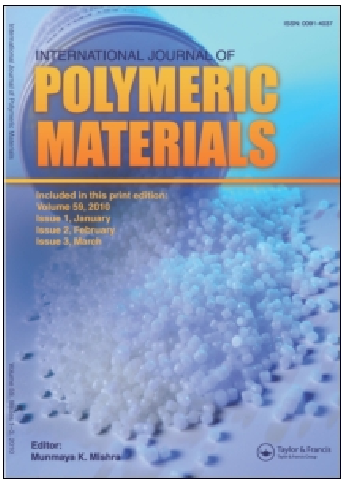

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Poly (1,1,2-Trichlorobutadiene-1,3) and its Compositions: Part II—Adhesives and Adhesive Compositions for Rubber to Metal Bonding

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Poly (1,1,2-Trichlorobutadiene-1,3) and its Compositions: Part II—Adhesives and Adhesive Compositions for Rubber to Metal Bonding

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The adhesive characteristics of polymers and copolymers of 1,1,2-trichlorobutadiene-1,3 are reviewed.

KEY WORDS 1,1,2-trichlorobutadiene-1,3, polymers, copolymers, adhesives, adhesive compositions, bonding to metals.

INTRODUCTION

Elastomers are traditional compounds that are widely used for producing various elastomer-metallic and multilayer elastomeric articles. A complex of operation properties of such products, as well as their durability depend to a great extent on the strength and stability of bonding between constituting elements.

Hot bonding, by use of adhesives, is the most reliable method among those known. Progress in the commercial production and manufacture of new machines and apparatus impose heavy and frequently conflicting demands on adhesives; these demands stimulate further synthesis of new elastomers and modifiers for adhesive purposes.

Adhesive compositions based on halogen-containing polymers (chlorinated and hydrochlorinated rubbers, brominated polybutadienes and others) have found wide use for rubber-to-metal bonding. Adhesives and adhesive compositions based on PTCB and PTCB modified by various reactive functional groups are highly promising.[1-2]

1. Adhesives and Adhesive Compositions for Rubber-to-Metal Bonding

According to Reference 7, an adhesive is obtained by dissolution of PTCB in an organic solvent.

The authors of paper[8] investigated the possibility of preparing adhesive compositions on the basis of PTCB and other halogen-containing polymers, which provide sufficiently reliable bonding with metals of promising rubbers obtained from nonpolar elastomers in the vulcanization process. Besides the study of bonding strength (at tearing, shearing and peeling) special attention was paid to determination of the hydrolytic resistance of the adhesive joint. Based on rather limited literature data the procedure consists in keeping the rubber-metallic specimen in water at 94–97°C for 2 h under a 2-kg load. Such a test is of great importance because the hydrolytic resistance of adhesive joint predetermines to a great extent the strength of rubber-metallic products under actual operating conditions.

The directed studies of several compositions prepared according to various formulations showed that at least three adhesive compositions surpass adhesives Leikonat and Chemosil 220 in indexes of bonding under static conditions, and are close to the two-layer system Chemosil 211/220.

Table I shows that adhesive compositions based on PTCB and chlorinated polymers provide not only reliable strength but the high hydrolytic resistance of the bonding between metals and nonpolar rubbers. After the samples were kept for 2 h under load in near-boiling water the peel strength did not change much, and the sample failure occurred mainly across the rubber.

Rubber–metal articles produced with the use of the formulated adhesive compositions were tested in operation over 15 years and showed high efficiency under various conditions.

Adhesive compositions do not provide reliable metal-to-rubber bonding in the case of elastomers with low unsaturation.[8] Bonding strength at the rubber–metal interface is lower than rubber cohesion strength.

To eliminate this drawback there were formulated some adhesive compositions

TABLE I

The bond strength of SKMS-30ARK and SKO

	Formulated Adhesive Composition					
Characteristics	Leikonat	Chemosil 220	Chemosil 211/220	Formulated adhesive composition		
				1	2	3
Pull (GOST 209-75) (MPa)	3,0-4,0	8,0-9,0	8,0-8,5	7,5-9,0	7,0-8,0	8,0-8,5
Failure of rubber	0	100	100	80-100	90-95	100
Shear (GOST 410-41) (MPa)	4,5-5,0	8,0-12,0	12,0-17,0	10,0-12,5	11,0-14,5	12,0-17,0
Failure of rubber	100	40	100	70	65-90	20-100
Peel,(kN/m)	2-3	13-16	10-16	10-12	11-14	12
(Failure of rubber,%)	0	0	100	70-100	80-100	100
Hydrolytic resistance	Does not withstand	Does not withstand	withstands	withstands	withstands	withstands

based on PTCB, chlorinated polyisoprene (natural and synthetic), chlorinated nairit and chlorosulfonated polyethylene (CSPE).[9–11] The adhesives contain fillers, cross-linking agents, stabilizers and other additives for special purpose. Laboratory investigations showed that adhesive compositions provide the reliable bonding of brass to rubbers (butyl rubber, butyl rubber + SKEPT, halogenated butyl rubber, and SKI-3); in all these cases failure occurs across the rubber bulk.

The strengths of rubber-to-brass bonding (MPa) measured according to GOST 209-75, are presented below:

Butyl rubber (the mixture for coating of valves)	4.0–6.2
Butyl rubber + SKEPT	4.9–6.4
SKI-3	7.0–8.0
Brombutyl rubber (the mixture for tubes)	3.1–4.1

Rubber-to-metal bonding depends significantly on the quality of metal-surface treatment. With formulated adhesive compositions the strength of butyl rubber-to-brass bonding is independent, however, of the method of metal-surface treatment (emery, sand-blast, ultrasonic); in all cases failure occurs across the rubber.

