life of the adhesive with the accelerator is 16 to 24 hours, dry residue 10% to 15%.

Application

BF-2 and BF-4 adhesives are suitable for bonding of metals, plastics, and ceramics. It is recommended that BF-4 adhesive be used for bonding of thermoplastics. BF adhesives are also suitable for bonding of such materials as organic glass, wood, plywood, fiber board, leather, ebonite, and paper. BF-2 and BF-4 adhesives are used as films, produced by pouring the liquid adhesive on the surface of glass or polyvinyl chloride plastic and subsequent removal of the solvent.

Heat-resistant adhesive types RAF-10 and RAF-50 have been described, based on phenol-formaldehyde resins. The first of these adhesives is recommended for bonding of plastics, phenoplasts, organic glass, capron, and acrylonitrile fiber. Composition RAF-50 can be used to bond metals; the shear strength of bonds in duralumin at 20°C is 120 to 160 kg/cm², at 300°C--20 to 50 kg/cm². The adhesive is used in the manufacture of resistance tensometers for measurement of deformation at high temperatures.

A combination of VS-10 composition with various phenol-aldehyde resins was used to produce the adhesives VS-10T and VS-350. These adhesives are designed for bonding of metals and heat-resistant nonmetallic materials. Steel of various types (30KhGSA, ST3, ST20, EYalT, etc.), anodized aluminum with aqueous, and bichromate filler are firmly bonded by these adhesives. The adhesives are suitable for joining textolites of various types and bonding them to metals, and also for bonding heat resistant gas-filled plastics (foam plastics) of types FK, K-40, etc.

Technological Status

Research -----	1947 through 1965 (est)
Development -----	--
Engineering -----	--
Production -----	1950 (early types) (est) 1963 to 1964 (Modified types) (est)

Properties

Adhesive joints of BF-2 and BF-4 adhesive are resistant to temperature drops between -60° and +60°C. After 50 cycles of varying application of

these temperatures, the shear strength exceeds 100 kg/cm². Joints using BF-2 adhesive have satisfactory shear strength at various temperatures (from -60° to +60°C), and also after cyclical application at high and low temperatures (3 cycles of heating to 200°C and cooling to -70°C). The shear strength of BF-2 adhesive joints does not change after heating to 60°C for 500 hours.

Strength of Adhesive Joints of Various Materials Using BF Adhesives

Materials Bonded	Type of Adhesive	Shear Strength kg/cm ²
Steel + Steel	BF-2	300 to 350
Copper + copper	BF-2, BF-6	150 to 200
Metal + polystyrene	BF-4	40 to 50
Ceramic + polystyrene	BF-4	100 to 140
Phenoplast + polystyrene	BF-4	40 to 50
Phenoplast + phenoplast	BF-2, BF-4	150 to 200

The long-term strength and endurance of adhesive joints between metals using BF-2 adhesive are relatively low. Joints made with BF-2 and BF-4 adhesives have satisfactory water resistance. The shear strength drops after exposure to water for 30 days (for BF-2 adhesive), after which it does not change for 7 months. Adhesive joints using BF-4 adhesive (due to the high content of poly[vinyl butyral]) are less water resistant; the decrease in water resistance continues for 70 days and reaches 42%, after which the water resistance does not drop any further for 7 months. The strength of adhesive joints using BF-2 adhesive, following holding for 500 hours in oil and alcohol-glycerine mixture, does not change; the action of gasoline (500 hours) leads to a drop in strength of 3%.

Strength of Adhesive Joints Using VS-10T Adhesive

Materials Bonded	Type of Test	Shear Strength, kg/cm ²		
		At 20°C	At 150°C	At 300°C
Steel 3 + steel 3	Shear strength	185	140	60
D16 aluminum alloy + D16 aluminum alloy	do	130	100	40
Textolite, VFT-S + 30KhGSA steel	do	160	100	58
Steel 3 + honeycomb of textolite	Even separation strength	12	8	2.3
Foam plastic K-40 + 30KhGSA steel	Same	5*	2.5*	---

*Ruptures through foam plastic.

FRAM-30 adhesive has good adhesion to duralumin, steel, copper, silver, and other metals and their alloys and to chemically treated teflon. The materials are bonded with liquid adhesive and with films of adhesive with liquid adhesive sublayers. The film adhesive is produced by pouring out the liquid adhesive; a film 0.16 to 0.3 mm thick is used for bonding.

Strength of Adhesive Bonds on Chemically Treated Teflon Using FRAM-30 Adhesive

Material Bonded	Shear Strength, kg/cm ²	Even Separation Strength, kg/cm ²
Teflon	67 to 95	128 to 148
Duralumin + teflon	60 to 90	---

Designation

Trademark ----- Unknown
 Generic type ----- Phenol-formaldehydes modified with
 glycidyl ethers of oximes

Description

Soviet work has been directed to the modification of PF resins with epoxy compounds by making mixed compositions to include oxime containing epoxies.

Application

No specific application is known for these variants. They may have use where a moderate increase in electrical and thermal properties is required, such as in dielectric coatings and binders.

Technological Status

Research ----- 1966 (est)
 Development -----
 Engineering -----
 Production ----- 1964 (est) May be limited. The oxime
 variants appear to be prototype
 forms.

Properties

Properties of PF Resins Modified With Nitrogen-Containing Epoxy Compounds
 (8-19%)

Epoxy compound	Adhesion strength, kgf/cm ²	Electric strength, kV/mm	Epoxy compound	Adhesion strength, kgf/cm ²	Electric strength, kV/mm
I*	49.0	26.0	I**	25.0	33.0
II*	59.4	37.5	II**	23.0	35.0
III*	50.0	32.5	III**	27.0	24.0
IV*	34.0	34.0	IV**	21.0	24.0
V*	36.0	36.0	V**	23.0	26.0

*Resins produced in alkaline medium (pH=9-10); hardening conditions:
 t=140-150°C; Time: 5 hours

**Resins produced in acidic medium (pH=2-3); hardening conditions:
 t=140-150°C; Time: 8 hours

The modification of the PF resins by the nitrogen-containing epoxy compounds is carried out in acidic (pH=2 to 3) and alkaline (pH=9 to 10) media. The glycidyl ethers are oximes of benzaldehyde (I), methyl ethyl ketone (II), isovaleraldehyde (III), cyclohexanone (IV), and acetophenone (V). Chemical analysis of the resulting resins shows the presence of secondary hydroxyl groups and the absence of epoxy groups.

Higher adhesion and electrical strengths are found with the resins produced in an alkaline medium with aliphatic nitrogen-containing glycidyl ethers (II, III). The adhesion strength is considerably less in the resin modified with the glycidyl ether of cyclohexanone oxime (IV). An intermediate position in certain characteristics is occupied by resins modified with the glycidyl ethers I and V.

The characteristics of the resins modified with nitrogen-containing epoxy compounds of the aliphatic, aromatic, and cycloparaffin series are higher than the analogous characteristics of phenolic resin modified with epoxy compounds of the cycloparaffin and aromatic series.

Designation

Trademark -----	BF
Generic type -----	Complex phenolic resins modified with cyclic unsaturated compounds

Description

Cyclic unsaturated modifiers include coumarone-indene, styrene, and cyclopentadiene. To produce cold-hardening compositions, the phenolic resin is modified with the propargyl ester of β -(cyclohexene-3) glycidic acid. The resulting resin is a viscous liquid and light yellow in color. It dissolves in almost all hydrocarbons, chlorinated hydrocarbons, oxygen-containing solvents, and alcohol.

With the addition of the modifier (the propargyl ester of β -[cyclohexene-3] glycidic acid), secondary hydroxyl groups are formed as a result of opening of the epoxide ring. The resin also contains a small amount of epoxide groups, probably as a result of partial combination of the propargyl ester of β -(cyclohexene-3) glycidic acid with phenol. The presence of hydroxyl and epoxide groups in the resin makes it amenable to hardening by the usual methods.

Application

Coumarone-indene resins are used in the coatings, paint, and varnish industries. Some resins are soluble in acetone and can be used as adhesive compositions where moisture may be present. The adhering of floor tiles and the fabrication of chipboard panels are specific applications.

Technological Status

Research -----	1968 (est)
Development -----	
Engineering -----	
Production -----	Unknown

Properties

These modified phenolic resins show improved properties over conventional heat-cured phenol-formaldehyde BF resins. The mechanical and dielectric properties of the synthetic resin, hardened with various hardeners, and the properties of ED-6 epoxy resin and standard BF are shown.

Mechanical Properties of the Hardened Synthetic Resin

Property	Composition			ED-6 resin, + phthalic anhydride	BF resin, heat hardening
	I	II	III		
Density, g/cm ³	1.2	1.3	1.3	1.2	1.4
Tensile strength, kg/cm ²	600	700	700	700	up to 500
Impact strength, kg-cm/cm ²	8.5	10	10.5	12	4
Martens yield temperature, °C	---	90	100	110	110
Shrinkage in hardening, %	---	2.5	2.5	up to 2.3	---
Electric strength, kV/m	18	17	16	15.7	10
Dielectric strength at 10 ³ Hz	3.6	3.63	3.7	3.65	6.0

The hardening agent for composition I is polyethylenepolyamine (PEPA) (resin: PEPA; 100:1); composition II is phthalic anhydride (resin: phthalic anhydride; 10:3); composition III is maleic anhydride (resin: maleic anhydride; 10:3).

The conditions of curing of these compositions are as follows:

Composition	<u>I</u>	<u>II</u>	<u>III</u>
Hardening temperature, °C	-- 20	150	150
Time, hr:			
gelling -----	1.5	7	2
setting -----	3	18	8
complete hardening -----	24	24	24

A composition consisting of 100 parts by weight of synthetic resin and 10 parts by weight of PEPA has adequate strength of adhesion to metal. In lap-bonding of two metal sheets, the shear strength of the bond seam, 1 day after bonding, is 200 kgf/cm².

One claimed advantage of the synthetic resin is that in making chip-board panels, the hardening of the composition does not require high temperatures. The panels were molded at 60° to 80°C and have high mechanical strength, a flexural strength of 550 to 700 kgf/cm², and low water absorption in 24 hr (3% to 4%).

Designation

Trademark ----- BFR-2, BFR-4
 Generic type ----- Modified phenolic butanol

Description

Adhesives BF-2 and BF-4 are described as butvar-phenolic adhesives. BFR-2 and BFR-4 are solutions in alcohol of a modified phenol-formaldehyde resin FR-200.

Application

These heat-resistant phenolic-butyral s are used primarily to bond metals or glass-reinforced plastic sheeting to metallic or nonmetallic honeycomb structures. The BFR-2 and BFR-4 resins are used in fabricating thin film dielectrics for circuit-board technology.

Technological Status

Research ----- 1964 (est)
 Development ----- 1965 to 1966 (est)
 Engineering ----- 1966 to 1967 (est)
 Production ----- 1968 (est)

Properties

The bond strengths after testing under various climatic conditions are as follows:

	<u>BFR-2</u>	<u>BFR-4</u>
Shear strength, kgf/cm ² :		
In initial state -----	128	165
After 48 hr at -60°C -----	124	144
Heat impact (2 hr at -60°C and 2 hr at 200°C, 3 cycles with transition from -60 to +200°C in 1 min) -----	108	150
After 5 days at 40°C under conditions of 98% relative humidity -----	125	155

An important factor in the production of thin film dielectrics is the choice of the adhesive for bonding the copper and for joining it to Getinaks (a laminated paper material using phenol-aldehyde resin) and

GRP's. BFR-2 and BFR-4, which are capable of operating for long periods at 180° to 200°C, may be used for bonding metals and non-metals and are claimed to give service under various climatic conditions.

The best results are reported with BFR-4. Data on the bond strength, in gf/cm, of copper foil and Getinaks or GRP in the initial state and after holding under various climatic conditions are given below:

<u>Conditions of Testing</u>	<u>Getinaks</u>	<u>GRP</u>
Bond strength, gf/cm:		
In the original state -----	1600 to 2100	1900 to 2050
At 180°C -----	---	400 to 800
After holding for:		
100 hr at 180°C -----	---	1400 to 1500
5 hr at 150°C -----	1550 to 2000	---
6 hr at -60°C -----	---	1950 to 2150
After holding in molten solder (t=260°C) for 15 sec -----	1700 to 2400	---
After holding under conditions of 98% relative humidity		
48 hr -----	---	1850 to 2150
30 days -----	---	1750 to 1850

Designation

Trademark -----	VIAM B, VIAM F-9 modified with NVB-2; RFT
Generic type -----	Cold-hardening phenol-formaldehyde modified with liquid polysulphide (thiokol); resorcinol-formaldehyde-sulphide rubber binder (RFT)

Description

Phenol-formaldehyde A stage liquid resins are widely used for the preparation of different cold-hardening polymer materials. The brittleness of the hardened A stage resins limits their range of application. To make the products of hardening more elastic, the liquid A stage resins are normally treated with rubber solutions. This increases the content of inert solvent in the binder; however this is not always practical.

PF resins can also be modified by combining them with liquid rubbers. A liquid rubber used for the modification of cold-hardening PF binder resins must have unlimited compatibility with the liquid A stage resins and should be capable of being cold-hardened.

A rubber satisfying these conditions is the liquid polysulphide rubber NVB-2 thiokol; its viscosity does not exceed 150 cP. Phenolic VIAM B and VIAM F-9 and resorcinol-formaldehyde (RF) are modified with this rubber.

Application

A possible application of these materials could be in GRP's and glass-fiber laminates.

Technological Status

Research -----	1967 (est)
Development -----	1968 (est)
Engineering -----	1969 (est)
Production -----	1970 (est); probably restricted to limited quantities of resorcinol-formaldehyde-thiokol material.

Properties

The preparation of the RFT binder resin consists of dissolving the resorcinol in the furfural and then mixing the solution with the thiokol.

The storage life of RFT binder containing no hardener is up to 10 days at 20°C, and up to 20 days at 0° to 2°C. In the presence of the hardener, the storage life of the binder varies from 20 min to 3 hours, depending on the amount of hardener and whether or not a filler is present. Materials based on this resin are hardened at 20°C for a period of 36 to 48 hours or at 80°C for 2 to 4 hours.

Some mechanical properties of materials based on RFT binder resin containing 70% thiokol are given as follows:

Mechanical Properties of Materials Based on RFT Binder Resin

Material	Tensile strength, kgf/cm ²	Flexural strength, kgf/cm ²	Impact strength, kgf-cm/cm ²	Elongation at break, %
Hardened binder containing no filler	15	Material is elastic	12	15 to 20
Composition with quartz powder filler (75%)	70	110	13.8	2.5
"Asbotekstolit" (i.e., hot-pressed resin impregnated asbestos fabric laminate)	---	600	---	7

Designation

Trademark -----	Unknown
Generic type -----	Phenol-formaldehyde-epoxy-sulphide resins

Description

Epoxy sulphides are obtained by the reaction of 1-thiol-3-chloropropanol-2, cyclohexene, and dicyclopentadiene, with subsequent treatment of the product by NaOH in ether.

Similarly, epoxy sulphides are synthesized by the combination of 1-thiol-2-acetoxy-3 (sic)-propane with acrylonitrile and butoxyvinyl (sic) with subsequent hydrolysis of the acetates to the corresponding chlorohydrins and treatment with NaOH in ether.

The modification of PF resins by the epoxy sulphides is carried out at the following phenol to formaldehyde to epoxy sulphide molar ratios: 3/3.5/1 (for an alkaline medium with pH value 9-10) and 3.5/3/1.17 (for an acidic medium with pH value 2-3).

The catalyst used for the alkaline medium was a 25% aqueous solution of ammonia (5% on the phenol), and for the acidic medium it was hydrochloric acid (density 1.19g/cm³, 1% on the phenol). The resins synthesized ranged in color from light brown to dark brown. These are readily soluble in acetone and alcohol.

Application

Epoxy sulphide modified phenol-formaldehydes can be used as bonding agents for various substrates at temperatures up to 120°C.

Technological Status

Research -----	1966 (est)
Development -----	1968 (est)
Engineering -----	1970 (est)
Production -----	1972 (est)

Properties

The physical properties of modified PF resin are shown as follows:

Physical Properties of PF Resin, Modified with Epoxy Sulphides

Property	Initial PF resin 1	PF resin, modified with epoxy sulphides			
		I	II	III	IV
Electric strength, kV/mm	18 to 20/14 to 18	32/30	28/26	24/22.5	33.5/31.2
Brinell hardness, kgf/mm ²	25 to 30/22 to 25	32/30	30.2/28.3	29.3/27.1	33.2/31.4
Martens yield temperature, °C	115 to 140/110 to 125	145/140	140/137	138/132	150/145
Impact strength, kgf-cm/cm ²	2.5 to 10/2.5 to 9	9.5/8.2	8.4/7.1	7.8/6.4	10.2/9.5
Flexural strength, kgf/cm ²	600 to 700/580 to 650	730/700	650/600	610/580	750/720
Adhesion strength, kgf/cm ²	25 to 30/20 to 28	47.5/45.2	40.2/38.1	32.4/30.3	49.2/46.1

Note. Figures before the stroke, for alkaline medium; after, for acidic medium.

Designation

Trademark -----	FR-12, KF-12; DFK-1A, DT-1, DT-2, DT-3
Generic type -----	Resorcinol-formaldehydes; diphenolic aldehydes

Description

Resorcinol-formaldehyde adhesives, designed for bonding of wood and porous materials, include FR-12 adhesive. FR-12 adhesive includes type KF-12 resorcinol-formaldehyde resin (100 wt parts) and a curing agent, paraformaldehyde (13 wt parts). To produce the adhesive the resin and curing agent are carefully mixed until a homogeneous solution is produced with a viscosity of 16° to 18° FE. The shelf life of the adhesive is 3 to 4 hr. KF-12 resin is the product of condensation of resorcinol with formaldehyde, with the addition of a plasticizer. The resin contains 32% water; pH = 7.2 to 7.4.

An adhesive used to bond teflon and polyethylene is produced by mixing a resorcinol-formaldehyde resin and polyvinyl acetals with copolymers of trifluoroethylene or hexafluoropropylene with vinylidene fluoride. The mixture is dissolved in organic solvents. The curing agent used in the composition is paraform; a 5% solution of caustic soda is used as an accelerator. This adhesive is prepared in three stages: (1) production of the intermediate product, (2) production of the combined product, (3) production of the adhesive solution. The intermediate product is produced by grinding 10 to 30 g trifluoroethylene-(vinylidene fluoride) copolymer at 20° to 40°C for 3 to 5 minutes. Then, 20 g resorcinol-formaldehyde resin, produced by condensation of 1 mol resorcinol with 0.5 mol formaldehyde, is introduced, and the mixture is ground for another 20 to 40 minutes. To prepare the combined product, 50 to 70 g poly(vinyl butyral)-furfural are ground at 120° to 140°C. The intermediate product is added (produced in the first stage), and the mixture is ground for an additional 10 to 30 minutes. The adhesive is prepared by dissolution at room temperature of 100 g of the combined product (produced in the second stage of the process) with 900 g of a mixture of equal parts of styrene and acetone. The resorcinol-formaldehyde resin may be replaced by resorcinol and paraformaldehyde taken individually.

Application

Adhesives based on diphenol resins (for example, DFK-1A) have good adhesion to wood and asbestos cement and can be used for bonding of various construction materials.

Technological Status

Research ----- 1952 (improved types) (est)
 1959 (diphenolics) (est)
 Development -----
 Engineering -----
 Production ----- 1956 (improved types) (est)
 1963 (diphenolics) (est)

Properties

The strength of adhesive joints from these polymers is shown below.

Strength of Adhesive Joints Made Using Adhesive Based on
 Poly(Vinyl Butyral)-Furfural, Resorcinol-Formaldehyde Resin
 and Fluorine-Derivative Copolymers

Materials bonded	Even separation strength, kg/cm ²	Shear strength, kg/cm ²
Teflon + teflon	up to 30	---
Polytrifluoroethylene + polytrifluoroethylene	up to 35	---
Teflon + duralumin	up to 30	---
Polyethylene + polyethylene	---	25-27
Polyethylene + duralumin	---	25-27

Strength of Adhesive Joints Made With Diphenol Adhesives

Adhesive type	Composition, wt parts		Shear strength at 20°C (kg/cm ²) for bonding of		
	diphenol resin	thiokol	Steel	KAST-V plastic	asbestos cement
DFK-1A	100	--	45	30	32
DT-1	100	40	85	70	45
DT-2	100	70	72	60	41
DT-3	100	100	42	--	35

Designation

Trademark -----	FR-12, DM-12, RAF-10, RA-6, FRAM-30, FRAM-70, FR-1, FEN-1, 9M-35
Generic type -----	Resorcinol-formaldehydes and variants

Description

Details on the chemical structures of these materials are lacking. Variants include types based upon dimethyl resorcinol or incorporation of various elastomers.

Application

The range of materials based on resorcinol resins and the range of the products for modifying these with other polymers are very considerable, including bonding agents, sealants, and dipping compositions. The first industrial product based on resorcinol was FR-12 resorcinol-formaldehyde resin. FR-12 bonding agent, used for bonding wood, plastics and other materials, was prepared on the basis of this resin.

Compositions for sealing oil wells have been prepared from FR-12 resin. Cementing of oil wells with a sealing composition makes it possible to obtain water-free oil on the surface, which affords a considerable savings. FR-12 resin is the basis for dipping compositions for tire cord. (The dipping is effected by secondary condensation of the resin in latices.) Dipping compositions based on FR-12 resin augment the bond strength of rubber-cord systems, increase the general life and work capacity of tire, and insure a number of advantages during processing.

A cheap bonding resin DM-12, used for bonding wood, asbestos-cement, chipboard, and other materials has been developed, based on dimethyl resorcinols extracted from the processing products of shales. The water-impermeability and bond strength obtained with this resin are claimed not to be inferior to those obtained with the better bonding agents based on phenol-formaldehyde resins.

Modified resorcinol-aldehyde resin is the basis for RA-6 sealant and RAF-10 bonding agent. RA-6 sealant hardens at room temperature and is characterized by good adhesion to metal.

RAF-10 belongs to the cold-hardening group of bonding agents and is intended for bonding of nonmetallic materials - (organic glass, nylon-6, acrylonitrile fiber, polystyrene, phenolic plastics, aminoplastics, and others).

New types of polymers were obtained by the mechano-chemical interaction of resorcinol resins with rubbers, and FRAM-30 bonding agent and FRAM-70 sealant were developed from these resins.

FRAM-30 bonding agent is characterized by high adhesion to duralumin, steel, copper, silver, and other metals and their alloys, and high adhesion to fluorine-containing plastic (chemically treated).

FR-1, another promising resin, is used as a basis for the preparation of bonding agents for use in bonding various vulcanizates to each other and to metal. FEN-1 and 9M-35 bonding agents are based on this resin.

FEN-1 bonding agent is intended for bonding vulcanizates based on butadiene-nitrile rubbers to metal during vulcanization, and for bonding vulcanizates based on butadiene-nitrile or fluoroorganic rubbers with fluorine-containing plastics (with a chemically treated surface) during vulcanization.

Technological Status

Research -----	1963 to 1964 (est)
Development -----	1965 to 1966 (est)
Engineering -----	1966 to 1967 (est)
Production -----	1967 to 1968 (est)

Properties

The advantages of FR-12 bonding agent over many cold-hardening phenol-formaldehyde bonding agents include its neutrality, its high bond strength (see below), and its resistance to water, vibration, and tropical climatic conditions.

Bond Strength of Oak Specimens With FR-12 Bonding Agent

Preparation of Specimens	Simple shear strength, kgf/cm ²	Number of specimens showing failure in the wood, %
Normal conditions	Up to 200	100
Wetting of wood, %		
Up to 25	150	Up to 25
Up to 30	115	
Heating at 100°C, hours		
6	165	Up to 90
20	185	
Keeping at -45°C, hours		
4	170	Up to 80
12	175	
Keeping in water, days		
10	95	Up to 100
100	100	
Alternate drying-out and soaking (cycles)		
2*	185	Up to 70
6	185	
10	144	
Keeping in atmosphere, months		
3	130	Up to 100
9	200	
12	105	

*Cycle: 24 hr holding in water, drying at 60°C to the original weight.

