ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 548–564. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © E.Ya. Beider, A.A. Donskoi, G.F. Zhelezina, E.K. Kondrashov, Yu.V. Sytyi, E.G. Surnin, 2009, published in Rossiiskii Khimicheskii Zhurnal, 2009, Vol. 52, No. 3, pp. 30–44.

An Experience of Using Fluoropolymer Materials in Aviation Engineering

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Received February 1, 2008

Abstract—The main grades of fluorine-containing materials, including solid and powder materials, paint-and-lacquer coatings and films, organic glasses, rubbers and sealants used in aviation engineering are described in the paper. The main operating performances are given as well.

DOI: 10.1134/S1070363209030372

Among multiple polymers produced by the chemical industry fluoropolymers to a greater extent provide for the requirements placed upon aviation materials. They have a complex of unique properties: increased thermal and fireresistance, exclusive resistance to the chemical action, superior mechanic, dielectric, antifriction, and antiadhesive properties, and also the capability of retaining these properties over a wide range of operating temperatures and pressures. Owing to these properties the materials and products from fluoropolymers are distinguished by their dependability in operation, fire safety, and by a sufficiently large period of service.

Thickening and Antifriction Materials Based on Fluoroplastics

Fluoroplastic-4 (F-4, polytetrafluoroethylene) is used in the aviation engineering to produce the details of thickening and antifriction purpose, in the friction blocks operating without lubricant among them. A drawback of flioroplastic-4 is a relatively low resistance to wear and an increased creep (deformation) on prolonged action of compressing load, which limits the operation resource and the opportunities for its wider application. One of the approaches to increasing the resistance to wear and decreasing the creep of fluoroplastic-4 is the synthesis of compositions on its basis filled with powders and fibers of various composition and quantity.

Thickening and antifriction details are produced by mechanic treatment of plates, sockets, and bars obtained by the method of cold pressing of fluoroplastic-4 powder and of the compositions on its basis with the following sintering at the temperature 370°C.

Table 1 gives the properties of F-4 and compositions on its basis developed by OAO "Plastpolymer" and of radiation modified fluoroplastic F-4RM developed by FGUP "Karpov NIFChI."

As is seen from Table 1, in comparison with fluoroplastic-4 its compositions with fillers have enhanced strength properties. Thus, the creep (residual deformation) of compositions on compressing with the load of 14 MPa for 24 h is lower by factors of 1.4–3.3, and resistance to wear is higher by factors of 15–150.

Radiation modified fluoroplastic (F-4RM) surpasses the starting F-4 in its resistance to wear by a factor of 150, its deformation on compressing under the load of 14 MPa is by a factor of 2.3 less, the residual deformation after taking off the compressing load being notably low (0.6%), which is a positive factor when mobile thickenings and antifriction details are operating.

F-4KS2, F-4S15, F-4K20, and F-4K15UV5 fluoroplastics are efficient materials for thickening and antifriction purpose for the details of pneumato-, hydro-, and fuel systems of aviation engineering

Table 1. Properties of fluoroplastic-4 and of the compositions on its basis

Index	F-4	F-4KS2 (F-4 filled with 2% of cobalt blue)	F-4S15 (F-4 filled with 15% of glass fiber)	F-4K20 (F-4 filled with 20% of type KL-1 casting coke)	F-4K15UV(F-4 filled with 15% of coke and 5% of carbon fiber)	F-4RM (radiation modified F-4)
Density, kg m^{-3}	2180	2170	2190	2100	2000	2180
Tensile strength, MPa	25	24	15	13	17.5	14.2
Relative elongation on rupture, %	350	300	200	120	150	125
Modulus of tension, MPa	350	400	480	630	700	630
Compression stress on 10% deformation, MPa	15	16.5	20	22	28	24
Compression deformation on loading by 14 MPa for 24 h, %	16	11.2	9.6	7.6	4.8	6.8
Residual deformation in 24 h after taking off the load of 14 MPa, %	9.8	5.4	6.8	5.5	3.5	0.6
Intensity of wear on friction over 30KhGSA steel loaded by 2.5 MPa and with the velocity of 0.3 m s^{-1}, mm km^{-1}	3,0	0,2	0,05	0,03	0,02	0,02
Coefficient of friction over steel	0.08	0.14	0.15	0.20	0.20	0.08
Brinell hardness, MPa	35	40	45	50	50	–
Water absorption for 24 h, %	0	0.05	0.04	0.03	0.07	0

operating in the temperature range from –60 to +250°C.

Fluoroplastic F-4KS2 is used for creating mobile thickenings in the thickening devices of hydro-aggregates of passenger aircrafts since it does not cause the wear of chrome-plated surfaces of the plungers and cylinders of the aggregates. Thickening seals for combined thickening details of fuel pumps used in all the products of aviation engineering are made of fluoroplastic F-4S15. Fluoroplastics F-4K20 and F-4K15UV5 are the materials for antifriction details operating without grease at high velocities of slide and low specific loads (0.1–1 MPa). Upon testing under conditions of back and forth movement with the velocity 5–80 mm s^{-1} and the load of 0.1 MPa antifriction details of fluoroplastic F-4K20 sustain 6 million of cycles and retain their working capacity, whereas similar details of F-4 sustain 300 thousand cycles up the a complete wear, i.e. their resource is substantially lower (more than by a factor of 20).

Construction Materials: Fluoroplastic F-40LD and Plyimidofluoroplastic PMF-L

Fluoroplastic F-40LD is a copolymer of tetrafluoroethylene and ethylene. It retains many positive properties of fluoroplastic-7 (chemical stability in various aviation media, inflammability, resistance to atmosphere etc.). But in contrast to F-4 on heating to the temperature higher that the melting point of the crystalline phase it passes into a viscous-flow state, which makes possible its treatment by pressure-die casting and obtaining the details of complex configuration. Fluoroplastic-40LD is recommended for producing by pressure-die casting of the items for construction and electroinsulating purposes operating in the temperature range from –60 to +150°C in air, in the aviation fuels, oils, and liquids for hydrosystems. In the aviation engineering it is used for producing by pressure-die casting of the details of fuel measuring apparata (clamps, cantilevers, etc.) instead of fluoroplastic-4, which made possible an increase in the coefficient of material use and a decrease in the man-hours per job of producing the details by factors of 5–10.

Polyimidofluoroplastic PMF-L (Technical Conditions 1-595-9-636-2001) developed by FGUP “VIAM” is a multilayer material consisting of polyimide films welded together with a unilateral and bilateral fluoroplastic coating of the PMF-351 and PMF-352 type. In this multilayer material the polyimide films,

Table 2. Properties of fluoroplastic F-40LD and polyimidofluoroplastic PMF-L

Index	F-40LD	PMF-L
Density, kg m^{-3}	1650	1620
Tensile strength, MPa	36	110
Relative elongation on rupture, %	20	60
Compression stress on deformation 10%, MPa	23	70
Flexure modulus, MPa	1100	1400
Brinell hardness, MPa	58	54
Deformation on compressing for 24 h, % with the load		
14 MPa	5.7	1.8
28 MPa	16	4.1
Water absorption for 24 h, %	0.01	0.2
Maximum operating temperature, °C	150	150
Combustibility	Difficultly combustible	

PM, ensure a high strength and resistance to creep, and the fluoroplastic layers, F-4MB) (copolymer of tetrafluoroethylene with hexafluoropropylene) ensure the elastisity and an interlayer adhesion.

Polyimidofluoroplastic PMF-L is produced by pressing at the temperature 345±10°C and the pressure 1.4±0.15 MPa. It is produced in the form of plates (108×134 mm and up to 3 mm thick).

This material has the highest mechanic properties (tests for stretch, flexure, and compressing) among all the modified materials based on F-4. It is used as thickening elements for pneumovalves of high pressure, which increases the dependability and the resource of the product operation by factors of 3-5 compared to rubbers and fluoroplastic-4 of similar purpose.