Laboratory data were confirmed on trials of rubber-coated valves under industrial conditions (Table II). Table II indicates that the reliable attaching of rubber to the brass valve is provided even without treatment of the body surface. An oil-free valve surface is a necessary condition for attaining the high bonding strength. Grease can be removed with benzene or with soda ash. The latter procedure is best suited under industrial conditions because benzene is flammable and toxic.

TABLE II

The strength of bonding of rubbers to valves TK115 under different treatments with and without the use of adhesive compositions (AC)

Characteristics	Method of the valve surface treatment					
	Acid-alkaline			Alkaline	Degreasing with benzene	Without treatment
	without AC	Chemosil 211/220	Proposed AC	Proposed AC		
			Bk rubbers			
Bonding strength (N)	30-90		130-220			
Failure mode	at metal surface		across rubber			
			BK + SKEPT rubbers			
Bonding strength (N)	20-40	130-160	130-230	150-220	130-210	130-190
Failure mode	At metal surface	At metal surface partly	Across rubber	Across rubber	Across rubber	Across rubber

TABLE III

The bonding strength of coating rubbers to metal cord covered with different compositions

Characteristics	Covering of steel cord			
	Brass plated	Chemosil 220	A-157	A-169
	SKI-3 rubber			
Bonding strength under usual conditions	28	40	40	38
Failure mode	M*	R**	R	R
Bonding strength after aging, (120° C, 1 hr)	25	35	35	40
Failure mode	M	R	R	R
	Natural Rubber			
Bonding strength under usual conditions	28	42	42	40
Failure mode	C	R	R	R
Bonding strength (kN/m) after aging, (120° C, 1 hr)	24	36	37	35
Failure mode	C	R	R	R

*M - Mixed mode of failure across the rubber and at the rubber and adhesive interface
**R - Across the rubber

Stand-and-service trials of an experimental batch of inner tubes with valves treated with the formulated adhesive compositions and coated with different rubbers showed that the adhesive compositions provide high strength of bonding of rubber-to-valve body under dynamic conditions.

Papers[12,13] show the possibility of substitution of the polymer coating for the brass adhesive coating of a metal cord. PTCB and halogen-containing polymers, vulcanizing agents, fillers and other additives were dispersed in 15–30% xylene solution in order to prepare the adhesive compositions. The adhesive compositions obtained were spread on the degreased or chemically-treated metal-cord surface with a brush or with the use of a dipping bath. After the complete removal of the solvent, the metal cord was coated with natural or synthetic rubber, vulcanized and tested, according to GOST 14863-69.

Experimental data presented in Table III show that the strength of bonding of the metal cord without brass plating but with adhesive coating is higher than that of the brass-plated metal cord.

The adhesive compositions A-157, A-169, and Chemosil 220 provide the bondings of similar strength, and in all cases a failure proceeds across the rubber. After the thermal ageing of the rubber–metal cord specimens, rubber failure occurs under lower loadings.

Corrosion resistance of the metal cord with the adhesive coating is more than

TABLE IV

Fatigue resistance of rubber-metal coard specimens according to (GOST 17443-80, R = 9 K of H = 60%, v = 250 rev/min

Characteristics	Metal cord coating	
	Brass-plated	Adhesive A-157
Fatigue resistance (cycles 10^3):		
Minimum	70	713
Maximum	92	1296
Average	72	1123
Temperatures in sample, °C	61-71	55-66
Failure mode	At metal-cord rubber interface	Metal cord rupture

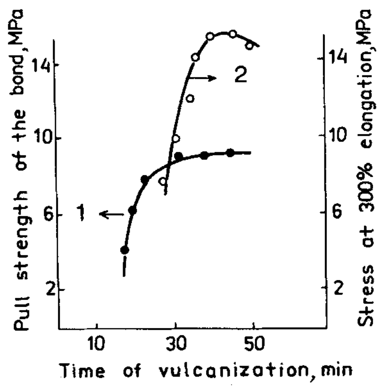


FIGURE 1 Dependencies of bond pull strength (1) and conventional stress (2) at 300% elongation of the SKI-3 rubber on vulcanization time.

twenty times higher than that of the brass-plated metal cord. Fatigue-resistance tests of the rubber–metal cord specimens showed that the strength of bonding of the metal cord with polymer coating is markedly (more than tenfold) higher than the bonding strength in the case of the brass-plated metal cord (Table IV). In the specimens with the brass-plated metal cord the failure proceeds at the brass–rubber interface, whereas in the specimens with the adhesive coating the metal cord itself ruptures. This fact demonstrates the high reliability of the adhesive bonding of the metal cord to rubber.

The universal PTCB-based adhesive composition was formulated designed for attaching various metals to polar and nonpolar rubbers that can be used in different fields.[14] A reliable rubber-to-metal bonding can be obtained when the rate of covulcanization of the adhesive film with rubber exceeds or equals the rate of crosslinking in the rubber itself.

Figure 1 shows that the maximum strength of the bond for SKI-3 and ST-3 rubbers (curve 1 solid dots) is attained earlier than the maximal stress at 300%

TABLE V

Strength of rubber-to-steel bonding with the use of adhesive composition

Elastomer	Pull, (MPa)	Shear (MPa)	Peel, kN/m)
Natural rubber	8,0	13,0	13,0
Isoprene	8,7	15,0	13,0
Butadiene	7,5	8,9	16,0
ButadieneOstyrene	6,0	6,8	8,9
Butadiene-nitrile	8,5	10,6	14,5
Chloroprene	7,0	9,2	12,0
Butyl	5,0	6,2	7,0
Chlorobutyl	3,6	4,7	5,0
Bromobutyl	3,5	5,2	—

rubber elongation (curve 2 open circles). It should be emphasized that the pull and peel tests of the rubber–metal specimens showed that the specimens vulcanized to the optimal degree break in all cases across the thin rubber film adjacent to the adhesive. This fact testifies that the covulcanization of the adhesive film with the rubber surface proceeds more rapidly than the vulcanization of the rubber bulk. In the optimal point and following it, rubber ruptures near a center (pull test), and at peeling the failure proceeds across the rubber. The adhesive composition provides the high strength of steel-to-rubber bonding both with polar and nonpolar rubbers (Table V). In all tests the failure of the rubber–metal specimens occurs across the rubber bulk.

