

NANOSTRUCTURED LIQUID EBONITE COMPOSITION FOR PROTECTIVE COATINGS

O.Figovsky, D. Beilin

Polymate Ltd.-International Nanotechnology Research Center, Migdal HaEmek , Israel
sitapolymate@gmail.com

ABSTRACT

Explores the possibility of preparing elastic and hard nanostructured ebonite coatings, utilizing the properties of oligobutadienes without ending functional groups. Examines the vulcanization processes leading to formation of rubberizing ebonite coatings on samples of oligobutadienes. Finds that the most effective bonding materials for non-solution compositions are ebonite coatings. . These covering allow to get rid of the deficiencies intrinsic to conventional rubber shut and liquid rubberizing compounds

Keywords: Coatings, Rubber, Protective Coverings, Rubberizing, Liquid Ebonite Mixtures, Low-molecular rubber, Oligobutadiene, Polybutadiene, Chemical resistance

INTRODUCTION

Rubber covering (rubberizing) finds wide application in chemical and other industries where it is used to provide corrosion protection for apparatus, equipment and pipelines. However, the use of sheet rubber and traditional liquid rubberizing compounds, based on polychloroprene (Neoprene), polysulphide (Tiokol), polyurethane and other caoutchoucs, isn't enable, to ensure long-time, reliable and effective protection. It demands adhesive substrate and fails to afford safety because of organic solvents present in the compounds. LEM are protective lining products whose function is superior to the current rubber products that are used in the marketplace. LEM is a cost-effective and functional solution for rubber-coating applications.

The novel Liquid Ebonite Mixtures (LEM) for rubberizing based on linear low-molecular polybutadiene contained nanosize black carbon fillers allow to get rid of the deficiencies intrinsic to conventional rubber sheet and liquid rubberizing compounds.

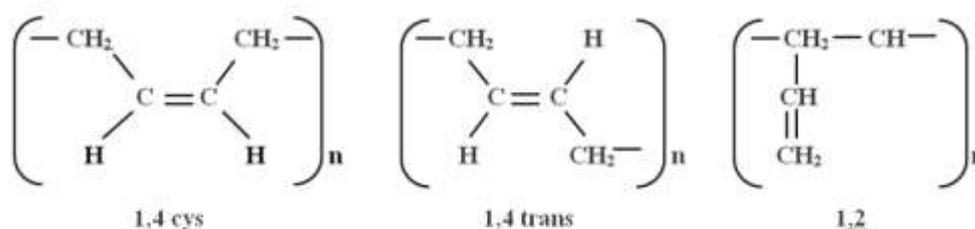
With value-added design and engineering flexibility, LEM has the ability to effectively cover hard to reach places, successfully coating the complex surfaces of such areas as the mesh of sieves otherwise considered impossible to coat with conventional rubber sheets. With increased chemical resistance, LEM maintain material integrity by assuring long-term durability and effective corrosion protection. In addition to high performance properties, material production of LEM meets environmental safety standards, further elevating LEM as an advanced product that outperforms conventional rubber coatings and coverings. The cost benefit factors based on anticorrosion reliability and application functionality will satisfy the demands of the high-performance coating industry.

Depending on the purpose and the type of rubber, used as a base, the LEM my be one - or double – pot composition. The one-pot LEM is low-viscous trixotropic compositions, solvent-free and hence safe in handling; their shelf life by 20 -30 °C is practically unlimited. The double-pot LEM are high-viscous compositions intended to make thick-layer (up to 2.5mm) coverings .

LEM is based on oligobutadienes without functional groups which are liquid polymers with a hydrocarbon structure and a high degree of non-saturation . The oligobutadienes are characterized by low values in molecular weight, the contrary to similar structured high-molecular elastomers. Oligomers of this type are mostly used as plastifying rubber mixtures based on high-molecular rubbers [1] and as a film-forming base of lacquer or paint coatings, for the complete or partial replacement of plant raw material [2]. We explored the possibility of preparing elastic and hard ebonite coatings, utilizing the properties of oligobutadienes without ending functional groups [3-6].

STRUCTURE AND PROPERTIES OF OLIGOBUTADIENES

Oligobutadienes without functional groups are similar in a structure and microstructure of its links to high molecular butadiene rubbers (polybutadienes) and contain links of three different types:



Depending on the conditions of polymerization and kind of catalyst can synthesize the oligobutadienes with various microstructure and molecular weight. Effect of kind of the catalyst is shown in Table 1 [7]

Table 1. Dependence of liquid oligobutadiene's microstructure on kind of catalyst

Process of polymerization	Catalyst	Structure of polymer, %		
		1,4-cis	1,4-trans	1,2
Anionic	Sodium, potassium	30-40	10-30	30-50
	Lithium	40		20
	Sodium, potassium + ether	-	15	85
	Lithium-butyl+ ether		8	92
Kationic	Boron fluorides	≤5	70-90	10-25
Radical	Potassium persulphate or cumene hydroperoxide	≤40	30-60	10-30

The study of the rheological properties of more viscous polybutadiene oligomer (NMPB¹) and less viscous (PBN²) shows the decisive influence of the latter, which can be explained by the role of low-viscosity polybutadiene oligomer as a intramolecular plasticizer. At the same time dependence of the viscosity of mixtures NMPB and PBN on temperature points to the influence of high-viscosity oligobutadiene (Figure 1) [7].