DM-12 resin is a good hardener for epoxy resins. The GRP based on the product of combination of dimethyl resorcinol resin with an epoxy resin (Lak 512) possesses high mechanical properties:

Impact strength, kgf-cm/cm ² -----	350 to 400
Flexural strength, kgf/cm ² -----	4000 to 4500
Tensile strength, kgf/cm ² -----	4000 to 5000
Compression strength, kgf/cm ² :	
perpendicular to the plies -----	4500 to 5000
parallel to the plies -----	1800 to 2000
Martens yield temperature, °C -----	250

RAF is nontoxic and does not cause corrosion of steel or aluminum alloys, but it has limited water impermeability. RA-6 film is resistant to petrol, kerosene, and mineral oil and can seal effectively at -60° to +135°C.

Data on the change in the mechanical properties of RA-6 sealant after keeping in kerosene are as follows:

	<u>20°C</u>	<u>100°C</u>	<u>-60°C</u>
Tensile strength, kgf/cm ² -----	$\frac{452}{623}$	$\frac{43}{76}$	$\frac{491}{543}$
Elongation at break, % -----	$\frac{15}{8}$	$\frac{11}{18}$	$\frac{17}{12}$

Note: The numerator gives the value after keeping in kerosene at 135°C for 100 hr; the denominator gives the value after 150 hr.

Some properties of RAF-10 when it is used to bond various substitutes are shown below.

Strength of Bonded Joints of Different Materials With
RAF-10 Bonding Agent

Bonded Material	Shear strength, kgf/cm ²	Character of failure
Aminoplastic	90 to 150	In the material
FKPM-15 (phenol-rubber solid)	100 to 150	In the material
FKPM-10	160 to 200	In the material (50%)
Fenolit-4 (phenolic solid)	120 to 175	At the bond
Resin-dipped fabric laminate	70 to 120	At the bond
Glass fabric laminate with filter	60 to 70	In the material
PMMA	220 to 390	Failure of surface of the PMMA

As indicated below, FRAM-30 shows high adhesion to various metals.

Bond Strength of Materials With FRAM-30 Bonding Agent

Bonded Material	Strength, kgf/cm ²	
	Direct Tension	Shear
D-16 Duralumin*	300 to 650	222 to 350
30 KhGSA steel**	---	250 to 280
45 steel	350 to 500	360 to 500
45 N alloy	---	300 to 400
79 NM alloy	---	280 to 360
Copper	---	80 to 100
Silver	---	60 to 100
LS-62 brass	280 to 550	300 to 500

*The shear strength at 80°C is 165 to 280 kgf/cm², and the peeling strength at 20° and 80°C, 40 to 70 and 30 to 58 kgf/cm, respectively.

**The specimen was sand-blasted.

The following mechanical data are given on FRAM-30 after various exposures to temperature and time:

Strength of Bonded Joints With FRAM-30 After the Action of Temperature

Condition of specimens	Strength*		
	-60°C	+20°C	+80°C
Control	$\frac{269 \text{ to } 284}{48 \text{ to } 62}$	$\frac{240 \text{ to } 324}{55}$	$\frac{155 \text{ to } 229}{21 \text{ to } 40}$
After 500 hr at 80°C	$\frac{287 \text{ to } 312}{43 \text{ to } 76}$	$\frac{301 \text{ to } 219}{39 \text{ to } 52}$	$\frac{216 \text{ to } 252}{21 \text{ to } 27}$
After 1000 hr at 80°C	$\frac{275 \text{ to } 291}{27 \text{ to } 75}$	$\frac{304 \text{ to } 366}{48 \text{ to } 60}$	$\frac{264 \text{ to } 276}{8 \text{ to } 25}$
After 500 hr at 100°C	$\frac{264 \text{ to } 283}{45 \text{ to } 78}$	$\frac{298 \text{ to } 321}{39 \text{ to } 48}$	$\frac{228 \text{ to } 282}{28 \text{ to } 39}$

*The numerator indicates the shear strength, kgf/cm²; the denominator indicates peeling strength, kgf/cm.

FRAM-70 gives reliable strength of bonded joints at 80°C for 1000 hr, and at 100°C for 500 hr. The bonded joints are resistant to oils, water, and alcohol. FRAM-70 sealant is employed for sealing metal articles that work in a medium of air and fuel at temperatures from -50° to +300°C (see below) and may find a wide application in various branches of technology.

Mechanical and Adhesive Properties of FRAM-70 Sealant

Medium	Conditions of heat treatment		Tensile strength, kgf/cm ²	Elongation at break	Tension set	Adhesion to D-16 duralumin (anodized), kgf/cm ²
	T, °C	time, hr				
Air	Without heat treatment		28.7	210	8	1.6
	200	100	33.0	283	6	1.65
	200	200	37.0	320	12	1.39
	250	200	43.8	390	--	----
	300	75	67.0	23	--	----
Kerosene	200	100	33.3	124	4	1.39
	200	200	70.0	22	4	1.49

Bonds based on FEN-1 bonding agent are fuel- and petrol-resistant, and can work at temperatures from -50°C to +170°C (see below). The rubber-to-metal bond strength (for gaskets, seals, etc.) obtained with FEN-1 bonding agent is greater than that by the method of brass-plating. This means that this bonding agent can be used in the flow-line production of large types of rubber-metal articles.

Bond Strength of Different Materials With FEN-1 Bonding Agent

Bonded materials	Strength*			
	Direct tension,* kgf/cm ²	Peeling kgf/cm		
		18° to 25°C	-50°C	+170°C
Metal + vulcanizate**	40 to 70	5 to 6	6.3	2.5 to 3
PTFE + vulcanizate***	---	5 to 6.5	6.6	2.8 to 3.5
PTFE + vulcanizate**	---	4.5 to 5.0	---	---

*Failure in the vulcanizate in all cases.

**Butadiene/nitrile vulcanizate.

***Fluoro-organic vulcanizate.

In addition to good adhesion to metal and fluoroorganic rubbers, 9M-35 possesses high heat (200°C) and fuel resistance. These data are shown as follows:

Rubber-to-Metal Bond Strength With 9M-35 Bonding Agent

Metal	Direct tension, kgf/cm ²	
	20°C	200°C
Titanium	73.8 to 70.0	16.2 to 14.8
Stainless steel	61.2 to 78.3	17.5 to 18.0
D-16 Duralumin	60.0 to 72.3	16.4 to 15.8

- Notes: 1. Numerator - with IRP-1144 vulcanizate; demoninator - with IRP-1225 vulcanizate.
 2. Failure occurred in the vulcanizate in all cases.

Strength of Bonded Joints With 9M-35 Bonding Agent

Medium	Conditions of heat treatment		Direct tension strength*, kgf/cm ²	
	T, °C	Time, hr	20°C	200°C
Air	without heat treatment		65.9 to 77.0	17.2 to 25.2
	200	200	59.1 to 62.7	15.8 to 23.5
Kerosene	200	100	66.1 to 45.2	14.4 to 5.5
	200	200	57.8	13.4

*Numerator - IRP-1144 vulcanizate; denominator - IRP-1225 vulcanizate.

Designation

Trademark ----- MF-17, MF, MFS-1, M-4, M-48, M-60,
M-70, MFSM, Bartrev type
Generic type ----- Urea-formaldehyde

Description

These adhesives are formed by condensation of urea with formaldehyde. Acid substances are used as catalysts--hydrochloric, sulfuric, acetic, oxalic and lactic acids, and the ammonium salts of strong acids. At pH of 6 to 5.5, the resins cure at high temperatures; at pH of 3 to 5, it cures at room temperature.

Application

These adhesives are widely used as adhesives for bonding of lumber, plywood, and other wooden materials.

Technological Status

Research ----- 1945 or earlier (est)
Development -----
Engineering -----
Production ----- 1950 (most variants) (est)

Properties

The following properties of urea-formaldehyde adhesive resins are provided:

Properties of Urea-Formaldehyde Adhesive Resins

Indicators	Resin Type									
	MF-17	MF	MFS-1	M-4	M-48	M-60	M-70	MFSM	Bartrev	
Concentration, %	at least 70	at least 65	55 to 60	55 to 60	48 to 50	57 to 63	67 to 70	59 to 61	60±1	
Refraction Coefficient	1.475 to 1.500	1.165 to 1.168	1.440 to 1.450	1.440 to 1.450	1.417 to 1.425	1.448 to 1.452	1.470 to 1.475	1.448 to 1.452	1.462 to 1.465	
Viscosity According to VZ-4, sec	---	---	Pasty Mass	40 to 60	13 to 20	90 to 240	60 to 300	20 to 90	7.5 to 7.8	
Ford-Engler viscosity	30 to 150	30 to 150	---	---	---	---	---	---	---	
Free formaldehyde content, %	2.5 to 3.5	3 to 4	1.0 to 1.2	1.0 to 1.5	0.0 to 1.2	1.0 to 2.5	1.5 to 2.5	0.8 to 1.0	4.0 to 7.0	
Shelf life with 1% ammonium chloride, hr	24 to 48	2 to 15	12 to 24	2 to 4	2.5 to 4	2 to 8	0.5 to 2	10 to 30	0.5 to 2.5	
Curing time with 1% ammonium chloride, sec	90 to 120	60 to 100	70 to 90	55 to 60	55 to 70	50 to 65	30 to 50	60 to 100	40 to 60	
Storage life	4 mo	2 mo	1.5 days	30 days	12 days	2 days	3 to 4 days	2 days	3 to 4 days	

Composition and Properties of Urea-Formaldehyde Adhesives

Adhesive Type	Urea-formaldehyde		Hardener		Shelf life, hr	Use
	Type	Quantity, wt parts	Type	Quantity, wt parts		
K-17*	MF-17	100	Ammonium chloride	7.5 to 22.0 1.0 to 1.2	3 to 5 24 to 48	Hot and cold bonding of plywood in furniture
MF	MF	100	Ammonium chloride	1.0	2 to 15	Same
MFS-1	MFS-1	100	Ammonium chloride	0.5 to 1.0	12 to 24	Hot bonding of plywood in furniture
M-4	M-4	100	Ammonium chloride	0.5 to 1.0	2 to 4	Hot and cold bonding of wood
M-48	M-48	100	Ammonium chloride	1.0	2.5 to 4.0	Hot bonding of wood, plywood in furniture
M-60	M-60	100	Ammonium chloride	0.5 to 1.0	2 to 8	Hot and cold bonding of wood
M-70	M-70	100	Ammonium chloride	0.5 to 1.0	0.5 to 2.0	Same
MFSM	MFSM	100	Ammonium chloride	1.0	10 to 30	Hot bonding of wood, plywood in furniture
Bartrev	Bartrev	100	Triammonium nitrate	6.5	---	Manufacture of wood-chipboards

*Filler: 8% to 10% wood flour.

Designation

Trademark ----- UKS; KP-8; PVAC on UBGAF modifications
 Generic type ----- Urea-formaldehyde resin (oligomer):
 poly(vinyl acetate) or ureabenzo-
 guanamine-formaldehyde modifications

Description

These adhesives consist of oligomer (UKS urea resin) modified during synthesis with a poly(vinyl acetate) (PVAC) emulsion and of a urea-benzoguanamine-formaldehyde oligomer (UBGAF).

Catalysts used with the PVAC-modified resin are phthalic acid monoureide (PAMU), oxalic acid neutralized with hexamethylenetetramine, and ammonium chloride. PAMU (3% to 5%) is the preferred hardener because it imparts greater service life to the binder than do the other catalysts.

Application

These adhesives are probably used as binders for substrates, such as wood and fibers, where enhanced water resistance and flexibility are required.

Technological Status

Research -----	1965 (est)
Development -----	1967 (est)
Engineering -----	1967 (est)
Production -----	1969 (est) A reasonably high interest in this general purpose resin may exist

Properties

The optimum pressing temperature for these adhesives is 135° to 140°C. The time of hardening at this temperature is 6 to 8 min, and the gel time is 40 to 60 sec. An improvement in the mechanical properties and water resistance of GRP's based on aminealdehyde resins is achieved by treating the glass fibre with aminosilanes. The aminosilanes AGM-3, ADE-3, and AGM-9 (AGM-9 is γ -aminopropyltriethoxysilane) are used. The results of adhesive strength tests show that UKS resin has an adhesive strength of 330 kgf/cm² to the untreated glass fibre and adhesive strength of 290 to 350 kgf/cm² to the glass fibre treated with aminosilanes. Finishing does not permit any appreciable increase in the adhesive strength of these resins,

but, after finishing, there is an increase in the water resistance of the GRP's. (After 0.5 hours boiling in water, the GRP based on the untreated fabric retains 5% to 10% of its initial flexural strength, and the GRP based on a fabric finished with aminosilanes retains 30% of its initial strength.)

The properties of the molded specimens obtained from the glass resin material based on PVAC (KP-8) are as follows:

Density, g/cm ³ -----	1.7 to 1.9
Flexural strength, kgf/cm ² -----	1600
Impact strength, kgf-cm/cm ² -----	60 to 80
Water absorption,% -----	3 to 4
Martens yield temperature, °C --	120
Surface resistivity, ohms -----	2x10 ¹²
Volume resistivity, ohm-cm -----	10 ¹²
Dielectric permittivity	
(f=10 ⁶ Hz) -----	6.1
Tan δ (f=10 ⁶ Hz) -----	0.04
Breakdown strength, kV/mm -----	12

Triazines can improve the water resistance, heat resistance, and other properties of urea resins. Benzoguanamine (2,4-diamino-1,3,5-triazine) has been used in the modification of phenol- and urea-formaldehyde resins utilized in the production of binder materials and paper treatment resins.

Mechanical properties of GRP's based on urea-benzoguanamine-formaldehyde binder resin and TS-8/3-250 glass fabric treated by different methods are shown below:

Method of treatment of glass fabric	Flexural strength, kgf/cm ²			Impact strength, kgf-cm/cm ²	Water absorption (in 24 hr), %
	In dry specimen	After 2 hr holding in distilled water	% strength retention		
Heat treatment	2555	1803	70.5	37.3	1.2
Treatment with 752 size	3040(3506)	2770(3015)	90(86)	88.7(84)	1.4(3.4)

*In brackets, data for a GRP based on a resin modified with PVAL.

Designation

Trademark -----	"K" binder
Generic type -----	Urea-formaldehyde resin modified with PVAL or furfural resins

Description

"K" binder is a urea-formaldehyde resin modified with poly(vinyl alcohol), containing a small amount of free formaldehyde (not above 0.5%). It is readily soluble in water. "K" binder also refers to MFF-M urea-formaldehyde-furfural resin and its mixtures. The working aqueous solutions of the resins are hardened with complex hardeners: oxalic + orthophosphoric acids, oxalic + hydrochloric acids (and also each of these acids individually). The polymer based on "K" binder is a hard water-insoluble material, with adequate strength and rates of hardening suitable for various practical purposes. Solutions of "K" binder have good adhesion to limestone and cement rock. After hardening of the solutions the permeability of the medium is reduced.

Application

The use of solutions of synthetic resins (such as "K" binder) in mining structures (for sealing off water and other purposes) is based on their capacity for forming strong water-impermeable products which bind "quick" and heavily broken-up rock into a dense "monolithic" mass. For consolidating mining rock, water-soluble urea resins (urea-melamine-, urea-formaldehyde, etc.) are used.

Designation

Trademark ----- UKS modified with S-89 or PVAL
 (poly[vinyl alcohol])
 Generic type ----- Urea-formaldehyde modified with
 amino-epoxides or polyvinyl alcohol

Description

This adhesive consists of grade UKS urea-formaldehyde resin, containing 2% of free formaldehyde, modified with S-89 resin as a 30% aqueous solution of pH 3.3, and in amounts of 0.4% to 4.0%, based on the dry weight of urea resin. Another modifying additive is poly(vinyl alcohol). The blended resins are hardened in air at 20° and 100°C.

Application

The use of urea-formaldehyde resins in the production of chipboard panels, veneer, and furniture is important. It is expected that the Soviets are using the S-89 modified UKS or other amino-epoxide modifier to reduce toxicity and increase fabrication speeds.

Technological Status

Research ----- 1967 to 1968 (est)
 Development ----- 1968 (est)
 Engineering ----- 1969 (est)
 Production ----- 1970 (est)

Properties

Urea resins have certain basic disadvantages: low water resistance, low resistance to cracking of injection molded articles, and the liberation of free formaldehyde during processing and service. The latter is particularly important when urea resins are used for articles to be utilized in living quarters.

Results of modifying the urea resin with PVAL are shown below:

Amount of PVAL added, % -----	0	0.1	0.3	0.5	1.0	1.5	2.0
Hardening time*, relative units -----	1	1	1	0.95	0.85	0.70	0.80
Free formaldehyde, content, relative units -----	1	1	1	0.9	0.7	0.4	0.4

*The hardening time was assessed by the increase in resistance to the movement of a metal rod of diameter 1 cm into the resin as it hardened. The hardener was ammonium chloride.

The following are results of the addition of S-89 resin on the content of free formaldehyde in hardened specimens of UKS resin.

Hardener:

Oxalic acid	{	0/3.9
		0.4/3.0
		1.2/2.2
		2.0/0.75
Ammonium chloride	{	0/2.2 to 3.0
		0.4/1.3
		0.8/0.9 to 1.0
		2.0/0.5 to 0.7
<u>Without hardener:</u>		2.0/0.9
		4.0/0.3

Note: Figures before the stoke, amount of S-89 resin added, in %; after, free formaldehyde content, %.

The characteristics of chipboard panels based on the urea resin, hardened in the presence of ammonium chloride or the aminoepoxide, are as follows:

<u>Hardener</u>	<u>NH₄Cl</u>		<u>S-89</u>
Amount, % -----	1.0	2.0	4.0
Pot life, hours -----	24	---	4 to 6
Hardening time, sec -----	120	105	42 to 45
Strength, kgf/cm ²			
flexural -----	150 to 170	190 to 205	220 to 240
tensile -----	3.0 to 3.5	4.5 to 5.0	6.5 to 7.0
Swelling, % -----	28	22	18

Tests show that the properties of chipboard panels, based on urea resin with the addition of PVAL, do not change with up to 1.5% PVAL content. Addition of PVAL in amounts greater than this reduces the strength of the panels. The most complete binding of the formaldehyde is found with the addition of 1.0% to 1.5% of PVAL.

Modification of the urea with S-89 amino-epoxide in amounts of 2.0% to 4.0% shortens the hardening time of the resin and considerably reduces the free formaldehyde content. Physicomechanical properties of the

articles based on the urea are improved. Following are the characteristics of solid oak wood bonded with UKS resin:

<u>Hardener</u>	<u>NH₄Cl</u>		<u>S-89</u>
Amount, % -----	1.0	2.0	4.0
Molding conditions:			
t, °C -----	120	---	---
p, kgf/cm ² -----	5	---	---
Shearing strength, kgf/cm ² :			
in dry state -----	115	120	135
after wetting in water,			
24 hr -----	103	113	133
Resistance to boiling, hr ----	2	4	8

Designation

Trademark -----	VK-2, VK-8, VK-10, VK-15, TS-7-165-32, K-105, K-111, KT-9, KT-15, KT-25, MAS-1, VKT-2, VKT-3, #201, #202, U-2-28
Generic type -----	Organosilicon resins and variants

Description

Organosilicon adhesives (VK-2, VK-8, VK-10, VK-15, etc.) are compositions based on thermally stable organosilicon compounds, usually modified with various organic polymers. The composition of many organosilicon adhesives include asbestos filler. The use of asbestos results in a significant increase in strength and thermal stability of adhesive joints, which can be explained by the formation of nonorganosilicon (silicate) structures.

VK-2 adhesive is a composition based on an organosilicon resin and asbestos. VK-8 adhesive is a phenol-organosilicon composition, modified with synthetic rubber in order to increase mechanical strength and elasticity. The composition contains an inorganic fibrous filler. The shelf life is 6 months.

Phenol-organosilicon resin B-1, with a high concentration of aromatic rings and a coke number (in the cured state) of 87%, is used to produce thermally stable adhesives. The resin is modified with polyorganometallosiloxanes. It is produced by reesterification of polyphenyl alkoxy siloxane with dioxydiphenyl propane. The polymer formed contains three aromatic rings for each silicon atom. One has a hydroxyl group capable of reacting with urotropin or paraform. This forms methylol derivatives followed by cross-linking of the polymer chains. VK-10 adhesive is a thermally stable and heat-resistant adhesive based on B-1 phenol-organosilicon resin, polyorganoborosiloxane, and asbestos. VK-15 adhesive is distinguished by its resistance to thermal oxidative destruction, its thermal stability, and its elasticity.

Type TS-7-165-32 adhesive cement is based on hydrolyzed ethyl ester of ortho-salicylic acid and synthetic corundum. K-105 organosilicon adhesive is produced from poly(methyl phenylsiloxane) resin with hardener, while K-111 adhesive is based on poly(chloromethyl chlorophenylsiloxane) resin. KT-9 adhesive is a 25% solution of a rubber mixture and an organosilicon resin in benzene. IP-9 adhesive is a methyl phenyl polysiloxane resin, modified with an epoxy polymer plus titanium dioxide. KT-15 is a mixture of two organosilicon compounds, one of which is the curing agent.

KT-25 adhesive contains three components: a 50% solution of modified organosilicon resin in ethyl acetate, a 50% solution of hardener in ethyl acetate, and a filler (titanium dioxide type TS). The shelf life of the adhesive does not exceed 2 days.

MAS-1 adhesive is a solution of modified organosilicon resin and hardener in a mixture of toluene and butanol. The hardener is introduced to the solution at the rate of 0.25 wt parts per 100 wt parts dry substance. VKT-2 and VKT-3 adhesives are mixtures of modified organosilicon resin and a copolymer of butyl methacrylate with methacrylic acid in organic solvents with triethanolamine added. VKT-3 is produced by introducing a filler to VKT-2 immediately before use. The adhesives are cured at room temperature without the use of pressure.

U-2-28 adhesive sealer is a pasty mass designed for sealing and for bonding various organosilicon rubbers and certain facing materials (STAM, ANTM-1) at room temperature (contact pressure).

Application

Organosilicon polymer compounds have been used as components in various thermally stable adhesives designed for use in load-bearing and nonload-bearing applications. VK-2 adhesive can be used to bond metals, plastics, and thermally stable nonmetallic materials. The VK-8 adhesive is designed for bonding of metals and thermally stable nonmetallic materials (textolite, graphite, etc.) in products used briefly at temperatures up to 1000°C. VK-10 adhesive purportedly can be used to bond heat-resistant materials and nonmetallic materials at temperatures up to 1200°C. VK-15 adhesive is designed for bonding of steels, titanium alloys, and thermally stable metal materials operating for long periods of time at temperatures of 300° to 1000°C. Type TS-7-165-32 adhesive cement is used for mounting of tensometer sensors to measure dynamic stresses at temperatures of 800°C and higher. The K-105 and K-111 adhesives are used to bond metals and nonmetallic materials. KT-9 adhesive is used for attachment of polysiloxane rubber to metals. IP-9 adhesive can be used for bonding of vulcanized polysiloxane rubber to metals during heat treatment. Treatment of the bonded surfaces is as with KT-9 adhesive.

KT-15 adhesive can be used to fasten organosilicon rubber to steel, VT-1 titanium alloy, brass, and other metals. One peculiarity of the adhesive is the fact that it can be used to reduce the time of heat treatment of rubber-metal products. KT-25 adhesive is designed for attachment of vulcanized organosilicon rubber to metals during heat treatment. The MAS-1 adhesive is designed for bonding all known types of polysiloxane rubber to metals during vulcanization. The VKT-2 and VKT-3 adhesives are designed for bonding of fiberglass insulation to metals.

Technological Status

Research -----	1955 (for simple types)
	1967 (for advanced types)
Development -----	
Engineering -----	
Production -----	1960 (for simple types)
	1970 (for advanced types) (est)

Properties

The organosilicon adhesives in this series have relatively low strength at room temperature, but one peculiarity of these compounds is that they retain their strength at very high temperatures. The even and uneven layer-separation strength and long-term strength of adhesive joints made with VK-2 can be characterized by the data presented below:

Even separation strength at 20°C, kg/cm ² -----	220
Uneven separation strength, kg/cm ² :	
at 20°C -----	8 to 9
at 350°C -----	6

Long-Term Strength of Adhesive Joints in Steel Made Using VK-2 Adhesive

Test Temperature, °C	Shear Strength, kg/cm ²	Time to rupture, hr	Test Temperature, °C	Shear Strength, kg/cm ²	Time to rupture, hr
20	56	1000	425	25	300
350	27	300	1000	3 to 10	2 to 7

The fatigue strength of 30KhGSA steel adhesive joints at 350°C, made with VK-2 adhesive, is 35 kg/cm² (base of 3×10^6 cycles). The shear strength of adhesive joints made with VK-2 adhesive and the long-term strength of VK-8 adhesive joints are as follows:

Shear Strength of Adhesive Joints in Various Materials Made With VK-2 Adhesive

Materials Bonded	Shear strength, kg/cm ²	
	At 20°C	At 425°C
VT-4 titanium alloy	42	35
30KhGSA steel + graphite	51	23 (at 400°C)
VFT textolite	47	29

Long-Term Strength of VK-8 Adhesive Joints

Test Temperature, °C	Shear Strength, kg/cm ²	Time to Rupture
20	120	1300 hr (No rupture)
400	12.5	2 hr
1000	10	5 min

These adhesives (VK-2 and VK-8) do not cause corrosion of stainless steel or titanium alloys. Adhesive joints are resistant to the effects of oil and gasoline.