The properties of fluoroplastic 40LD (F-40LD) and polyimidofluoroplastic PMF-L are given in Table 2.

Fluoroplastic Films

Fluoroplast-4 films are obtained by planing intermediate products; the films of meltable fluorocopolymers are made by extrusion.

The properties of fluoroplastic films F-EN, F-4MB, F-2M, and F-10, which find use in aviation engineering, are given in Table 3.

Films of F-4 of various types serve as electroinsulators of wires, cables, in aviation devices, and also as antiadhesive materials when pressing the products of press-materials, carbon- and fiber glass plastics. F-4EN fluoroplastic tapes are used for making thickening seals. Electro insulating and thickening products of F-4 films and tapes are efficient in air and in liquid media (aviation fuels, oils, liquids for hydro systems) in the temperature range from –60 to +260°C.

Films of F-4MB are used for producing fuel tanks undergoing no complex bending deformations on operation and destined for operation in the temperature

Table 3. Properties of fluoroplastic films F-EN, F-4MB, F-2M, and F-10

Index	F-4EN	F-2M	F-2M	F-10
Tensile strength, MPa	30	30	48	30
Relative elongation on rupture, %	300	300	200	280
Flexure modulus, MPa	350	350	960	270
Resistance to flextures by the method of “hermetic little rhomb,” cycle	25	500	–	2500
Nitrogen permeability coefficient $P\times10^8$, cm^3 cm cm^{-2} atm^{-1} s^{-1}	–	94	90	88
Water absorption for 24 h, %	0	0	0	0
Combustibility	Difficultly combustible			
Coefficient of integral light transmission, % (thickness 100 μm)	–	94	90	88
Maximum operating temperature, °C	260	200	130	100
Resistance to atmosphere	Perfect			

range from –60 to +150°C. They also serve as antiadhesive separating layer upon autoclave molding at the temperature of up to 200°C of the products of composition materials of single and double curvature.

Films of F-10 having a high resistance to flexure (withstand 2500 cycles of complex bending before loosing the impermeability) are used for producing elastic compensation capacitances, fuel tanks, products of special purpose with operating temperature from –40 to +50°C.

A ZPPK type multilayer protective film coating was developed in FGUP "VIAM" (Technical conditions 1-595-14-996-07) on the basis of a film of fluoroplastic-2M with a glue layer. This film coating is destined for operative repair of damaged sites of paint and varnish coating on the external surface of the products of aviation engineering and can be exploited in the temperature range from –60 to +80°C.

Fluoroplastic Tubes and Flexible Pipes

Fluoroplastic tubes are used in aviation engineering for electro insulation of the wires and cables operating in a wide temperature range (from –60 to +260°C) in various operating media.

Fluoroplastic tubes are prepared by extrusion of F-4D powder adding a grease, benzene being used as the latter (16–22% from the total mass of the composition). The extrusion is carried out at the temperature 25–30°C with the following drying at 90–140°C for removing the grease and sintering at the temperature 370–390°C. If necessary, fluoroplastic tubes are thermally treated at 370°C with the following quenching with the aim of decreasing the anisotropy of mechanic properties and increasing the elasticity.

In the pneumo- hydro-, and fuel systems of aviation engineering of wide use are fluoroplastic flexible pipes, which have a number of advantages in comparison with rubber and metal flexible pipes: a high stability in the operating media; an increased working capacity upon pulsating pressure and hydraulic strokes; a low hydro resistance; a smaller mass (by 50%); almost unlimited period of storage; the operating temperature from –60 to +230°C; and the operating pressure up to 28 MPa. Fluoroplastic flexible pipes are a construction consisting of a fluoroplastic tube playing the role of hermetic chamber reinforced by a single or double metal braid and an end connection for joining the aggregates. On exploiting the fluoroplastic flexible pipes some cases were observed when the fluoroplastic chambers were cracking and lost their impermeability, which limited the operation resource of the flexible pipes. In this context the study was carried out to reveal the influence of various technological and operation factors on the properties of fluoroplastic tubes and their resistance to cracking.

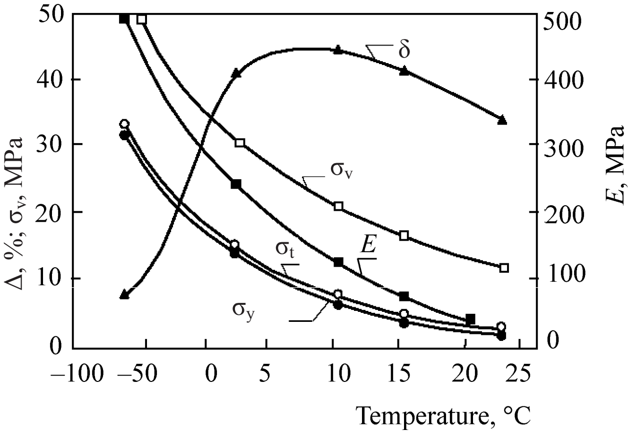

Fig. 1. Temperature dependence of the strength σ_v, the yield stress σ_y, the modulus of elasticity *E*, of relative elongation on rupture δ upon tension of fluoroplastic tubes and rupturing tangential stress σ_t (tests under pressure).

The mechanic properties of fluoroplastic tubes after prolonged storage in the TC-1 fuel almost do not change. Another pattern is observed on simultaneous action of tensile stress and TC-1 fuel.

The temperature dependence of mechanic properties of fluoroplastic tubes under conditions of uniaxial tension and also rupturing tangential (radial) stress (tests under the pressure of compressed air) are given in Fig. 1.

As is seen from Fig. 1, the mechanic properties of fluoroplastic tubes substantially depend on temperature. In this case under condition of complex stressed state of fluoroplastic tubes the rupturing tangential stress resulting from pressure corresponds to the yield stress of the tubes recorded in the tests under conditions of uniaxial tension.

Under simultaneous action of a stretching load and of TC-1 fuel the strength of fluoroplastic tubes decreases. The TC-1 fuel has a viscosity by a factor of 17 lower than the 7-50C-3 liquid used in the hydro aggregates. Consequently, it has a higher rate of surface diffusion; hence its influence on the fatigue limit of fluoroplastic tubes shows itself stronger.

Table 4. Indices of structure and properties of fluoroplastic tubes as a function of thermal treatment regimes

Index	Thermal treatment (t.t.) at 370°C			
	for $t_{t.t}$ + cooling in air		for 3 h + quenching in water with the rate	
	$t_{t.t}$ = 3 min	$t_{t.t}$ = 3 h	6 m min^{-1}	60 m min^{-1}
Degree of crystallinity, %	58	54	46	44
Average width of permolecular formations (fibrils), μm	0.5	0.4	0.3	0.2
Deformation resistance to cracking, %	2.5	7.0	18	24
Time until loosing the tube impermeability upon radial 10% deformation and pressure of 2.6 MPa, min	0.5	3	840	1200
Coefficient of anisotropy of mechanic properties of the tubes in the radial and axial directions	0.7	0.9	0.9	0.9
Tensile strength, MPa	25	31	33	36
Relative elongation on tension, %	500	470	420	400

The results of testing fluoroplastic tubes under the pressure of TC-1 fuel show that as the stretching tangential stresses increase from 8 to 12 MPa, the time until the first visual fractures appear and the tubes lose their impermeability at the expense of the through intergrowth of the fractures decreases by a factor of ~40, i.e. the operating resource of the tubes decreases.

We emphasize that on testing fluoroplastic tubes under conditions of uniaxial tension and under the pressure of the operating medium in the free state the special features of operation of fluoroplastic flexible pipe chambers are not taken into account. This means that a fluoroplastic chamber has a metallic braid on the exterior, which limits its radial deformation on action of the inner pressure of an operating liquid exceeding by an order of magnitude the rupturing pressure of the tube (2.5 MPa) in the free state.