Thixotropic structuring reflects the ability of rubberized composition to form a physical and chemical structure of the relatively thick coating layer applied to the protected surface. The process of thixotropic recovery of the destroyed structure in the state of rest is characterized by an increase of strength in time. Modification compositions based on oligobutadiene by carbon black or surface-active substances such as lecithin, increase the thixotropic properties of the filled composition. Loading-unloading curves of compositions based on SKDNN³ filled with a modified carbon black shows a hysteresis loop; area of this loop is far exceeds the hysteresis loop are for the composition, modified lecithin, and even more so for non-modified composition (Figure 2) [7].

¹ Loss-molecular polybutadiene rubber, Russian Standard (TU) 38.103290-75

² Loss-molecular polymer, Russian Standard (TU) TU 38.103641-87

³ Loss-molecular cis-polybutadiene rubber, Russian Standard (TU) 38.103515-82

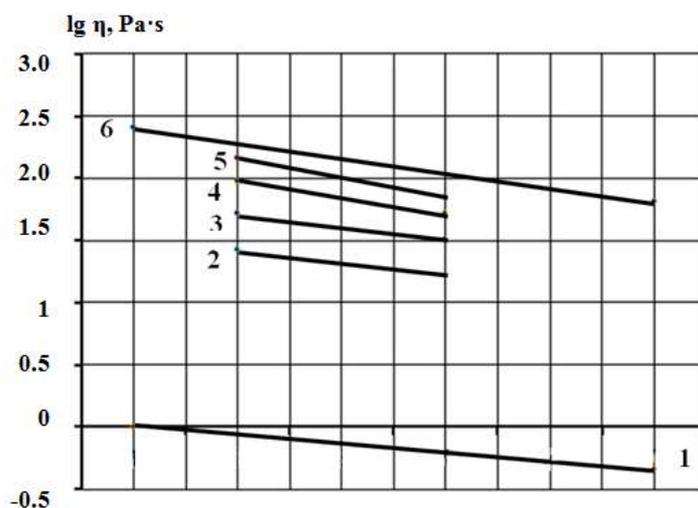


Figure 1. Dependence of viscosity η of NMPB and PBN mixtures (% mass) on temperature T :
 1- 0/100; 2-30/70; 3-40/60; 4-50/50; 5-75/25; 6- 100/0

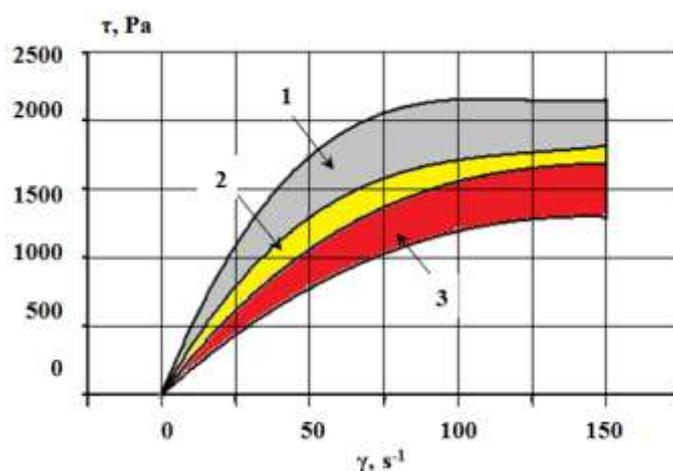


Figure 2 . Hysteresis deformation loop of the composition based on SKDNN with no modified and modified by carbon black as a filling agent . Time of the deformation 140 s^{-1} is 20 minutes.
 1- carbon black modified by n-hexane; 2- carbon black modified by lecithin; 3- no modified carbon black

VULCANIZATION

The vulcanization of low-molecular polymers of butadiene is traditionally carried out using the same vulcanizing systems, which are employed in the vulcanization of analogous high-molecular butadiene rubbers, i.e. by sulfur with accelerators, organic peroxides, parachinonedioxime combined with lead, or manganese dioxides, among others . Rubber-like vulcanized products prepared with such systems are characterized as having insufficient mechanical durability and elasticity, caused by the high number of defects in the rare vulcanization net due to the low length of molecular chains of the oligomer (Figure 3) .

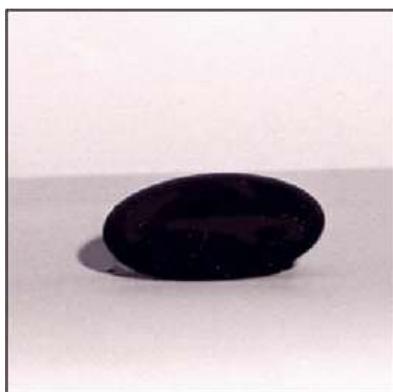


Figure 3. Solidified Sample of LEM

The study examined the vulcanization processes leading to formation of rubberizing ebonite coatings on samples of oligobutadienes of various molecular parameters and microstructures (Table 2),[4].

Vulcanization was carried out by high-frequency current using sulfur with accelerators (bithiocarbamates, thiazoles and thiurames) in the temperature interval of 100-170°C to form ebonites. The ebonites were evaluated according to the value of durability characteristics against the following: strain, firmness, content of bonded sulfur in the vulcanite, relative density of the vulcanite net, and the value of swelling in physically and chemically aggressive media and, following the elaboration of protective coatings their adhesion to carbon steel. The technical findings are discussed throughout.