Data on the strength of adhesive joints made with VK-8 adhesive are presented below:

Strengths of Adhesive Joints in Various Materials Made With VK-8 Adhesive

Materials Bonded	Test Type	Indicators			Nature of Rupture
		At 20°C	At 350°C	At 425°C	
30KhGSA steel to 30KhGSA steel	Shear strength, kg/cm ²	160	45	35	Through adhesive
VT-4 Ti Alloy to VT-4 Ti Alloy	do	170	--	24	do
E1651 steel to graphite	do	106	--	--	Through graphite
30KhGSA steel to VFTS textolite	?	182	--	44	Through textolite
30KhGSA steel to 30KhGSA steel	Even separation strength, kg/cm ²	250	--	--	Through adhesive
30KhGSA steel to 30KhGSA steel	Uneven separation strength, kg/cm ²	15	5-6	--	do

Exposure to water for 30 days reduces the strength of the VK-8 joints at 20°C by 5% and at 400°C by 10% to 12%. The strength of adhesive joints exposed to tropical climate conditions does not change for 1 month.

The strength of adhesive joints in various materials made with VK-10 adhesive are as follows:

Strength of Adhesive Joints Made With Phenol-Organosilicon Compositions
Containing Polyorganometallosiloxanes (VK-10)

Element Introduced	Content, %	Shear strength, kg/cm ²		Shear strength after aging, kg/cm ²				Uneven separation strength, kg/cm ²	
				At 350°C, 24 hr		At 425°C, 4 hr			
		At 20°C	At 425°C	At 20°C	At 425°C	At 20°C	At 425°C	At 20°C	At 250°C
Initial data	---	76	25	32	19	22	17	7.5	--
Boron	0.30	160	48	80	45	80	47	14	8
Titanium	0.16	110	50	30	32	81	48	11	6
Aluminum	0.12	56	24	47	34	36	42	--	--

Strength of Adhesive Joints in Various Materials Made
With VK-10 Adhesive

Materials Bonded	Shear Strength, kg/cm ²		
	At 20°C	At 300°C	At 425°C
1Kh18N9T stainless steel	125	---	37
VT-4 Ti Alloy	122	---	35
SK-9F textolite	54	---	12
Graphite	70	10	---
Asbestos Cement*	50	---	20

*Rupture through material

The layer separation strength of adhesive joints of VK-10 and 30KhGSA steel is shown as follows:

Separation Strength of Adhesive Joints in 30KhGSA
Steel Made With VK-10 Adhesive

Test Temperature, °C	Even separation strength, kg/cm ²	Uneven separation strength, kg/cm ²
20	185	13
250	---	8
275	---	7

VK-10 adhesive has high thermal stability and heat resistance. Data on the strength of adhesive joints in 30KhGSA steel following thermal aging are presented below:

Thermal Aging of Adhesive Joints in 30KhGSA Steel Made With VK-10 Adhesive

Aging Conditions		Shear strength, kg/cm ²		Aging Conditions		Shear strength, kg/cm ²	
Temperature, °C	Time, hr	At 20°C	At 425°C	Temperature, °C	Time, hr	At 20°C	At 425°C
Initial Data		127	37	700	5	30	31
200	3000	59	78	700	100	24	19
250	2000	40	38	900	100	34	16
350	5000	41	30	1000	0.5	28	23
600	100	30	18	1200	0.25	20	19

Data are presented below on the long-term strength of adhesive joints in 30KhGSA steel made with VK-10 adhesive as a function of temperature. The effects of 30 days exposure to water reduce the strength of adhesive joints by 10% at 20°C and leave it unchanged at 425°C. The shear strength of specimens held in a tropical climate chamber for 3 months is reduced by 30% at 20°C but is unchanged at 425°C. The adhesive joints are resistant to the effects of MK-8 mineral oil and T-1 fuel. The shelf life of the adhesive is 6 months. The technology of bonding consists of application of the adhesive to carefully degreased surfaces with a spatula, in two coats, each of which is held for 1 hour. The adhesive is cured under a pressure of 8 kg/cm² at a temperature of 200°C for 3 hours.

Long-Term Strength of 30KhGSA Steel Adhesive
Joints Made With VK-10 Adhesive

Test Time	Shear strength, kg/cm ²			Test Time	Shear strength, kg/cm ²		
	At 20°C	At 425°C	At 1000°C		At 20°C	At 425°C	At 1000°C
0.1	100	28	18	10	52	20	--
1	70	24	12	100	40	--	--

The dependence of the shear and even separation strength of specimens bonded with VK-15 adhesive and data on the thermal aging of adhesive joints are presented below:

Even Separation Strength of Adhesive Joints in 30KhGSA
Steel Made With VK-15 Adhesive

Materials Bonded	Even Separation strength, kg/cm ²		
	At -60°C	At 20°C	At 300°C
30KhGSA Steel	94	109	44
30KhGSA Steel + TZFN Heat insulating material	--	10*	Ruptured without load

*Rupture through TZFN material.

Change in Uneven Separation Strength of Specimens of 30KhGSA Steel Bonded With VK-15 Adhesive Under the Influence of Various Factors

Test Conditions	Uneven separation strength, kg/cm ²				Test Conditions	Uneven separation strength, kg/cm ²		
	At 20°C	At 250°C	At 275°C	At 300°C		At 20°C	At 275°C	
Initial state	11	8	7	6	After aging at 300°C			
After holding in water for 5 days	9	--	--	--		250 hr	6	4
						500 hr	7	4
						1000 hr	5	--

Thermal Aging of Adhesive Joints in 30KhGSA Steel Made With VK-15 Adhesive

Aging Conditions		Shear strength, kg/cm ²				Aging Conditions		Shear strength, kg/cm ²			
Temp, °C	Time, hr	At 20°C	At 300°C	At 350°C	At 425°C	Temp, °C	Time, hr	At 30°C	At 350°C	At 20°C	At 425°C
Initial data		110	35	36	40	500	500	20	--	--	15
							1000	20	--	--	15
300	1000	31	33	--	--	600	500	33	--	--	33
	5000	29	28	--	--		1000	31	--	--	30
350	1000	24	--	25	--	700	250	19	--	--	--
	5000	22	--	17	--	800	50	25	--	--	--
						1000	10	15	--	--	--

TS-7-165-35 adhesive cement allows wire tensometer sensors to be used to measure dynamic deformations on rotating and nonmoving parts at 800°C and higher. The cement is frost resistant. The specific resistivity of the insulation between the tensometer sensor and the part at 800°C is over 10⁵ ohm. The adhesive is resistant to the effects of water, kerosene, and oil.

The bonding mode for K-105 and K-111 adhesives is as follows: open holding at room temperature for 20 minutes, and curing under a pressure of 5 kg/cm² for 2 hours at 200°C. The adhesive joints in metals have shear strengths at 20°C of 75-100 kg/cm², at 300°C of 15-25 kg/cm².

Bonding with KT-9 adhesive is performed as follows: The metal, preliminarily sand blasted and degreased with gasoline, is coated with two coats of adhesive. The first coat is dried for 30 minutes at 100°C, the second coat at room temperature for 60 minutes. The rubber mixture is degreased with gasoline or benzene before bonding. The adhesive joint is cured during vulcanization of the rubber. The bonded products are vulcanized by being placed in a cold press, put under pressure, and gradually heated to 150°C. The process requires 30 minutes. The parts are cooled under pressure. The strength of adhesive joints between 14r-2 and 5r-129 polysiloxane rubber and metals is shown below. Heat treatment of the rubber-metal products at 200°C for 240 hours does not decrease the properties of the adhesive joints.

Strength of Adhesive Joints Between Polysiloxane Rubber and
30KhGSA Steel Made With KT-9 Adhesive

Test Temp, °C	Even separation strength, kg/cm ² *		Test Temp, °C	Even separation strength, kg/cm ² *	
	14r-2 resin	5r-129 resin		14r-2 resin	5r-129 resin
-40	18 to 20	24 to 26	150	10 to 12	6 to 8
20	15 to 18	13 to 14	200	8 to 9	6 to 8
100	11 to 13	9 to 11			

*Rupture in all cases occurs through the rubber.

Data on the strength of IP-9 adhesive joints are presented below:

Strength of Adhesive Joints Made With IP-9 Adhesive

Type of Rubber	Test Temp, °C	Even separation strength, kg/cm ²		Nature of Rupture
		30KhGSA Steel	Duralumin	
14r-2 (Shore hardness 35-45)	20	7 to 12	7 to 10	Adhesive remains on metal
	100	5 to 10	5 to 9	do
	150	5 to 10	5 to 9	do
	200	4 to 9	4 to 9	do
14r-6 (Shore hardness 35-50)	20	6 to 11	6 to 9	do
	100	5 to 9	5 to 8	do
	150	5 to 9	5 to 8	do
	200	4 to 8	4 to 7	do
5r-129 (Shore hardness 45-65)	20	7 to 12	6 to 11	Through thin layer of rubber
	100	7 to 11	6 to 11	do
	150	7 to 11	6 to 11	do
	250	6 to 10	6 to 11	do

KT-15 adhesive joints are reliable in the temperature interval from -40°C to +200°C and withstand long exposure to high temperatures.

The results of aging tests of KT-25 adhesive joints indicate that after thermal aging the strength indicators remain at the previous level or decrease slightly, although rupture of the specimens occurs primarily through the rubber. Although the strength of the mounting produced decreases with increasing temperature, specimens rupture only through the rubber; the adhesive joints can be used in the temperature interval from -40°C to +250°C.

Influence of Aging on Strength of Adhesive Joints in Rubber
Made With KT-25 Adhesive

Type of Rubber	Even separation strength, kg/cm ²						Nature of Rupture
	Before aging		After aging at 200°C for 200 hr		After aging at 250°C for 500 hr		
	At 20°C	At 200°C	At 20°C	At 200°C	At 20°C	At 200°C	
IRP 1265	26.6	6.0	20.7	12.2	12.3	6.0	Through rubber
IRP 1266	28.4	4.8	21.9	14.0	10.5	5.0	do
IRP 1267	18.0	8.5	17.5	11.7	--	--	do
IRP 1225	64.0	9.1	30.4	12.2	--	--	do
IRP 1144	65.2	5.5	74.8	16.4	--	--	Release of rubber
IRP 1287	91.6	6.8	72.1	13.0	--	--	do

Data on the strength of adhesive joints between rubber and various metals made using KT-25 adhesive are presented.

Strength of Adhesive Joints Between Rubber and
Metal Made With KT-25 Adhesive

Rubber	Even separation strength, kg/cm ²		
	30KhGSA Steel	Duralumin	Titanium Alloy
IRP 1265	16.3 (Through rubber)	16.2 (Through rubber)	17.7 (Through rubber)
IRP 1266	10.8 (Separation of rubber)	10.9 (Traces of rubber on metal)	17.2 (Traces of rubber on metal)
IRP 1267	15.6 (Separation of rubber)	18.1 (Traces of rubber on metal)	16.5 (Traces of rubber on metal)
IRP 1287	43.5 (Traces of rubber on metal)	68.8 (Through rubber)	53.3 (Through rubber)
IRP 1225	61.0 (Through rubber)	60.9 (Through rubber)	58.3 (Through rubber)

Strength of Adhesive Joints Made With KT-25 in Various Mediums

Medium	Heat Treatment	Even separation strength, kg/cm ²	
		At 20°C	At 200°C
Initial data	---	6.7 Rupture through rubber	43.0 Rubber released; rupture through rubber
Water	30 days	45.5 Rupture through rubber	----
B-3V oil	150°C, 200 hr	20.1 Adhesive on metal	5.0 Adhesive on metal
70-50S-3-oil	200°C, 400 hr	50.2 Rupture through rubber	42.1 Rubber released

Before bonding with MAS-1, the metal surface is water and sand blasted and degreased. The adhesive is applied in two layers, each layer successively dried in air for 1 hour, after which the rubber and metal parts are joined and vulcanized in a press, using the rubber vulcanization mode. Data on the bonding strength of 14r-6 rubber with metal using MAS-1 adhesive are as follows:

Strength of Adhesive Joints in 14r-6 Rubber With Metal, Made Using MAS-1 Adhesive

Metal Bonded	Even separation strength, kg/cm ²		Metal Bonded	Even separation strength, kg/cm ²	
	At 20°C	At 200°C		At 20°C	At 200°C
30KhGSA Steel	20.0	8.4	Duralumin	20.0	12.2
3I268 Steel	24.1	11.9	VT-1 Ti Alloy	23.5	11.8

The properties of the VKT-2 and VKT-3 adhesives are as follows:

Physical Properties of VKT-2 and VKT-3 Adhesive Compositions

Properties	VKT-2	VKT-3
External appearance	Homogeneous, opalescent solution, yellow to dark brown in color. Some sediment may precipitate, but is easily dissolved when mixed	White viscous product
Dry residue, %	40 to 45	---
Viscosity, sec	6 to 15	---
Shelf life	At least 6 months	45 to 60 min

The strength characteristics of adhesive joints between fiberglass insulation and stainless steel at various temperatures show that VKT-2 and VKT-3 adhesives can be used at temperatures up to 400°C. Long-term exposures to high temperatures cause significant increases in bond strength due to the more complete curing of the adhesive. The strength of adhesive joints is not reduced by exposure to water, oil, or kerosene.

Peeling Strength of Adhesive Joints in Fiberglass Insulation
With Stainless Steel Made With VKT Adhesives

Test Temperature, °C	Peeling Strength, kg/cm ²		Test Temperature, °C	Peeling Strength, kg/cm ²	
	VKT-2	VKT-3		VKT-2	VKT-3
-60	19.8	19.5	300	2.8	4
20	57	63	350	1.6	2
60	13.8	22	400	1	2.4

Strength of Adhesive Joints Between Fiberglass Insulation and
Stainless Steel After Exposure to Various Physical and Chemical Factors

Nature of Influence	Peeling strength, kg/cm ²	
	VKT-2	VKT-3
Exposure for 5 hr to temperature*: 300°C 350°C 400°C	7.9 6.2 2.4	9.9 2.3 4.8
Exposure to 96-98% rel humidity for 3 days: Test At 20°C At 300°C	39.2 3.1	31.7 3.7
Exposure to transformer oil for 5 days: Test At 20°C At 300°C	42.8 3.2	41.7 4.1
Exposure to kerosene for 5 days: Test At 20°C At 300°C	2.1 2.9	2.3 4.7

*Tested at the same temperature.

There is interest in organoborosilicon compounds as a base for thermally stable adhesives. Data on the strength of adhesive joints made with these adhesives at various temperatures are as follows:

Influence of Temperature on Strength of 30KhGSA Steel Joints Made With
Organoborosilicon Adhesive Compositions (#201 and #202)

Adhesive Composition	Shear strength, kg/cm ²						
	At 20°C	At 300°C	At 350°C	At 400°C	At 425°C	At 450°C	At 500°C
201	140	--	68	58	56	48	36
202	180	65	65	50	50	49	40

**Influence of Holding at High Temperatures on Strength of 30KhGSA
Steel Adhesive Joints Made With Organoborosilicon Adhesives**

Adhesive Composition	Shear strength, kg/cm ²				
	Initial data		After 2 hr at 400°C		After 1 hr at 500°C
	At 20°C	At 400°C	At 20°C	At 400°C	At 20°C
201	140	48	89	40	70
202	130	50	37	36	33

Adhesive joints made with compositions 201 and 202 have low water resistance after 30 days in water, the shear strength drops to 30 kg/cm² for composition 201 and to 83 kg/cm² for adhesive 202. At 425°C, the strength is 49 and 47 kg/cm², respectively. After boiling the adhesive joints in water for 2 hours the strength of adhesive joints made with composition 201 is 32 kg/cm² (20°C) and 46 kg/cm² (425°C), 68 and 49 kg/cm², respectively for adhesive 202.

Joints with U-2-28 adhesive can operate for extended times at 200° to 250°C. The adhesive does not cause corrosion of metals.

Strength of Adhesive Joints in Metals Made With U-2-28 Adhesive Sealer

Indicators	Test Temperature, °C				
	-60	20	200	250	300
Peeling strength, kg/cm ²	2.5 to 5.0	1.3 to 2.0	0.37 to 0.60	0.32 to 0.36	0.24 to 0.28
Shear strength, kg/cm ²	57 to 64	13 to 30	6.5 to 8.0	4.2 to 5.6	3.0 to 3.7

Properties of Glass Fiber Laminates Based on PFS and Other Organosilicon Resins

Properties	Glass fiber laminates based on		
	PFS	SKM-1	STK-41
Density, g/cm ³	1.76	1.74	1.7
Impact strength, kgf-cm/cm ²	100	60	110
Strength kg/cm ²			
flexural	1500	1400	1000
tensile	1800	--	2000
compression along the piles	650	610	--
perpendicular to the piles	1600	--	--
Martens yield temperature, °C	280	215	250
Water absorption in 24 h, %	0.1	0.5	0.35
Tan δ at f = 10 ⁶ Hz			
20°C	0.010	0.006	0.002
200°C	0.014	0.08	0.02
300°C	0.018	0.55	--
Dielectric permittivity at f = 10 ⁶ Hz			
20°C	4.6	4.5	--
200°C	4.6	--	--
300°C	4.7	--	--
Surface resistivity at 20°C, ohm	5x10 ¹⁴	1.2.10 ¹⁴	10 ¹⁴
Volume resistivity, ohm-cm			
20°C	1x10 ¹⁵	5x10 ¹³	10 ¹⁴
200°C	9x10 ¹²	10 ¹²	10 ¹²
300°C	2x10 ¹⁰	--	--
Electric strength at 20°C kV/mm	10	11	18

The laminate based on PFS has a high heat distortion temperature and retains 61% of the initial strength at 200°C and 44% at 300°C (the specimens being heated at each temperature for 40 min):

Temperature of testing, °C	20	100	200	300	400
Flexural strength, kg/cm ²	1500	1100	915	665	270

The dielectric permittivity and $\tan \delta$ of the glass fiber laminate based on PFS, in contrast with commercial organosilicon glass fiber laminates, changes only slightly up to 300°C. Note that the Martens yield temperature of the PFS laminate is 30° to 65°C higher than the "control" laminates. In these laminates the filler was ASTT(b)-S₂ low-alkali glass fabric. The content of resin in the glass fiber laminate was 32% to 35%. The following conditions of hardening were used: 150°C for 5 hours, 200°C for 1 hour, and 200°C for 6 hours.

The PFS type laminate is resistant to water, organic solvents, and dilute alkaline solutions; it is not resistant to acids or high concentrations of alkali.

Results of the Action of Various Reagents on a Glass Fiber Laminate Based on PFS

Reagents	Gain in wt, %	Flexural strength, % of initial
Water	0.12	98.6
Acetone	0.14	98.4
Alcohol	0.12	99.0
Benzene	0.23	97.5
Dichloroethane	0.41	96.0
Hydrochloric acid		
10%	0.14	63.7
36%		Specimens broke up
Sulphuric acid		
10%	21.65	Specimens peeled
96%		Specimens broke up
Nitric acid		
10%	1.35	57.4
64%		Specimens broke up
Caustic soda solution		
10%	0.25	95.3
50%	4.6	64.6

Note - The specimens were kept in the media for 36 hours.

Designation

Trademark ----- DEMPS-3M
 Generic type ----- Diorganosiloxane variants of
 ω, ω' -diethoxymethacrylates

Description

These adhesives can be prepared by curing ω, ω' -diethoxymethacrylates of polydiorganosiloxanes at 50°C for 1 hour in the presence of 1% dicyclohexyl peroxydicarbonate (DPD). In the series of polymers of ω, ω' -diethoxymethacrylates of polydiorganosiloxanes, the resistance to thermooxidation rises with increase in the number of diorganosiloxyl units in the main chain of the polymer. With an identical number of units, the polymers containing the methylphenylsiloxane units are more heat resistant than are the polymers containing dimethylsiloxyl units.

Application

No specific application is known; however, the overall chemical structures of these siloxane variants of methacrylates suggest that they may be developed into novel high-temperature adhesives and binders.

Technological Status

Research ----- 1966 (est)
 Development ----- 1969 (est)
 Engineering ----- 1969 (est)
 Production ----- Not known

Properties

As indicated by resulting data, the temperature at which the weight of the specimens begins to decrease, as a consequence of degradation, increases regularly in the sequence: TGM-3* < DEMPS-3M < DEMPS-3MF < DEMPS-9M < DEMPS-100M. In accordance with this series, a regular reduction in the total weight loss of the polymers at high temperature is seen.

*Triethyleneglycol dimethacrylate

Weight Losses of the Polymers in Thermooxidative Degradation

Polymer	Temp at beginning of wt loss °C	Weight loss of the specimens, %						
		200°C	300°C	350°C	400°C	450°C	500°C	550-600°C
TGM-3*	110	3.5	20.9	47.9	68.1	87.1	95.4	--
DEMPS-3M	110	1.9	9.7	20.3	39.6	75.8	87.5	--
DEMPS-3MF	130	1.9	6.9	15.0	26.1	50.0	69.6	79.2
DEMPS-9M	180	--	6.7	12.9	22.9	31.4	41.5	74.2
DEMPS-100M	200	1.6	3.2	6.4	9.2	17.2	34.0	--

*Triethyleneglycol dimethacrylate

Designation

Trademark ----- MF-50
 Generic type ----- Silicone resin

Description

MF-50 is an organosilicon resin used as an adhesive in a 40% to 50% by weight solution, with a gelling time of 5 to 15 minutes at 200°C. SMF-50 glass fabric laminate, based on MF-50 organosilicon resin (dry solids 40% to 50%, gelling time at 200°C 5 to 15 minutes), has good heat resistance and retention of mechanical and dielectric properties at high temperatures.

Application

Silicon adhesives are widely used by the Soviets. SMF-50 glass fabric laminate (using MF-50 as binder) has good heat resistance and retention of mechanical and dielectric properties under high-temperature conditions. This laminate can be used as electrical insulation and structural material in the radio and electronic industries, at temperatures from -50° to 300°C over long periods, at 350°C for not more than 500 hours, and at temperatures of 600°C and above for 5 to 10 minutes.

Technological Status

Research ----- 1964 (est)
 Development ----- 1965 to 1966 (est)
 Engineering ----- 1967 to 1968 (est)
 Production ----- 1969 (est)

Properties

The strength of SMF-50 glass fabric laminate is maintained under the prolonged application of temperatures in the 200° to 300°C range.

Mechanical Properties of SMF-50, Based on ASTT(b)-S₁, After Holding at High Temperatures

Property	At room temperature	1000 hr at 200°C	1000 hr at 250°C	500 hr at 300°C	250 hr at 350°C
Strength, kgf/cm ²					
flexural	2480	970	850	620	480
compression	1880	750	450	320	--
tensile	2900	2300	900	1600	--
Impact strength, kgf-cm/cm ² *	200	80*	65*	50*	35*

*Testing at 200°C

Mechanical tests of specimens show that SMF-50 glass fabric laminate can operate for short periods at high temperatures (400° to 600°C). Test results are as follows:

Temperature*, °C	Flexural strength, kgf/cm ²
300	1200
400	850
600	675

*Time 20 min

Dielectric Properties of SMF-50 Based on ASTT(b)-S₁

Property	In original condition	After holding for 24 hr in a medium of relative humidity 100%	At 200°C
Tan δ of dielectric loss (f=10 ⁶ Hz)	0.0018	0.028	0.002
Volume resistivity, ohm-cm	1x10 ¹⁵	1x10 ¹³	1x10 ¹⁴
Surface resistivity, ohm	1x10 ¹⁵	1x10 ¹³	1x10 ¹⁴
Dielectric permittivity (f=10 ⁶ Hz)	3.9	4.2	3.7
Electric strength, kV/mm	7.6	7.5	---

Dielectric Properties of SMF-50 At Elevated Temperatures

Temperature, °C	Tan δ ($f=10^6$ Hz)	Dielectric permittivity ($f=10^6$ Hz)
20	0.0032	4.8
100	0.0038	4.8
200	0.0045	4.7
300	0.0052	4.85
400	0.0058	4.93
500	0.0084	4.93
600	0.0088	4.9

SMF-50 glass fabric laminate has high thermal stability; in the course of prolonged heat aging (up to 3000 hours) at 250° to 350°C, it is claimed that the weight loss does not exceed 1%.