The minimal relative radial deformation resulting in the tube loosing its impermeability owing to the formation of through fractures was measured by an express method of estimating the deformation resistance of fluoroplastic tubes to cracking (the tests under the pressure of TC-1 fuel 2.6 MPa given various radial deformations, the use of metallic limiting sockets with the slots for the control over the tube impermeability). It was found that the higher is the deformation resistance of the fluoroplastic tubes to cracking, the greater is the operation resource of fluoroplastic flexible pipes.

Table 4 gives the results of studying the influence of the regimes of fluoroplastic tubes thermal treatment on their structure and properties.

An increase in the duration of the thermal treatment of fluoroplastic tubes at 370 to 3 h and the following quenching with the rate of 60 m min^{-1} allow a material to be obtained with a decreased degree of crystallinity and lower sizes of permolecular formations (fibrils), and, as a consequence, the deformation resistance to cracking to be increased by a factor of 10 and the working capacity (the time until loosing the impermeability) to be increased by a factor of 2400. We emphasize that the tensile strength and the relative elongation on tension of fluoroplastic tubes scarcely vary with the regimes of thermal treatment, i.e. they are insufficient indices for estimating the structure changes in the material.

The studies carried out in FGUP "VIAM" together with OAO "Plastpolymer" and Construction bureau "Hydromechanics" made possible the optimization of technological regime of producing fluoroplastic tubes and the construction of flexible pipes and the required resource of their operating in the products of aviation engineering to be ensured.

Coatings Based on Fluorocopolymers

With the aim of estimating the possibility of using soluble thermoplastic copolymers of trifluorochloroethylene and tetrafluoroethylene as film-forming substances for moisture protecting paint and varnish coatings capable of being used at the temperatures up to 300°C the studies were carried out of their heat resistance and diffusion permeability in comparison to other film-forming substances.

By the heat resistance of a paint and varnish coating is meant the capability of retaining the protective properties after the action of temperature. An estimation of the heat resistance of film-forming substances by studying their thermal oxidation stability by the method of thermogravimetric analysis (DTGA) gave no reliable results. The results obtained by the DTGA method on comparative study of the heat resistance of fluorocopolymers, K-23-E(3N) organosilicon polymer, and KO-861 enamel based on KO-928 organosilicon varnish do not correspond to the actual heat resistance of these polymer film-forming substances determined by the method of gravimetric analysis on isothermal aging. Hence on estimating the heat resistance of thermoplastic copolymers of trifluorochloroethylene and tetrafluoroethylene with vinylidene fluoride both the method of DTGA and the method of gravimetric analysis on isothermal aging were used. As follows from the results of these studies, the method of DTGA does not permit the duration of heating to be estimated in the temperature range 200–250°C, during which the mass loss of a copolymer does not exceed 10%. At the same time, the method of DTGA makes possible the estimation of comparative heat resistance of copolymers, which is supported also by the results of gravimetric analysis on isothermal aging.

The study of thermal resistance of heterogeneous systems of “polymer film-forming substance–dispersed filler (pigment),” oxides and aluminosilicates being used as the latter, revealed no signs of any chemical reaction between the surface of the filler and the film-forming substance. The results of chromatographic analysis and the data of IR and Moessbauer spectroscopy confirmed this.

At the same time the results of chromatographic analysis of these heterogeneous systems point to a change in the rate of film-forming substance destructtion in these systems. Since the influence of the dispersed filler on the rate of thermal oxidation destruction shows up mostly in the polymer – filler interface, the specific surfaces of the most used pig-ments and fillers were determined (thus, for example, the specific surface of zinc oxide is 7.35 m^2 g^{-1}, and that of silicon dioxide is 31.4 m^2 g^{-1}). The mass losses of polymer film-forming substances were also determined. Those latter depend not only on the nature of the dispersed filler, but on temperature, the duration of heating, and on the volume of filling (for example, the mass loss of copolymer of trifluorochloroethylene and vinyliden fluoride is 8.5 % for 250 h of heating at 250°C, on introduction of zinc under the same conditions of heating is 2.8%). The obtained results of chromatographic analysis allow the dispersed fillers to be assigned to catalysts and anticatalysts of thermal destruction (they change the reactivity of adsorbed molecules).

A substantial part of dispersed fillers and pigments (oxides of Fe, V, Cu, Mn, Pb, Zn, Mg, Al, sulfides of W, Mo, Zn, aluminosilicates etc.) are classified as semiconductors, which is accounted for by the admixtures and a deviation from the stoichiometric composition.

If the width of the forbidden band attains several electron-volts, the concentration of electrons in the conduction band was found (by S.Z.Roginskii) to be negligibly small, and a dielectric is formed, in which the electron conductivity and the color in the visible part of the spectrum are almost absent. And quite the reverse, given the forbidden band width of 1.2–1.4 eV, the electron conductivity is attained typical for semiconductors, and the intensity of the color in the visible part of the spectrum increases.

The external indicators were also revealed, which confirm the participation of the electrons of the forbidden band in the thermal oxidation destruction and in the grouping of active centers on certain sites of the filler surface.

A comparison of the intensity of the color of fluorocopolymer thermal resistant coatings, in which thermal resistant colored pigments with the forbidden band width of 1.2–1.4 eV were introduced to impart a necessary color, before and after heating shows that after heating the intensity of the coating color decreases to a greater or lesser extent in all the cases. Whereas the heating of the same pigment under the same conditions but outside the polymer matrix does not result in a notable change in color intensity. On heating colored thermal resistant coatings the spots 2–5 mm in diameter very often appear on their surface, the intensity of their color being substantially lower than the intensity of the remaining surface. According to the theory of “active ensembles” this points to the grouping of active centers on certain sites of the surface of fillers and pigments.

The obtained experimental data on the estimation of the influence of dispersed media (fillers) on the thermal oxidation resistance of polymer film-forming substances were used when developing the formula of thermal resistant enamels based on fluorine containing copolymers.

Table 5. Diffusion permeability of polymer membranes (H_2O vapors, 30°C)

Polymer	Diffusion flow, mg cm^{-2} h^{-1} given the pressure gradient, atm					Coefficient of diffusion permeability $P\times10^{10}$, cm^3 cm cm^{-2} s^{-1} atm^{-1}, given the pressure gradient, atm				
	0.03	0.028	0.024	0.016	0.01	0.03	0.028	0.024	0.016	0.01
Copolymer of trifluorochloroethylene and vinyliden fluoride	0.0015	0.0015	0.0015	0.0015	0.0011	0.69	0.74	0.87	1.30	2.1
Copolymer of tetrafluoroethylene and vinyliden fluoride	0.0079	0.0079	0.0079	0.0057	0.0049	3.66	3.91	4.40	4.94	6.8
EP-571 epoxy varnish	0.0335	–	–	–	–	15.5	–	–	–	–
PSKh-LS perchlorovinyl resin	0.0497	–	–	–	–	23	–	–	–	–
EP-730 epoxy varnish	0.0715	0.0611	0.0546	–	–	23.17	21.20	22.10	–	–
SKF-32 fluorine-containing elastomer	0.0945	0.0798	0.0694	–	–	43.75	39.58	40.16	–	–
Stereoregular polyphenyl cloride sesquioxane	0.1017	–	–	–	–	47.08	–	–	–	–
SKF-26 fluorine-containing elastomer	0.1204	0.1006	0.0873	–	–	55.74	49.9	50.52	–	–
SFZh-309 phenol-formaldehyde resin	0.1522	–	–	–	–	70.46	–	–	–	–
PM-1 polyimide resin	0.2352	–	–	–	–	108.9	–	–	–	–
MCh-025 ureaformaldehyde resin	0.2522	–	–	–	–	116.7	–	–	–	–
Clorosulfonated polyethylene	0.2675	0.2357	0.1820	–	–	123.84	116.91	105.30	–	–
K-23-E(ZH)organosilicon copolymer	0.3070	0.2272	0.2238	–		142.12	112.70	129.50	–	–
KO-945 organosilicon varnish	0.3998	–	–			185.1	–	–	–	–
AS-16 acryl varnish	0.4195		–			194.2	–	–	–	–

An important operating characteristic of the materials is the thermal shock resistance by which it is generally meant the temperature of the material (polymer) loosing its mechanic strength upon the action of one or other load.