Table 2. Principal characteristics of studied oligomers

Samples	Molecular weight	Microstructure percentage of links			Viscosity		Non-saturation (against iodine-number)
		Mn	1,4-cis	1,4-trans	1,2	Characteristics	
	Pa·s						
1	740	25	19	56	0.08	1.4	343.3
2	2,140	40	45	15	0.11	1.0	401.7
3	1,750	24	34	42	0.08	1.3	414.5
4	2,350	35	44	21	0.10	1.1	422.3
5	2,130	75.5	23	1.5	0.11	1.2	440.4

In general terms vulcanization reaction of 1,4-cis-oligobutadiene at 150 ° C can be described by the equation [7]:

$$\ln (S_{bb} - S_{cb}) = -K\tau + \ln S_{bb}$$

where S_{bb} - the amount of sulfur introduced into the oligobutadiene, % by mass weight; S_{cb} - the amount of sulfur bonded with oligobutadiene in the course of vulcanization, % by mass weight; K – constant of speed of vulcanization; τ - duration of the vulcanization time, hours. The amount of bounded sulfur during the vulcanization depend on the process time presented in Table 3, [7].

Organic accelerators such as thiuram, dithiocarbamate, thiazole, guanidine etc. introduce in ebonite composition for acceleration of sulfur vulcanization process (Table 4), [7]

For the comparative estimation of the ability of oligomers with a different structure to vulcanize, studies were carried out on model mixtures with sulfur content 23% of the mass, at a temperature of 150°C. After sodium-initiated polymerization, the oligobutadiene sample 1 displayed low values of the molecular weight and non-saturation, and a high content of vinyl links. Results characterize the sample as very slow vulcanization, low durability of ebonites, a low content of bonded sulfur and considerable swelling in hexane.

Table 3. Dependence of quantity of bound sulphur in the vulcanizates based on oligobutadiene (OB)

Quantity of introduced sulphur		Quantity of bound sulphur (% mass) at 150°C							
		Time of vulcanization, (hours)							
Mass parts per 100 mass parts of OB	% mass	1	2	3	4	5	6	8	10
20	16.7	37.4	67.7	-	69.2	-	66.0	68.1	
30	23.0	47.8	71.2		72.2		75.7	77.4	73.5
40	28.5	50.8	76.0	72.5	85.1	75.4	-		
50	33.3	47.8	79.0	54.7	99.8	98.8	99.7	-	
70	41.2	61.1	78.0	63.5	63.4	-			

Table 4. Main accelerators of vulcanization

Chemical name	Chemical formulae	Technical name
Zink diethyldithiocarbamate	$\begin{array}{c} \text{S} \\ \\ [(\text{C}_2\text{H}_5)_2\text{N-C-S-}]_2\text{Zn} \end{array}$	Ethyl Zimate ®
Zinc dimethyldithiocarbamate	$\begin{array}{c} \text{S} \\ \\ [(\text{CH}_3)_2\text{N-C-S-}]_2\text{Zn} \end{array}$	Methyl Zimate ®
Tetramethylthiuram disulfide	$\begin{array}{c} \text{S} \\ \\ [(\text{CH}_3)_2\text{N-C-S-}]_2 \end{array}$	Thiuram
Diphenylguanidine	$[(\text{C}_6\text{H}_5)\text{NH-}]_2\text{C}=\text{NH}$	Guanide
2-Mercaptobenzothiazole		Kaptax

Oligobutadienes from the lithium initiated polymerization (samples 2-4, Table 2) contain mainly linear monomeric links. They are less saturated and therefore, vulcanize more actively. Like oligobutadienes from sodium polymerization, oligomers of this type have a larger induction period before the start of vulcanization.

Out of samples tested, sample 5 - the vulcanization of oligobutadiene synthesized on nickel catalyst was the most effective with the least period of induction. The structure of this sample is mostly linear with predomination 1, 4-cis links, characterized by a high-degree of non-saturation. Vulcanizates prepared from this oligobutadiene are very durable, contain a high concentration of bonded sulfur (17%) and display nearly no swelling in hexane, which means a high number of crosslinks in the oligomer. The microstructures of the monomeric links, confirmed by the roughly equal incline of the curves in Figure 4 for all oligobutadiene samples, were shown to have little influence on the vulcanization rate in its active period (Table 5) [4].