Designation

Trademark ----- KM-9K
 Generic type ----- Polymethylsiloxane

Description

KM-9K is a standard siloxane binder resin that has been commercially available for about 6 to 7 years.

Application

The siloxane, alone and with fillers, can be used in electrical and electronic applications where high performance is required. It is claimed that this class of binders has potential use in high-voltage insulator lines, high-performance transformers, and high-amperage circuits.

Technological Status

Research ----- 1965 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1970 to 1972 (est) (production may
 be limited)

Properties

PK-9 and KPZh-9 plastics based on KM-9K binder resin show high arc resistance and high tracking resistance.* PK-9 is filled with silica cuttings, and KPZh-9 is filled with asbestos fiber.

*T. V. Morogova, et al., "Changes in Electrical Properties of Plastics based on a Polymethylsiloxane Resin." Soviet Plastics, No. 1, 19-20 (1971).

Designation

Trademark ----- ETS-40, ETS-50 (Etilsilikat)
 Generic type ----- Ethyl silicates

Description

Etilsilikat adhesives are a mixture of a monomer, tetraethoxysilane, and polyalkoxysiloxanes. These are polymers of linear structure. Etilsilikat-40 (ETS-40) cannot be used as a binder without additional hydrolysis and hydrolytic condensation of the resulting products. Etilsilikat-50 is a mixture of alkoxyxiloxanes with branched and partially cross-linked structure. It has 50% to 55% silicon content, making it useful as a ceramic mold binder.

Application

ETS-40 and ETS-50 can be used in making ceramic shell molds for casting of metals.

Technological Status

Research -----	1965 (ETS-40) (est)
	1968 (ETS-50) (est)
Development -----	1968 (ETS-40) (est)
Engineering -----	?
Production -----	1969 (ETS-40) (est)

Properties

The fluxural strength of a ceramic based on ethyl silicate decreases with increase in the content of silicon. This is due to premature gelling of these alkoxyxiloxanes in the course of production of the ceramic. The following data indicate the influence of impurities on the strength of a ceramic based on ethyl silicate:

<u>Results of analysis of the products, %</u>	<u>A</u>	<u>B</u>
Si -----	24.3/25.3	23.8/22.6
-Si-OC ₂ H ₅ -----	58.9/54.7	60.4/63.6
Si(C ₂ H ₅) ₄ (sic) -----	---	-/0.9
C ₂ H ₅ OH -----	1.5/-	2.5/2.0
Fe -----	10 ⁻³	0.22/10 ⁻³
Drying time of film, hours -----	24/4.5	4.03/5.5
Flexural strength, kgf/cm ² -----	46.0/29.8	12.6/28.6

(Note: A: Figures before stroke, ethyl silicate before heating; after stroke, ethyl silicate after heating. B: Figures before stroke, ethyl silicate containing iron compounds; after stroke, containing tetraethoxy-silane.)

Designation

Trademark ----- Unknown
 Generic type ----- Silicon containing phosphazenes

Description

This generic type is based on the reaction product of butoxycyclophosphazene and chloromethylorganosiloxanes. They are commonly called poly(silico-phosphazenes).

Application

This adhesive class can be used in glass-reinforced plastics (200° to 250°C) having a short-term capability of a few hours at 350°C.

Technological Status

Research ----- 1967 (est)
 Development ----- 1968
 Engineering ----- 1970
 Production ----- ?

Properties

The poly(silico-phosphazenes) display the following properties when used as binder resins for GRP's (using Grade T glass fabric).

Properties of GRP's Based on the Silicon-Containing Polyphosphazenes

Binder resin	Binder content, %	Flexural strength, kgf/cm ²		
		at 20°C	After 2 hrs in boiling water	After 30 min holding at 350°C
HBPh + OChMS	14.0	585	438	198
TPhTB + OChMS	21.8	1172	244	243

Note: HBPh = hexabutoxycyclotriphosphazene
 TPhTB = triphenoxytributoxycyclotriphosphazene
 OChMS = oligomeric chloromethyl siloxanes

The GRP's were produced by molding at 200°C and at a pressure of 5 kgf/cm², followed by heat treatment. The binders were synthesized by condensation at 160°C in a nitrogen atmosphere. The resulting composites purportedly have good heat resistance and hydrolytic stability.

Designation

Trademark ----- PTGS, DPDGS
 Generic type ----- Poly(phenyltriglycidoxysilane),
 Poly(diphenyldiglycidoxysilane)

Description

Active diluents used for epoxy resins are aliphatic epoxy resins based on various glycols. PTGS is prepared by the ester exchange reaction of phenyltrialkoxysilanes with glycidol in the presence of alkaline catalysts.

PTGS-M is obtained by the ester exchange reaction of phenyltrimethoxysilane. PTGS-E is obtained by the ester exchange reaction of phenyltriethoxysilane. Diphenyldiglycidoxysilane is prepared by the ester exchange reaction of diphenyldimethoxysilane.

Application

It is expected that the Soviets are using these materials as adhesives and GRP binders where reliable performance under hot and/or wet conditions is desired.

Technological Status

Research ----- 1968 (est)
 Development ----- 1969 (est)
 Engineering ----- 1970 to 1971 (est)
 Production ----- 1972 (est)

Properties

Dielectric properties of the hardened phenylglycidoxysilanes are as follows:

<u>Product</u>	<u>PTGS-M</u>	<u>PTGS-E</u>	<u>DPDGS</u>
tan δ -----	0.002/0.013	0.002/0.012	0.001/0.008
ϵ -----	2.2/2.8	2.0/3.0	2.8/3.3
$\rho_v \times 10^{-16}$, ohm, cm -----	3.0	3.4	2.5
$\rho_s \times 10^{-16}$, ohm -----	6.0	6.0	1.9
E_s , kV/mm -----	18.9	21.4	20.0

(Note: Figures before the stroke, at frequency 10^3 Hz; after stroke, at 10^6 Hz)

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When methyltetrahydrophthalic anhydride (in an amount of 0.85 mol per epoxy group) is used as the hardener, the following hardening schedule is observed:

- 2 hours at 100°C;
- 4 hours at 120°C;
- 4 hours at 140°C;
- 2 hours at 150°C;
- 12 hours at 200°C.

Properties of resins based on ED-5 epoxy resin diluted with PTGS-M and PTGS-E (hardened with POFT-3 polyorganophosphotitanoxane or PEPA polyethylenepolydiamine) are as follows:

Components parts by weight	Hardening conditions, °C-hr	Strength, kgf/cm ²		Brinell hardness, kgf/cm ²	Impact strength, kgf-cm/cm ²	Vicat softening temp., °C
		flexural	compression			
ED-5(100) POFT-3(15)	160-6 180-6	900 to 1000	2000	8 to 19	7 to 8	193
ED-5(100) PTGS-E(20) POFT-3(15)	160-6 180-6	600 to 700	1035	19 to 20	8 to 9	183
ED-5(100) PEPA	--	800 to 1000	1200 to 1600	10 to 12	3 to 13	--
ED-5(100) PTGS-M(20) PEPA(10)	20-24 100-1 120-5 140-2	900 to 1000	--	--	13 to 15	--
ED-5(100) PTGS-E(20) PEPA(10)	20-24 100-1 120-5 140-2	900 to 1000	1150	12	16	175

Designation

Trademark ----- AMK, DGMS, and TM-60
Generic type ----- Polyester and variants

Description

AMK adhesive is an adhesive composition based on polyester resins. The storage life is 1 year. DGMS adhesive composition is the product of interaction of an unsaturated polyester with styrene. The composition is prepared by mixing DGM polyester (75%) with styrene (25%) and benzoyl peroxide (0.5% to 1% of the mass of the composition) just before use. To decrease shrinkage and prevent cracking, a filler can be added to the composition (for example, ground quartz sand). Type TM-60 adhesive is prepared by dissolution of resin TF-60 (a polyester based on ethylene glycol, terephthalic, and sebacic acids) in methylene chloride. The adhesive is designed for bonding of polyethylene terephthalate films.

Application

The polyester resins can be used for the manufacture of adhesives designed for attachment of metal to glass, asbestos to copper, and aluminum foil to cork, and for bonding of glass-reinforced plastics and other materials. The adhesive properties of polyesters are due to the presence of carboxyl and hydroxyl groups in the polymer molecule.

AMK adhesives are suitable for bonding of wool, glass, and cotton thermal insulation to metal surfaces. DGMS is suitable for use as a filler.

Properties

The adhesive consumption is 180 to 200 g/m² applied in two coats. Bonding modes are: a) at 15° to 35°C, drying time of first coat 2 hours, second coat with thermal insulation--24 hours; b) at temperatures up to 70° to 100°C, 6 to 8 hours. The peeling strength of adhesive joints when AOD fabric is bonded to clad duralumin, following drying for 4 hours at 100° to 105°C, is at least 75 kg/m. The adhesive joints can be used at temperatures up to 80° to 100°C. The adhesive does not cause corrosion of metals and has good resistance to the effects of water and petroleum hydrocarbons.

Curing of DGMS is performed at high temperatures. Bonding can be performed by holding the adhesive joint at 60° to 100°C for 2 to 5 hours under a pressure of 1 to 3 kg/cm². The shear strength of an adhesive

joint in duralumin produced with DGMS adhesive (with 0.5% benzoyl peroxide) is 100 kg/cm² at 20°C, 45 kg/cm² at 60°C, and 18 kg/cm² at 100°C.

Adhesive joints made with TM-60 adhesive can be used in products in the temperature interval from -150° to +100°C. Bonding is performed by applying the adhesive to both surfaces, with subsequent rolling, using a roller heated to 150° to 170°C. The adhesive joints are transparent, oil-, water- and frost-resistant.

Technological Status

Research -----	late 1930's (first types)
	1958 (newer variants) (est)
Development -----	?
Engineering -----	?
Production -----	1945 (first polyesters)
	1965 (newer variants) (est)

Designation

Trademark ----- TF-60 (S series and SF series)
 Generic type ----- Copolyester bonding agents for use
 in bonding polyethyleneterephthalate
 film

Description

TF-60 is a reaction product of ethylene glycol with terephthalic and sebacic acids. It is the standard for the bonding of PETP (mylar-like) films. The S and SF types are more heat resistant adhesives than TF-60. They are based on the reaction products of ethylene glycol with terephthalic and isophthalic acids for the S series, and on ethylene glycol with terephthalic and 2,5-furandicarboxylic acids for the SF series.

Application

These adhesives can be considered to be specific adhesives for PETP film; however, they can be used for other substrates which contain polar groups.

<u>Technological Status</u>	<u>TF-60</u>	<u>"S Series"</u>	<u>"SF Series"</u>
Research Development Engineering	1955 (est)	1968	1968 (est)
Production	1960 (est)	1971 to 1972	1971 to 1972 (est)

Properties

The maximum working temperature of joints bonded using TF-60 copolyester is 100°C; the strength of the bond at this temperature is 40% to 50% of that of the PETP film. The SF copolyesters containing less than 25 mol% of ethylene 2,5-furandicarboxylate or ethylene isophthalate units are not soluble in low-bp solvents. Copolyesters with a content of ethylene isophthalate units in excess of 30 mol% and of ethylene 2,5-furandicarboxylate units in excess of 35 mol% dissolve completely in methylene chloride, dichloroethane, and tetrachloroethane.

Properties of Copolyesters

Grade of copolymer	Specific viscosity	Shear strength, kgf/cm ²	Temperature of adhesion failure of the bonds, °C
SF-25	0.09	1500	--
SF-25	0.14	1550	99
SF-25	0.16	1600	98
SF-25	0.19	1600	107
SF-25	0.32	1800	180
S-25	0.12	1550	90
S-25	0.20	1600	150
S-25	0.30	1750	170

Designation

Trademark ----- PSK-1 and 4 Variants
 Generic type ----- General-purpose polyesters and modified variants

Description

Adhesives in this series are:

- PSK-2 (ED-5 epoxy resin modified polyester.)
- PSK-4 (Variant with unsaturated epoxy resin ester.)
- PSK-8 (about 5% α -methylstyrene in base polyester.)
- PN-10 (unsaturated polyester copolymerized with styrene. The base polyester is probably polyester maleate)

Application

PSK-1 and its variants can be used as binders for glass fibers, molding powders, and general high-performance adhesives for various substrates.

<u>Technological Status</u>	<u>PSK-1</u>	<u>PSK Variants</u>
Research -----	Before 1960 (est)	1968 (est)
Development -----		
Engineering -----		
Production -----	1960 (est)	1974 (est)

Properties

The properties of PSK-1 and PSK-8 are shown below.

<u>Properties</u>	<u>PSK-8*</u>	<u>PSK-1</u>
Impact strength, kgf-cm/cm ² -----	16 to 23/30 to 32	25 to 30
Flexural strength, kgf/cm ² -----	800 to 900/800 to 1000	800 to 1000
Martens yield temperature, °C -----	110 to 135/168 to 223	180 to 240

*The figure before the stroke signifies without heat treatment; the figure after the stroke, signifies after heat treatment.

<u>Properties</u>	<u>PSK-8*</u>	<u>PSK-1</u>
Water absorption in 24 h, % -----	0.08 to 0.12/0.09 to 0.1	0.25 to 0.5
Shrinkage, % -----	0.1 to 0.15/-	0.4 to 0.6
Breakdown strength, kV/mm:		
A -----	16.0/15.0	13.8
B -----	15.0/15.0	9.3
C -----	15.0/-	4.5
D -----	15.0/-	2.5
Volume resistivity, ohm-cm:		
A -----	$10^{13}/10^{13}$	10^{14}
B -----	$10^{12}/10^{13}$	10^{10}
C -----	$10^{10}/-$	10^8
D -----	$10^{10}/-$	10^6
Surface resistivity, ohms:		
A -----	$10^{13}/10^{13}$	10^{13}
B -----	$10^{11}/10^{12}$	10^9
C -----	$10^{10}/-$	10^7
D -----	$10^{10}/-$	10^7
Dielectric permittivity, (f=1 MhZ) -----	3.0 to 4.0/-	4.0 to 6.0
Tan δ (f=1 MhZ) -----	0.015 to 0.02/-	0.02 to 0.03

Note: A gives the value in the initial state; B, C, and D give values after keeping in water for 1, 7, and 14 days, respectively.

*The figure before the stroke signifies without heat treatment; the figure after the stroke, signifies after heat treatment.

The Effects of Moisture on the Properties of Various Premixes for Adhesives in the PSK Series:

Type of premix	Change in weight, %		Volume resistivity, ohm-cm		Surface resistivity, ohms		Breakdown strength, kV/mm		Reduction in flexural strength after 366 days keeping in water, %
	Time of keeping, days		Time of keeping, days		Time of keeping, days		Time of keeping, days		
	14	146	0	14	0	14	0	14	
Control of PSK-1 premix based on ZHS-1 glass fibre	1.62	2.90	10 ¹⁴	10 ⁶	10 ¹⁴	10 ⁷	13.8	2.3	62.1
Premix based on glass fibre with finish:									
Z	1.22	2.80	10 ¹³	10 ⁸	10 ¹⁴	10 ⁸	13.3	12.0	55.4
ZV	1.20	2.80	10 ¹³	10 ⁸	10 ¹⁴	10 ⁸	13.3	12.0	51.8
Premix containing 1:1 mixture of kaolin and talc (1:1)	0.97	2.50	10 ¹⁴	10 ⁷	10 ¹⁴	10 ⁸	13.8	11.3	46.5
Premix with addition (3%) of organosilicon compounds VIES (vinyltriethoxyisilane;Transl.)	1.42	3.50	10 ¹¹	10 ⁸	10 ¹²	10 ⁸	14.2	2.1	58.7
PMS-50 (polydimethylsiloxane; (Transl.))	1.42	3.50	10 ¹¹	10 ⁷	10 ¹²	10 ⁸	13.2	1.3	58.7
GKZh-94 (ethylhydrosiloxane liquid; (Transl.))	1.42	3.50	10 ¹³	10 ⁷	10 ¹³	10 ⁸	7.7	2.0	58.7
GVS-9 (a silane derivative; Transl.)	1.42	3.50	10 ¹⁰	10 ¹⁰	10 ¹¹	10 ⁸	14.0	2.3	58.7
Premix with addition of ED-5 epoxy resin (PSK-2)	0.83	2.30	10 ¹⁴	10 ¹⁰	10 ¹³	10 ¹¹	17.0	16.0	38.8
Premix based on PH-10 (resin based on an unsaturated polyester copolymerised with (or in solution in) styrene; Transl.)	1.53	2.40	--	--	--	--	--	--	42.2
Premix based on unsaturated epoxy resin ester (PSK-4)	0.10	0.70	10 ¹³	10 ¹¹	10 ¹³	10 ¹⁰	15.0	15.0	43.5

PSK-4 premix is stable even when tested under tropical conditions. It has high heat resistance, in addition to high water resistance. The nominal decomposition temperature of the binder in PSK-4 premix is 250° to 260°C, which is 30°C higher than that of PSK-1 premix. PSK-1 premix shows irreversible changes in strength as early as after 150 days aging at 155°C, whereas the strength of PSK-4 premix is somewhat increased under these conditions.

Designation

Trademark ----- PN-1 with "Fosfakrilat" flame retarder
 Generic type ----- Polyethylene glycol maleate phthalate (ester) with organophosphorus ester

Designation

"Fosfakrilat" (FA) is a mixture of esters of linear and cyclic structures that are synthesized from pentaerythritol and alkylphosphoric and methacrylic acids. Incorporation of FA into the commercial polyester resin PN-1 (polyethylene glycol maleate phthalate) gives flame resistant GRP's. "Fosfakrilat" contains 6% to 10% phosphorus.

Application

The modified PN-1 materials have been used in several general purpose structures as binders. They can also be used as general adhesives and as binders in flame resistant GRP's.

<u>Technological Status</u>	<u>PN-1</u>	<u>PN-1 with Fosfakrilat</u>
Research	Prior to 1960 (est)	1964 (est)
Development	--	--
Engineering	--	--
Production	1962 (est)	1971 (est) (production may be limited)

Properties

FA is able to copolymerise with the PN-1 polyester, forming a three-dimensional structure; with this there is a considerable increase in the hardening time. The dependence of the hardening times of the PN-1 + FA system in various conditions is shown below:

Initiator and accelerator	Hardening temperature, °C	Hardening time, min, with FA amount (%)						
		0	5	10	20	25	33	50
CuHP (3%) CoNa (8%)	20	90	1440	2500	5500	6700	8700	--
CuHP (3%) CoNa (3.5%)	60	13	20	28	46	60	80	130
CuHP (3%) CoNa (1.5%)	80	4	7	10	12	13	19	35
Benzoyl peroxide (1%) dimethyl- amiline (2%)	80	2	2.5	3	4	4.5	5	7
CuAP (1%) V (0.4%)	80	2	2	2.5	3	4	5	6
CuHP (3%) V (1%)	20	26	28	31	33	35	36	37

CuHP = cumene hydroperoxide; AP = acetyl peroxide; HA = Napthenate;
V = V₂O₅

Designation

Trademark ----- PN-11
 Generic type ----- Polyester (no styrene or volatile
 content)

Description

In the hardened state, PN-11 is superior to PN-1 in heat resistance. (PN-1 is specified by MRTU-6-05-1082-67, polyethylene glycol maleate phthalate. PN-11 is specified by TUP-457-66; composition is not defined.)

Application

Taking into account the good properties of PN-11 resin (its relatively low viscosity and the absence of styrene) and its relatively low cost, it is recommended as a replacement of PN-1 resin as a binder for parts and structures of GRP's functioning at temperatures up to 100°C. PN-11 is used in the production of glass fiber-reinforced tubes.

Technological Status

Research ----- 1964 (est)
 Development ----- 1965 (est)
 Engineering ----- 1966 (est)
 Production ----- 1966 to 1967 (est)

Properties

The following are the mechanical properties of the hardened polyester resins PN-1 and PN-11:

	<u>PN-11</u>	<u>PN-1</u>
Strength, kgf/cm ² :		
compression -----	1270	830
tensile -----	485	650
Elongation at break, % -----	1.69	4.70
Elastic modulus in		
flexure, kgf/cm ² -----	40,200	23,000
Impact strength,		
kgf-cm/cm ² -----	2.4	5.0
Martens yield temper-		
ature, °C -----	67	43
Vicat softening point, °C -----	185	87

Properties

Tests of bonded joins of Stal' 3 steel based on polyester (PN-1) and epoxy (ED-6) bonding agents are shown below:

<u>Bonding Agent</u>	<u>PN-1</u>	<u>ED-6*</u>
Strength in uniform direct tension or in shear, kgf/cm ² days:		
1 -----	384/154	209/40
2 -----	428/167	261/82
5 -----	424/182	278/92
10 -----	401/188	300/145
25 -----	396/191	292/139
50 -----	399/189	--

Note: Figures before the stroke, strength in uniform direct tension; after, shear strength.

*With dibutyl phthalate plasticizer, and polyethylene polyamine room temperature hardener.

Designation

Trademark ----- PN-11, modified with allyl
mellitates
Generic type ----- Allyl mellitate modified polyester

Description

These adhesives are copolymers of unsaturated polyesters with monomers of the allyl series having more than one double bond per molecule, such as diallyl phthalate, diallyl isophthalate, allyl cyanurate, and others.

Application

These materials have potential application as binders and adhesives for moderately high-temperature use. They appear adequate for moderate-load structural and general purpose bonding.

Technological Status

Research ----- 1963 (est)
Development ----- 1966 (est)
Engineering ----- 1966 (est)
Production ----- 1969 to 1970 (est)

Properties

The following are some of the properties of allyl esters of aromatic acids:

	<u>TATM</u>	<u>TAPM</u>
Elementary composition, %		
C -----	64.94/65.45 ^a	62.9/63.7
H -----	5.24/5.45	4.99/5.29
Bromine number -----	143.3/145.5	147.8/154.5
Ester number -----	505/509	537/540
n_D^{20} -----	1.5298/-	1.5220/-
Density, g/cm ³ -----	1.1737/-	1.1705/-
B.p., °C -----	195-205/- (3 mm Hg)	200/205/- (3 mm Hg)

a: Figures before the stroke, found; after, calculated.

The following are some properties of the hardened resin based on PN-11 polyester and allyl esters of polycarboxylic acids:

	<u>TATM</u>	<u>TAPM</u>	<u>TGM-3^a</u>
Vicat softening point, °C -----	300	300	170-190
Martens yield temperature, °C -----	155	177	60-70
Brinell hardness, kgf/mm ² -----	36.4	48.0	12-16

a: triethyleneglycol dimethacrylate

Hardening is effected in the presence of 1% of tert-butyl perbenzoate with step-wise raising of the temperature in the 80° to 140°C range. During the period of 5 hours, 50% of the monomer is added to the resin.

Designation

Trademark ----- Evinol-1
 Generic type ----- Polyester acrylate

Description

Modification of properties of unsaturated polyesters by copolymerization with various vinyl monomers is widely used. Methods are also known for producing low-toxicity binder resins using the low-viscosity oligoester acrylates TGM-3 (triethyleneglycol dimethacrylate), MGF-9 (dimethacrylate of bistriethyleneglycol phthalate), and others (instead of styrene).

Evinol-1 is an unsaturated oligomeric binder resin containing double bonds of a mixed type, both on the ends and in the middle units of the oligoester. Evinol-1 is a light-yellow liquid with a slight odor. It does not contain any volatile and toxic monomers and solvents. Evinol-1 resin hardens at room and elevated temperatures, using the same initiator systems as ordinary polyester resins.

Application

Compositions based on Evinol-1 resin can be used as potting compositions for starter-control gear, instead of using a composition based on epoxy resins. Production tests show that Evinol-1 can be used with good results as a binder resin for impregnating and potting compositions. Evinol-1 is recommended as a low-toxicity binder resin for heat-resistant GRP's, for making large articles of GRP's, and also for potting and impregnating compositions. This resin may also be used as a binder for varnishes, core mixes, coated sands for foundry work, and also in all fields of use of unsaturated polyester resins.

