ISSN 1070-3632, Russian Journal of General Chemistry, 2011, Vol. 81, No. 5, pp. 1042–1046. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © V.T. Minakov, A.N. Babin, N.S. Kitaeva, E.I. Alekseeva, E.V. Sokolyuk, 2010, published in Rossiiskii Khimicheskii Zhurnal, 2010, Vol. 54, No. 1, pp. 85–89.

Intermediate Layers for Laminated Glazing Materials

V. T. Minakov[a], A. N. Babin[a], N. S. Kitaeva[a], E. I. Alekseeva[b], and E. V. Sokolyuk[b]

[a] *All-Russian Scientific Research Institute of Aviation Materials Federal State Unitary Enterprise,*
State Research Center of the Russian Federation (RIAM), ul. Radio 17, Moscow, 105005 Russia
e-mail: admin@viam.ru

[b] *State Order-of-the-Red-Banner-of-Labor–Awarded Research Institute of Chemistry and Technology*
of Organoelement Compounds Federal State Unitary Enterprise (SRICTOEC),
sh. Entuziastov 38, Moscow, 11123 Russia
e-mail: eos2004@inbox.ru, chteos@yandex.ru

Received December 1, 2009

Abstract—Laminated glazing is used in architecture, automotive, aviation, and other industries, where there is a demand for imparting to transparent constructions shatter-proof, impact-proof, bird- and bullet-proof, and certain special properties. The article describes organosilicon compositions for intermediate adhesives for triplexes. The compositions and properties of laminated glazing materials are presented.

DOI: 10.1134/S1070363211050380

Triplex (laminated glass) is a combination of glasses manufactures by adhesion over the whole surface of two or several colorless, tinted, or reflecting glass layers with a transparent, colored, white, or colorless polymer film between them. Laminated glazing is applied in architecture, automobile and aircraft building, and other industries, where there is a demand for imparting to transparent constructions shatter-proof, impact-proof, bird- and bullet-proof, and certain special properties.

Not only traditional silicate glass triplexes, but also laminated organic glass materials are of interese for aviation industry. Laminated glazing allows, due to redistribution of thermal and force stresses, enhancement of thermal stability, strength, reliability, and service life. By combining the composition of materials in the laminated glazing one can endow hybrid materials with unique properties and protect functional coating by arranging them inside the triplex.

Triplex Production Technologies

Intermediate adhesive layers in glazing materials can be made of films or potting compositions of varied compositions. With films, the laminated material is obtained by pressing, autoclaving, or vacuum-bag molding. With potting compositions, the latter are poured into the air space between glasses, and then it polymerizes. These are oligomers of different nature, depending on the requirements to heat and freeze resistance of the glazing material.

The principal technologies of production of laminated materials of organic glasses with an elastic potted intermediate layer:

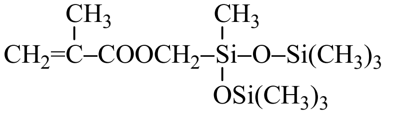
– choice of monomers (a mixture of monomers) or oligomers, whose polymerization involves formation of an adhesive bond between the intermediate layer and organic glass, as a result of swelling of the organic glass surface;

– use of monomers or oligomers whose adhesion to organic glass is provided by treatment of glass surface.

In the framework of the first technology, research groups headed by B.V. Petrov and E.S. Osikina to developed potted intermediate layers on the basis of low-substituted esters of acrylic and methacrylic acids with various dopants, including cross-linking agents. In the framework of the second technology, various organo-silicon compounds were tested.

Organosilicon compounds chosen as the base for intermediate adhesive layers of laminated glazing materials should be low-viscosity transparent liquids cured at moderate temperatures to form highly elastic polymers without isolation of by-products.