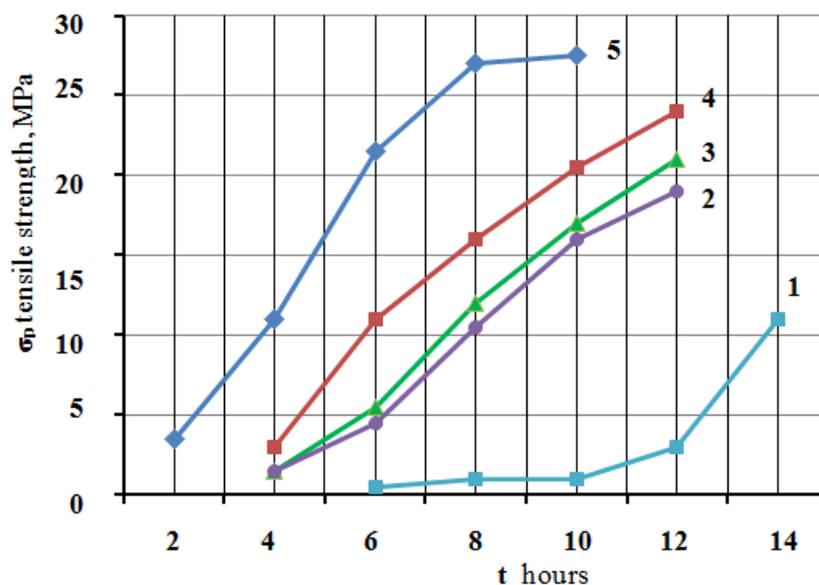


Figure 4. Tensile strength of sulfur vulcanizates based on various oligobutadienes (Table 2) depending on the duration time of the vulcanization at 150°C where the initial dose of sulfur in the composition is 23 % of the mass

Table 5. Oligobutadiene influence on the properties of vulcanizates prepared from a composition with 23% of its mass, sulfur.

Parameter	Sample number by Table 2				
	1	2	3	4	5
Tensile strength (MPa)	1.5	8.4	10.5	16.8	25.5
Swelling in hexane at 20°C during 10 hours (%)	5.7	1.3	4.9	4.0	0.0
Content of bonded sulfur in the vulcanite, mass (%)	11.0	12.2	12.1	12.2	17.0

The increased dose of sulfur in the composition treated by vulcanization does not change the general influence character of the microstructure of the oligobutadiene links on its vulcanization. Vulcanization of 1,4-cis oligobutadiene is much more active than that of 1,2 oligobutadiene with a sulfur content of 23 or 33 % of the composition mass.

The durability dependence, bonded sulfur content in the vulcanizate, and the relative density of the vulcanization net of the duration time of vulcanization of compositions based on high-active 1,4-cis oligobutadiene are shown in Figure 5 [4]. If the content of sulfur is less than 16.7 % of the mass, the rate of vulcanization reduces and the prepared vulcanizate display low durability (Figure 5a). The content of bonded sulfur in the vulcanite prepared from such a mixture seems high enough just after two hours of vulcanization when the durability of the vulcanite and the relative density of the net are still very low.

Similar results have been obtained when the dose of sulfur in the composition increased to 23% of the mass that corresponds to 30% of the mass from the amount of oligobutadiene (Figure 5b). The same results were found by increasing the dose of sulfur to 28.6 % and 33.3 % of the mass (Figure 5c and 5d) .