Since paint and varnish coatings, as a rule, do not undergo the action of loads, the concepts of "thermal resistance" and "thermal shock resistance" are generally accepted as identical. As applied to the paint and varnish coatings in the aircraft the concept of thermal shock resistance has a quite real sense, since the paint and varnish coatings of the aircraft are prone to the action of aerodynamic flow and, as a consequence, to the action of friction stresses. This is confirmed by the data on the dependence of friction stresses arising on the surface of an aircraft on the velocity and height of its flight, which attain 7 kPa at the height of 10 km given the velocity of the flight 3600 km h^{-1}.

The thermal shock resistance of a coating can be estimated by the temperature interval T_s–T_f in the thermomecanic curve (T_s is the temparature of softening, T_f is the temperature of fluidity). With the help of a specially designed device given the really acting loads the temperature of softening the pigmented coatings was found to exceed the operating temperature (the heat resistance) of the coatings based on thermoplastic copolymers of trifluorochloroethylene and tetrafluoroethylene with vinyliden fluoride.

An important characteristic of polymer films is the diffusion permeability for water vapors (Table 5). As follows from the data of Table 5, copolymers of vinyliden fluoride with trifluorochloroethylene and tetrafluoroethylene have a record low permeability to water vapors and are of interest for developing moisture protecting coatings on polymer composition materials.

On the basis of soluble thermoplastic copolymers of vinyliden fluoride with trifluorochloroethylene and tetrafluoroethylene the formula and technologies were advanced for depositing moisture protecting coatings resistant to gas erosion wear given the velocities of the gas flow up to 900 m s^{-1}. This became possible owing to the study of the influence of dispersed inorganic pigments and fillers on thermal resistance and thermal shock resistance, and also on the diffusion permeability of the coatings based on fluorocopolymers. In particular, zinc oxide was found to inhibit the thermal oxidation destruction of the copolymer of trifluorochloroethylene with vinyliden fluoride and to the least extent influences the diffusion permeability of the films based on it. At the same time, the introduction of dispersed fillers to the composition of fluorocopolymers made possible an increase in the temperature of fluidity of the coatings based on them to 250–300°C.

Coatings based on copolymers of vinylidene fluoride have high physico-mechanic and moisture protective properties, thermal and thermal shock resistance and are used in the case, when fiber glass require protection from moistening (Fig. 2).

Coatings based on copolymers of trifluorochloroethylene and vinylidene fluoride can be ex-ploited at temperatures up to 250°C, and on the basis of tetrafluoroethylene and vinylidene fluoride up to 300°C. Unfortunately, up to now the copolymer of trifluorochloroethylene with vinylidene chloride failed to be synthesized. This copolymer judging from theoretical calculations must have even lower diffusion permeability.

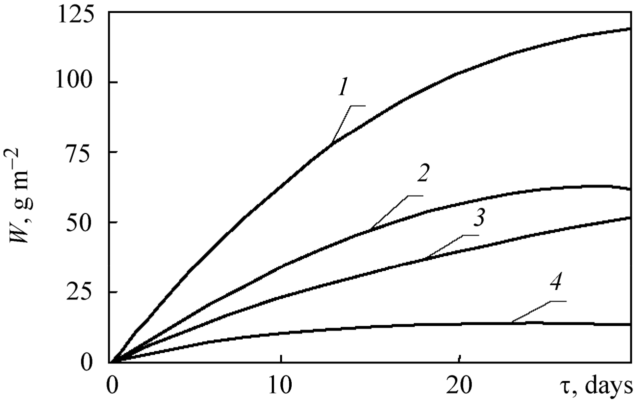

Fig. 2. Plot of moisture swelling, *W*, of a fiber glass on a phenol-furfural binder vs the duration of moistening, τ. Samples under test: (*1*) colorless, (2–4) painted by perchlorovinyl, epoxy, and fluoroplastic enamel, respectively.

To protect the above mentioned coating systems from gas erosion and gas drop wear fluorine containing elastomer coatings are suggested to be deposited on their surface.

On the basis of the studies on estimating the thermal and thermal shock resistance, diffusion permeability, and erosion resistance of fluorocopolymers the enamels were developed: FP-5105 (TC 6-10-954-75), FP-5190 (TC 6-10-1930-84), and KCh-5185 (TC 6-10-1932-84) (Table 6), which from 1965 are used for protecting the construction elements of polymer composition materials in supersonic aircrafts.

Table 6. Properties of fluorine containing enamels used in industry

Index	FP-5105 (TC 6-10-954-75)	FP-5190 (TC 6-10-1930-84)	KCh-5185[a] (TC 6-10-1932-84)
Heat shock resistance, °C	250	300	250
Hardness of the coating[b], conv. units, no less than	0.4	0.5	0.12
Elasticity of the film on bending, mm, no more than	1	1	1
Strength of the enamel film on impact[c], cm, no less than	–	50	50
Coating resistance to the action of water at the temperature 20±2°C, days, no less than	5	5	3
Tangent of the angle of dielectric losses at the frequency 10^6 Hz, no more than	0.03	0.005	0.2
Dielectric permeability at the frequency 10^6 Hz, no more than	3–5	3.5–4.5	10
Thermal resistance of the coating, h, no less than			
at 300±2°C	4	–	4
at 350±2°C	–	5	–

[a] Based on SKF-32 fluorine containing elastomer. [b] Measurements by an ME-3 pendulum device. [c] Measurements by a U-1A device.

Table 7. Requirements to the fluoroplastic powders

Index	F-30P	F-40DP	F-4M
Appearance	Homogeneous white powder without visual foreign inclusions		
Humidity, %, no more than	0.1	0.05	–
Filled density, g cm^{-3}	0.24–0.6	0.35–0.6	0.45
Dispersity, μm, no more	200	150	150
Temperature of loosing strength, °C	226–240	255–280	265–285
Spreadability, %, no less than	150	135–150	140
Thermal resistance, %, no more than	1.0	0.4–0.6	0.8

Table 8. Physical and mechanic properties of fluoroplastic coatings

Index	F-30P	F-40DP	F-4M
Shine, %	20–30	28–30	30–40
Density, g cm^{-3}	1.6800	1.6800	2.1100
Tensile strength, MPa	35–40	22–28	16–19
Relative elongation on tension, %	200	100–150	100–250
Resistance to impact, N cm	500/500	500/500	500/500
Elasticity, mm	5	5	5
Interval of operating temperatures, °C	From –60 too +130	From –60 to +180	From –60 to +220
Abrasion resistance, mm/cycle			
at 20 °C	0.0096	0.0096	0.0072
at 120 °C	0.007	0.0100	0.0072
at 190 °C	–	0.0100	0.0250

Coatings of Powder Fluoroplastics

Domestic industry produces a large number of fluoroplastic types suitable for obtaining the coatings by the method of air dispersed deposition. Of greatest use are powder fluoroplastics of the types: F-30P (TC P-236-70), F-40DP (TC P-193-68), and F-40MP (TC P-311-71), their coatings having high operation characteristics. The requirements to the starting powders of the coatings are given in Table 7.

High-quality coatings of fluoroplastics are obtained if the powders for spraying have a high filled density, good spread ability, thermal resistance at the temperature of film forming, and minimum possible molecular mass. To increase the filled density the powders are thermally treated before the beginning of the work. The coatings are deposited by electrojet spraying.

Physical and mechanic properties of fluoroplastic coatings are given in Table 8.