A.K. Dabagova, V.T. Minakov, and S. V. Antonova, under the supervision of K.A. Andrianov, synthesized 2-(methacryloyloxy)heptamethyltrisiloxane:



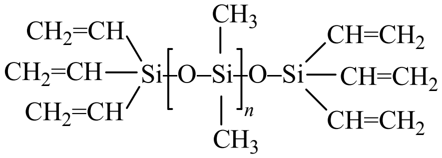
$$CH_2{=}\overset{CH_3}{C}{-}COOCH_2{-}\underset{OSi(CH_3)_3}{\overset{CH_3}{Si}}{-}O{-}Si(CH_3)_3$$

The films obtained by polymerization of 2-(methacryloyloxy)heptamethyltrisiloxane exhibit a good elasticity over a wide temperature range, but they are insufficiently resistant to thermooxidative destruction. To stabilize the polymer chain due to cross-linking and strength enhancement, we explored the possibility of co-polymerization of 2-(methacryloyloxy)heptamethyltrisiloxane with organic compounds of the acrylic and allylic series, as well as with α,ω-bis(methacryloyloxy)-dimethylpolysiloxanes (BMMPS) of different molecular weights. It was shown that 2–3% of a cross-linking agent stabilize the polymer chain and enhances the resistance to thermooxidative destruction by 30–50°C and strength by a factor of 2–5 (Table 1).

Polyadditive Organosilicon Intermediate Layers

One of the most interesting ways to preparing intermediate layers for glazing materials involves the use of liquid organosilicon oligomers vulcanized by the polyaddition reaction without isolation of volatile products.

The necessary starting compounds for preparing high-elasticity materials are a linear polyorganosiloxane with a molecular weight of up to 100000 and end vinyl groups:



as well as a linear polyorganosiloxane with ≡Si–H functional groups:

$$(CH_3)_3SiO{-}\{[(CH_3)SiO]_{0.5}[(CH_3)HSiO]_{0.4}\}_n{-}Si(CH_3)_3$$

The optimal characteristics of polymers can be reached with an excess of hydride groups. In air the latter undergo hydrolysis to form additional intermolecular cross-links on subsequent dehydrocondensation. The gel particles that form play the role of an active highly dispersed filler and favor enhanced strength of the resulting elastomers.

However, to produce a laminated glazing, such organosilicon formulations should be cross-linked in a closed volume in the absence of air moisture and without isolation of by-products, in our case water, which adversely affect the optical properties of the triplex. Therefore, to block unreacted hydride groups, introduction of an additional cross-linking agent, say hexavinyldisiloxane, was suggested.

To gain insight into the effect of the structure of films on their strength, we applied the method of forced resonance vibrations of a cantilever-fixed sample in the temperature range –15 to +20°C. The resulting data allowed us to estimate the average molecular mass between cross-links (M_{av}), as well as the temperature range of service without change of physicomechanical properties.

$$M_{av} = 3RT/C_0^2,$$

where $R = 8.31\times10^3$ kg m^2 kmol^{-1} K^{-1} and C_0, sound speed in the region of well-developed highly elastic state.

Curing Medium and Film Properties

On curing in air, increased excess of ≡Si–H groups decreases the average distance between cross-links M_{av}

Table 1. Effect of cross-linking agents on the physicochemical parameters of (methacryloyloxymethyl)dimethylsiloxane films

Cross-linking agent	Tensile stress, MPa	Tensile yield ε, %
No cross-linking agent	0.37	1460
Diallylformal	1.97	575
Triallyl trimellitate	2.80	325
Triallyl pyromellitate	1.50	300
Diallyl chlorendicate	1.90	475
2,3-Bis(methacryloyloxymethyl)-2,3-dimethylhexamethyltetrasiloxane	1.80	385
Bis(methacryloyloxy)dimethylsilane	2.50	525

Table 2. Characteristics of intermediate adhesive layers

Parameter	Intermediate layer		
	(methacryloyloxymethyl)dimethylsiloxane+ 2,3-bis(methacryloyloxymethyl)-2,3-dimethylhexamethyltetrasiloxane	SILON 864T	SIEL 159-476
Density, g cm^{-3}	1.02	1.05	1.02
Refractive index	1.445	1.5	1.405
Tensile stress, MPa	2.3	2.5	2.8
Tensile yield ε, %	320	185	190
Integral light transmittance, %	90	84	90

and enhances the film strength. The maximum strength values are attained at a 2.3-fold ≡Si–H excess. Therewith, side reactions form in the polymer structure a great variety of structural elements, which extends the elastic–glass transition range.