Technological Status

Research ----- 1968 (est)
 Development ----- 1970 (est)
 Engineering ----- ?
 Production ----- 1972 (est)

Properties

Mechanical properties of Evinol-1 resin hardened at 70° to 100°C for 4 hours at room temperature (holding for 1 month) are given below. The mechanical properties of specimens of Evinol-1 are slightly affected by

the hardening temperature, except for the compression strength. Compared with general purpose polyester (PN-1 and PN-2), Evinol-1 resin has higher heat resistance and may be rated, along with PN-3 and PN-4, as a heat-resistant resin.

Mechanical Properties of Hardened Evinol-1 Resin

Property	Hardened	
	at 70° to 100°C*	at room** temperature
Degree of polymerization, %	95 to 97	93 to 97
Brinell hardness, kgf/mm ²	20 to 22	14 to 22
Vicat softening point, °C	180	180
Strength, kgf/cm ²		
flexural	500 to 600	500 to 600
compression	1500 to 1700	2000 to 2200
Impact strength, kgf-cm/cm ²	7 to 8	--

*Initiator system: Cumene hydroperoxide-3%; cobalt naphthenate-7%

**Initiator system: Cumene hydroperoxide-0.3%; Accelerator VO₅-0.2%

Evinol-1 resin hardened at 70° to 100°C is not inferior in dielectric properties and impact strength to ED-6 epoxy resin.

Electrically Insulating Properties of Evinol-1 Resin Hardened at 70° to 100°C

Property	Evinol-1	ED-6+30% of maleic anhydride
Tan δ (f = 10 ⁶ Hz)	0.023	0.024
Permittivity (f = 10 ⁶ Hz)	4.9 to 5.3	4.1
Resistivity		
volume, ohm-cm	1.4x10 ¹⁴ to 1.9x10 ¹⁴	2.1x10 ¹⁴ to 1.5x10 ¹⁴
surface, ohm	3.2x10 ¹⁴	1.5x10 ¹⁴
Electric strength, kV/mm	18 to 19	18.6
Impact strength, kgf-cm/cm ²	20 to 22	17.0

A glass fabric laminate based on Evinol-1 resin has good mechanical and insulating properties, while its Martens yield temperature is considerably superior to that of glass fabric laminates based on PN-3 and PN-4 resins:

Strength, kgf/cm²

tensile -----	2700 to 3400
flexural -----	2800 to 3500
compression -----	2000 to 2500

Elastic modulus in tension,

kgf/cm ² -----	6.1x10 ⁴ to 1.22x10 ⁵
---------------------------	---

Impact strength,

kgf-cm/cm ² -----	220 to 370
------------------------------	------------

Martens yield

temperature, °C -----	240 to 270
-----------------------	------------

Water absorption in 24 hr, % --

0.4 to 0.52

Permittivity

(f = 10 ⁶ Hz) -----	3.1 to 4.0
--------------------------------	------------

Tan δ

(f = 10 ⁶ Hz) -----	0.02 to 0.021
--------------------------------	---------------

Resistivity

surface, ohm -----	1.7 to 3x10 ¹³
--------------------	---------------------------

volume, ohm-cm -----	3.7 to 6x10 ¹³
----------------------	---------------------------

Designation

Trademark ----- PNT-2, PNTS-1
 Generic type ----- Maleate acrylate

Description

PNT-2 resin is a solution in TGM-3 (triethyleneglycol dimethacrylate) of the product of polycondensation of maleic and phthalic anhydrides and diethyleneglycol: PNTS-1 is a solution in TGM-3 of the product of polycondensation of maleic and chlorendic anhydrides and ethylene glycol and diethyleneglycol.

Application

Maleate acrylate resins have high adhesion to glass fillers and other materials and are used as resins for GRP's (and molding compositions). Because of good adhesion to various materials, their sufficiently high heat resistance, their chemical resistance, and other properties, these resins can be used as electrical insulation and sealing compositions.

PNTS-1 resin, which includes chlorine, may (with the incorporation of a small amount of antimony trioxide) be used where the end products must have reduced flammability.

Technological Status

Research ----- 1964 (est)
 Development ----- 1965 (est)
 Engineering ----- 1966-67 (est)
 Production ----- 1968 (est)

Properties

Physicochemical properties of PNT-2 and PNTS-1 resins are as follows:

Properties	PNT-2	PNTS-1
Density, g/cm ³	1.16 to 1.20	1.28 to 1.31
Viscosity, cP	800 to 2000	1000 to 2000
Acid number, mg KOH/g	20 to 25	15 to 20
Cl content, %	--	17.5 to 18.5
Content of SbO ₃ , %*	--	2
Gelling time, min, at 20 ±0.2°C in the presence of 4.0 parts by wt. of cumene hydroperoxide A +4.5 parts by wt. of accelerator AK	120 to 300	120 to 600

*Added during processing of the resin.

These resins are of comparatively low viscosity and are easily processed by various methods to give GRP's. The properties of GRP's based on PNT-2 resin and ES-0,4-1 glass roving are as follows:

Density, g/cm ³ -----	1.39 to 1.41
Glass filler content, % -----	47.5 to 48.0
Strength, kgf/cm ²	
tensile -----	1200 to 1400
compression -----	1400 to 1500
Impact strength, kgf-cm/cm ² --	130 to 150
Tensile modulus, kgf/cm ² -----	0.7 x 10 ⁵

Flammability tests on a GRP, based on PNTS-1 and ASTT(b)-S₂-0 using the fire tube method, show that the weight loss is 12.3%. The time of independent combustion is 10 seconds with no smouldering. The results of all tests show that the GRP's based on PNT-2 and PNTS-1 resins have high mechanized indices. The GRP based on PNTS-1 are self-extinguishing. PNT-2 and PNTS-1 resins are comparatively easily colored with inorganic and organic pigments, making them useful for the production of decorative GRP's.

The Mechanical Properties of GRP's Prepared by Contact
Molding, Based on PNT-2 and PNTS-1

Properties	GRP based on	
	PNT-2	PNTS-1
Density, g/cm ³	<u>1.76 to 1.78</u> --	<u>1.69 to 1.71</u> 1.62 to 1.64
Content of glass filler, %	<u>46.5 to 47.5</u> 60.0	<u>50.5 to 51.5</u> 54.5 to 55.5
Strength, kgf/cm ²	1800 to 2000 <u>(1200 to 1400)</u>	1900 to 2100 <u>(1700 to 1800)</u>
compression	850 to 950 (850 to 950)	900 to 1000 (850 to 950)
flexural	3900 to 4100 <u>(2300 to 2500)</u> 1250 to 1350 (1500 to 1600)	4500 to 4700 <u>(3000 to 3200)</u> 1700 to 1800 (1300 to 1400)
tensile	2800 to 3000 <u>(1600 to 1800)</u> 2200 to 2400 (2200 to 2400)	3600 to 3700 <u>(1850 to 1950)</u> 2600 to 2800 (2900 to 3100)
Impact strength, kgf-cm/cm ²	160 to 180 <u>(55 to 65)</u> 160 to 170 (160 to 170)	140 to 300 <u>(100 to 110)</u> 80 to 100 (110 to 120)
Elastic modulus, kgf/cm ²		
tensile	<u>1.52 x 10⁵</u> 1.49 x 10 ⁵	<u>2.15 x 10⁵</u> 1.64 x 10 ⁵
compression	--	<u>1.7 x 10⁵</u> --
Elongation at break, %	--	<u>1.67</u> --
Interlayer shear strength, kgf/cm ²	--	<u>280 to 230</u> --

Designation

Trademark ----- OEA 7-20T
 Generic type ----- Oligoester acrylate (triethylene glycol dimethacrylate with "7-20" oligoester)

Description

OEA 7-20T consists of 85 parts by weight of triethylene glycol dimethacrylate (TGM-3) and 15 parts by weight of 7-20 oligoester. OEA 7-20T is a brown product of density 1.094 to 1.098 g/cm³. It mixes well with other oligoesters of methacrylic acid and dissolves in aromatic hydrocarbons and acetone. OEA's can harden in the presence of various peroxides at relatively high temperatures or in the presence of redox systems at room temperature. The initiators used are cumene hydroperoxide (CuHP), a 15% solution of cyclohexanone hydroperoxide in CuHP (Giperiz A), a 35% solution of cyclohexanone hydroperoxide in cyclohexanone (CHHP), and the accelerator "Accelerator K."

Application

Oligoester acrylates are used extensively as medium temperature service (60° max.) adhesives for general purpose use on all types of substrates. They have been used for some time as binders for glass-structured products.

Technological Status

Research ----- 1963 to 1964 (est)
 Development ----- 1966
 Engineering ----- 1967
 Production ----- 1968 (using redox system as hardeners)

Properties

The following are the properties of OEA 7-20T cold-hardened over 7 days, compared with those of OEA 7-20T cold-hardened with subsequent heat treatment (holding for 24 hours at room temperature, then heat treatment for 2 hours at 60°C and 6 hours at 80°C):

Compression strength,
 kgf/cm² ----- 2050/2100
 Flexural strength, kgf/cm² --- 600/-

Elastic modulus in compression,
kgf/cm² ----- 20,000/21,000
Brinell hardness, kgf/mm² ---- 13.3/13.4
Impact strength, kgf-cm/mm² -- 5.20/5.25
Vicat softening point, C ----- 255/250
Amount of extractibles in:
acetone in 6h, % ----- 4.5/4.2
Volume shrinkage, % ----- 14.0/14.0

Note: Figures before the stroke, specimens cold-hardened for 7 days;
figures after the stroke, specimens cold-hardened and given heat
treatment.

In the cold-hardening of OEA 7-20T in the presence of the redox
system CuHP + accelerator K for 7 days, the degree of conversion and
the properties of the products of hardening reach the same figures as
for OEA 7-20T cold-hardened with subsequent heat treatment.

Designation

Trademark ----- OEA-7/MDF-1 copolymers (also called F-70, F-50, and F-30)
 Generic type ----- Copolymer of oligomer acrylates with dimethacrylate of bis-ethylene glycol phthalate.

Description

These adhesives consist of copolymers of varying composition based on the oligoester acrylates 7-20 (OEA-7) and MDF-1 (dimethacrylate of bisdiethyleneglycol phthalate). The polymerization of the OEA-7 and its copolymerization with the MDF are carried out "cold" in the presence of 3 parts of cumene hydroperoxide (CuHP) and a corresponding amount of cobalt accelerator, with subsequent heat treatment at various temperatures.

Application

By the copolymerization of the oligoester acrylates OEA 7-20 and MDF-1, it is possible to obtain copolymers resistant to the action of high temperatures and having high mechanical characteristics. These materials have potential utility as adhesives and binders for steel, metals, glass, and other substrates.

Technological Status

Research ----- 1967 (est)
 Development ----- 1968 (est)
 Engineering ----- 1969 (est)
 Production ----- 1971 (est)

Properties

The following are data on the changes in the degree of hardening with time and data on the influence of the temperature of heat treatment on the degree of hardening:

	<u>MDF</u>	<u>F-70</u>	<u>F-50</u>	<u>F-30</u>
Degree of hardening, % cold with subsequent heat treatment at temperature*, °C				
40 -----	96.0	89.8	82.0	76.0
60 -----	96.0	91.2	85.0	79.8
80 -----	96.0	93.0	85.6	81.9
100 -----	-	94.4	89.5	85.0
120 -----	-	94.3	90.0	85.0
140 -----	-	94.0	90.0	85.4
160 -----	-	94.0	90.0	85.0
'cold' for, days				
1 -----	96.0	88.4	80.8	57.1
2 -----	-	88.7	82.8	60.2
3 -----	-	90.0	83.9	60.2
6 -----	-	90.0	83.9	65.2
14 -----	-	90.2	85.0	65.5
21 -----	-	90.0	85.0	68.0

*Holding at room temperature for 24 hours with subsequent constant heating to the particular temperature and holding at it for 5 hours.

These data show that in "cold" hardening, the degree of hardening of OEA+MDF copolymers differs, and the hardening process is practically complete in 3 days for F-70, or 14 days for F-30; with increase in the time of exposure, there is no essential change in the degree of hardening.

Data on the OEA+MDF copolymers hardened under the optimum conditions are as follows:

<u>Copolymers</u>	<u>F-70</u>	<u>F-50</u>	<u>F-30</u>
Degree of hardening, % -----	90.6/94.3	84.4/91.6	65.5/75.0
Strength, kgf/cm ² :			
compression -----	1840/2050	1900/2300	1980/2350
flexural -----	540/580	576/896	587/720
Brinell hardness, kgf/mm ² ----	16.40/17.00	17.70/18.80	18.00/20.80
Impact strength, kgf-cm/cm ² -----	8.00/6.00	5.30/4.50	4.20/3.40
Vicat softening temperature, °C -----	205/215	220/260	260/280

Note: Figures before the stroke, the properties of copolymers hardened cold for 14 days; after, the strength hardened cold with subsequent heat treatment at 100°C for 5 hours.

The best schedule of hardening of OEA+MDF copolymers is holding at room temperature for 24 hours, followed by heat treatment with gradual heating to 100°C and holding at this temperature for 5 hours. Copolymers hardened according to this schedule have the best mechanical properties.

The following are data on the changes in the compression strength, σ_c , of OEA-7+MDF copolymers:

	<u>F-70</u>	<u>F-50</u>	<u>F-30</u>
Initial value of σ_c , kgf/cm ² -----	2050	2300	2350
Change in σ_c , % temperature, °C			
60 -----	76.6	90.2	97.7
80 -----	73.2	80.0	93.0
100 -----	47.2	60.6	67.2
120 -----	35.6	44.0	54.5
140 -----	12.2	26.0	36.4
160 -----	9.4	18.6	20.9
180 -----	8 (sic)	12.0	20.0
200 -----	5.6	9.6	16.4

Designation

Trademark ----- Unknown
 Generic type ----- Maleic anhydride oligoesters
 reacted with alkylene oxide adducts
 of phenol-formaldehydes (novolaks).

Description

The novolaks are synthesized by a standard method. The MW of the products are regulated by varying the phenol-formaldehyde ratio in the range of 1:0.5 to 1:0.87. The novolaks are rinsed with hot distilled water to remove unreacted reaction products. The content of free phenol in the rinsed products is 1% to 3%. For oxypropylation of novolaks, an excess of propylene oxide relative to the amount of hydroxyl groups in the phenol (50 mol. %) is used. Sodium hydroxide (5% based on the weight of novolak) is used as a catalyst. The rinsed and dried products do not contain free phenol and range from light-yellow to light-brown in color.

Application

The Soviets may be using these more economical oligoesters as binders in glass-reinforced plastics and also as casting or encapsulation agents.

Technological Status

Research ----- 1964 (est)
 Development ----- 1965 to 1966 (est)
 Engineering ----- 1966 to 1967 (est)
 Production ----- 1968 (est)

Properties

The drop point of the oxypropylated products is slightly lower than that of the initial novolaks, as a result of the plasticizing action of the oxypropylene units. The drop point of the novolaks and polyols increases with increase in their MW. The MW's of the polyols agree well with the MW's of the initial novolaks.

Description of Novolaks

Novolak	Drop point, °C	MW	n_{sp}	Content* of OH groups, %
F-1	84	245	0.192	15.9/17.0
F-2	87	330	0.225	17.0/16.7
F-3	88	360	0.227	16.9/16.5
F-4	94	610	0.285	17.5/16.3

*Numerator - found values; denominator - calculated values.

Description of Polyols

Polyol	Drop point, °C	MW	n_{sp}	Content of OH groups, %
OF-1	66	415	0.164	10.8/10.8
OF-2	68	520	0.175	10.8/10.6
OF-3	77	560	0.187	10.5/10.5
OF-4	80	950	0.215	11.3/10.5

With increase in the MW of maleates the drop point of the products increases. The oligoesters combine well with different polyester acrylates. The viscosity of 40% solutions of oligoesters in TGM-3 increases with increase in the MW of the maleates.

Description of Oligoesters and of Solutions of Them

Oligoester	Drop point, °C	Acid number mgKOH/g	Density of 40% solutions in TGM-3 at 20°C, g/cm ³	Viscosity of 40% solutions in TGM-3, cP
PF-1	71	220	1.145	795
PF-2	78	220	1.150	1330
PF-3	85	220	1.154	1780
PF-4	87	227	1.153	2550

A 40% solution of the oligoesters in glycol dimethacrylates hardens at room and elevated temperatures. Products show high hardness.

Designation

Trademark ----- Unknown
 Generic type ----- Methyl methacrylate (MMA) - Triallyl
 cyanurate (TAC) and isocyanurate
 (TAIC) copolymers.

Description

Copolymerization is carried out in bulk in the presence of 0.1% to 0.3% of azobisisobutyronitrile at 60° to 80°C over a period of 6 hours. The products of copolymerization are colorless translucent glasses and are a mixture of copolymers, homopolymers, and crosslinking agent triallyl cyanurate or isocyanurate that has not taken part in the reaction.

Application

The copolymers can be used as bonding agents for joining metals, glass fabric laminates, and other heat-resistant materials.

Technological Status

Research ----- 1958 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1968 (est)

Properties

Optimum weight ratios of MMA to crosslinking agent are 80:20, 90:10, and 95:5. The copolymers containing TAC, for the same monomer ratios, have a higher content of gel fraction than the copolymers containing TAIC. Softening temperatures for 95:5 (MMA) TAC (or TAIC) are 113°C for TAC variant and 105° for TAIC variant.

The incorporation of TAC or TAIC into PMMA leads to an increase in the heat resistance of the polymer; the weight loss of such copolymers in heating for 3 hours at 210°C is approximately 1%. This makes it possible to use a copolymer of 95% MMA + 5% TAC as a binder resin for GRP's. The following are some mechanical properties of GRP's based on this resin:

Strength, kgf/cm ²	
flexural -----	4110
tensile -----	4000
compression -----	4300
Impact strength,	
kgf-cm/cm ² -----	444
Brinell hardness,	
kgf/mm ² -----	200

The strength values of this GRP are similar to the comparable properties of epoxy-phenolic plastics and higher than values for GRP's based on polyester binder resins. It is claimed that these adhesives are cheaper than epoxy resins and are less toxic, having higher resistance to aging and weathering.

Designation

Trademark ----- ED-5, ED-6, E-40, E-41, E-33, ED-13,
 E-44, ED-15, E-49, E-05
 Generic type ----- Unmodified epoxies

Description

These adhesives are based on epichlorohydrin and bis-phenols. Curing agents for epoxy resins include amines, amides, anhydrides of dibasic organic acids, boron trifluoride and its complex compounds, and certain polymer products (for example phenol-formaldehyde resins). Acid anhydrides, frequently including maleic or phthalic acid anhydrides, help to increase the mechanical strength and hardness of cured epoxy polymers, in comparison to products hardened with polyamines.

Application

Epoxies hardened with anhydrides are used for bonding of aluminum and its alloys, steels, organic glass, phenol-formaldehyde plastics, wood, ceramic materials, and porcelain.

<u>Technological Status</u>	<u>Amine, amide Cured</u>	<u>Anhydride Cured</u>
Research	1955 (est)	1962 to 1963 (est)
Development	1956 (est)	1963 (est)
Engineering	1958 (est)	1965 (est)
Production	1958 to 1959 (est)	1965 (est)

Properties

Physical and Chemical Constants of Epoxy Resins

Resin Type	Melting point*, °C	Epoxy number	Mean molecular weight
ED-5	Liquid	25 to 27	450
ED-6	Liquid	20 to 22	500
ED-40	Liquid	17 to 21	600
E-41	72 to 82	9 to 12	1000
E-33	70 to 80	9 to 11	1000
E-13	50 to 55**	8 to 10	1500
E-44	83 to 92	6 to 8	1600
ED-15	60 to 70**	5 to 7	2200
E-49	95 to 100	>4	2800
E-05	115 to 125	15 to 2.5	3500

*Ring and ball method

**In capillary

Physical and Mechanical Properties of Cured ED-6 Resin

Curing agent	Brinell hardness, kg/mm ²	Static bending strength, kg/cm ²	Specific impact toughness, kg-cm/cm ²
Polyethylene polyamine, 6.5%	1.83	100	7.1
Maleic anhydride, 30%	17.2	1000	8.6

The physical and mechanical properties of Soviet epoxy resins hardened with maleic anhydride are presented below:

	<u>ED-13</u>	<u>ED-15</u>
Brinell hardness, kg/mm ² -----	26.5	28.9
Martens thermal stability, °C -----	76	68
Static bending strength, kg/cm ² ---	814	614
Specific impact toughness, kg-cm/cm ² -----	4.89	5.02
Water absorption in 24 hours, % ---	0.062	0.159

Designation

Trademark ----- EDP, EDL, L-4, VK-9, VK-32-EM,
MATI-K-2, Epoksid Pr, Epoksid P,
Epoksid 201
Generic type ----- Unmodified epoxies

Description

These adhesives include amine and anhydride cured resins.*

Application

They are appropriate for bonding metals, wood, ceramics, and plastics. VK-32-EM can be used in adhesive welded joints (glue welding).

<u>Technological Status</u>	<u>Amine Cured</u>	<u>Anhydride Cured</u>
Research	1955	1962 to 1963
Development	1956	1963
Engineering	1958	1965
Production	1958 to 1959	1965

Properties of EDP and EDL Epoxy Resins

<u>Properties</u>	<u>Resin Type</u>	
	<u>EDP</u>	<u>EDL</u>
Epoxy number -----	11 to 14	8 to 11
Volatile substance content -----	1	1
Melting point (ball and ring method), °C -----	--	40 to 60
Chloron-ion content -----	0.007	0.007
Total chlorine content, % -----	1.5	1.5

L-4 adhesive is a composition based on E-40 epoxy resin, polyethylene polyamine, and dibutyl phthalic acid. The adhesive is designed for bonding of metals and nonmetallic materials, primarily in nonload-bearing structures, for blocking of bolt joints, and for other purposes.

*Nitrogen-containing epoxies include EA (aniline diene epoxy), EMDA (diaminodiphenylmethane diene epoxy), EFF (phenolphthalein-containing epoxy), and EAF-400 (nitrogen-containing epoxy).

Adhesive joints made with L-4 adhesive have low strength and low heat resistance. Heating the adhesive seam to 120°C for 4 hours significantly increases its heat resistance.

Strength of Adhesive Joints Made Using L-4 Adhesive

Materials Bonded	Holding		Test Temp °C	Shear strength kg/cm ²	Even separation strength, kg/cm ²
	Temp °C	Time, hr			
Duralumin	20	72	-60	53	405
			20	60	147
			60	8	12
EI-654 Steel	20	72	-60	15	223
			20	60	133
			60	10	20
Duralumin	120	4	-60	47	420
			20	138	398
			60	58	123

Epoxy adhesives cured with low-molecular polyamides include type VK-9 adhesive. This adhesive contains no solvent. It is used for bonding of metals and nonmetallic materials (plastics, ceramic, wood, etc.). The adhesive joints can operate at 125°C over 500 hours, and briefly at 250°C.

Strength of Adhesive Joints Made with VK-9 Adhesive

Materials Bonded	Shear strength, kg/cm ²				
	at -60°C	at 20°C	at 125°C	at 150°C	at 250°C
30KhGSA	256	229	49	32	10
OT-4 Ti alloy	137	180	78	50	10
FN textolite*	-	79	20	18	10
RTPK ceramic	-	127	131	40	-

*Rupture through material

Strength of VK-9 Adhesive Joints with Even and
Uneven Layer Separation

Characteristics	Test Temperature, °C			
	-60	20	60	125
Even separation strength, kg/cm ²	340	204	-	43
Uneven separation strength, kg/cm	11	24	40	4

A typical adhesive composition based on epoxy resin (ED-6 or E-40) and a dibasic acid anhydride is type VK-32-EM adhesive. VK-32-EM adhesive also contains a mineral filler. The adhesive is used for bonding of metals (steel, duralumin) to each other and to heat-resistant foam plastics. The shelf life of the adhesive is 6 to 10 days. Bonding is performed at 150°C in 3 hours at a pressure of 0.5 to 1.0 kg/cm². The usage temperatures of adhesive joints in metals are ±60°C. The usage temperatures of joints between foam plastic and metals correspond to the usage temperatures of the foam plastics themselves (up to 140°C). Strength data of adhesive joints for anodized duralumin and steel are presented below:

Strength of Adhesive Joints in Metals Made with
VK-32-EM Adhesive

Metal Bonded	Shear strength, kg/cm ²			
	at -60°C	at 20°C	at 60°C	at 100°C
Anodized duralumin	115	165	195	30
30KhGSA steel	247	270	275	60

The even-layer separation strength of adhesive joints of duralumin, in the temperature interval from -60° to +60°C, is 450 kg/cm²; the strength of adhesive joints between duralumin and type FK-20 foam plastic at 20°C is 6 to 10 kg/cm². The uneven-layer separation strength of adhesive joints in duralumin at 20°C is 15 to 20 kg/cm. The shear endurance limit (base of 5x10⁶ cycles) at 20°C is 30 kg/cm². Adhesive joints in duralumin have quite satisfactory long-term strength; with a shear stress of 95 kg/cm², they do not rupture at 60°C in 180 hours, can withstand a temperature of 80°C for 500 hours, and can resist the

effects of variable ($\pm 60^{\circ}\text{C}$) temperatures for 30 cycles. They are resistant to gasoline, kerosene, and oil. After 30 days exposure to water, the bond strength drops at 20°C by 40% to 50% and at 60°C , by 15% to 18%. The significantly lower reduction in the strength of bond specimens tested at 60°C can be explained by the partial removal of the water upon heating. VK-32-EM adhesive does not cause corrosion of the metals bonded and has satisfactory resistance to the effects of microorganisms.