Fluoroplastic coatings can operate for long at elevated temperatures. Mechanic properties of the F-30P, F-49DP, F-4m films almost do not change after 2000 h of exposure at the temperatures 130, 180, and 220°C respectively. Adhesion properties of the coatings to a greater extent are determined by the method of preparing the surfaces of plated products. The chemical modification of the surface allows not only the adhesion of fluoroplastic coatings to aliminum products to be increased by factors of 2–3, but also the adhesion to be stabilized in time including on operating in liquid media.

Protective properties of the coatings of F-30P and F-40DP are sufficiently high. The tests of the samples under the most various conditions (in a tropical chamber, hydrostate, sea water, 35 solution of NaCl, 10% solution of H_2SO_4, boiling solution of $Ca(NO_3)_2$+$NaNO_2$, washing compositions, in the solutions of galvanic tubs for chemical and electrochemical treatment of metals) showed that the properties of protective films after testing remain at the starting level, no corrosion was found.

The coatings of F-30P and F-40DP fluoroplastics endured the tests in the tropic climate for 6 months: no corrosion was found, the loss of shine was 5–15%, a decrease in the mechanic properties was from 5 to 20%. The side of the coating that was not irradiated remained unchanged.

Fluoroplastics differ by their resistance to fungi: F-30P and F-40DP are not stable (correspond to ball 3); F-4M is stable (ball 1). However, fungi and mold are easily removed from the surface of the coatings, the mechanic properties of the films remaining at the starting level. Owing to the presence of micro pores the coatings of F-4M are not recommended to be used for a long time anticorrosion protection of the products.

The dielectric properties of the coatings are high and almost do not depend on the conditions of the heat aging.

Powder fluoroplastics are used for creating protecting, electro insulating, abrasion resistive and anti-adhesion coatings.

Antifriction Organoplastics Based on Polytetrafluoroethylene

Fluoropolymers are a perfect material for producing the constructions functioning under the conditions of friction and wear. They allow an important technical problem to be solved: the provision of efficiency without using grease, i.e. under the conditions of dry friction.

In the mechanical engineering of wide use is an antifriction material: metal fluoroplastic. The basis of this material is a low carbon steel, a porous layer of spherical particles (about 0.1 mm in diameter) of tin bronze 0.3–0.4 mm thick being deposited through a copper layer on it. The pores are filled for the whole depth with fluoroplastic containing molybdenum disulfide. A thin surface layer is formed from this very mixture, which covers the apexes of external spherical particles of the bronze. In the aviation engineering the use of metal fluoroplastic is limited since the material does not insure a sufficient durability under conditions of hinged joint operation, namely: the action of alternative dynamic loads, vibrations, exceeding the admissible norm of P_v (the product of specific load in the contact zone by the amplitude value of the sliding velocity).

For the necessities of aviation engineering FGUP "VIAM" developed and promoted into helicopter and airplane constructions antifriction organoplastics: Orgalon AF-1M-260 and Orgalon AF-1M-500 (TC 1-595-11-391-2006).

Orgalon AF-1M is a polymer composite material reinforced with a combined cloth of polymer fibers of two types: based on polyimide and polytetrafluoroethylene fibers. Polyimide fibers in the composition of Orgalon AF-1M fulfill the function of the power framework ensuring the efficiency of the friction joint on action of increased mechanic loads. Owing to polytetraflioroethylene fibers the required coefficient of friction is provided and also the capability of the friction joint to work without grease during operating.

A phenol caoutchouc binder, AFK-101, is used in antifriction organoplastics as a polymer matrix, at the expense of which a solidity of antifriction material is created, a high strength of linkage to the metal base and the efficiency of the organoplastic at the temperatures up to 200°C are attained.

For the friction joints based on antifriction organoplastic Orgalon AF-1M a stable working capacity is typical (the coefficient of friction does not depend on the duration of the work up to a complete wear of the coating) and also the absence of the wear of counter body material. This makes possible a substantial facilitation of the repair of the friction joints, in which only the coating is replaced on the old carrier with the same counter body. The material of Orgalon AF-1M is passive to corrosion relative to construction steels 12Kh18N9T, 30KhGSA, aluminum and titanium alloys. The operation resource of the bearings coated with antifriction organoplastic is by factors of 2.0–2.3 greater than with metal fluoroplastic.

The recommended regions of using organoplastic Orgalon AF-1M are: the production of heavy loaded joints of sliding friction operating without grease at the temperatures from –60 to +200°C, the protection against fretting-corrosion of contacting surfaces of metals operating at high loads and ratingly immobile, but undergoing small periodic relative shiftings, as sealing and antifriction layings in various mechanisms and aggregates.

Table 9. Properties of fluorine containing coating materials

Index	STF-A	STF-B	STF-26	AzTc[a]	ANAMc[a]
Surface density, g m^{-2}	45–60	45–60	45–60	110	245
Width of the produced material, cm	65.0	65.0	65.0	82.0	74.0
Tensile load of a 25×100 mm band, H, no less than					
along the warp	147(15)	147(15)	147(15)	205(20)	150(15)
along the welf	98(10)	98(10)	98(10)	160(16)	135(13)
Combustibility	Difficultly combustible			Self-extinguishing	
Smoke-forming capability, D_4[b]	1	1	1	–	–
Toxicity, category of danger	4	4	4	2	2

[a] (AZTc) is on the basis of a caprone fabric and (ANAMc) is on the basis of cotton fabric with fireproofing nitrocellulose coat. [b] (D_4) is specific optic density of smoke for 4 min of testing.

Heavy loaded friction joints produced using antifriction organoplastic Orgalon AF-1M are present in the construction of Ka-32, Ka-50, Ka-52. Mi-28, Mi-34 and other helicopters (hinges of the supporting system aggregates, hinges of the control system, hinges of the legs of landing gear, hinges of the blade damper attachment etc.), in the construction of Tu-204, Su-38, Su-27 airplanes (sockets in the deviation cantilevers, the mechanism of thrust, sockets in the flap control, hinges of the shock absorbers and of the system of removing the bow and main landing gear, etc.).

The accumulated experience in operation showed a high efficiency of the working capacity of antifriction organoplastic Orgalon AF-1m in the heavily loaded friction joints of aviation constructions: an increase by factors of 2–5 in the resource of moving joints and in their reliability under conditions of increased dust content, which is especially important for helicopters. The use of Orgalon AF-1M allows the time and expenses on technical service and repair to be decreased, and also the number of details, metal capacity, and dimensions of the bearings to be decreased.

Fabric Film Materials Based on Fluoroplastics

One of the first fluorine containing materials used in the aviation engineering is a coating material STF (TC 1-92-82-83). This material is a fiber glass varnish fabric impregnated with the solution of low molecular fluoroplastic F-42L or fluoroplastic F-26 in a mixture of organic solvents. It is used for coating fibro porous heat and sound insulating materials.

Fiber glass varnish fabrics made on the basis of F-42L and F-26 fluoroplastics differ by their operating temperatures: fiber glass varnish fabrics based on F-42L have the operating temperature up to +80°C, based on F-26 up to +150°C. The properties of type STF fiber glass varnish fabrics in comparison with other coating materials based on cotton or caprone fabric with an one-sided fireproofing nitrocellulose coating used for coating fibro porous heat insulation are given in Table 9.

With the aim of producing elastic difficultly combustible tanks and also for using as a protective material in the products of special purpose a fluorolon varnish fabric of type FLT-42 (All Union Standard 6-05-5019-80) was developed, which is a fabric of fluorinated fiber (a copolymer of tetrafluoroethylene and hexafluoropropylene) impregnated with the solution of F-42L fluoroplastic in a mixture of organic solvents.

For coating the details of complex profile, with double curvature among them, in the passenger air planes and space vehicles elastic decorative materials are required. A drawback of fluoropolymers as such materials is their increased rigidity. A composition consisting of copolymers of trifluorochloroethylene and vinylidene fluoride given their certain relationship has the required elasticity. Such compositions were developed and also the recipes of painting, the procedure of introducing the fillers and pigments. The producing procedure of decorative and finishing materials ATDM, ATDM-1, and ATDM-F was composed.