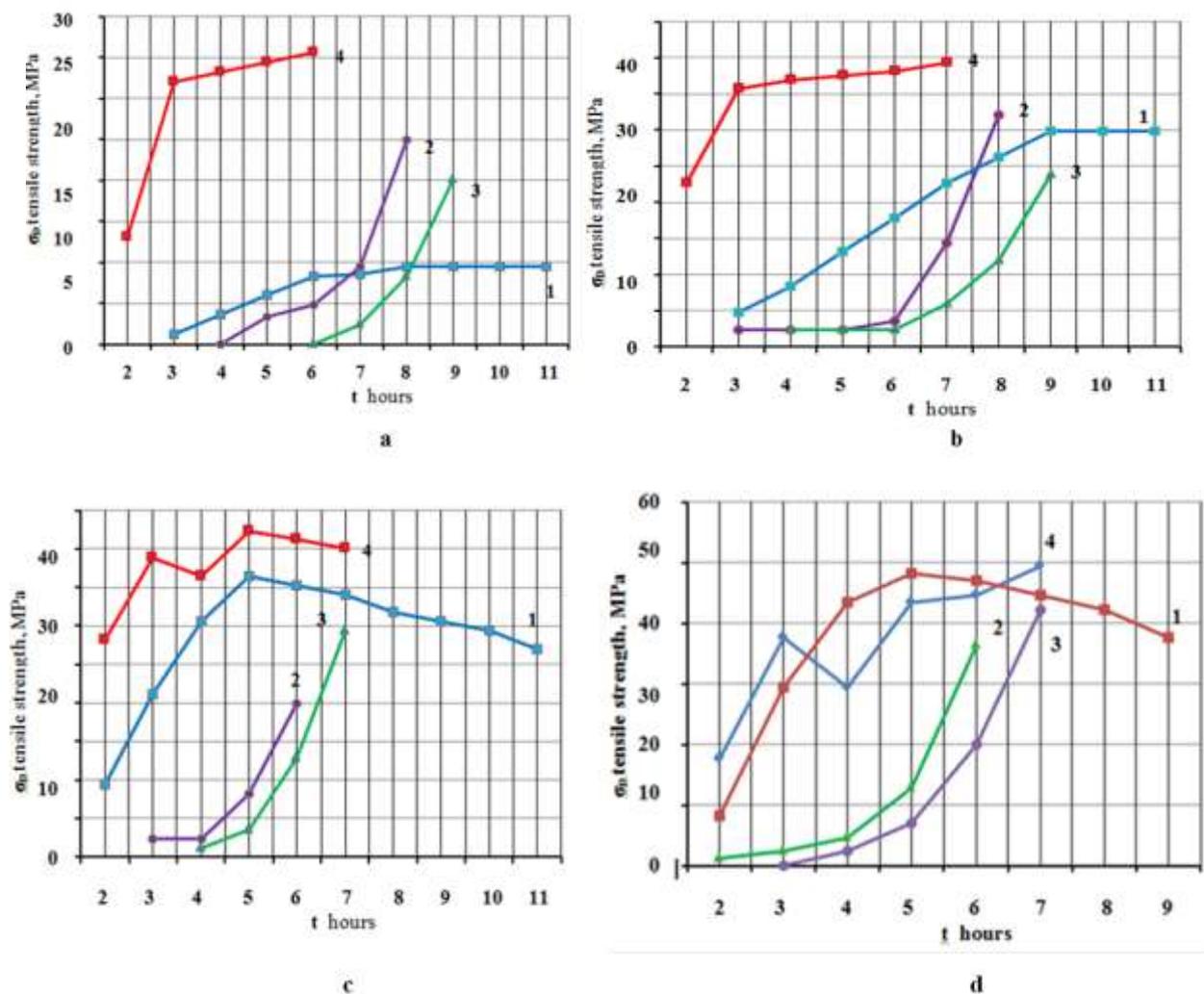


Figure 5. Correlation of the tensile strength in MPa(1), relative density of the vulcanizate net form the equilibrium swelling in hexane at 20°C (2) and 50°C (3) and the content of bonded sulfur in vulcanizate (4) with sulfur's initial dose: (a-16.7%, b-23.0%, c-28.6%, d-33.3%) vs the vulcanization duration time at 150° C

The increase in the duration time of vulcanization does not lead to a significant change in the amount of bonded sulfur interacting with oligobutadiene during the first two hours; however, the durability of the vulcanite and the density of the vulcanization net seriously rise. Moreover, with a high enough dose of sulfur (28.6 and 33.3%), the increase in vulcanite durability of and the density of the vulcanization net in the period between two and four hours of the vulcanization, may be accompanied by the reduction of the content of bonded sulfur after several moments.

The obtained experimental data prove that in the first stage of vulcanization, sulfur joins oligobutadiene to form rare polysulfide bonds which do not assure enough density of the vulcanization net and the vulcanite durability. In the second stage of vulcanization the polysulfide bonds are broken up on account of their insufficient durability, and transformed into bonds with a lower content of sulfides while the released sulfur forms new horizontal low-sulfide bonds that raise the density of vulcanization net. The results indicate that the process mechanism of the vulcanization of low-molecular polybutadiene by sulfur with the forming of ebonite, occurs in the following two-stages [4]:

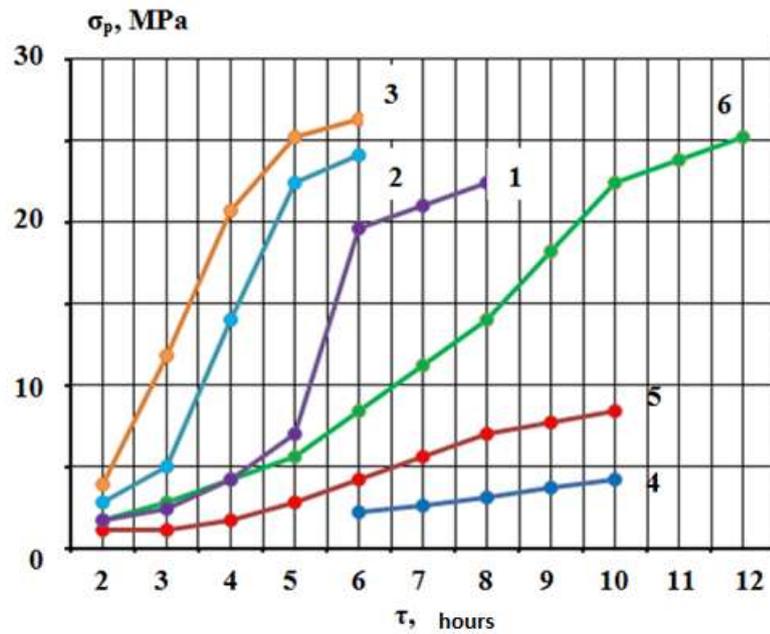


Figure 6. Dependence of strength of the vulcanizates (σ_p) based on oligobutadiens SKDSN (curves **1-3**) and PBN (curves **4-6**) on time of vulcanization (τ) at 150°C. Sulphur quantity (% mass): curves **1,4** – 23%; curves **2,5** – 28.6%; curves **3,6** – 33.3%.

The temperature of vulcanization significantly influences the strength of the vulcanizates and adhesive properties of ebonite coatings. At 100°C, without effective accelerators, the sulfur vulcanization of the studied oligobutadienes cannot be carried out. Using ultraaccelerators like zinc biethylthiocarbamate or tetramethylthiurambisulfide, enables the vulcanization of oligobutadiene to form ebonite coatings with enough durability and chemical stability coatings at 100°C within 20-25 hours of vulcanization.

Raising the temperature of vulcanization from 125 to 175°C leads to a near linear increase of the tensile strength of vulcanizates prepared from compositions on the base of 1,4-cis oligobutadiene with sulfur without accelerators for the vulcanization duration of six to eight hours (Table 6), [4].

The correlation between the temperature and the adhesion value of the coatings, prepared from the same compositions, is characterized by obvious extreme values, the maximum being at 150°C.