The paper[15] describes adhesive properties of single-component adhesives based on copolymers of TCB with peroxydisubstituted esters of acrylic acids. The dependence of the bonding strength of metals to the SKI-3 rubber on the content of peroxyester groups (PEG) in the copolymer, exhibits an extremum. The maximal bonding strength is observed when the copolymer contains 5–25 mol.% PEG. The further increase in their content leads to a decrease in the strength of the adhesive bonding and changes the failure mode from cohesive (across the rubber) to adhesive.

The results presented in Table VI show that the copolymers provide high strength of bond between steel and the polar and nonpolar rubbers. In all tests the failure of the rubber–metal specimens occurs across the rubber.

Copolymers of TCB with derivatives of α-cyanoacrylic acid (CAA) exhibit high adhesive properties in relation to metals and rubbers.[16–18] Test results showed that the adhesive properties of the copolymers are highly competitive with those of the widely-known two-layer adhesive system Chemosil 211/220 (Table VII). In both cases the failure occurs across the rubber bulk (100%).

TABLE VI

Strength of rubber-to-steel bonding with the use of copolymers

Elastomer	Pull (MPa)	Peel,(kN/m)
Natural rubber	8,5	11,8
Butadiene	7,2	14,3
Butadiene-styrene	6,8	7,4
Butadiene nitrile	9,7	12,5
Chloroprene	6,6	9,2

TABLE VII

Strength of rubber-to-steel bonding with the use of copolymers of TCB with derivatives of cyanoacrylic acid (CAA), MPa

Elastomer	Adhesive	
	Copolymer of TCB with CAA derivatives	Chemosil 211/220
SKN-26	7,3	7,5
SKN-18/SKN-40	10,9	8,5
SKMS-30ARK	7,8	7,1
SKI-3	8,2	8,6

The copolymers of TCB with CAA derivatives impart the heat stability and the temperature resistance, as well as the resistance to an action of aggressive media, to the rubber–metal systems. The copolymers, their solutions in organic solvents and their films covering metal surfaces retain the adhesive properties in prolonged storage at room temperature. Industrial tests of these adhesives showed positive results.

The authors of papers[3,6] investigated a mechanism of an interaction between chlorine-containing polymers and polydienes in the presence of amines. They found that PTCB and polyisoprene react when heated forming the total three-dimensional system. IR spectra of vulcanizates, as well as of sol and gel fractions of the samples, confirm this conclusion. The following absorption bands were compared: the band at 835 cm^{-1}, characteristic of deformation vibrations in repeating units of *cis*-1,4-polyisoprene, and one of the PTCB bands at 710, 755 and 780 cm^{-1}, derived from vibrations of C—Cl bond. The vulcanization time was found not to influence a ratio of intensities of these bands in the vulcanizate spectrum. An examination of relative concentrations of the polymers in the sol and gel fractions showed that PTCB dominates in the sol fraction, and polyisoprene constitutes a high proportion of the gel fraction, the interaction between the polymers leading to the loss of the system's solubility. The rate and extent to which the interaction of PTCB and polyisoprene proceeds are increased significantly in the presence of SKMVP and pyridine which also accelerate the dehydrochlorination of PTCB at heating.

The authors of work[19] studied the effect of the elastomer substrate (SKN-26) on interaction of adhesives of different chemical types with metals. It was shown that at the same thickness of the adhesive (the PTCB composition) peeling velocity, which is a characteristic of the adhesive–metal interaction, depends upon the elastomer's nature. This relation is clearly recognized when the adhesive thickness is small. The maximal bonding strength is attained when the rates of the adhesion processes at the adhesive–elastomer and adhesive–metal interfaces coincide to each other. The processes at the adhesive–elastomer interface are activated by introducing *p*-dinitroso-aromatic compounds into the adhesives based on the chlorine-containing polymers.[20] Formation of the adhesion bonds at the interface elastomer–adhesive composition, containing a polymer binder and *p*-dinitrosobenzene (*p*-DNB), during vulcanization was studied.[21] PTCB and chloro-sulfonated polyethylene (CSPE) acted as binders. SKN-26, SKI-3 and SKEP were used as substrates. Chemical transformations in the polymer–*p*-DNB system were studied by IR spectroscopy. Comparison of the IR spectra of vulcanizates obtained from the SKN-26–*p*-DNB composition pre- and post-heating, showed disappearance of the bands at 1140 and 1250 cm^{-1} related to valency vibrations of the nitroso-group. A new band in the region 3500 to 3480 cm^{-1} appeared, however, assigned to the hydroxyl-group absorption; a band of the C—N bond in a tertiary amine increased as well. The authors suppose formation of a compound with hydroxyl groups, obviously, *p*-quinone dioxime. Addition of *p*-DNB to the polymer proceeds simultaneously; this reaction is confirmed by appearance in the IR spectra of the absorption band at 1670 cm^{-1} characteristic of valency vibrations of the C═N bond, conjugated with an aromatic cycle at one side and with C═C bond, at the other. In the authors' opinion, the Pol C═NPh structure (Pol is the polymer chain, Ph is phenyl) is formed. The similar chemical reactions and the elastomer crosslinking occur in the compositions based on SKI-3 and SKEP, but their depths are different. SKI-3 is more susceptible to such reactions than SKEP which contains no double bonds in the reactive functional groups. Thus, the IR spectroscopic method points to the intersurface chemical interaction of *p*-DNB with the adhesive and substrate polymers. The interaction is accompanied by the crosslinking of the polymer molecules and by the elimination of free *p*-quinone dioxime, because *p*-DNB is a highly reactive, bifunctional compound insoluble in elastomers.