Curing in a closed volume in the absence of oxygen and moisture increases M_{av}, decreases the deformation strength characteristics of the polymer, narrows the elastic–glass transition range, and imparts a more uniform structure to the polymer. In this case, optimal film characteristics are obtained at a stoichiometric vinyl-to-hydride ratio.

The intermediate adhesive layer SILON 864T was developed for a glazing material on the basis of siloxane oligomers with vinyl and hydride groups, cured by the polyaddition reaction. The working range of SILON 864T is from –60 to +250 C, and its deformation strength parameters are listed in Table 2.

The RIAM together with SRICTOEC has performed optimization of SIEL series compounds for use as intermediate layers of glazing materials. The compound consists of two parts which are mixed directly before use. The components of the compound are:

(a) low-molecular rubber with end vinyl groups

$$(CH_2{=}CH)_xCH_{3-x}SiO[Si(CH_3)_2O]_n{-}Si(CH_3)_{3-x}(CH{=}CH_2)_x,$$

where $x = 1$ or 3;

(b) oligomer G-5 having Si–H bonds in the siloxane chain framework:

$$(CH_3)_3SiO{-}\{[(CH_3)_2SiO]_a\,[(CH_3)HSiO]_b\}_nSi\,(CH_3)_3,$$

where $n = 10$–12;

(c) complex platinum catalysts providing curing by the hydrosilylation reaction at 60–120°C.

Curing Catalysts for SIEL Compound

The catalysts were chosen amongcomplexes V-2, V-4, and V-6, obtained by the reactions of chloroplatinic acid with hexavinyldisiloxane, tetravinyldimethyldisiloxane, and divinyltetramethyldisiloxane, respectively, in the presence of ethanol and potassium bicarbonate. The catalyst activity decreases in the order: V-2 > V-4 > V-6, in line with increasing number of vinyl groups. Quite an important characteristic of a catalyst is its stability on storage. All the catalysts were tested for stability which was measured by activity versus time for model systems. The activity was defined as the rate of gel formation for model systems at the same temperature. As model systems we used α, ω-bis(tri-vinylsiloxy)oligodimethylsiloxane (MVK-3) or α,ω-bis-(methyldivinylsiloxy)oligodimethylsiloxane (MVK-1) in combination with α,ω-bis(trimethylsiloxy) oligodi-methyl(methylhydride)siloxane (G-5), model systems **I** and **II**, respectively.

The most active catalyst V-2 loses activity the most rapidly, and the least active catalyst V-6 is the most stable on storage. It should be noted that the activity of catalyst V-6 reaches a kind of minimum in within a month and then remains almost invariable for about half a year, catalyst V-4 preserves activity for about 3 months, and the activity of catalyst V-2 steadily decays over the entire observation period. Catalyst V-6, in view of its fairly low activity, requires the temperature above 120°C to induce polymerization, whereas with catalysts V-2 and V-4 the polymerization reactions can be brought to completion at 60–80°C within several hours, which makes these systems suitable for virtually all existing organic glasses, oriented inclusive.

All group V catalysts are solutions in toluene. The presence of solvents in composite materials applied in

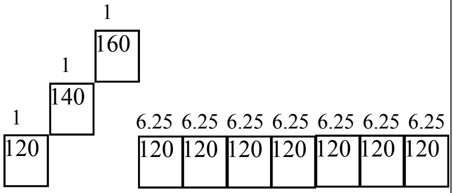
Table 3. Dynamics of catalyst activity on storage

Catalyst	Gelation life, min					
	Model system I			Model system II		
	after preparation	after 1 week	after 1 month	after preparation	after 1 week	after 1 month
V-2	5–10	15–20	30–40	10–15	20–30	45–60
V-4	20–30	30–45	60–80	40–50	60–80	90–120
V-6	40–50	60–70	70–90	60–80	80–90	90–100

Table 4. Physicomechanical properties of modified compound SIEL 159-476

Curing mode	Immediately after preparation		After 1-month storage	
	σ, MPa	ε, %	σ, MPa	ε, %
80°C, 4 h	2.23	193	2.64	191
100°C, 2 h	2.52	190	2.30	193
120°C, 1 h	2.67	196	2.83	187