MATI K-2 adhesive is an epoxy adhesive containing dicyandiamide and a filler. The adhesive is suitable for bonding of steel and other metals. The strength of adhesive joints for even separation, when bonded at 150° to 160°C , increases with increasing holding time at this temperature.

Influence of Curing Time at 150° to 160°C Upon Even Separation Strength of Adhesive Joints in Steel Made with MATI K-2 Adhesive (Without Filler)

Curing time at 150° to 160°C , min	Even separation strength, kg/cm^2	Curing time at 150° to 160°C , min	Even separation strength, kg/cm^2
15	23	120	615
30	345	180	730
60	475	240	740

Epoksid Pr and Epoksid P (powder) have shelf lives of at least 6 months. Bonding with these adhesives is performed with a pressure of 0.5 to $3.0 \text{ kg}/\text{cm}^2$ at the following temperatures:

Bonding temperature, $^{\circ}\text{C}$ ----- 240 220 200 180 150 120
 Holding time, min ----- 5 15 40 120 300 600

The adhesive joints in metals can be used in the temperature interval from -60° to $+100^{\circ}\text{C}$. Adhesive joints withstand long (500 hr) heating to 100°C and are resistant to variable temperatures (from -60° to $+100^{\circ}\text{C}$) and the effects of water, fuels, and oil. The endurance limit in shear of adhesive joints in duralumin (base of 3×10^6 cycles) at 20°C is $40 \text{ kg}/\text{cm}^2$. The adhesives are resistant to the effects of microorganisms, do not cause corrosion of metals, and are nontoxic.

Long-Term Shear Strength of Adhesive Joints in
Metals Made with Epoksid Pr Adhesive

Metal Bonded	Test Temp, °C	Shear stress, kg/cm ²	Test time, hr
Anodized duralumin	60	100	>344
	100	90	>200
Clad brushed duralumin	60	110	>245
	100	90	>400
Type 20 steel	60	180	>150
	100	80	>400

Shear Strength of Adhesive Joints of
Various Materials Using
Epoksid Pr Adhesive

Materials Bonded	Shear strength, kg/cm ²			
	at -60°C	at 20°C	at 60°C	at 100°C
Anodized duralumin	97	123	136	139
Clad brushed aluminum	161	211	223	245
30KhGSA steel	312	342	355	316
Oxidized MA8 magnesium alloy	86	88	111	200
Duralumin + textolite	-	94*	-	44*

*Rupture through textolite

Separation Strength of Adhesive Joints in Metals
Made with Epoksid Pr

Metal Bonded	Even separation strength, kg/cm ²				Uneven separation strength, kg/cm ²	
	at -60°C	at 20°C	at 60°C	at 100°C	at 20°C	at 100°C
Clad brushed duralumin	500	445	443	445	10	32
30KhGSA steel	500	486	451	372	19	58

Designation

Trademark ----- VK-7
 Generic type ----- Epoxy-triazine

Description

VK-7 adhesive is a composition containing a high-molecular epoxy resin that has triazine rings. The adhesive is heat resistant to 250°C. It is a single-component adhesive and contains a hardener, filler, and solvent, in addition to the resin. The concentration of the adhesive is 60%. It can be stored for 2 months.

Application

The adhesive is employed for forming adhesive and weldable-adhesive joints with steel and with aluminum and titanium alloys.

Technological Status

Research ----- 1963 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1966 (est)

Properties

The adhesive is applied in a single layer, using 150 to 160 g/m². During curing, the joint must be held in the open at 20°C for 24 hours and at 60°C for 2 hours, under a pressure of 0.5 to 1 kg/cm². It can be held under pressure under one of the following conditions:

	Duration, hrs		Duration, hrs
205±5°C	1	155±5°C	5
185±5°C	2	125±5°C	12

Data on the strength of joints employing the VK-7 adhesive are as follows:

Strength of Weldable-Adhesive Joints of Duraluminum and
L2 Brass* Employing the VK-7 Adhesive

Bonds	Shear strength, kg/cm ²		
	60°C	230°C	250°C
Weldable-adhesive duraluminum	1015	730	575
Duraluminum with drilled welding spot	420	220	215

*Joints having a 25x25-mm lap with a single welding spot.

Adhesive joints of duralumin resist a shear stress of 50 kg/cm² at 20°C for 180 hours, and 35 kg/cm² at 250°C for 36 hours. At 20°, 230° and 250°C, adhesive joints employing VK-7 resist shear stresses of 60, 35 and 30 kg/cm², respectively, for 10x10⁶ cycles. The adhesive joints withstand changing temperatures (between -60°C and +250°C) for 30 cycles. Strength of the adhesive joints does not change appreciably after being subjected to the action of water for 30 days.

Designation

Trademark ----- DEG and TEG and TGM-3 variants
 Generic type ----- Modified epoxies

Description

DEG-1, DEG-F, DEG-Zh, DEG-19, TEG-1, and TEG-17 are modified with aliphatic glycidyl esters. TGM-3 and MGF-9 are modified with polyester acrylates. The introduction of glycidyl esters to epoxies allows the control of viscosity, elasticity, and cure rate.

Application

No information available.

Technological Status

No information available on status of research, development, engineering, or production.

Properties

Properties of Epoxy Oligomers

Properties	DEG-1	DEG-F	DEG-Zh	DEG-19	TEG-1	TEG-17
Viscosity, cp, not over	-	80	40	80	100	100
Content of volatiles, %, not over	1.5	2.0	1.5	2.5	2.5	2.5
Epoxy groups, %	26	10 to 14	6 to 10	17 to 22	18	15 to 20
Hydroxyl groups, %	-	-	-	7 to 9	-	7 to 9
Organic chlorine, % not over	1.5	1.5	1.5	2.5	2.5	-
Chlorine ion, % not over	0.06	0.8	0.01	0.1	0.1	-

Of the polyester acrylates, TGM-3 (the product of interaction of methacrylic acid and triethylene glycol) and MGF-9 (the product of interaction of methacrylic and phthalic acids and triethylene glycol) are most widely used. Some of their properties are below.

	<u>TGM-3</u>	<u>MGF-9</u>
External appearance -----	Light brown	liquid
Viscosity at 20°C, cp -----	10 to 40	100 to 350
Acid number, mg KOH, not over -----	5	5
Polymerization rate at 100°C with 1% benzoyl peroxide, min -----	1 to 3	1 to 3

Phenol-formaldehyde modified epoxies

Epoxy-phenol adhesives have higher thermal stability than unmodified epoxy adhesives. At 150° to 200°C, the epoxy groups in the resin interact both with the phenol hydroxyls and with the methylol groups of the resol resin, leading to curing of the system. When epoxy resin type ED-6 is fused with K-21 resol resin at 95° to 100°C, adhesive compositions are produced with high strength of bonds in steel under even tension. The highest strength is achieved when the ratio of epoxy to resol resins is 60:40. The strength of adhesive joints in steel under even tension for this composition depends on the curing time. The highest strengths are produced with 8-hour holding at 150° to 160°C.

Designation

Trademark ----- K-153, KLN-1
 Generic type ----- Modified epoxies

Description

These adhesives are modified with polysulphides and have high elasticity. They are less thermally stable than unmodified epoxies. Organic amines are used as hardeners.

Application

They are suitable for metal-to-metal bonding, and textolite-to-metal and fabric-to-metal bonding. Type K-153 domestic epoxy-polysulphide adhesive is designed primarily for bonding of textolite to metals, plus bonding of aluminum alloys, steels, magnesium alloys, and brass. KLN-1 adhesive is designed for bonding of metals and nonmetallic materials, as well as the manufacture of adhesive-welded joints.

Technological Status

No information available on status of research, development, engineering, or production.

Properties

K-153 adhesive consists of ED-5 epoxy resin, plasticized with polysulphide, hexamethylene diamine, and a filler (type-400 portland cement). Still residue produced in the production of hexamethylene diamine, or complex amines, may be used in place of the hexamethylene diamine. The adhesive is cured under a pressure of 1.5 to 2 kg/cm² for 18 hours at a temperature of at least 20°C and 4 hours at 100°C (or 6 hours at 80°C). The bonding strength (duralumin + textolite) does not drop following aging for 500 hours at 100°C. Type K-153 adhesive has good dielectric properties. The adhesive joints are resistant to the effects of atmospheric conditions, fuels, mineral oils, and acetone.

Shear Strength of Adhesive Joints Made with K-153 Adhesive

Materials Bonded	Shear strength, kg/cm ²		
	at -60°C	at 20°C	at 60°C
Duralumin + textolite	69 to 83	105 to 128	67 to 84
30KhGSA steel (with sublayer of BF-2 adhesive) + textolite	76 to 97	96 to 123	58 to 69

Even Separation Strength of Adhesive Joints Made
with K-153 Adhesive

Materials Bonded	Even separation strength, kg/cm ²		
	at -60°C	at 20°C	at 60°C
Duralumin	108	136	125
MA8 magnesium alloy	82	107	106
Brass	136	174	134
30KhGSA steel	-	258	170
Duralumin + textolite	96 to 114	91 to 113	101 to 117
30KhGSA steel (with sublayer of BF-2 adhesive) + textolite	95 to 117	100 to 109	98 to 115

Type KLN-1 adhesive is an epoxy-polysulphide composition, cured with polyethylene polyamine. To reduce viscosity and increase shelf life, a reactive diluent is included in the adhesive. The shelf life of the mixture is 2 hours. The adhesive is applied to the bonded surfaces in one layer, consumption 150 to 250 g/m². Preliminary holding is 30 minutes at room temperature. Bonding is performed under 0.5 to 2.0 kg/cm² pressure at 18° to 25°C for 24 hours. Satisfactory strength is achieved following 7 to 10 days. The thermal stability of adhesive joints is not over 60° to 80°C. The uneven separation strength at 20°C is 20 kg/cm; the long-term strength of adhesive joints at 20°C, with a shear stress of 80 kg/cm² and at 80°C with a shear stress of 8 kg/cm², is over 500 hours. The fatigue strength at 20°C, at a stress of 50 kg/cm², is 0.2x10⁶ cycles. Following exposure to water for 30 days, the strength of the adhesive joints is decreased by 16% to 30%. Adhesive joints made with KLN-1 adhesive are resistant to the effects of fuel, transformer oil, and ethyl alcohol. The shear strength of adhesive joints in duralumin at 20°C is 524 kg/cm²; at 80°C it is 63 kg/cm². KLN-1 adhesive does not cause corrosion of anodized aluminum alloys or galvanized steel.

The curing agents for epoxy-polysulphide adhesives may be fatty organic amines, dimethyl aminomethyl phenol or trisdimethyl aminophenol (not over 10% of mass of epoxy resin). Use of the latter hardener in a composition consisting of thiokol LP-3 and liquid epoxy resin produces the highest strength indicators for even separation of all adhesive joints made with this type of adhesive, with the resin-thiokol ratio as 1:2.

Designation

Trademark ----- PFED, PED, FL-4S, BOV-1, BOV-3
 Generic type ----- Modified epoxies

Description

PFED and PED are epoxies modified with poly(vinyl chloride) or chlorinated poly(vinyl chloride). FL-4S and BOV variants are epoxies modified with furans.

Application

PFED and PED are used to bond vinyl resins to each other, to metals, and to plastic foams. FL-4S is designed for bonding metals and for glue-welded joints in duralumin. BOV-1 is used to bond ferrites, brass, steel, aluminum, copper, etc. It is recommended for use for anticorrosion protection of parts made of steel, brass, and aluminum. The adhesive is water resistant and is a satisfactory insulator. BOV-3 can be used to bond teflon and polyethylene.

Technological Status

No information available on status of research, development, engineering, or production.

Properties

The composition (in wt. parts) of PFED and PED adhesives is as follows:

	<u>PFED</u>	<u>PED</u>
Epoxy Resin (ED-5) -----	100	100
Polyvinyl chloride -----	3	-
Perchlorovinyl resin -----	-	20
Dioctyl phthalate -----	3	-
Cyclohexanone -----	55	10
Toluene -----	34	-
Methylene chloride -----	-	90
Polyethylene polyamine -----	15	15

Type FL-4S adhesive is an alcohol-acetone solution of combined epoxy-furyl-phenol-acetal resin, plasticized with dioctyl sebacinate. The adhesive is designed for bonding of metals and primarily for production of adhesive-welded joints in duralumin. The hardener used is hexamethylene diamine (or the still residue produced in its

manufacture) in a quantity of 10% of the mass of the adhesive composition. The adhesive is hardened at 155° to 160°C for 2 hours. The following method is recommended for production of adhesive-welded joints using FL-4S:

Raising temperature to 80°C --	<u>hrs</u> 1.5
Holding at 80°C -----	1
Raising temperature to 120°C -----	0.5
Holding at 120°C -----	8
Raising temperature to 140°C -----	0.5
Holding at 140°C -----	0.5

The shear strength of adhesive joints of duralumin made with FL-4S adhesive at 20°C is 90 to 100 kg/cm². The adhesive is resistant to the effects of acid and alkaline corrosive media usually used in anodizing aluminum alloys.

Type BOV-1 adhesive is produced by combining ED-5 epoxy resin and FA monomer (furfural-acetone resin), styrene, and a hardener--polyethylene polyamine or the still residue of hexamethylene diamine. The adhesive is prepared in two operations: preparation of varnish and preparation of adhesive. The varnish is produced by simultaneous dissolution of ED-5 resin, FA monomer, and styrene in an agitated reactor at room temperature or at 40° to 50°C, with careful mixing for 20 to 30 minutes. The finished varnish can be stored 2 to 3 years. Depending on the intended use of the adhesive, various fillers are added: sand, cement, graphite, mica, quartz or asbestos flour, aerosil, carbon black, or aluminum powder. The quantity of filler is not over a ratio of 1:1 or 1:2. The viscosity of the adhesive is 21 to 60 sec on the VZ-4 viscosimeter. Materials are bonded at temperatures above 16°C. The shelf life of the adhesive is 4 to 6 hours; it is cured in 24 hours with a minimum pressure of 0.1 to 0.5 kg/cm². When joining wood and wood-based plastics, a filler is used (multilayer plastics are bonded without preliminary surface coating).

BOV-3 adhesive is based on a combined epoxy resin with an amine-type hardener. It can be used for bonding of teflon and polyethylene at room temperature, without preliminary chemical treatment of surfaces. Strength indices of adhesive joints of various materials made with BOV-3 adhesive are:

Shear strength
at 20°C, kg/cm²

Polyethylene + polyethylene -----	up to 17
Teflon + teflon -----	8
Brass + brass -----	20
Aluminum + aluminum -----	30
Textolite + textolite -----	35

The adhesive is resistant to corrosive media, and after curing is insoluble in acetone, kerosene, water, alcohol, dichloroethane, and mineral oils. The bonding pressure is 0.1 to 0.5 kg/cm²; curing time is 3 to 4 hr. Thermal stability of the adhesive is 170°C.

Designation

Trademark ----- ME-1, VK-1, VK-1M, VK-1MS
 Generic type ----- Modified epoxies

Description

Type ME-1 adhesive is an epoxy resin modified with poly(vinyl butyral); the hardener is dicyandiamide (resin ratio 1:1). The adhesive is produced as a solution and as a film on polyamide fiber gauze. The storage life is 1 year.

Type VK-1 adhesive consists of a liquid epoxy resin modified with a hetero-organic compound (which is also the curing agent) and a filler.

Modified adhesives types VK-1M and VK-1MS have been produced to improve the technological properties of VK-1 adhesive.

Application

The main application of ME-1 adhesive is in the manufacture of honeycomb fillers of aluminum foil.

VK-1 is used in adhesive, adhesive-welded, adhesive-riveted and adhesive-threaded joints in duralumin and titanium alloys operating in the temperature interval from -60° to 150°C .

Technological Status

No information available on status of research, development, engineering, and production.

Properties

ME-1 adhesive is used as a solution; it is applied to both surfaces to be bonded: the consumption is 150 to 200 g/m². Following application of the first coat, the specimen is held in air for 45 minutes, then for 30 minutes at 60° , 80° , and 105°C . After cooling the specimen to room temperature, a second coat of adhesive is applied and dried as with the first coat. The joint is then closed and held under a pressure of 2 to 3 kg/cm² at $153 \pm 2^{\circ}\text{C}$ for 4.0 hr; at $163 \pm 2^{\circ}\text{C}$ for 2.5 hr; and $173 \pm 2^{\circ}\text{C}$ for 1.5 hr. When the adhesive film is used, it is washed in gasoline and applied to a polyethylene film washed with acetone, then dried in a thermostat at $30 \pm 2^{\circ}\text{C}$ for 1 hour. Bonding is performed in the same manner as when the liquid adhesive is used. At

80°C, the shear strength is 260 kg/cm². The uneven separation strength at 20°C is 5 to 7 kg/cm, and at 80°C, 8 to 10 kg/cm.

The bonding modes of VK-1, VK-1M, and VK-1MS adhesives are presented.

Bonding Modes of Epoxy Adhesives (VK-1, VK-1M, VK-1MS)

Adhesive Type	Pressure, kg/cm ²	Bonding temp, °C	Holding time under pressure, hr	Number coats Applied	Adhesive consumption per coat, g/m ²	Shelf life, hr
VK-1	0.3-3.0	120-160	5-1	1	200-250	72
VK-1M	0.5-1.0	100	5	1	250-350	2
VK-1MS	0.5-1.0	120	3	1	150-200	2

After the adhesives are held in water for 30 days at 20°C, the strength of adhesive joints made with VK-1 adhesive drops by 30% and remains the same for VK-1M adhesive. Adhesive-welded joints using these adhesives can be produced by pouring into the welded seam and welding over a layer of adhesive applied to one of the surfaces to be welded. The joints are resistant to the effects of water and tropical climate conditions, to microorganisms, oil, kerosene, gasoline, mineral, and fuel; they do not cause corrosion of metals.

Strength of Adhesive-Welded Joints of Duralumin Made with Epoxy Adhesives VK-1 and VK-1MS

Test Conditions	Shear strength, kg/cm ²			
	VK-1		VK-1M	
	at 20°C	at 80°C	at 20°C	at 80°C
Before testing	745	1030	1607	849
After exposure to water for 30 days	743	956	1068	909
After exposure to tropical climate for 30 days	716	937	921	812

Uneven Separation Strength of Adhesive
Joints Made with Epoxy Adhesives

Adhesive Type	Uneven separation strength kg/cm ²			
	at -60°C	at 20°C	at 60°C	at 150°C
VK-1	20	20	16	15
VK-1M	12	16	11	14
VK-1MS	17	32	30	4

Long-Term Strength of Adhesive Joints Made
with Epoxy Adhesives at 20° C

Adhesive type	Shear stress, kg/cm ²	Time to rupture, hr
VK-1	110	500
VK-1M	80	500
VK-1MS	85	500

Fatigue Shear Strength of Adhesive Joints in
Duralumin Made with Epoxy Adhesives at 20°C

Adhesive type	Maximum cycle stress, kg/cm ²		
	10 ⁵ cycles	10 ⁸ cycles	10 ⁷ cycles
VK-1	62	53	45
VK-1M	62	52	40
VK-1MS	60	52	50

Designation

Trademark ----- K-400, EF-9, K-10, EFK-9
Generic type ----- Modified epoxies

Description

K-400 adhesive is a composition based on an epoxy-organosilicon resin (100 wt. parts) and L-20 polyamide (40 wt. parts), with the addition of Cr₂O₃ or boron nitride (60 wt. parts).

Application

K-400 is designed for bonding of metals and nonmetallic materials. The shelf life of the composition is 4 hours.

Technological Status

No information available on status of research, development, engineering, or production.

Properties

K-400 adhesive is hardened for 48 hours at room temperature and at 0.5 to 1 kg/cm² pressure. The service temperature interval is from -60° to +250°C.

Of the epoxy adhesives modified with organosilicon compounds, descriptions have been published for EF-9 and K-10 adhesives (epoxy resins mixed with chlorophenyl polysiloxane resin). These adhesives differ from each other in the ratio of these components used. The adhesives are designed for bonding of metals, nonmetallic materials and for sealing. When duralumin is bonded with EF-9 adhesive, the shear strength of the adhesive joints produced reaches 200 kg/cm² at 20°C.

An epoxy-phenol resin modified with methyl phenyl polysiloxane resin is the basis for EFK-9 adhesive, used for bonding various metals and nonmetallic materials during the manufacture of high-power filament light bulbs. This adhesive has the capability for long-term operation at 300°C and for brief operation at 400°C.

Epoxy adhesive compositions have been described, consisting of glycidic esters of diphenols, combined with organo-silicon compounds and fatty acids.

Designation

Trademark ----- ED-6 (modified)
 Generic type ----- Modified epoxy

Description

ED-6 resin is hardened with an α , β -dipiperidyl.

Application

Modified ED-6 is suitable for use at 100°C for electronic component bonding.

Technological Status

Research ----- 1963 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1968 (est)

Properties

Hardening of Epoxy Resin ED-6 with Different
 Amounts of an α , β -Dipiperidyl

Composition, parts by weight			Hardening temperature, °C	Hardening time, min	Bond Strength, kgf/cm ²
resin ED-6	dibutyl phthalate	α , β -dipiperidyl			
100	15	18	120	25	610
100	15	20	120	20	640
100	15	26	120	27	520

Data on Modified ED-6 are as follows:

Density (gm/cm³) ----- 1.27
 Tensile strength
 (kgf/cm²) ----- 640
 Flexural strength
 (kgf/cm²) ----- 1150
 Impact strength
 (kgf-cm/cm²) ----- 12
 Compressive strength
 (kgf/cm²) ----- 1100

Dielectric constant	
(at 10^6 Hz) -----	336 (at 10^6 Hz)
Dissipation factor	
(at 10^6 Hz) -----	0.0180 (at 10^6 Hz)
Volume resistivity	
(ohm-cm) -----	8.4×10^{14} (25°C)
Service temperature	
($^\circ\text{C}$) -----	-50° to $+100^\circ$
Heat distortion temperature	
(low kgf/cm ² at low	
$^\circ\text{C}$) -----	120°

Designation

Trademark ----- ETF
 Generic type ----- Polyfunctional epoxy

Description

Polyfunctional resin ETF (the reaction product of 1,1,3-tri (hydroxyphenyl)propane and epichlorohydrin), has a MW of 540 to 700 and contains 20% to 24% of epoxide groups. On hardening this resin with amine or acid-hardening agents, specimens can be obtained that have higher heat stability than do the diene epoxy resins.

Application

ETF is probably being used where long-term service above 150°C is desired in polymer concrete and glass-reinforced plastics.

Technological Status

Research ----- 1961 to 1962 (est)
 Development ----- 1963 to 1964 (est)
 Engineering ----- 1965 to 1966 (est)
 Production ----- 1967 (est)

Properties

The heat distortion temperature of specimens of the resin, hardened with the hardening agents shown at a stress of 24 kgf/cm², is above 250°C. The highest flexural strength is given by specimens hardened with aniline-phenol-formaldehyde resin 211. The highest compression strength is observed in specimens hardened with maleic anhydride.