p-DNB with isocyanates are widely used in the adhesive compositions, therefore the studies of peculiarities of their combined action were of interest. The results of studies showed that the degree of the polymer crosslinking increases markedly in the presence of Leikonat. It was concluded that an increase in the strength of the adhesive compounds is caused by formation both of interface chemical bonds during the reaction of the polymers with *p*-DNB and of the interpenetrating networks in the process of the isocyanate diffusion into the rubber and polymerization in it. The authors of paper[22] have formulated a single-layer adhesive involving chlorinated polymer, isocyanate and C-nitroso-aromatic compound which provides the strength of bonding of most rubbers (obtained from general-purpose elastomers) to metals in the vulcanization process. The authors of work[23] investigated the peculiarities of the effect of polymer binder and of the ratio of the components, isocyanate (Leikonat) and C-nitroso-aromatic compound (*p*-DNB), in the single-layer adhesive. The adhesive was applied for bonding of steel (steel 3) to SKN-26, SKI-3 and SKEP rubbers. Diffusion of isocyanate into the rubber mixture and its subsequent polymerization in an elastomer were shown to result in the formation of interpenetrating graft networks derived from the polymerized isocyanate and the vulcanized elastomer. The interaction of *p*-DNB appeared to be essential: it reacts with the adhesive and substrate polymers that lead to their crosslinking at the interface. As this takes place, the hydroxylamine derivatives bonded with elastomer are formed; they promote linking of the network of the polymerized isocyanate and the three-dimensional network of the vulcanizate together, due to the reactions with free NCO groups.

The maximum strength of the rubber-to-metal bonding is obtained when the adhesive compositions involve PTCB, CSPE and the butadiene nitrile elastomer SKN-26. It was noticed that when the adhesives containing these binders were applied for bonding the SKN-26 rubbers the bond strength increased significantly with increasing Leikonat content in the adhesive composition. However, in bonding of steel to the SKI-3 and SKEP rubbers the Leikonat content has little effect. This may be ascribed, apparently, to its high solubility in the polymer binder SKN-26 and low solubility in the mixtures of SKI-3 and SKEP rubbers. An increase in the *p*-DNB content in adhesive compositions is shown in all cases to result in an increasing bonding strength of the rubber–metal compounds. Based on the investigations the authors formulated an adhesive-foundation for hot bonding of SKEP rubbers to metals. It should be noted, however, that the use of the adhesive-foundation does not exclude the necessity of additional applying of the adhesive-primer (Armlok O1) which is deposited on a metal surface and a polychloroprene-based adhesive which is used for covering the adhesive-primer. Thus the procedure of bonding nonpolar rubbers to metals involves the subsequent depositions of three adhesive layers on to the metal substrate. Such technology of the metal-to-rubber bonding is used for coating chemical apparatus with the rubber highly resistant to aggressive media.

PTCB may be used in two-layer adhesive systems. Thus in the proposed method of bonding[24] the adhesive primer based on polychloroalkadienes such as (poly[3,5,5-trichloropentadiene-1,3] or poly[1,3,7-trichloroheptadiene-1,3] is deposited on the metal surface and then covered by the PTCB-based adhesive. When the adhesive bonding is carried out with nonpolar rubber the emphasis is on producing the strong bond at the adhesive–rubber interface. For this purpose the special covering adhesives are applied. Thus, the following method of SKEP rubber-to-metal bonding leads to increased heat resistance. Two layers of the adhesive containing the mixture of PTCB with triisocyanatetriphenylmethane are deposited on the rubber surface, and the solid-substrate surface is coated with the composition based on phenol–formaldehyde resins (FFS) and SKN.

An examination of literature data[24–31] allows us to conclude that the adhesives and the adhesive compositions based on PTCB and PTCB modified with various reactive functional groups may be successively used for the reliable bonding of both the polar and nonpolar rubbers to metals in the manufacturing of the rubber–metal articles.

2. Water-Based and Cold-Setting Adhesives

Water-dispersible adhesives are very promising glues. Their advantage consists in elimination of organic solvents from adhesive compositions and in their environmentally-friendly nature. The use of water-based adhesives improves workplace conditions and leads to the economical consumption of oil-refining products.

According to literature data,[25–31] the active search for water-based adhesives competitive with those dissolved in organic solvents continues. It is Ozelli's opinion[32] that this problem cannot be solved with certain because it is unlikely that metal corrosion can be avoided in the industrial use of water-based adhesives. Therefore, the author offers the application of a two-layer adhesive system involving the water-based coating glue and a primer based on an organic solvent.

According to work,[33] the use of water-based adhesives for bonding elastomers together and to substrates during the vulcanization process has some peculiarities. It has been noticed that the appropriate treatment of surface before bonding provides the required wetting of a substrate with an adhesive. Thus, it is essential to phosponate the metal surface or cover it with the solution adhesive. Water-based adhesives must be resistant to dilution by hard water, and mixing during their production must not create foaming. For this purpose stirring with low-rotation velocity or antifoaming agents which do not deteriorate the operation characteristics of the adhesive bonding is used. The author indicates that water-based adhesives must be resistant to freezing and thawing; they are best stored and transported at 10–30°C, and containers and tubings must be coated with rubber, epoxies or phenolics. It should be noted that the author thinks, just as does Ozelli, that when elastomers are attached to metals only with the water-dispersible adhesives, the use of passivating primer can reduce corrosion. It is found that water-based adhesives are effective in bonding natural, SKI, SKS, SKN and polychloroprene rubbers and are less effective in the case of rubbers obtained from elastomers with a low degree of unsaturation (butyl rubber, SKEP, SKEPT). It is noted that for SKT and fluorinated rubbers the solution adhesives are preferable.