Table 5. Temperature dynamics of the optical properties of triplexes

Triplex composition	Light transmittance before thermal treatment, %	Test program[a]	Light transmittance after thermal treatment, %	Defects
SO-120T/SIEL159-476/PK	88		83.5	No defects

[a] Each cycle is shown by a square with indication of cycle time (h) and test temperature (°C).

closed volumes is undesirable and can lead to negative results (blistering during exploitation of the laminated glazing material, etc.). To solve this problem, α,ω-bis(trimethylsiloxy)methyldivinyldimethylsiloxane was introduced at the synthesis stage preceding preparation of group V catalysts from a concentrated toluene solution, after which the solvent was removed in a vacuum. With a vinyl-containing oligomer, catalytic systems analogous to group V catalysts were obtained: V-2/MV and V-4/MV. The quantity of the vinyl-containing oligomer required for stabilization of the catalytic system was selected.

Studying the mechanic properties and activity of the catalysts showed that the most suitable is catalyst V-4/MV. The mechanical properties of the composition cured with this catalyst are higher by 10–20% compared with the composition cured with catalyst V-2/MV. Technologically, this allows the gelation life of the composition to be maintained for 2–6 h, and for curing 60–80°C would suffice. The SIEL compound with the V-4/MV catalytic system was given the name SIEL 159-476. The properties of the composite are presented in Table 4 and Fig. 1.

The developed compound was used for manufacturing triplexes and assessing the effect of temperature on the properties of the material. The thermal stability of organic glass SO-120T/SIEL 159-476 (2 mm)/polycarbonate (4 mm) triplexes was studied

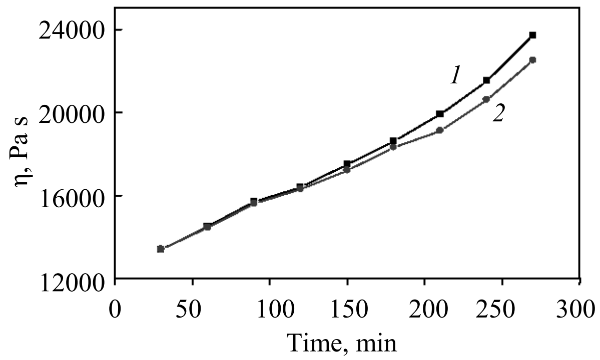


Fig. 1. Dynamics of the viscosity of SIEL 159-476 compound with time: (*1*) immediately after production of components and (*2*) after 1-month storage of components.

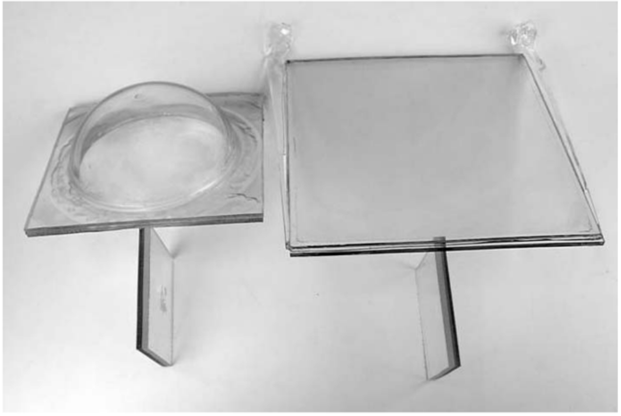


Fig. 2. Triplex as a plane sheet and experimental sample of molded triplex.

under the conditions of step (120–140–160°C) and isothermal (120°C) heating (Table 5), under cyclic exposure to temperature (–60°C to +120°C), and in a tropical climatic chamber (+50°C, humidity 98%).

The triplex with a SIEL 159-476 intermediate layer and appropriate finishing agent for the organic glass is resistant to temperature and moisture and preserves about 80% the integral light transmission. The developed compositions for intermediate layers and laminated materials makes it possible to produce curvilinear items by molding triplex sheets like block organic glass (Fig. 2).