Properties of ETF Resin, Using Different Hardening Agents

Hardening Agent	Flexural strength kgf/cm ²	Compression strength, kgf/cm ²	Tensile strength, kgf/cm ²	Tensile elastic modulus Ex10 ⁻³ kgf/cm ²	Elongation at break, %
m-Phenylenediamine	650	1500	-	-	-
Triethanolamine titanate	800	1500	350	31.2	1.9
Aniline-phenol-formaldehyde resin ·211	950	1400	550	28.3	2.2
Maleic anhydride	650	1700	-	-	-
Methyltetrahydro-phthalic anhydride	750	1520	-	-	-

The weight loss of ETF resin specimens, hardened with different agents, and after heat ageing at 200°C for 1000 hours, is 20% to 30% lower than weight loss in ED-5 resin hardened with the same hardening agents. (ED-5 is obtained by condensation of diphenylolpropane and epichlorohydrin.)

ETF resin softens in the range 35° to 55°C; it may be used for the preparation of GRP's by the dry method. Since maleic anhydride is comparatively volatile and toxic, the main hardening agent selected for ETF resin (when used as a binder) is the aniline-phenol-formaldehyde resin 211. The binder resin, which is a composition of resins ETF and 211, has received the designation T-71-S.

Designation

Trademark ----- EAF-400
 Generic type ----- Epoxy derivative of spiro-bis(1,3-dioxane)

Description

Epoxy derivatives of spiro-bis(1,3-dioxane) are prepared by the condensation of pentaerythritol with unsaturated aldehydes or ketones, followed by epoxidation of the double bonds or attachment of the phenol to the resulting acetal, and further etherification with epichlorohydrin.

Application

It is expected that the Soviets use EAF-400 as structural adhesives and binder resins for glass-reinforced plastics where better fatigue resistance and performance at high temperature (150°C) is required.

Technological Status

Research ----- 1963 to 1964 (est)
 Development ----- 1965 to 1966 (est)
 Engineering ----- 1967 (est)
 Production ----- 1968

Properties

EAF-400 resin has the following characteristics:

Density, g/cm³ ----- 1.22 to 1.25
 Molecular weight ----- 540 to 640
 Content, %
 of epoxide groups ----- 13.5 to 15.5
 of chlorine ----- 1.0
 of volatiles ----- 1.0
 Kramer-Sarnow softening
 point, °C ----- 100 to 120

The elongation at break of hardened EAF-400 resin is 5% to 7%, which is 2 to 3 times that of polymers based on diene resins.

Main Properties of Hardened EAF-400 Resin

Property	Hardner			
	m-phenylene-diamine	phthalic anhydride	maleic anhydride	methyltetrahydrophthalic anhydride
Impact strength, kgf-cm/cm ²	18 to 25	10 to 17	14 to 20	11 to 17
Brinell hardness, kgf/mm ²	15 to 17	17 to 22	16 to 19	17 to 22
Strength, kgf/cm ²				
flexural	1000 to 1160	1100 to 1500	1100 to 1300	1100 to 1400
compression	1200	1170 to 1230	1150 to 1300	1100 to 1140
tensile	800 to 830	750 to 790	920 to 930	880 to 890
Elongation at break, %	5.8 to 6.9	4.2 to 6.1	6.1 to 6.6	4.6 to 5.2
Strength in simple shear, kgf/cm ²				
20°C	514	452	468	453
100°C	322	241	219	309
150°C	93	21	19	-
Martens yield temperature, °C	110 to 118	106 to 110	96 to 102	90 to 95
Water absorption in 24h, %	0.08	0.06	0.07	0.06
Volume resistivity*, ohm-cm				
1	4.4x10 ¹⁵	7.6x10 ¹⁵	6.2x10 ¹⁵	4.6x10 ¹⁵
2	2.7x10 ¹⁵	3.7x10 ¹⁵	2.7x10 ¹⁵	5.0x10 ¹⁵
3	1.2x10 ¹⁴	1.3x10 ¹⁴	1.3x10 ¹⁴	1.0x10 ¹⁴
Surface resistivity*, ohm				
1	7.4x10 ¹⁵	7.4x10 ¹⁵	7.3x10 ¹⁵	7.1x10 ¹⁵
2	4.9x10 ¹⁵	1.0x10 ¹⁶	2.8x10 ¹⁵	1.3x10 ¹⁶
3	8.3x10 ¹³	1.6x10 ¹⁴	3.0x10 ¹³	7.4x10 ¹³
Tan δ at f = 10 ⁶ Hz*				
1	0.023	0.017	0.012	0.015
2	0.026	0.019	0.016	0.015
3	0.010	0.0046	0.015	0.0077
Dielectric permittivity at f = 10 ⁶ Hz*				
1	4.3	4.0	3.2	3.9
2	3.9	3.7	3.6	3.8
3	4.8	4.3	5.4	4.7
Electric strength*, kV/mm				
1	16.0	16.9	18.8	17.2
2	20.0	16.1	18.8	15.5
3	20.0	21.7	21.5	18.6

*1 - in the initial state; 2 - after holding for 48 hr in an atmosphere of 98% relative humidity; 3 - after heating at 100°C for 1 hr.

The glass transition temperature of certain EAF-400 hardened variants is 10° to 20°C lower than that of ED-5 epoxies containing the same hardeners. EAF-400 adhesives have double or triple the elongation of ED-5 and related epoxies.

GRP specimens, prepared from TS 8/3-250 glass fabric, were dipped in EAF-400 resin. The fabric was compressed under a pressure of 20 kgf/cm².

The content of binder resin in the GRP was 21% to 23%. The properties of the resulting GRP's are given. The data show that GRP's using EAF-400 and aniline-phenol-formaldehyde resin 211 have the highest strengths and best heat resistance.

Properties of GRP's Based on EAF-400 Resin

Hardner	compression	Strength, kgf/cm ²						
		flexural				simple shear		
		20°C	100°C	150°C	200°C	20°C	100°C	150°C
Aniline-PF resin 211	4350	6050	5000	4500	2150	350	260	140
m-Phenylenediamine	4000	6350	3070	1500	1050	420	160	30
Maleic anhydride	3230	3600	2370	700	450	330	60	20
Triethanolamine titanate	3000	5350	2800	1300	580	-	-	-

Designation

Trademark ----- ED-5 (flexibilized), K-115,
 K-153, K-156, K-139, K-147, K-160.
 Generic type ----- Epoxy (low molecular weight
 oligomer)

Description

ED-5 is a standard commercial resin. Flexible ED-5 has reduced brittleness when it is modified by additives.

Application

The adhesives are suggested for use where minimal stress buildup is required.

Technological Status

Research ----- 1968 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- ?

Properties

Modifying additives include:

K-115 ----- MGF-9 oligoester acrylate
 K-153 ----- MGF-9 oligoester acrylate,
 NVT-B thiokol
 K-156 ----- DEG-1 aliphatic diepoxide
 K-139 ----- MGF-9 oligoester acrylate,
 SKN-26-1 carboxylated nitrile
 rubber
 K-147 ----- SKN-26-1
 K-160 ----- Dibutyl phthalate

Hardeners are aliphatic amines.

Change in Some Characteristics of Epoxy Compositions According to the Hardening Conditions

Compo- sition	Hardening Conditions										
	I			II			III				
	Swelling in ace- tone, %	t_g , °C	δ_t , kgf/cm ²	Swelling in ace- tone, %	t_g , °C	δ_f , kgf/cm ²	δ_t , kgf/cm ²	Swelling in ace- tone, %	δ_t , kgf/cm ²	Swelling in ace- tone, %	δ_t , kgf/cm ²
ED-5	17.1	50	480	0.13	155	1100	560	0.18	-	0.18	-
K-115	9.5	60	540	0.23	88	1400	675	1.25	540	1.25	540
K-153	12.0	70	480	1.15	95	1200	630	2.01	530	2.01	530
K-156	11.0	50	475	0.07	110	1500	620	-	560	-	560
K-130	12.5	75	400	0.98	95	1200	600	4.4	540	4.4	540

Designation

Trademark ----- 6E18N60, 6E18N50
 Generic type ----- Block copolymers of ED-6 diene
 resin and novolak.

Description

Block copolymers 6E18N60 and 6E18N50, produced by copolymerization of ED-6 epoxy resin and No. 18 novolak at 120°C for 30 minutes and containing, respectively, 60 and 50 parts by weight of the epoxy resin, have improved storage characteristics at room temperature. They are heat cured and require no additional hardeners.

Application

The epoxy-novolaks (prepeg forms) are high-performance adhesive binders for structural glass-reinforced plastics. They are claimed to be used in shipbuilding and in storage tanks. Since they contain phenol-formaldehyde as part of the system, they are less expensive than conventional epoxies.

Technological Status

Research ----- 1966 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1974 (est)

Properties

These block copolymers may be dissolved in acetone and alcohol. (The impregnation of the glass fabric can be effected with a 50% alcohol-acetone solution using a vertical impregnating-drying machine at 80° to 100°C.) The epoxy-novolak block copolymers, their solutions, and the impregnated fabric, may be kept for a long time at room temperature with no great change. It is claimed that the solutions of epoxy-novolak block copolymers show practically no change in viscosity for 180 days, whereas, in 70 days, epoxy-A stage resins change to the gel state. In the case of impregnation with epoxy-A stage resin binders, the storage time for glass fabric with paraffinic size is 7 to 10 days at room temperature, or 3 to 5 days with a hydrophobic-adhesion size.

The range of use of epoxy-novolak GRP's based on epoxy novolak resin and ASTT(b)-S₂ glass fabric is shown. The hold-on time is 18 minutes per 1 mm of thickness of sheet. The mechanical properties of the resulting GRP specimens are as follows:

	S6E18N-60	S6E18-50	STER-S-30	EDT-10
Strength, kgf/cm ² :				
tensile -----	6700	6400	6500	6800
flexural -----	8200	7800	8200	8000
compression -----	6100	6300	6300	6000
in inter-ply shear -----	760	760	750	750
Impact strength, kgf-cm/cm ² --	480	400	520	480
Water absorption after 2 hr				
boiling, % -----	0.18	-	0.19	0.29

Designation

Trademark ----- ENBC
 Generic type ----- Unfilled and filled epoxy-novolak
 block copolymers

Description

Unfilled forms are designated 6E18-N50-2, 6E18-N60-2, and 6E160-2. They are based on ED-6 epoxy and novolak resins.

Filled forms are designated as ENKP-1, ENKP-1.5, ENKP-2, ENKP-2.5, ENT, ENT-2, ENV, ENAL, ENS-60, ENOS-1/1, ENO-1, ENM-20, ENG-30, and ENTA-25. These filled types are based on 6E18N-60 block copolymer.

It appears that the Soviets have a continued interest in epoxy-novolak development and modification.

Application

The ENBC (filled and unfilled) are suspected to have wide use as high-performance adhesives (at 200°C). Since they contain phenol-formaldehyde, they are less expensive than conventional epoxies.

Technological Status

Research ----- 1963 (est)
 Development ----- 1965 (est)
 Engineering ----- 1965 (est)
 Production ----- 1968 (est)

Properties

In contrast with composition D-1 based on ED-6 epoxy resin and maleic anhydride, hardening of ENBC's is not accompanied by any heat liberation. This makes it possible to maintain temperature conditions of hardening accurately to avoid overheating of the compositions, thus preventing the formation of internal stresses in the article. Decomposition of ENBC's begins at 300°C; however, the presence in the macro-chain of the ENBC's of a phenolic resin and the formation of an ether bond during hardening give ENBC's increased heat stability and hardness and high chemical resistance.

The mechanical properties of the hardened unfilled ENBC's used as dipping and casting compositions are as follows:

	<u>6E18N50-2</u>	<u>6E18N60-2</u>	<u>60E160-2</u>	<u>D-1</u>
Density, g/cm ³ -----	1.22	1.21	1.21	1.23
Flexural strength, kgf/cm ² -----	800 to 1000	1000 to 1200	1200 to 1300	1100 to 1400
Compression strength, kgf/cm ² -----	1400 to 1600	1400 to 1500	1600 to 1700	1500 to 1700
Impact strength, kgf-cm/cm ² -----	7 to 8	10 to 15	10 to 16	8 to 18
Brinell hardness, kgf/mm ² -----	20	18 to 20	17 to 19	20
Vicat softening point, °C -----	115 to 120	120 to 125	115 to 120	125 to 135
Coefficient of linear expansionx10 ⁶ , per °C -----	64	65	65	65
Weight loss at 300°C, % -----	4.2	4.0	4.5	16
Thermal conductivity, w/m ^o K -----	-	0.18	-	0.16

The introduction of fillers results in an improvement in the strength characteristics of the compositions, a reduction in the coefficient of linear expansion, and the conferring of predetermined properties. To give the compositions antifrictional properties, molybdenum disulphide, graphite, and powders of tin or lead are used. The fillers for the compositions based on the 6E18N-60 type of ENBC are as follows:

	<u>Filler</u>
ENKP-1 -----	PKP (100)*
ENKP-1.5 -----	PKP (150)
ENKP-2 -----	PKP (200)
ENKP-2.5 -----	PKP (250)
ENT-1 -----	Titanium dioxide (100)
ENT-2 -----	Titanium dioxide (200)
ENV -----	Vermiculite
ENAL -----	Al sifer (Al-Si-Fe alloy RJM) (500)
ENS-60 -----	Lead powder (60)
ENOS-1/1 -----	Tin powder (30), Lead powder (30)
ENO-1 -----	Tin powder (60)
ENM-20 -----	Molybdenum disulphide (20)
ENG-30 -----	Graphite (30)
ENTA-25 -----	Talc (25)

*PKP is a powdery quartz sand.

Figures in parentheses show parts by weight.

	<u>ENKP-1</u>	<u>ENKP-2</u>	<u>ENT-1</u>	<u>ENT-2</u>	<u>ENV</u>
Density, g/cm ³ -----	1.54	1.8	1.45	2.2	1.23
Flexural strength, kgf/cm ² -----	1300 to 1400	800	1300	950 to 1000	800
Compression strength, kgf/cm ² -----	1800	2000	-	-	-
Impact strength, kgf-cm/cm ² -----	8 to 10	6 to 9	12	16	4 to 6
Brinell hardness, kgf/mm ² -----	33	35	30	-	-
Coefficient of linear expansionx10 ⁶ , per °C -----	40	34	48	-	-
Vicat softening point, °C -----	125 to 140	150 to 180	-	250 to 300	-
Thermal conductivity, W/mx°C -----	0.440	0.656	0.420	-	0.315
Thermal diffusivityx10 ⁸ , m ² /sec -----	29.8	37.5	23.5	-	22
Specific heat, J/kg°C -----	960	940	912	-	956
Volume resistivity, ohm-cm at 20°C -----	-	10 ¹⁶	10 ¹⁵	10 ¹⁵	10 ¹⁶
Dielectric loss tangent at 10 ⁶ Hz -----	-	0.009	0.01	0.01	0.09
Dielectric permittivity at 10 ⁶ Hz -----	-	3.8	4.2	4.0	3.8

	<u>ENM-20</u>	<u>ENG-30</u>	<u>ENT-25</u>
Density, g/cm ³ -----	1.32	1.29	1.28
Flexural strength, kgf/cm ² -----	1000 to 1200	800 to 1000	1100 to 1200
Compression strength, kgf/cm ² -----	1700 to 1800	1200 to 1400	1500 to 1600
Tensile strength, kgf/cm ² -----	450 to 500	400 to 500	500 to 600
Young's modulus in bend, kgf/cm ² -----	41,000 to 44,000	20 to 22	22 to 25
Brinell hardness, kgf/mm ² -----	20 to 22	120	120
Vicat softening point, °C -----	125 to 130	0.33	0.33
Poisson's ratio -----	0.33		
Coefficient of friction with a lubricant -----	0.18	0.16	0.22
Coefficient of friction on a clean polished surface at v = 1.11 cm/sec -----	0.09	0.12	0.11
Linear abrasion over 1 km at a pressure of 50 kgf/cm ² without a lubricant -----	0.0025	0.006	0.004

Designation

Trademark ----- 6E18N-60-0.5 with SKN-18-1
 Generic type ----- Epoxy novolak block copolymer
 modified with carboxyl containing
 butadiene-acrylonitrile rubber.

Description

Epoxy-novolak block copolymers are products of interaction of epoxy and novolak resins. To increase their use, they are blended with rubbers. An example of this blending is interaction of an epoxy-novolak block copolymer with SKN-18-1 low molecular carboxyl-containing butadiene-acrylonitrile rubber.

Application

These adhesives are generally similar to epoxy novolak nitrile adhesives. They may be used as moderate- to high-temperature structural adhesives, with increased resistance to vibration. Aerospace and aircraft applications appear possible.

Technological Status

Research ----- 1965 (est)
 Development ----- 1968 (est)
 Engineering ----- 1970 (est)
 Production ----- 1971 (est)

Designation

Trademark ----- ENBC with ACCP or APCP
 Generic type ----- Epoxy novolak block copolymers
 modified with aminocyclotriphos-
 phazenes.

Description

Polyphosphazenes and polymers based on cyclophosphazenes are introduced into epoxy and PF resins to increase their thermal stability and fire resistance. The use of aminochloro- and amino-organocyclophosphazenes as hardeners of epoxy resins makes it possible to obtain materials with a Vicat softening point of 215°C and a flame resistance of 2 on the Schramm scale.

Heat-resistant epoxy novolak block copolymers are obtained by modification with aminocyclotriphosphazenes (ACP's): 2,2-diamino-4,4,6,6-tetrachlorocyclotriphosphazene (ACCP) and 2,2-diamino-4,4,6,6-tetraphenoxycyclotriphosphazene (APCP).

Modified ENBC's are obtained by heating ED-6 epoxy resin with PF novolak resin 18 in the presence of the ACP's at 90° to 110°C for a period of 0.5 to 1 hour. Block copolymers containing 5% to 40% ACP on the weight of the ENBC are light-brown, translucent, solid, brittle materials, melting in the range 55° to 70°C.

Application

Epoxy-novolak block copolymers modified with aminocyclophosphazenes have self-extinguishing properties, a high softening point, satisfactory thermal stability, and valuable mechanical properties. They are of interest as polymeric materials that can work at elevated temperatures.

Technological Status

Research ----- 1965 (est)
 Development ----- 1967 (est)
 Engineering ----- 1969 (est)
 Production ----- 1972 (est) (probably limited)

Properties

The mechanical properties of the ENBC's obtained under the conditions of hardening mentioned, and also the properties of the ENBC of type 6E18N60 and of epoxy resin hardened with ACCP (for comparison) are given below.

	<u>ENBC</u>	<u>ENBC-10-ACCP</u>	<u>ENBC-20ACCP</u>	<u>ENBC-35-APCP</u>	<u>Epoxy resin ACCP</u>
Compression strength, kgf/cm ² -----	1400 to 1500	1700 to 1800	1500 to 1600	1800 to 1900	1900
Brinell hardness, kgf/mm ² -----	17	22	21	22	20
Impact strength, kgf-cm/cm ² -----	10 to 14	8 to 10	5 to 6	-	5
Vicat softening points, °C -----	120	170	255	240	215
Content of insolubles, % --	90	97	98	99	99
Water absorption in 24 h, % -----	0.02	0.24	0.28	0.33	0.66
Weight loss in 5 hr, %:					
at 250°C -----	1.2	1.0	0.2	1.3	13.1
at 300°C -----	1.8	-	19.0	-	58.2
Volume resistivity, ohm-cm -----	1.0x10 ¹⁶	-	2.0x10 ¹⁶	-	5.1x10 ¹⁵
Dielectric loss tangent at f = 10 ⁶ Hz -----	9.0x10 ⁻³	-	1.6x10 ⁻³	-	8.1x10 ⁻³
Schramm flame resistance, points -----	Flammable	Self-extinguish- ing	Self-extinguish- ing	-	Self-extinguish- ing

Modified ENBC's have a higher softening point than that of the epoxy resin hardened with ACCP. The use of aminocyclophosphazenes for modifying ENBC's is more effective than the use of these compounds as hardeners for epoxy resins. Complete hardening of epoxy resins such as ED-5 and ED-6 requires the introduction of 35 to 40 parts by wt. of ACCP, whereas to obtain materials with a Vicat softening point of 255°C, the addition of 20% of ACCP on the weight of the ENBC is adequate.

Hardness and compression strength show a rise as a result of increase in the crosslink density. A decrease in the impact strength of modified ENBC's, compared with the epoxy-novolak block copolymers is found (impact strength decreasing from 10 to 14 to 5 to 6 kgf-cm/cm²). Of these materials, the initial ENBV's have the greatest thermal stability; their weight losses at 300°C, after keeping for 5 hours, are 1.5% to 3%. The weight losses of the modified ENBC's under similar conditions are 20%. At 250°C there are practically no weight losses in the modified ENBC's. Weight losses of the epoxy resin hardened with ACCP are considerable, amounting to 13.0% at 250°C and 58.0% at 300°C. These materials can be ranked in descending order of thermal stability as follows: ENBC>modified ENBC>epoxy resins hardened with ACP's. The lower thermal stability of modified ENBC's, compared with that of the initial ENBC's despite their high crosslink density, is attributed to the content of nitrogen and chlorine in the block copolymer. ENBC's modified with ACP's, after keeping for 100 hours at 200° to 230°C not only do not change in their mechanical properties, but actually increase their compression strength and hardness. This is probably because of the additional crosslinking arising from a more complete reaction of the remaining functional groups.

Designation

Trademark ----- ED-6 hardened with various polyorganosilazanes.
 Generic type ----- Diamine epoxy with hexamethylcyclotrisilazane, polymethylsilazane, or polymethylphenylsilazanes as hardeners.

Description

Modifying epoxy resins with organocyclosilazanes enhances heat stability of the polymer. Improvement of the heat resistance of epoxy resins is achieved by employing as hardeners hexamethylcyclotrisilazane $[(CH_3)_2 SiNH]_3$ or polyorganosilazanes containing di- and trifunctional structural units, of the general formula



(where $R = CH_3$; $R' = CH_3, C_6H_5$; $n = 1$ or 3) as hardeners.

Polymethylsilazane (MSN-7) is reported to be the preferred hardener for epoxy resins ED-5 and ED-6.

Technological Status

Research ----- 1963 (est)
 Development ----- 1965 (est)
 Engineering ----- 1968 (est)
 Production ----- 1970 to 1971 (est) (possibly limited use)

Properties

The mechanical and dielectric properties of ED-6 epoxy resin hardened with polymethylsilazane and endic anhydride are shown below:

Property	Hardner	
	Polymethylsilazane (MSN-7)	Endic anhydride
Tensile strength, kgf/cm ²		
20°C	232	440
155°C	152	7
Impact strength, kgf-cm/cm ²	6	14
Martens yield temperature, °C	182	120
Electric strength, kV/mm	40	47
20°C	1.1x10 ¹⁶ *	1.2x10 ¹⁵ *
155°C	9.8x10 ¹³ *	1.2x10 ¹³ *
tan δ at 50 Hz		
20°C	0.0002	0.002
155°C	0.002	0.085

*resistivity values

The improvement of tensile strength of the ED-6/MSN-7 system upon heat treatment is shown below:

Tensile strength, kgf/cm²:

20°C ----- 197/232
 155°C ----- 38/152

Elongation at break, %:

20°C ----- 3.3/-
 155°C ----- 4.5/4.0

(Note. Figures before the stroke, after heat treatment at 150°; after stroke, after heat treatment at 200°C.)

Designation

Trademark ----- ES-9 (also called TPPGTS-based epoxy)
 Generic type ----- Epoxy-organosilicone

Description

ES-9 adhesive is a resin diluent based on triphenylpentaglycidoxytrisiloxane (TPPGTS). Diluents are used to reduce the viscosity of epoxy resins so that wetting properties of the adhesives are enhanced. Other diluents available are the diglycidyl ether of diethyleneglycol and phenyl glycidyl ether.

Application

Epoxy variants using ES-9 in high percentages (30% to 50%) may give improved binder resins (for glass reinforced materials) and produce adhesives having extended durability under hot/wet exposure. It is postulated that these type agents are used in various electrical and electronic items.

Technological Status

Research ----- 1967 (est)
 Development ----- 1967 to 1968 (est)
 Engineering ----- 1969 (est)
 Production ----- 1969 (est)

Properties

The compatibility of TPPGTS with epoxy and modified epoxy resins makes it possible to use this product as an active diluent. The addition to ED-6 epoxy resin of even minimal amounts of TPPGTS (5%) reduces the viscosity of the composition at 50°C almost to one-twentieth. A sharp reduction in the viscosity is also observed with the addition of ES-9 to T-10 epoxy-organosilicon resin.