Table 10. Properties of decorative materials based on fluoropolymers

Index	ATDM	Talka[a]	ANDM-F	ADDM-P	Vinylisleather-T[a]
Surface density, g m^{-2}	200–260	480–520	120–160	500–540	320–420
Combustibility (critical concentration of oxygen), %	41	40	36	41	22
Smoke formation (D_{max}) in the regime of:					
glowing	40	90	32	95	173
combustio	45	84	28	83	102
Degree of danger	3	–	2	3	4
Resistance to fungi, ball	1	3	0	1	3
Specific surface electric resistance, Ω	10^8	10^{10}	10^8	10^8	10^{14}

[a] Artificial leather Talka on a tricot base of arimide fiber with the coating of F-26 fluoropolymer (developed at IVNIIPIK (Ivanovo) together with NPO “Plastpolymer”); aviational Vinylisleather-T is a cotton fabric with a fireproof impregnation, a fireproof polyvinyl chloride coating being deposited on it.

The ATDM decorative material (TC 1-595-155-83) is a fiber glass with a one-side painted fluoropolymer coating, and the ATDM-1 decorating material with a two-side coating.

The base of the ANDM-F material (TC 17-21-08-07-82) is a Phenylone fabric with a painted fluoropolymer coating. This material is recommended as a soft decorative finishing of “Ruslan” air plane.

A drawback of the fluoropolymer composition containing fluoroelastomer is the increased contaminability of the surface of a fabricated material. One of the ways of solving the problem of providing the surface of fluoropolymer material with mud repulsive properties is an increase in the content of end CF_3 groups in the chain (the surface tension is decreased). The best results among the fluoropolymers under study were obtained on depositing the copolymer of trifluorochloroethylene and vinylidene fluoride on the surface of ATDM, ATDM-1, and ATDM-F materials.

The ATDM-1 material is destined for obtaining type ADDM-P (TC 1-595-67-366-91) decorative coating material with a relief design by doubling the ATDM-1 material with type ANM volume nonwoven fabric made of arimide (phenylone) fiber by the pressing thermal method. An inventor’s certificate (no. 1669224 from 08.04.1991) was obtained for this material.

The properties of decorative materials based on fluoropolymers are given in Table 10.

With the aim of decorating the details of the interior of passenger air planes and helicopters (the panels of the walls, the ceiling panels) a multilayer protective decorating material, “Polyplex” (TC 8729-022-003003311-2003), was designed, which meets the international requirements of IKAO (FAR-23, FAR-25) and national AP-25 norms by its refractoriness, smoke and heat release – both in a free state and in the composition of three layer honeycomb panels and glass plastics (Table 11).

The material is a glass fabric with an one-side painted polymer coating based on fluoroplastic and fluoroelastomer of trifluorochloroethylene with vinylidene fluoride. It is produced in a single color version of smooth texture. A drawback of “Polyplex” is a limit in its use only for flat details and the details with single curvature.

Material “Polyplex” is recommended for decorating the details of glass plastics and three layer honeycomb panels, and also for repair of decorative coatings of the interior details of air plane and helicopter salons. “Polyplex” retains its properties in the temperature range from –60 to +80°C.

Fluoroacrylate Organic Glasses

A unique achievement of native science and industry was the creation of highly heat resistant fluoroacrylate organic glasses E-2 and SO-200 having no analogs in the world, capable of operating in the plane constructions at the temperatures higher than 200°C. These glasses made possible the creation of light, reliable, safe details of windows, which are used in the high-speed native air planes of OKB “MiG” along with highly strong constructions of aluminum,

Table 11. Properties of multilayered protective decorating material "Polyplex"

Property	Results of the tests
Mass of 1 m^2, g	220±25
Combustibility	Difficultly combustible (1)
Time of residual combustion, s	0
Height of burning through, mm	40
Smoke formation in the combustion regime[a]:	Weakly smoking (2)
D_2	6
D_4	7
$D_{макс}$	13
Heat release	
Maximal rate of the heat release (peak), kW m^{-2}	27
Total heat released during 2 minute test, kW min m^{-2}	3.0
Heat release in the composition of a tree layer honeycomb panel on a phenol binder the peak, kW m^{-2}	41.0
Total heat for 2 min, kW min m^{-2}	59.0

[a] (D_1, D_4, and D_{max}) are specific optical density of smoke for 2, 4 min, and maximal, respectively.

titanium alloys and steels. Under operating conditions given an one-side aerodynamic heat-up type E-2 and SO-200 fluoroacrylate organic glasses withstand the temperature up to 230–250°C. The details of windows are successfully exploited for 10, 15, and more years.

The results of scientific researches stand tests, and also the experience of many years exploiting fluorine organic glasses practically proved the efficiency of fluoroacrylate glasses in the details of windows in the air plane construction at the temperatures higher than the temperature of the glass softening under conditions of the temperature gradient along the thickness of an organic glass. Given the maximal regimes of the flight, the temperatures of the external surface of organic glasses correspond to the temperatures fitting the region of highly elastic state of the material.

A number of the main indices of mechanic properties of fluoroacrylate organic glasses CO-200 and E-2, of the new heat resistant organic glass VOS-2 and of the series-produced polymethylmethacrylate glass SO-120-A (for comparison) is given in Table 12.

Table 12. Mechanic properties of fluoroacrylate glasses

Index	VOS-2	SO-200	E-2	SO-120A[a]
Tensile strength, MPa	83	78	83	81
Relative elongation on rupture, %	5.7	6.0	3.8	4.0
Modulus of elasticity at 20°C, MPa	4200	2910	3400	3400
Specific impact viscosity, kJ m^{-2}	23	28	21	16.5

[a] Polymethylmethacrylate glass.

Fluorosiloxane Hermetics

Polysiloxanes containing γ-trifluoropropyl radical found application as the base for hermetics. By introduction of this radical into siloxanes and also of some other, including hexafluoropropene and perfluoroalkyl groups it has been possible to obtain fluorosiloxanes varying by their structure and properties: a new class of high-molecular compounds combining the properties of carbon–chain fluoropolymers and polyorganosiloxanes.

The industrial production of elastomers containing γ-trifluoropropyl radical is mastered in various countries, but the most successful and wide production of these materials was organized in the USA and USSR for aviation and space industry. The firms "Dow Corning" and also "General Electric" and "SWS Silicones" (USA) are the main producers of fluorosiloxane elastomers and hermetics on their basis.

The firm "Dow Corning" developed hermetics 94-002, 94-011, and 94-031 on the basis of fluorosiloxanes. Hermetic 94-002 is efficient at the temperatures from –57 to +260°C, it is resistant to nitrogen tetra oxide, ozone, dimethylhydrazine, and also to aviation fuels and oils. It has a high adhesion not only to aluminum and titanium alloys, stainless steel, but also to glass, polysiloxane rubbers, and phenol and polyester resins. No heating is required for the hermetic vulcanization on sealing.

Hermetic 94-002 can be used also as a coating for 94-009 deposited from the solution of the hermetic in methylpropylketone and vulcanized also without heating.

Hermetics 94-011 and 94-031 are nonvulcanizing pastes resistant to the action of fuels and oils in the temperature range from –57 to +204°C, to vibration, impact and cyclic temperature loadings. Special manual extruding devices are used for sealing.

The listed materials found a wide use for sealing the air planes DC-8 and DC-9 of the firm “McDonnel-Duglas” and of T-38 and F-5 of the firm “Northrop.” These hermetics have a high thermal and chemical resistance, to aviation fuels in particular and also good mechanic and dielectric properties.