The authors of paper[34] have formulated water-dispersible PTCB-based adhesive designed for metal to rubber (to nonpolar and unsaturated elastomers) in the vulcanization process. The covering adhesive contains PTCB latex combined with latex of an elastomeric adhesion-active film-forming compound (DMVP-10x), as well as a highly dispersed carbon filler and a nitroso-aromatic adhesion promoter. The solution adhesive, for instance, Armlok-0.1 is used as a primer deposited onto metal substrate. Systematic studies on various water-dispersible adhesive compositions[33] make it possible to reveal the dependence of their adhesion properties on the degree of coagulative structuring of the adhesive components and on the thermostructuring of the adhesive film.

The maximal structuring in the mixture of latexes depends on the degree of PTCB modification with ammonia which is required to combine acid PTCB with alkaline latex. The optimal degree of structuring and the adhesion properties of adhesive compositions increase with increasing degree of filler dispersity and using a micelle-forming surface-active substance needed for filler dispersion. The filler is found to adsorb the adhesive and substrate polymers on its surface (in the boundary layer). The PTCB reactivity increases in this process due to a decrease in the activation energy of the polymer dehydrochlorination. In the presence of the dinitroso-aromatic compound the polymers react intensely with one another and with the filler surface producing strong adhesion bonds of a chemical nature. The author has proposed the main principles of formulating water-borne adhesives.

A variation in the PTCB structure, as well as introducing different functional groups, for example aromatic, acidic, peroxide, ester and so on, in its molecules, result in the production of the modified PTCB with interesting physicochemical characteristics, and enlarged markedly the field of its practical use as an adhesive. Thus, the introduction of esters of α-cyanoacrylic acid into the molecule opens up limitless possibilities for regulating adhesive properties. Both cold- and thermosetting adhesives may be obtained depending on the copolymer composition. Cold-setting adhesive compositions based on copolymers of TCB with ethyl (ECA) and allyl (ACA) esters of α-cyanoacrylic acid are proposed for bonding of rubbers, metals, as well as rubbers to metals. As is seen from Table VIII, their strength characteristics are 7–8 times higher than those of the PTCB-based adhesives (in the cold-setting adhesives); their resistance to thermooxidative destruction in air increases by 80–100°C compared with polycyanoacrylates.

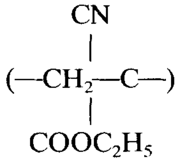
The mixture of TCB with ECA and ACA partially polymerized in the presence of radical initiators is proposed for bonding metals, rubbers, as well as rubbers to metals; the content of the copolymers in the composition ranges from 20 to 80 mol.%. The bonding of vulcanized polar rubbers is possible also when solutions

TABLE VIII

Physical properties of cold-setting adhesives PTCB-Cyacrin

Adhesive	Initial strength MPa	Strength after H_2O treatment (240 h) MPa	Fire resistance
1. Monomer TCB	0	0	non-burning
2. Composition based on PTCB in monomer TCB	1,9	0	non-burning
3. Composition; copolymer TCB: ECA 50:50 (10%) In monomer ECA (90%)	16,0	9,5	non-burning
4. Composition copolymer TCB:ECA 75:25 (5%) In monomer ECA (95%)	16,5	11,5	non-burning

of the copolymers in esters of α-cyanoacrylic acid are used as adhesives. The introduction of



$$(\text{—}CH_2\text{—}\overset{CN}{\underset{COOC_2H_5}{C}}\text{—})$$

fragments (30 and 50 mol.%) into the macromolecular chain decreases the resistance to shearing of the adhesive compounds of aluminum alloy D^{16} (obtained by the use of pure ECA) from 18 to 16.0–16.5 MPa; however, the operation temperature increases by 80–100°C, and this reflects in the elasticity. In the case of the copolymers with allylcyanoacrylate the operation temperature of the adhesive increases still further.[4,5,35,36]

Presently, a variety of requirements have been imposed upon adhesives: they concern, in particular, the necessity of bonding untreated surfaces with oil or fuel remains; this is an especially urgent problem when agricultural equipment is repaired under field conditions.

The cold-curing adhesive compositions based on the copolymers of TCB with fluorocyanoacrylates show increased adhesive strength in bonding of greasy surfaces compared with the compositions based on fluorocyanoacrylates.[37] The adhesive strengths are fairly high when the proposed compositions are used with untreated surfaces both of steel and duralumin. The values of shear strength of attaching steel with spindle-oil remains amount to 8–19.0 MPa depending on the composition structure and the curing time. The high bonding strength (2.7–9.8 MPa) is attained for the steel surface with the diesel-fuel traces after a 1-h curing and with diesel-oil traces (2.4–6.5 MPa). The bond strength is retained also after storing the samples in a 13% solution of sea salt for 240 h: it is 9–16.2 MPa for steel with the spindle-oil traces (at shearing), and 4.0–7.0 MPa for aluminum.

The compositions based on the pure fluorocyanoacrylates show the zeroth strength on bonding for 1 h; after 6 h the strength is 0.9 MPa for a surface with the diesel–oil traces and 3.2 MPa for that one with diesel–fuel traces. The authors noticed that the greater the alkyl substituents of fluoro-derivatives of α-cyanoacrylic acid in the TCB copolymer, the less the strength of the adhesive composition.

Thus, the introduction of a definite amount of esters of α-cyanoacrylic acid into the PTCB molecule makes it possible to obtain cold-setting adhesives with the enhanced thermal stability and water resistance. Modification of cyanoacrylates of TCB allows introduction of metal powders into the composition and producing electrical-conducting adhesives as well as adhesives operating at low temperatures and on surfaces. However, the cold-setting adhesives mentioned are not suitable for bonding metals to elastomers, for example to polyurethanes in the process of hot vulcanization.