The addition of TPPGTS to ED-6, T-10, or other epoxy resins (in the ratio 1:1) makes it possible to produce resins of novel quality of the contact type for GRP's and casting compositions, having low viscosity and almost no voids.

Property data for liquid TPPGTS are:

MW -----	712
Dry residue, % -----	95 to 98
Viscosity, cP	
20°C -----	300 to 400
50°C -----	60 to 70
Content, %, of	
epoxy groups -----	20 to 22
silicon -----	11 to 12
nD ²⁰ (refractive index) -----	1.5279
solubility -----	In esters, alcohols, ketones, aromatic hydrocarbons

Conventional hardeners can be used for diluent epoxy systems. The data below are given for a system containing 62phr of methyl tetrahydrophthalic anhydride as hardener (24 hour cure over 100° to 200°C gradual temperature range).

Flexural strength, kgf/cm ² ---	650
Brinell hardness, kgf/mm ² ----	6
Impact strength, kgf-cm/cm ² --	8 to 10
Water absorption, %	
in 24 hours -----	0.09
after 3 hours boiling -----	0.6
Dielectric permittivity at	
10 ⁶ Hz -----	3
Tan delta -----	0.0078
Surface resistivity, ohm -----	3.4x10 ¹⁵
Volume resistivity, ohm-cm ---	3.9x10 ¹⁵

Designation

Trademark ----- T-10
 Generic type ----- Epoxy-organosilicone

Description

T-10 is an epoxy-organosilicone resin. It has high dielectric and water resistant properties. A modified form of T-10 contains polydimethylsiloxane rubber that enhances the strength and water repellence of the resin.

Application

T-10 and modified T-10 are probably used as binders in laminates for high-temperature use (180°C) and in electronic equipment.

Technological Status

Research ----- 1965 (est)
 Development ----- 1966 (est)
 Engineering ----- 1967 (est)
 Production ----- 1968 to 1969 (est)

Properties

Mechanical and Electrical Properties of GRP's Based on T-10 Epoxy-Organosilicon Resin

Property	Glass fabric				
	E-0.1	KT-11-E			
		20x20	10x8	10x9	10x10
Impact strength, kgf-cm/cm ²	240(230)	90	164	166	163(186)
Flexural strength, kgf/cm ²	4200 (4300)	2910	3550	3670	2970 (2600)
Elastic modulus E.10 ⁻⁵ , kgf/cm ²	1.8(1.7)	1.1	1.1	1.2	1.2(0.9)
Brinell hardness, kgf/mm ²	41.2 (39.9)	35.6	34.2	35.6	36.8 (28.5)
Water absorption in 24 h, %	0.06-0.07 (0.06)	0.06	0.06	0.05	0.06 (0.04)
Tan delta at 10 ⁶ Hz	0.007 (0.007)	0.008	0.008	0.008	0.010 (0.007)
Dielectric permittivity at 10 ⁶ Hz	3.9 (4.1)	4.2	4.1	4.2	4.1(4.5)

Note: In parentheses, GRP based on resin T-10, modified with SKTN rubber.

Best properties are shown by the material based on KT-11-E glass fabric (10x10 count) with 48% to 50% T-10 resin binder content. Laminates based on synthetic fibers are superior to GRP's in water-resistant and dielectric properties, but their mechanical properties are inferior.

Mechanical and Electrical Properties of Laminates Based on Synthetic Fabrics and T-10 Epoxy-Organosilicone Resin

Properties	Fabric				
	Lavsan		PP		
	initial	treated with hot air	initial	treated with $K_2Cr_2O_7$	treated with H_2SO_4
Impact strength, kgf-cm/cm ²	26.0/20.1	-/18.3	100/97	118/86	-/116
Flexural strength, kgf/cm ²	825/667	-/790	576/970	720/442	-/424
Elastic modulus $E \cdot 10^{-4}$, kgf/cm ²	3.7/2.9	-/3.5	8.1/1.5	3.1/2.1	-/2.0
Shear strength, kgf/cm ²	32.7/9.4	-/15.6	10.0/6.3	10.0/6.2	-/5.5
Brinell hardness, kgf/mm ²	19.6/19.2	-/19.5	18.3/9.4	18.3/9.3	-/5.1
Water absorption in 24 h, %	0.04/0.04	-/0.03	0.05/0.03	0.65/0.03	-
Tan delta at 10^6 Hz	0.009/0.008	-/0.009	0.006/0.006	0.007/0.009	-/ 0.006
Dielectric permittivity at 10^6 Hz	3.9-4.1/3.9	-/4.0	3.2/3.5	3.2/3.6	-/3.6

Note: Figures before the stroke, resin T-10; after the stroke, T-10 resin modified with SKTN rubber.

Designation

Trademark ----- MVTsG and DCPDD-Epoxies
 Generic type ----- Modified epoxies

Description

DCPDD-epoxies are based on dicyclopentadiene dioxide, while MVTsG-epoxies are based on 4-vinyl-1,2-epoxycyclohexane and can function as reactive diluents for epoxies in lowering viscosity. These variants have high temperature stability.

Application

These materials are high-temperature binder resins useful for structural glass-reinforced plastics.

Technological Status

Research ----- 1968 (est)
 Development ----- 1969 (est)
 Engineering ----- 1970 (est)
 Production ----- 1972 (est)

Properties

Composition I: 60 parts MVTsG
 40 parts maleic anhydride

Composition II: 12.1 parts MVTsG
 48.3 parts DCPDD
 39.6 parts maleic anhydride

Composition III: 9.3 parts MVTsG
 23.2 parts DCPDD
 23.2 parts ED-5
 43.3 parts maleic anhydride

Composition IV: 16.2 parts MVTsG
 48.9 parts ED-5
 34.9 parts maleic anhydride

[Curing initiated by peroxides]

The above GRP's were prepared with ASTT (b)-S₁ glass fabric. The glass fabric was impregnated with the binder containing no solvent.

The GRP was pressed in the form of flat sheets about 10 mm thick under stepwise temperature conditions (from 80° to 220°C) at 10 kgf/cm² for 20 min/mm. Binder content is 25% to 28%.

Composition I has a relatively low heat stability. The higher heat stability of compositions, containing ED-5 in the range 300° to 400°C, results from the greater degree of hardening.

The data show the change in flexural strength of the glass fiber laminates after the short-term effect of high temperatures. The introduction of DCPDD and ED-5 into compositions based on MVTsG (composition I) increases the flexural strength of the glass fiber laminate. A laminate based on composition IV retains almost 84% of its initial strength at 250° to 300°C, and up to 51% at 360°C; a laminate based on compositions II and III retains about 55% of its initial strength. The strength of a laminate based on composition I at 300°C is less than 28% of its initial strength, and the strength of a laminate based on ED-5 resin (composition V) at 200°C is only 20% of its initial value.

Flexural Strength of Glass Fiber Laminates After Short-Term Action of High Temperatures

Binder	Flexural strength, kgf/cm ²				
	20°C	200°C	250°C	300°C	350°C
I	3370*	2180	1200	950	-
II	4340	3170	2970	2760	1160
III	5170	3430	3330	2840	1510
IV	4500	4400	4100	3800	2300
V	5000	800	-	-	-

*Content of binder - 36%

Dielectric tests on the glass fiber laminates show that these materials have satisfactory electrotechnical properties. It is claimed that glass fiber laminates based on compositions II and III are suitable for long-term use at temperatures of up to 250°C, and glass fiber laminate based on composition IV may be recommended for long-term use at 200°C.

Designation

Trademark ----- DM-6T, DM-6, DM6S
 Generic type ----- Epoxy modified with acrylates

Description

These adhesives are based on ED-6 modified with dimethacrylates and triethyleneglycol dimethacrylate (TGM-3). DM-6 is the designation for the latter. Synthesis of DM-6 is performed at 100°C in the presence of lithium chloride catalyst (0.2%) and at 120° to 140°C without a catalyst. DM-6S is a solution of DM-6 in styrene.

Application

The dimethacrylic esters of epoxy resins may be used with appropriate hardening systems as binder resins for fabricated GRP's and as prepegs. Improved water and chemical resistance and heat resistance are characteristic. The dimethacrylic esters may be used also as binder resins in compositions for making chemically resistant floor coverings.

Technological Status

Research ----- 1967 to 1968 (est)
 Development ----- 1968 (est)
 Engineering ----- 1970 (est)
 Production ----- 1971 (est)

Properties

The properties of DM-6T resin, hardened in the presence of 3% of isopropylbenzene hydroperoxide and 8% of cobalt naphthenate accelerator at room temperature, and with subsequent heat treatment at 80°C for 12 hours are as follows:

Flexural strength, kgf/cm² --- 500 to 600
 Compression strength,
 kgf/cm² ----- 1250 to 1350
 Impact strength, kgf-cm/cm² -- 4 to 5
 Brinell hardness, kgf/mm² ---- 18 to 24
 Martens yield temperature
 °C ----- 80 to 85

Solutions of DM-6 in TGM-3 (DM-6T resin) are more stable than are solutions of DM-6 in styrene (DM-6S resin). At 120°C specimens of DM-6T resin produced in the presence of various catalysts have the following pot life:

<u>Catalyst</u>	<u>Pot life, hours</u>
Pyridine -----	5
No catalyst -----	<6
Lithium chloride -----	9

The strength and dielectric properties of GRP's made by contact molding on the basis of DM-6S and DM-6T resins and ASTT (b)-S₂-0 glass fabric are higher than or equal with the comparable properties of polyester GRP's based on polymaleates. With regard to heat resistance they are superior to the polymaleate GRP's (i.e., PN-1).

Properties of Contact Molded GRP's Based on the Resins DM-6S, DM-6T and PN-1 and ASTT(b)-S₂-0 Glass Fabric

Property	DM-6S*	DM-6T	PN-1
Strength, kgf/cm ² flexural (along the warp)	3540 to 4360	4110 to 4720	3700
tensile	2890 to 3150	2600 to 3000	3200
compression	1320 to 1590	-	900 to 1100
Impact strength, kgf-cm/cm ²	302 to 392	116 to 162	250 to 350
Martens yield temperature, °C	300	-	80 to 100
Surface resistivity, ohm	10 ¹⁴	-	10 ¹³
Volume resistivity, ohm-cm	10 ¹⁵	-	10 ¹⁴
Dielectric loss tangent (f = 1 MHz)	0.013	-	0.015 to 0.03
Dielectric permittivity (f = 1 MHz)	5.3	-	4.5 to 5.4
Electric strength, kV/mm	25.3	-	-

*GRP's based on DM-6S have higher thermal and chemical resistance than those based on polymaleates.

Designation

Trademark ----- ETs, ETsD-13
 Generic type ----- Polyglycidyl ester of cyanuric acid.

Description

ETs resin is based on polyglycidyl ester of cyanuric acid and has an epoxide content of 30% to 32%. ETsD-13 is a composition of ETs and ED-13 resin.

Application

These resins have potential application as high-strength adhesives. These compositions when used as GRP binders afford a 10% to 15% improvement in mechanical properties, as compared to GRP's made of ED-13 epoxy binder.

Technological Status

Research ----- 1966 (est)
 Development ----- 1968 (est)
 Engineering ----- 1969 (est)
 Production ----- 1971 (est)

Properties

ETs have high viscosity, but also has a high degree of shrinkage and brittleness in the cured state. Of a composition of ETs with ED-13 resin, the best technological and strength properties are observed in a composition consisting of 20% to 30% of ETs resin and 70% to 80% of ED-13 (ETsD-13).

Data on GRP's based on ED-13 and ETsD-13 resins are as follows:

	ED-13	ETsD-13
Tensile strength, kgf/mm ² ----	64.0/68.0	72.0/74.1
Compression strength, kgf/mm ² -----	46.2/52.0	51.5/59.0
Flexural strength, kgf/mm ² ---	72.0/77.0	76.0/84.0
Inter-ply shear strength, kgf/mm ² -----	6.9/7.1	7.2/7.4
Tensile elastic modulusx10 ⁻³ , kgf/mm ² -----	3.1/3.1	3.1/3.1

Notes: 1. The reinforcing material is ASTT(b)-S-8/3 glass fabric with size 752. 2. Curing agent: before the stroke, PF resin; after stroke, triethanolamine titanate.

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The composition based on ETsD-13 resin has not only good strength characteristics but also good use characteristics: the viscosity of the composition is $5-9 \times 10^4$ cSt, the epoxide group content is 19% to 22%, and the gel time is 15 to 45 min.

Designation

Trademark ----- ED-5 SKN-26-1 composition
 Generic type ----- Epoxy - butadiene acrylonitrile
 compositions.

Description

This class includes mixtures of ED-5 resin and SKN-26-1 (carboxylated butadiene - acrylonitrile rubber). Hardeners used include polyethylenepolyamine.

Application

This adhesive class is used for vibration resistant applications, and may be used in place of phenolic-nitriles where high temperature performance is not critical, such as aircraft honeycombs, metal structures, and flexibilized glass structures.

Technological Status

Research ----- 1966 (est)
 Development ----- 1968 (est)
 Engineering ----- 1969 (est)
 Production ----- 1971 (est)

Properties

With an increase in the rubber content, the decrease in the tensile strength is more gradual than the increase in the elongation at break.

Designation

Trademark ----- ED-5 SKN-26-5 composition
 Generic type ----- Epoxy-butadiene acrylonitrile
 compositions.

Description

This class is based on ED-5 epoxy resin modified with SKN-26-6 low molecular weight butadiene-acrylonitrile rubber. Triethanolamine titanate (TEAT) is used as hardening agent.

Application

This adhesive type can be used with many metallic substrates. Continuous-use temperature is no greater than 100°C.

Technological Status

Research ----- 1965 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1970 (est) (limited)

Properties

The shear strength of bonded short-blasted 30KhGSA steel is 400 kgf/cm²; for D16AT aluminum alloy (surface treated with abrasive sheet) the shear strength is 250 to 300 kgf/cm²; for D16AT aluminum alloy with anodized surface it is 150 to 180 kgf/cm².

The incorporation of fine-particle strontium chromate (SrCrO₄) into the epoxy-rubber composition, in an amount of 5 parts by weight, leads to an increase in the strength of the bonded joints, in particular in the bonding of sheets of D16AT aluminum alloy with anodized surface. The incorporation of fine-particle strontium chromate into the epoxy-rubber composition leads to a change in the supermolecular structure of the composition, and at the same time there is less tendency for the composition to form bubbles. The shear strength of such bonded compositions increases from 200 to 250 kgf/cm² (without chromate) to 250 to 300 kgf/cm².

Designation

Trademark ----- EPF
 Generic type ----- Epoxy-phenol-furan resins

Description

The epoxy-phenol-furan resins (called EPF's, although this is probably not an official designation) based on α -glycidyl furfuryl ether are solid products of dark-brown color, with a softening temperature of 90° to 100°C. At 25°C they are hard and brittle; at 70° to 80°C they are elastic and can be drawn into threads. They dissolve readily in acetone and alcohol.

EPF's are found in two stages. At the beginning of the condensation of the phenol with excess of furfural in an alkaline medium, a resin of C stage type is formed. This condensation product is a carbinol. This then condenses with the α -glycidyl furfuryl ether and formaldehyde, forming the EPF resin. Upon addition of formaldehyde (37% formalin), there is formed a methylol group at the para and partly the ortho position of the phenolic ring. The latter enters into reaction with epoxide groups. The epoxide rings open forming a secondary hydroxyl group, which takes part in the crosslinking of the resin.

Application

Epoxy-phenolic resins are used widely as binders for various substrates and as general adhesives and coatings. These types show low impact strength and low elasticity. The furfuryl ether modifications, however, have additional flexibility and elasticity.

Technological Status

Research ----- 1965 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1969 (est) (probably limited)

Properties

It appears that the USSR has extensive and current programs related to increasing flexibilization (brittleness reduction) of phenolic resins. It is surmised that some forms of "flexibilized"

phenolics have been in production for a number of years. Typical properties of EPF and standard phenolic K-18-2 are shown:

	<u>EPF</u>	<u>K-18-2</u>
Shear strength, kgf/cm ² -----	50	45
Raschig flow, mm -----	200	90 to 180
Shrinkage, % -----	1.0	0.6 to 1.0
Water absorption, mg/gm -----	60	55
Brinell hardness -----	35	30 to 40
Flexural strength, kgf/cm ² ----	800	700
Impact strength, kgf-cm/cm ² -----	6	6
Dielectric strength, kV/cm -----	600	600
Heat distortion temperature (Martens, °C) -----	125	125
Density -----	1.45	1.40

Designation

Trademark ----- Unknown
 Generic type ----- Poly(amide-imides)

Description

Poly(amide-imides) are based on trimellitic acid derivatives condensed with aromatic diamines. Poly(amide-imides) contain amide groups as well as imide and aromatic rings. Poly(amide-imides) combine the properties of polyimides and polyamides (high heat resistance, good mechanical and dielectric properties, radiation resistance, and good processibility). Poly(amide-imides) are inferior to polyimides in heat resistance but have better heat resistance than epoxy polymers, phenol-formaldehydes, and others.

Application

Poly(amide-imides) can be used as high-temperature adhesives, binder resins for glass-reinforced plastics, and electric insulation. Specific Soviet applications are not known. Crosslinked adhesives based on poly(amide-imides), consisting of glass fabric impregnated with a resin solution, can be used for joining different types of stainless steel and also titanium, and they retain their high-strength bond characteristics for 1000 hours at 315°C.

Technological Status

Research ----- 1965 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- ?

Properties

Glass-reinforced plastics based on poly(amide-imides) retain high mechanical properties after aging at 289°C for 1000 hours. Crosslinked poly(amide-imides) can be used at 315°C and have higher strength properties than do linear polyimides. The following tables list properties of poly(amide-imides); however, these properties, although reported in the Soviet literature, may be based on Western data.

Change in Strength of GRP's Based on Poly(Amide-Imides)* With Aging

	Test temperature, °C		After aging at 289°C**			
	24	289	250 hr	500 hr	750 hr	1000 hr
Flexural strength, kgf/cm ²	4922/5040	3500/3290	2870/2961	2387/2674	2380/2744	2100/2408
Elastic modulus in flexure, (kgf/cm ²)x10 ³	225/245	157.5/161	146.3/158.2	138.6/142.1	126/150.5	113.4/140.7

*Numerator - GRP's based on poly(amide-imide) type 10; denominator - GRP's based on poly(amide-imides) type 11.

**The strength was determined at 289°C.

Strength of Bonded Joints (Duralumin D-16) Based on Poly(Amide-Imides)*

Temperature for testing and thermal Aging, °C	Shear strength of bonded joint kgf/cm ²	
	SP-95	SP-92
20	120 to 125	110 to 133
300	80 to 100	117 to 120
350	65 to 70	64 to 67
		SP-77
		110 to 120
		87 to 92
		65 to 70

*GRP's based on crosslinked poly(amide-imides) have high strength characteristics even at 350° to 400°C. The flexural strength of SN-95 (a poly(amide-imide)-based GRP) is 2125 kgf/cm² at 350°C, after aging at 350°C for 100 hours it is 2000 kgf/cm², and at 400°C it is 1800 kgf/cm².

Strength of GRP's Based on Poly(Amide-Imides)

Type of polyamide-imide	at 24°C	at 300°C	Flexural strength, kgf/cm ² after thermal aging at 300°C*				
			250 h	500 h	1000 h	1500 h	2000 h
SP-95	5350	4980 to 5500	2600 to 4350	2800	1870 to 1950	1570 to 1300	1050 to 1170
SP-96	6650 to 6850	4600 to 5850	5180 to 5380	3190 to 3850	2400 to 1500	-	-
SP-92	5880 to 6620	3800 to 4500	4100 to 4300	4100 to 4300	2200 to 2800	-	-

*The strength was determined at 300°C

(a) L. I. Chudiva, A. M. Chukurov, "Poly(amide-imides)," Soviet Plastics, No. 8, 7-12 (1970).

(b) S. R. Rafikov, et al., Vysokomol. Soedin, B11, No. 3, 165 (1969).

(c) M. I. Bessonov, et al., "Polyimides - A New Class of Thermally Stable Polymers," Technomatic Publication Company, Stamford, Conn. 1970.

Designation

Trademark ----- Unknown
 Generic type ----- Poly(methylidene phthalide)
 copolymers.

Description

Poly(methylidene phthalides) contain a lateral cyclic group in which at least one of the atoms forms part of the main polymer chain. A bulk homopolymer of methylidene phthalide is an amorphous, transparent, brittle plastic. To obtain products with better mechanical properties than poly(methylidene phthalide), copolymers of methylidene phthalide (MP) with acrylonitrile (A), methacrylic acid (MAA), styrene (S), methyl methacrylate (MMA), methyl acrylate (MA), ethyl acrylate (EA), and butyl acrylate (BA) are synthesized. Crosslinked copolymers are also included. The crosslinking agents used are dimethacrylic ester of ethylene glycol (DMG) and hexamethylene- α,ω -bis(methacryloyloxyethyl)urethane (HMU).

Application

This adhesive class is appropriate for high-performance bonding applications and binder resins (240° to 270°C). The Soviets probably have been studying thermal stabilizers for these adhesives.

Technological Status

Research ----- 1968 (est)
 Development ----- ?
 Engineering ----- ?
 Production ----- 1973 (est)

Properties

Copolymers of poly(methylidene phthalide) are less brittle than the parent polymer. Softening points and decomposition temperatures are high for the copolymers.

Heat Resistance of Some MP Copolymers (Tests in Air)

Molar ratio of monomers	Temp. of start of decomposition, °C	Temp. of semi-decomposition of the polymer, °C
	MP:S	
0.7:0.3	250	350
1.0:0.0	290	350
0.0:1.0	250	360
	MP:MA	
0.7:0.3	240	350
0.0:1.0	320	380
	MP:MMA	
0.7:0.3	230	330
0.0:1.0	220	320
	MP:A	
0.7:0.3	280	360
0.5:0.5	280	360
0.0:1.0	290	530
	MP:MAA	
0.7:0.3	200	330
	MP:S:DMG	
0.7:0.27:0.03	270	340
	MP:S:HMU	
0.7:0.29:0.01	260	340
	MP:A:HMU	
0.5:0.49:0.01	270	340

The appearance of the copolymers depends on the initial monomer ratio. Transparent copolymers are obtained with particular ratios of methylenediphthalide and the other comonomer, the maximum amount of the other monomer diminishing with decrease in its polarity. For copolymers of MP with acrylates, the maximum amount of acrylate giving a transparent copolymer decreases with increase in the length of the hydrocarbon radical. Any decrease in the content of MP below a certain value no longer results in a transparent polymer.

GLOSSARY

- ASTT(b)-S₁--Soviet designation for woven E-glass fabric with satin 8/3 type weave.
- ASTT(b)-S₂-0.--Soviet designation for woven treated E-glass fabric with satin 8/3 type weave.
- Centipoise (cP)--One one-hundredth of a poise. The poise is the metric system unit of viscosity, and has the dimensions of dyne-second per square centimeter.
- Duralumin--A common aircraft aluminum alloy.
- HMDI--Abbreviation for 1,6-hexamethylene diisocyanate.
- Kapron (capron)--Soviet trade name for nylon-6.
- Leykonat--Soviet designation for polyurethane.
- MGF-9--Soviet designation for triethyleneglycol methacrylate-phthalate.
- Nairit--Soviet designation for polychloroprene rubber.
- NVB-2--Liquid polysulphide used to modify Soviet phenol-formaldehyde adhesives.
- PF--Abbreviation for phenol-formaldehyde resin.
- PMMA--Poly(methyl methacrylate).
- PUR--Soviet designation for polyurethane elastomers.
- PVAL--Soviet designation for poly(vinyl alcohol).
- PVB--Poly(vinyl butyral).
- PVF--Poly(vinyl formal)
- PVK--Poly(vinyl ketal)
- TDI--Abbreviation for 2,4-toluene diisocyanate.
- TGM-3--Soviet designation for triethyleneglycol dimethacrylate.

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13. ABSTRACT This report presents a narrative analysis of Soviet conventional and high-performance adhesive and tabular data on the properties, compositions, designations, and characteristics of the adhesive material. It presents potential or known uses of the adhesives, including glue welding technology. Comparative analysis of US and USSR adhesives programs is presented in a tabular form. A tabulation of major institutes and key personnel conducting adhesives research is presented.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Adhesives Glue-welding Thermoset adhesives Thermoplastic adhesives Elastomeric adhesives Polymers						

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