In what followed a single component hermetic 94-2817 was developed by the firm “Dow Corning,” which replaced hermetic 94-002 and was purposed for using in airspace, aviation, and automobile industry in the constructions, where the action on sealing layers of fuels, oils, and solvents is possible. The vulcanized hermetic has a solid rubber-like state. It retains elasticity in the temperature range from –57 to +260°C as the hermetic of 94-002 type. It has an adhesion to corrosion resistant steels, titanium and aluminum alloys, epoxides, polyesters, phenoplastics, rubbers based on siloxane rubbers, glass, and corks.

The materials of the firm “Dow Corning” have found a wide application for sealing the fuel caisson tanks: both as vulcanizing hermetics (for the surface sealing) and nonvulcanizing hermetics (for the intraweld sealing). Among the first type are the type 730 hermetic: moisture-resistant, weatherproof, efficient in the temperature range from –57 to +260°C and the type Q_4-2817 hermetic having a greater conventional tensile strength compared to the type 730 hermetic and better retaining its physical and mechanical properties at high temperatures. This material is used in the fuel caisson tanks of the F-111 plane. Noncorroding active hermetics of the type 58733 and X5878 also belong to vulcanizing hermetics.

The representatives of the second type of fuel and oil resistant fluorosiloxane hermetics operating in the temperature range from –57 to +232°C, being shock-resistant is the type Q_4-2804 (also as the type 94-011 noted above) being in use in The F-15, F-18, F-14, and A-6 planes, and also the type 94-031 hermetic used in the B-1B and F-4 planes. With the aim of decreasing the fluidity and increasing the quality of sealing in a number of cases the composition of both hermetics is introduced with polystyrene microsphere particles. The type X42885 hermetic developed together with the specialists of the “Wright Patterson” aviation base of BBC belongs to the same type. It is inserted with vulcanized fluorosiloxane elastomer as a filler, which assists in better filling the gaps.

The “General Electric” firm developed a single component type FRV1106 hermetic also vulcanizing at room temperature. It is used as a sealing layer in the pipe lines for combustible substances and solvents, in the fuel caisson tanks, and also for gluing rubbers based on fluorosiloxane caoutchouc with glass, aluminum alloys, polybuteneterephtalate, and phenol resins.

The “Shin-Etsu Chemical Corporation” firm developed quickly vulcanizing fluorosiloxane hermetics. They contain (mass parts): 100 of polyorganosiloxanes; 5–100 of silicon dioxide as a filler; 0.01–5 of organic peroxides of composition ROOCOR or ROOCOROCOOR, 0.01–2 of joining agents with the molecular mass up to 10000 containing ≥2 of allyl, metacryl, epoxy, or alkoxy groups per molecule. Polyorganosiloxanes correspond to the formula $R^1_aR^2_bR^3_cSiO_{4-a-b-c}$ (R^1 is trifluoropropyl; R^2 is C_{2-8} alkyl; R^3 is C_{1-8} alkyl or aryl; a = 0.96–1.01, b = 0.0001–0.01; c = 0.96–1.06; $a + b + c$=1.98–2.02; R^4–R^6 and R^8 are C_{3-10} alkyl; R^7 is C_{2-8} hydrocarbon radical, possibly with oxygen atoms).

The study of fluorosiloxane hermetics in the electric field in a humid medium for more than 1 year showed the instability of their dielectric properties. With regard to the prescription factors and the operating conditions a new fluorosiloxane compound was developed with the resistance of more than 10^{10} Ohm, which was retained after 18 months storage at 70°C under conditions of 100% of relative humidity.

Fluorosiloxane hermetics have found a wide use also in the constructions of European “Caravel” and “Concord” planes.

The first native siloxane hermetics were the VGF-1 and VGF-2 materials. These hermetics based on fluorosiloxane caoutchoucs do not contain a solvent, almost do not shrink on vulcanizing, and in the vulcanized form they are soft and elastic. The density of both hermetics is 1.75 g cm^{-3}, the conventional tensile strength is no less than 1.3 MPa, the relative elongation is no less than 130%, the working life of VGF-1 is 0.5–24 h, of VGF-2 is 3–7 h. They are purposed for sealing metal joints operating in the medium of T-5 T-6 and type naphthyl fuels in the temperature range from –60 to +250°C (VGF-1 is used for surface sealing, VGF-2 for intraweld sealing).

Further works in the field of creating hermetics allowed the operating characteristics of fluorosiloxane hermetics to be substantially improved. The main

Table 13. Properties of fluorosiloxane hermetics of native production

Index	VGF-4-10	VGF-7-10	VGF-4-8	VGFP
Consistence	Dough-like	Viscousflow	Dough-like	Dough-like
Цвет	White	Blue	White	White
Working life, h	3–7	1–3	3–10	2–8
Duration of vulcanization, h	24–72	18–30	72–120	72
Conventional tensile strength, MPa	2.3–3.5	2–2.4	2.5–3.8	2–3.2
Relative elongation on rupture, %	90–130	120–160	120–150	60–120
Shore hardness, conv. units	40–60	40–50	40–60	65–72
Stratification strength from aluminum D16 alloy, kN m^{-1}	1.2–1.5	1.3–1.6	1.2–2	1.1–1.4
Range of operating temperatures, °C	From –60 to +300	From –60 to +250	From –60 to +280	From –60 to +280
Temperature coefficient of linear expansion $\alpha\times10^6$, deg^{-1}	–	–	200	30

properties of VGF-4-10, VGF-7-10, VGF-4-8, and VGFP hermetics are given in Table 13.

VGF-4-10 (dough-like) and VGF-7-10 (viscous-flow) hermetics are purposed for surface sealing. Both hermetics are three component, are noteworthy for their high rate of vulcanization at room temperature. Their adhesion to metals and coatings is provided by a system of sublayers. VGF-4-8 and VGFP hermetics are purposed for intraweld sealing. They are resistant to destruction and retain their properties at an adequate level during heating at a high temperature upon a limited contact with fuel and atmosphere.

VGFP hermetic has one substantial advantage over silicon organic hermetics, including fluorosiloxane hermetics. High temperature coefficients of linear expansion are typical for silicon organic hermetics ($\alpha\times10^6$ = 180–200 deg^{-1}). On heating such materials in a closed contour owing to an essential increase in their volume a fraction of material is extruded, the stresses appear resulting in cracking the hermetic. The VGFP hermetic is devoid of this drawback. It has a lowered temperature coefficient of linear expansion and can be used for sealing the slots and sealing by filling a volume. Of all fluorosiloxane hermetics purposed for intraweld sealing the VGFP hermetic is the most resistant to destruction. The resource of this hermetic operation in a fuel and in the air medium at 280°C is 100 h.

The latest development in the field of fluorosiloxane hermetics is VGM-4 hermetic. The necessity of its development is associated with the fact that from 1996 the VGF type hermetics are produced of import raw materials. A new fluorosiloxane SKTNFT-100-Lest caoutchouc is used as the basis of the new hermetic. It is filled with zinc oxide of native production in contrast to all the fluorosiloxane hermetics, in which TC-type titanium dioxide produced at Sumy chemical plant (Ukraine) serves as a filler. The special features of the new hermetic are a high resistance to the heat ageing and lower toxicity.

Rubbers Based on Fluorosiloxane Elastomers

Fluorosiloxane caoutchoucs [polymethyl(3,3,3-trifluoropropyl)siloxanes] have a complex of unique properties. They retain the elasticity on action of solvents, oils, greases over a wide temperature range (from –60 to +250°C), have a high density, and, consequently, are noted for a lowered moisture and gas penetrability, and also for their ozone resistance and a high resistance to ageing in complex with good dielectric indices. Special properties of fluorosiloxane caoutchoucs are defined by a highly polar trifluoropropyl group.