3. Adhesives for Bonding Cast Polyurethanes to Metals

Cast polyurethanes (CPU) are widely used for manufacturing polyurethane–metal products due to their valuable complex of technical properties. Their efficiency and durability are governed to a great extent by the strength of the polyurethane-to-metal bonding. CPU exhibits, however, low adhesivity to metal surface. Therefore, great efforts have been made to produce adhesive and adhesive compositions with increased bonding strength in the modern technology of manufacturing reinforced polyurethane–metal products.

An examination of the literature data[38–50] showed that the adhesive compositions that are used for hot bonding CPU to metals belong mainly to the multilayer type; they are toxic and nondurable. To eliminate these defects, biphilic polymers were synthesized. They contain simultaneously in a macromolecule two or more reactive functional groups that interact intensely both with the metal surface and the polyurethane in the vulcanization process.

The peel strength of metal-to-CPU bond does not exceed 3 kN/m in the case of pure PTCB. When 0.5 mol.% of the reactive functional groups (for instance, carboxyl, amine, hydroxyl, derivatives of α-cyanoacrylic acid and others) are introduced into the PTCB macromolecule, the adhesivity of PTCB to CPU increases sharply.[51–54]

The dependence of the adhesive strength on the ratio of functional groups in the macromolecule exhibits an extremum, and the region of the optimal adhesion properties depends on the type of functional groups. In the CPU-to-metal bonding, PTCB is found to show optimal adhesion properties when the content of the functional groups containing a mobile hydrogen atom amounts to 1–15 (carboxyl), 4–19 (derivatives of cyanoacrylic acid), and 5–25 mol.% (peroxy-substituted esters of acrylic acid).

It should be noted that with all synthesized biphilic polymer adhesives, failure of the polyurethane–metal specimens occurs at the adhesive–polyurethane interface when the content of the functional groups is less than the optimal. Thus, the adhesives interact with the metal surface more intensely than with the elastomer. When the content of the functional groups is optimal the failure proceeds across the polyurethane bulk, i.e., the polymer reactivities in the interaction with both substrates are identical. When the content of the reactive functional groups is increased the specimens rupture at the adhesive–metal interface because the polymeric adhesives interact with the elastomer, in this case to the maximal extent. When the homopolymers of trichlorobutadiene and of the monomer with functional groups are used as adhesives the bonding strength decays practically to zero, and the failure occurs at the adhesive-polyurethane (PTCB) or the adhesive-metal interface (polycyanoacrylate).

Thus the maximum strength of metal-to-CPU bond is attained when the ratio of monomers in the copolymer provides the maximum interaction of halogenic groups with the metal surface and of the functional groups with CPU. The conditions of obtaining copolymers do not influence the adhesion properties if their molecular masses are different slightly. When the molecular mass decreases the adhesion properties and cohesion strength of the copolymers are deteriorated.

Table IX presents the data on the effect of some technological factors upon the strength of bonding of cast polyurethanes (based on oligodienediol) to metals by the use of the TCB copolymer with α-cyanoacrylic-acid derivatives. These data show that the most bonding strength is attained with shot-blast, sand-blast, and

TABLE IX

Effect of technological factors on the strength of bonding of cast polyurethane based on oligodienediol to metals

Technological Factor	Metal	Bonding strength (GOST 411-77), kN/m	Failure Mode
Method of metal - surface treatment:			
Ungreasing	Al	14.3	Coh*
with organic solvent	Steel-3	7,8	Coh
with emery paper	Steel-3	17.5	Coh
shot blasting	Al	19.8	PU*
	Steel-3	20.8	PU
sandblasting	Al	21.3	PU
	Steel-3	22.0	PU
chemical	Al	20.5	PU
Termperature of adhesive drying; ° C,			
23°	Steel-3	22.8	PU
30 - 60°	Steel-3	20.0	PU
Time of the adhesive film heating at 120°C, min:			
0	Al	21.4	PU
25	Al	24.1	PU
60	Al	23.0	PU
90	Al	17.1	Coh
180	Al	11.4	Coh
Solvent:			
Toluene	Al	24.3	PU
Methylene chloride	Al	23.0	PU
Tetrahydrofuran	Al	23.0	PU

* Coh - Failure at the adhesive-polyurethane interface
** PU - Failure across polyurethane

chemical treatment of the metal surface. When the adhesive film is heated at 120°C, more than 60 min the bonding strength decreases; this appears to be caused by chemical reactions in the adhesive film that reduce the adhesive reactivity in relation to CPU (the failure of the polyurethane–metal specimens at the adhesive–polyurethane boundary confirms this). Solvent and metal nature, conditions of adhesive-composition drying do not influence the bonding strength; the failure of the polyurethane–metal specimens is of cohesion type in all cases.

The effect of different aggressive media and increased temperatures on the strength of CPU-to-metal bonding has been investigated (Table X). Table X shows that the

TABLE X

Effect of temperature and aggressive media on the strength of bonding of CPU (based on oligodienediol) to metals

Metal	Aging conditions	Peel strength kN/m	Failure mode
Steel-3	Standard samples (23°)	22.7	PU*
Al	Standard samples (23°)	23.1	PU
Steel-3	Boiling in water for 6 hrs.	19.5	PU
Al	Boiling in water for 5 hrs.	20.2	PU
Steel-3	Boiling in 5% NaCl solution, 6 hrs	21.9	PU
Al	Boiling in 5% NaCl solution, 6 hrs	21.8	PU
Steel-3	Thermal ageing 100° C, 72 hrs.	24.4	PU
Al	Thermal ageing 100° C, 72 hrs.	23.2	PU
Al	Air vapor medium (94+/-1)° C, 7 hrs	17.4	Coh*
	15hrs	17.1	Coh
	24hrs	18.3	Coh
Steel-3	Test temperatures of polyurethane - metal samples		
	80° C	23.1	PU
	90° C	21.9	PU
	100° C	22.4	PU
	110° C	22.7	PU

* PU - Failure across polyurethane
** Coh - Failure at the adhesive - polyurethane interface

copolymers provide high thermal stability and temperature resistance, resistance to boiling water and NaCl solutions. In all the cases, the failure occurs across the polyurethane bulk. However, the bonding strength decreases somewhat under the tests in the air–vapour medium, and rupture of the specimens occurs at the adhesive–CPU boundary; this points to the destruction only of the weakest bonds between the adhesive and polyurethane. The high bonding strength on the treatment of the polyurethane–metal-cord specimens in the air–vapour medium testifies to this conclusion.