Table 7 [7] shows the increase in hardness of vulcanizates based on oligobutadiene samples NMPB with a viscosity 29-311 Pa·s at a low temperature vulcanization (20-25°C) in the presence of 1,4 benzoquinone dioxime and manganese dioxide. Rubbery vulcanizates get quite stable properties after 5-10 days of outdoor exposition.

Comparative properties of vulcanizates obtained at room temperature based on NMPB with use of various vulcanizing systems:

- 1,4 benzoquinone dioxime (1,4BD) with manganese dioxide (MD) ,
- sulphur with zink diethylthiocarbamate (ZDDC),
- benzoyl peroxide (BP)

are presented in Table 8 [7].

Table 6. Durability and adhesion of vulcanites and coatings prepared from compositions with a sulfur content of 23.3% of the mass

Vulcanization duration (hours)	Characteristics at the vulcanization temperature T, °C					
	Tensile strength, MPa			Adhesion at breaking, MPa		
	125	150	175	125	150	175
2	1.2	4.8	20.2	<0.1	2.3	1.2
4	1.3	10.2	29.6		3.1	0.8
6	2.4	18.8	38.4		4.8	1.2
8	3.5	25.2	51.3		8.0	2.0

Table 7. Hardness of the rubberlike vulcanisates based on oligobutadiene NMPB with 1,4 benzoquinone dioxime and manganese dioxide

Viscosity at 25°C Pa·s	Hardness (Shor A)					
	Cure time in air (days)					
	1	2	4	6	8	10
29	0	12	30	44	53	60
87	15	25		43	60	62
122	17	18		40	47	60
140	7	23	43	53	58	
165	15	27	42	56	60	
311	12	30	29	35	57	

Table 8. Properties of vulcanizates and covering from compositions based on oligobutadiene NMPB produced at temperature 20-25°C

Property	Vulcanization agents and their dosage (mass parts per 100 mass parts of NMPB)		
	1,4BD(5) +MD(15)	Sulpur (30) +ZDDC (15)	BP (4)
Tensile strength, MPa	0.2-0.4	-0.2-0.5	4.8
Eelongation per unit length	80-120	130-140	70-90
Rersidual elongation	10-25	8-10	3-5
Hardness (Shore A)	58-62	32-35	70-82
Change of mass an 20 °C in hexane, %	-23.9	-29.7	-21

By increasing the dosage of sulfur (50 mass parts per 100 mass parts of oligomutadiene) and postvulcanization at 120-150 °C can achieve a significant increase in the strength of vulcanizate (Table 9).The viscosity of the oligobutadiene has a significant impact on the strength of the vulcanizate obtained by the two-step process (Table 10), [7].

Table 9. Strength of vulcanizates based on the mixtures of oligobnutadiens NMPB and SKDNN during the after-vulcanization process at 120-150 °C

No	NMPB / SKDNN (mass parts)	Dosage of the agents of sulphur vulcanization (mass parts per 100 mass parts of the mixture)		Strength of vulcanizate (MPa)	
		Sulphur	Accelerator	150 °C, 6 hours	120 °C, 20 hours
1	95/5	30	-	9.6	7.3
2	90/10	50	-	26.1	6
3				Kaptax (2)	30.5
4	95/5		34.0	28.9	
5	90/10		Kaptax (3)	35.5	29.0
6			Kaptax + Thiuram (2+2)	35.7	29.7
7			95/5	Kaptax + Methyl Zimat®	35.3

Table 10. Tensile strength of the vulcanizates based on NMPB

Viscosity of NMPB (Pa·s)	Strength, (MPa) during time of vulcanization (hours)				
	2	4	6	8	10
27	10.0	19.8	21.4	23.2	28.4
208	6.5	12.3	15.0	17.3	17.4
465	3.5	4.8	9.2	12.5	16.8

PERFORMANCE CHARACTERISTICS OF VULCANIZATES

To investigate the principal application properties of ebonite vulcanizers and coatings, the study examined prepared samples based on the most active vulcanizable by sulfur 1.4-cis oligobutadiene with the optimal receipt and vulcanization regime that allowed a gain in the upper density of the vulcanization net characteristics in durability and adhesion. System properties are as follows.

Thermo-Mechanical Properties

Thermo-mechanical curves of ebonite vulcanizates in coordinates “relative lengthening vs temperature” are monotonically rising curves (Figure 7) which do not have a zone of glass transition, that proves the thermoplasticity of these polymeric materials. Using carbon black as a filler the thermo-deformation ability of ebonite vulcanite slightly decrease in comparison with a non-filled ebonite vulcanite [4].

Sorption and Diffusion Properties

Where water is considered the most widespread component of aggressive media acting, the study examined its effect on ebonite vulcanizates and coatings prepared from compositions based on oligobutadienes.

The kinetic curves of water sorption by ebonite vulcanizates have a long-lasting saturation plate. Involving the inert filler (technical carbon) reduces the amount of water sorbed in equilibrium. The initial parts of deformation curves of water sorption are straight lines (Figure 8) representing the Fick-like diffusion of water into ebonite vulcanizates. The study of the correlation of water-sorption of ebonite vulcanizates, and temperature between 20 and 80°C, revealed that the values of the diffusion coefficient well satisfy the Arrhenius equation [4].