Fluorosiloxane caoutchoucs better withstand the action of weak acids and aggressive salt solutions, nonpolar and low-polarity hydrocarbon solvents than other types of siloxane caoutchoucs. However, they are prone to the influence of some polar solvents (esters, ketones). Acetone and some other ketones and also esters produce swelling and favor softening the vulcanizing agents based of fluorosiloxanes. A combination of a fluorosiloxane caoutchouc and various

Table 14. Properties of native fluorosiloxane elastomers

Index	SKTFT-25	SKTFT-50	SKTFT-100	SKTFT-100S[a]
Molecular weight	500–700	500–700	500–900	700–2000
Heat resistance (3 h, 150°C), %	3.0	3.0	3.0	2.0
Tensile strength, MPa	6–7	6.4	5.9	8.8–1.1
Relative elongation, %	300–400	170	200	250–310
Residual deformation, %	10	10	10	5–10

[a] (S) is increased strength.

siloxane caoutchoucs allows the mixtures to be obtained having a resistance to particular solvents. Combining these caoutchoucs the resistance of vulcanizing agents to the action of both oils and acetone can be achieved.

All the siloxane caoutchoucs have very low temperatures of vitrification and, consequently, a high resistance to frost. And on replacing methyl groups by polar groups: alkyl halide, alkyl cyanide, aryl, polyfluoroaryl: the temperature of vitrification increases (as a rule, in proportion to the mole fraction of such groups). The temperature range of operation of rubbers based on native fluorosiloxane elastomers is from –60 to 150°C. Fluorosiloxane elastomers are produced in the pure state and in the state of mother mixtures (filled but without a vulcanizing group), which are vulcanized by a hot procedure using peroxides. The main properties of fluorosiloxane elastomers are given in Table 14.

Rubbers for the details of aviation industry are produced on the basis of types 51-1434, 51-1570, 51-1479 fluorosiloxane elastomers. The main advantage of types 51-1434, 51-1570, and 51-1479 fluorosiloxane rubbers is a wide temperature range of efficiency in various media (fuels, oils, and air). The type FS rubbers are also produced for other branches of industry:

FS-55-1, the operation temperature from –60 to +100°C; FS-55-2, the operation temperature from –60 to +100°C in the medium of solvents, oils, and greases; FS-55-3 and FS-55 for the needs of electro technical, automobile, and other branches of industry, the operation temperature from –55 to +175°C (FS-55-3), from –55 to +200°C (FS-55).

The properties of rubbers based on fluorosiloxane caoutchoucs depend on the content of trifluoropropyl siloxane units. The best resistance to fuels and solvents has the rubber based on the caoutchouc, in which all the units of the macromolecules include trifluoropropyl groups. However, an increase in the content of trifluoropropyl groups providing for the efficiency of the rubbers in liquid hydrocarbon media essentially decreases the resistance to cold of the rubbers on compression. Nevertheless, rubbers based on fluorosiloxane caoutchoucs are the most cold-resistant materials operating in the fuels and other hydrocarbon media.

As for mechanic properties of rubbers based on fluorosiloxanes, all of them lose their elasticity and strength as the result of ageing at 250°C, so that the operation temperature is limited by ~200°C.

The technologies of producing rubber mixtures in Russia and abroad substantially differ. Foreign technology includes two stages: at the first stage a mother mixture is prepared in a mixer (without a vulcanizing system), which is cooled after unloading from the mixer. The second stage occurs on rolls – the vulcanizing substances and pigments are added to the mother mixture, then the mixture enters the operation of removing foreign admixtures. In the two stage process the time of mixing decreases, the degree of dispersing the friable ingredients increases, and the physical and mechanic properties of rubbers are improved.

At the native plants the fluorosiloxane rubber is produced in one stage on the rolls by the technology of processing caoutchoucs of general purpose. In such a technology the macromolecular structure of a caoutchouc undergoes a mechanochemical destruction. Moreover, an uneven distribution of the components in the fluorosiloxane mixture takes place, which results in a decrease in the strength and in the loss of elasticity: the main operating properties of vulcanizates. Such a technology is used for producing the 51-1434 and 51-1570 fluorosiloxane rubbers.

A distinctive feature of fluorosiloxane elastomers is a low intermolecular interaction, which results in low-grade physical and mechanic properties of nonfilled vulcanizates. Hence the composition of fluorosiloxane mixtures is introduced by a number of ingredients: a filler, an anticross-linking and a thermal stabilizing additions, a vulcanizing agent.

Aerosil (silica with an essential number of hydroxyl groups of the silanol type) is used as a filler. Aerosil is highly active with respect to siloxane caoutchoucs and brings about the formation of a gel fraction in their mass even at room temperature. The reaction between silanol groups of a caoutchouc and Aerosil results in an abrupt increase in the viscosity of the rubber mixture even during a short time storage, which makes it unsuitable for processing. Hence the rubber mixtures based on fluorosiloxane caoutchoucs containing Aerosil are introduced with anticross-linking additions for regulating the cross-linking. Methylphenylmethoxysilane (the trade mark “product CM-2”) has found a wide utility. Other alkoxysilanes are recommended for use, and also dimethoxy- and diethoxydimethylpolysiloxanes, both containing and not containing vinyl groups. Such compounds may appear to be technologically more expedient than CM-2, what is more, their synthesis is more accessible.

Aerosil modified with organosilicon compounds at the stage of producing the mixture imparts the rubbers a decreased strength, which might be associated with a partial cross-linking at the starting moment of producing the mixture.

Vulcanizing agents are organic peroxides bringing about the formation of a vulcanizing net resulting from the reaction with vinyl groups incorporated into caoutchouc macromolecules. During ageing the products of thermal transformations of peroxides (free radicals and organic acids) favor, respectively, either an additional cross-linking, or the destruction of caoutchouc macromolecules.

Simultaneously with the radical hemolytic disrupttion the decomposition of the oxides may occur also in a heterolytic manner, which results in by-products (alcohols, ketones, acids). The products of peroxide disruption diffuse from the mass of a vulcanizate or remain in the polymer and influence the properties of vulcanizates; hence the regime of vulcanization has a great impact on the final properties of rubbers.

The influence of the type of organic peroxide is the most essential on ageing of the rubbers. By their influence on the thermal resistance of rubbers peroxides fall into the following order: di-*tert*-butyl > dicumyl > 2,5-dimethyl(2,5-di-*tert*-butyl)peroxyhexane > 2,4-dichlorobenzoyl > benzoyl. A too high content of peroxide also decreases the thermal resistance of vulcanizates. The greatest thermal resistance of fluorosiloxane rubbers is ensured when the fillers of neutral character and organic peroxides with neutral disruption products are in use.

Peroxide under the trade mark “Peroximon F40” [di-*tert*-butylperoxoisopropyl)benzene is used abroad as a vulcanizing agent. In Russia Perkados and Luperko (dicumylperoxide) type peroxides are mainly in use. As is shown by the tests, the physical and mechanic properties of vulcanizates based on these peroxides have no essential differences.

The heat resistance of vulcanizates may be increased with the help of thermal stabilizers, Fe, Ti, Ce and other oxides being used as such. Metal atoms seem to be able to intercalate into the siloxane chain of fluorosiloxane polymer and make an inhibiting impact on the thermo oxidizing destruction. In this case the heat resistance of the polymer is notably affected by the nature of the metal in the compound. The protecting action of the thermo stabilizers depends also on the conditions of the thermal ageing, on the prescription of the mixture, and on the caoutchouc structure. The efficiency of the thermo stabilizers essentially decreases in the presence of silica fillers and abruptly increases as the content of methylvinyl units in the caoutchouc increases. By the decrease in the efficiency the thermo stabilizers based on various metals may be listed in the following order: Zr > Ti > Fe > Cu > Co > Zn > Al.

Combining metal oxides results in a total action on the properties of vulcanizates. Cadmium oxide and α-aluminum oxide make a modifying impact only in the rubber mixture based of fluorosiloxane caoutchoucs. Such mixtures have an increased hardness and are distinctive by their smaller cross-linking on storage.

This review clearly demonstrates the important role of fluoropolymer materials and their products in the aviation engineering. It is evident that the functional properties of fluoropolymers are far from being realized, and these materials have prospects of wider application in the aviation and other high technology branches of industry.