The resistance to dynamic loading is an important characteristic of elastomer–metal products. A comparative estimation of fatigue resistance of the polyurethane–metal-cord systems obtained by the use of different adhesives was carried out according to GOST 17443-80 which is applied for the determination of the fatigue resistance of rubber–metal-cord systems under various fatigue conditions.

Preliminary statistical tests of polyurethane–metal-cord specimens by the H-method showed that the strength of CPU bonding to the brass-plated metal cord of 22L15 type covered with the biphylic adhesive film was 30 kN/m.

Table XI compares the fatigue-resistance values of the polyurethane–metal-cord systems obtained with the use of various adhesive systems. As is seen from the table, the fatigue resistance of the polyurethane–metal-cord systems produced with the use of Leikonat and the brass coating is markedly less than the fatigue resistance of the systems with the polymer coating. It should be noted that similar results were obtained when the metal cord without the brass plating was attached to CPU with the biphilic polymer adhesives.

When more severe loading conditions are used, for example when the metal cord is tested under 49 N, the fatigue strength of the brass-plated samples with Leikonat decays practically to zero ($[0.6-1.0] \times 10^3$), whereas in the case of the polymer coating it retains a reasonably high value (223×10^3). The adhesive films heated at 120°C for 40 min provide higher fatigue resistance than films heated for 65 min. This fact confirms the results obtained previously in statistical tests: the bonding strength decreases when the adhesive film is heated for longer than 60 min.

The copolymers, their solutions in organic solvents and their films deposited onto metal surface retain the adhesion properties in the prolonged (no less than two years) storage at 23–30°C.

The adhesive properties of the biphilic polymers with reactive functional groups are affected significantly by the nature of substituents in vinyl monomers employed for PTCB modification. For example, the pull strength of the polyurethane–metal specimens produced with the use of the copolymer of TCB with acrylic acid (TCB : AA = 85 : 15 mol.%) amounts to 20 MPa. When methacrylic acid (MAA) is used instead of acrylic acid (TCB : MAA = 85 : 15 mol.%) the polyurethane–metal specimens destruct at 9 MPa. The methyl group of MAA is supposed to diminish the area of actual contact of the polymer chains and the adhesive; therefore the strength of bonding with metal surface decreases. The failure of the samples at the adhesive–film interface justifies such a conclusion.

The influence of the type of substituent in the main chain and of the ester group

TABLE XI

Fatigue resistance of the polyurethane-metal cord systems obtained with the use of adhesives (brass-plated metal cord 22L15)

Adhesive	Time of heating of adhesive film at 120°C	Test conditions		Number of cycles $n \times 10^3$
		Load, N	Deformation V, %	
Brass	-	29.4	15	2.5
Leikonat	-	29.4	15	57.0
Copolymer of TCB	40	29.4	15	1511.0
with CAA derivatives	65	29.4	15	326.0

of α-cyanoacrylic acid (CAA) on the adhesion properties of the TCB copolymers with CAA derivatives was studied. When the substituents with long carbon chains (C_4–C_7) are introduced into ester groups and when the main chain contains bulky substituents (phenyl, furfuryl, etc.) the adhesion properties of the copolymers are shown to deteriorate.

The small-sized substituents (C_2H_5—, —$CH_2CH{=}CH_2$—) in the ester groups of cyanoacrylates promote the increased mobility of the macromolecular chains, the more effective wetting of the substrate surface with the adhesive and, as a result, the most entire interphase contact. This is confirmed by the failure of the polyurethane–metal samples across the polyurethane bulk.[55]

The synthesized polymers are very effective in bonding of CPU based on oligodienediols, oligoethers and oligoesters to metals; the oligomer molecular mass does not influence the bond strength of the polyurethane systems: in all cases the failure occurs across the polyurethane bulk. The adhesion properties of such ad-

TABLE XII

Strength of CPU-to-aluminum bonding with different adhesives

Starting compound for PU	Adhesive	Peel strength kN/m	Failure mode
oligodienediol	TCB-AA	23.3	PU
	TCB-CAA	22.8	PU
	Tixon AV-936	17.7	A-PU
	Desmocol 12-Desmodur L	21.6	PU

TABLE XIII

Effect of time of adhesive film heating on the strength of CPU-SPU bonding

Time of heating, mins.	Bond strength (GOST 6768-75, kN/m)	Failure mode
0	22.3	PU *
20	14.4	Coh*
40	11.1	Coh
80	8.8	Coh

* PU - Failure across polyurethane
* Coh - Failure at the adhesive - SPU interface

TABLE XIV

Resistance of two-layer polyurethane systems to heating and salt medium action

Conditions of ageing, adhesive	Bondstrength (GOST 6768-75, kN/m)	Failure mode
Before ageing, 23° C		
Leikonat	12.6	Coh*
MPTCB	19.4	PU**
Heat ageing (72 hrs., 100° C)		
Leikonat	6.1	Coh
MPTCB	20.4	PU
Boiling in 5% NaCl for 6 hrs		
Leikonat	9.5	Coh
MPTCB	16.7	PU

*Coh - Failure at the adhesive - CPU interface

** PU - Failure across polyurethane

TABLE XV

Strength of SPU-and-CPU to rubber bonding

Double samples	Bond Strength (GOST 6768-75 (kN/m)
SPU rubber based on:	
BSK, 23° C	12,3
SKN, 23° C	9,3
SKN, 100° C	8,7
BSK-CPU, 23° C (based on polyenediol vulcanizate)	10,3
BSK-CPU, 100° C	8.9

hesives are as good as those of the well-known cements Tixon AB-936 and Desmocol 12-Desmodur L (Table XII). The table shows the polyurethane samples produced with the use of the polymer adhesives destruct under tests across the polyurethane bulk; this fact points to the intense interaction of the adhesives with the substrates. The samples cemented with Tixon AB-936 destruct at the adhesive–polyurethane interface.