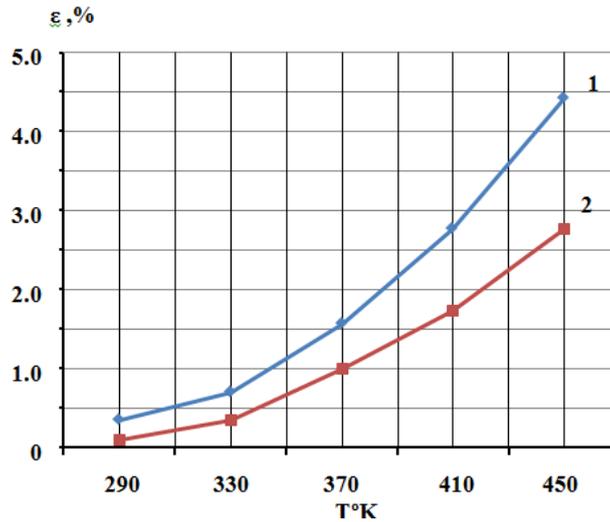


Figure 7. Thermo-mechanic curves for non-filled (1) and filled (2) ebonite vulcanizates

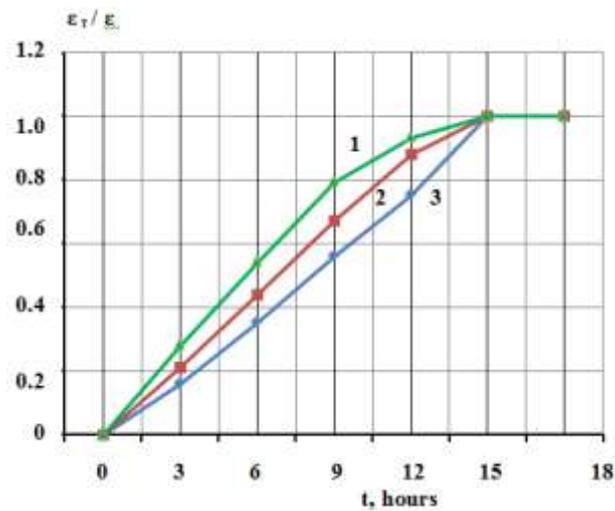


Figure 8. Correlation between the relative increasing of the linear deformation of ebonite and duration time of its staying in water at 80°C: **1** - without filler; **2** and **3** - with active carbon PM-15, 9 and 20 mass % respectively

One can see that values of the activation energy during the process of water diffusion in ebonite vulcanizates do not significantly depend on the presence of filler in the composition, which are 49-53 kJ/mole only.

The weakening of the adhesive bond "metal-ebonite coating," is observed during absorption of water after a certain period of delay time; numerical values of it are given in Table 11[7].

Table 11. Delay time of water penetration into ebonite covering

Composition	Time delay (hours) for thickness of the covering (mm)		
	0.2	1.0	2.0
No fillers	38.5	963	3861
PM (20% mass parts)	464	11583	46389

Chemical resistance

The density of the vulcanization net and the structure of vulcanization bonds are the main influence on the chemical stability of ebonite vulcanizates, which is determined by the type of vulcanization system selected and the conditions of carrying out vulcanization. Accelerators present in the vulcanizate increase chemical stability by reducing the amount of sulfides in the horizontal bonds as their density rises.

The chemical stability of the reagents also influences the chemical stability of ebonite vulcanizates. The comparison of the correlation between the rising of the mass of the sorbed liquid and the duration time of ebonites exposed in mineral acid solutions provides supporting evidence to conclude that their initial parts for water sorption are straight lines. The value of the coefficient of diffusion in acid solutions is equal to that of water and does not depend on their chemical composition. Nevertheless, after gaining saturation, water solutions of nitric and sulfuric acids exhibit a reduction of mass increase, meaning that chemical changes cause the removal of products for chemical reactions. The study found that nitric acid has a stronger reaction with ebonite vulcanizates, which can be attributed to its oxidizing ability. Solutions of hydrochloric and phosphoric acids cause positive swelling of ebonite vulcanizates [4].

Chemical resistance of the vulcanizates obtained at 150 ° C with use various types of oligobutadienes as a vulcanized basis is little different from each other (Table 12), [7].

Table 12. Chemical resistance samples of vulcanizates based on oligobutadiens modified by thermoelastoplasts (700 hours testing at 20 °C)

Bonding base		Hardness (Shore A)	Change of mass of the samples in media (%)		
Thermoelastoplasts	Oligobutadien		50% H ₂ SO ₄	35% HCL	20%NaOH
Styrene-Butadiene Thermoplastic Elastomer DST-30R	Polyoil-110	96-100	0.4	1.2	0.4
			0.1	0.9	0.2
	Polyoil-130	94-98	0.3	2.1	1.5
	SKDSN	89-92	0.5	4.0	2.3
Oil-extended thermoelastoplast TRS 75/90	Polyoil-110	81-85	0.8	29*	8*
	Polyoil-130	92-96	1.0*	13*	2.3*
		97-100	0.2`	8.2*	1.7*
	SKDSN	90-91	0.5	7.9	2.3
Thermoelastoplast TRS 75/90, no oil	Polyoil-110	97-100	0.3	4.5	4.1
	Polyoil-130		0.7	3.5	0.4
	SKDSN	95	0.8	3.3	0.6
		96-100	0.4	3.7	
			0.2	2.6	0.5

* Increase of the mass is continued

NPBM-oligobutadiene vulcanizates produced with use of mixed vulcanizing system consisting of (mass parts per 100 mass parts of NPBM):

- 1,4 benzoquinone dioxime (5 mass parts)
- Manganese dioxide (15 mass parts)
- Sulphur (30 mass parts)
- Technical carbonate (15 mass parts)

show satisfactory chemical resistance at a vulcanization temperature of 150 ° C (Table 13), [7].