The results obtained show that copolymers of TCB with the vinyl monomers containing various reactive functional group can be used for manufacturing polyurethane–metal products designed to operate under different conditions.

4. Adhesives for Bonding Elastomers of Different Nature

The multi-ply rubber articles based on elasomers of different nature with a high operation properties can be obtained only when a strong and stable bond between the articles is formed. The problem of repairs of the traditional and polyurethane tires (PU) may only be solved in this way.

It follows from literature data[56–64] that adhesives designed for hot bonding of elastomers in the process of manufacturing multi-ply rubber articles are basically of a multilayer type. They are sensitive to the composition of the materials to be bonded and to the method of treatment of the substrate surface; their production and application are rather complicated processes.

The copolymers of TCB and vinyl monomers with the reactive functional groups (peroxide, amine, sulfur-containing, nitrile, cyanoacrylate and others) may find good use for bonding different elastomers.

The dependence of the strength of the adhesive compounds on the content of the functional groups in the copolymer shows an extreme.[65,66] The optimal strength is attained when the content of the cyanoacrylate groups amounts to 4–19 mol.%.

Table XIII presents the results of an investigation of the effect of the time of the adhesive film heating at 120°C on the strength of bonding of CPU to the setted polyurethane (SPU).

According to the data of Table XIII, the maximum strength of the bond between CPU and SPU is reached without heating the adhesive film. An increase in the heating time results in a decrease of the strength of the adhesive compounds. The heating appears to induce chemical transformations in the film itself that reduce its adhesivity to SPU.

The effects of heat and salt medium upon the strength of the adhesive compounds have been studied because the plied-up rubber products must possess efficiency and durability under various operational conditions.

Bonding with the isocyanate adhesive is not efficient enough at 23°C and after aging (Table XIV) because failure of the samples occurs in all cases at the interphase boundary. After the action of heat and boiling in a NaCl solution the strength of the adhesive compounds decreases markedly.

Modified PTCB (MPTCB) provides reliable bonding of CPU to SPU based on an oligodienediol, confirmed by the cohesion mode of the polyurethane failure.

The high bonding strength is attained when CPU and SPU are bonded to polar and nonpolar rubbers (Table XV). As is seen from the table, the bond strength is not reduced much when the test temperature increases up to 100°C and in all cases cohesive failure of the rubber occurs.

Thus the results of research point to high efficiency of MPTCB in bonding of different elastomers in the process of hot vulanization.

CONCLUSIONS

Numerous investigations have shown that PTCB has high adhesivity to metals, rubber, elastomers of different chemical nature, and so on. Various types of PTCB-based adhesives designed for bonding the rubber–metal products have been formulated; they involve water-based adhesives, cold-setting adhesives, heat-setting adhesives for bonding the cast polyurethanes to metals and elastomers of different nature.

The PTCB-based adhesives may be successively used for reliable bonding of polar and nonpolar rubbers to metals in the manufacturing of different rubber–metal products. These adhesive compositions are highly competitive in their properties with the well-known two-solvent adhesive composition, Chemosil 211/220.

When the PTCB-based adhesive compositions are employed, the strength of the rubber-to-metal bonding is independent of a method of metal-surface treatment: in all cases, failure occurs across the rubber bulk.

The introduction of modifiers—esters of α-cyanoacrylic acid—into the PTCB macromolecule offers considerable scope for regulating the adhesive properties and producing the adhesives designed for bonding metals, rubbers and rubbers to metals. The strength indexes of cold-setting adhesives increase by seven to eight times as compared with PTCB-based adhesives.

Cold-setting adhesive compositions based on the copolymers of TCB with α-cyanoacrylic acid have been formulated; they operate at reduced temperatures and on greasy surfaces, and exhibit high thermal stability, water resistance, and resistance to the action of aggressive media.

When 0.5 mol.% of reactive functional groups (carboxyl, amine, hydroxyl, α-cyanoacrylic acid derivatives, etc.) are introduced into the PTCB macromolecule, the PTCB adhesion to the cast polyurethane increases sharply (compared with pure PTCB). As a result, heat-setting adhesives (based on modified PTCB) providing reliable bonding to metals, have been formulated. TCB copolymers provide high thermal stability, resistance to boiling water and NaCl solution; the fatigue resistance of such polyurethane–metal-cord systems is considerably higher compared with systems produced with the use of Leikonat or the brass plating. Under test conditions, in all cases the failure of polyurethane–metal-cord systems proceeds across the polyurethane bulk. Adhesives based on TCB copolymers are highly competitive in their adhesion properties with the well-known adhesives Tixon AB-936 and Desmocol 12-Desmodur L.

TCB copolymers containing reactive functional groups may be used for bonding different types elastomers, for example the cast polyurethane to the set polyurethane derived from an oligodienediol, as well as for their bonding to polar and nonpolar rubbers.

Thus, PTCB and its copolymers with various vinyl monomers are highly promising for use as adhesives and adhesive compositions. PTCB and the interpolymers of PTCB with different high-molecular amines may be used as special-purpose polymer coatings (resistant to aggressive media, electrical conducting, bactericidal).

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