Table 13. Chemical resistance samples of vulcanizates based on NPDM-oligobutadiene with application of mixed vulcanization system.

Aggressive medium 20°C	Time of after-vulcanization at 150°C, hours	Change of vulcanizate mass during exposition (days)			
		15	30	45	60
20% NaOH	2	0.8	1.1	1.2	
	6	0.3	0.4	0.45	0.48
	8	0.2	0.3		
	10				
20% H ₂ SO ₄	2	0.43	0.62	0.71	0.79
	6	0.35	0.45	0.56	0.60
	8	0.25	0.38	0.42	0.43
	10	-0.07	0.08	-0.08	
20% HCl	2	0.4	0.58	0.61	0.62
	4	0.38	0.5	0.60	
	6	0.65	0.42	0.43	
	8	0.18	0.27	0.32	
	10	0.1	0.16	0.17	0.19

High chemical resistance of NPDM vulcanizates is provided at 100°C (Table 14), in case of application of the vulcanization accelerator Ethyl Zimate® [7].

Structure of the composition (mass parts per 100 mass parts of NPBM):

- Ethyl Zimate® (15 mass parts)
- Sulphur 30 (mass parts)

Chemical resistance of the ebonite vulcanizates based on the various oligobutadienes modified by divinyl-styrene thermoelastoplast (48% of mass) is shown in Table 15 [7].

Increasing of chemical resistance of LEM-coverings is achieved by adding oxide-contained additives which are interacting with diffusing aggressive media and forming new phases of high-strength crystalline hydrate complex-nonorganic glue-cement (Figure 9), [3].

Adhesion Stability of Ebonite Coatings

The effectiveness and strength of ebonite coatings are determined by their adhesion properties, not only at the time of application, but over time after exposure to various factors such as: aggressive medium, temperature, electrical field, among others.

The adhesion of ebonite coatings is significantly influenced by internal resting tensions following the thermal vulcanization and causing compression by 3.2-4.5 percent. The optimal regime of vulcanization results in the initial value of adhesion to most steels at approximately 8-12 MPa (for breaking). With water sorption, the weakening of the adhesion bond “metal-coating” is observed as a result of “retard” due to a long duration time of water penetration to the interphase surface.

When the speed of water transportation on the frontier “metal-ebonite coating” was measured, it was found that in such a case, water transportation is not through the capillary, but rather following the diffusive law, or the value of the diffusion coefficient which is calculated from the water penetration constant. This parameter shows that the kinetics of the change of the adhesion durability of the ebonite coating in contact with water is determined by its diffusive properties, and one of the ways of stabilization of adhesion consists in the decrease of its diffusive properties. One way of stabilizing adhesion is by decreasing its diffusive permeability. This approach was considered as follows.

Table 14. Chemical resistance samples of vulcanizates based on NPDM-oligobutadiene with application Ethyl Zimate®

Aggressive medium 20°C	Time of after-vulcanization at 100/150°C, hours	Change of vulcanizate mass during exposition (days)			
		15	30	45	60
20% NaOH	2/2	-4/0.4	-6/0.6	-7/0.65	-8/0.66
	5/4	0.9/0.4	1.3/0.45	1.6/0.55	1.9/0.54
	10/6	0.5/0.18	1/0.3	1.1/0.4	1.2/0.45
	15/8	0.5/0.1	1/0.19	1.1/0.21	1.2/0.22
	20/10	0.4/0.1	0.6/0.19	0.9/0.21	0.9/0.22
20% H ₂ SO ₄	2/2	-1/0.1	-1.6/0.15	-2/0.18	-2.2/0.2
	5/4	0.2/0.09	0.25/0.1	0.23/0.17	
	10/6	0.2/0.08	0.24/0.09	0.22/0.11	0.26/0.18
	15/8	0.21/0.09	0.25/0.13	0.24/0.13	0.25/0.15
	20/10	0.2/0.08	0.26/0.09	0.25/0.17	0.25/0.16
20% HCl	2/2	3.8/0.8	6/0.45	7.9/0.62	9/2
	5/4	0.04/0.35	0.05/0.41	0.05/0.56	0.05/0.6
	10/6	0.04/0.3	0.05/0.38	0.05/0.55	0.05/0.5
	15/8	0.2/0.27	0.4/0.36	0.6/0.43	0.6/0.47
	20/10	0.2/0.25	0.4/0.32	0.6/0.4	0.6/0.42

Table 15. Chemical resistance samples of vulcanizates based on same NPDM-oligobutadienes modified by divinyl-styrene thermoelastoplast during exposition in 35% sulphur acid at 20°C (vulcanization at 150 °C)

Kind of oligobutadiene	Change vulcanizate mass during exposition (days)					
	2	4	10	14	35	261
Polyoil-110	0.46	0.47	0.49	0.60	1.0	2.2
Polyoil-110	1.0	1.24	1.48	1.76	2.5	6.0
SKDSN	1.1	1.76	2.24	3.25	4.3	9.2

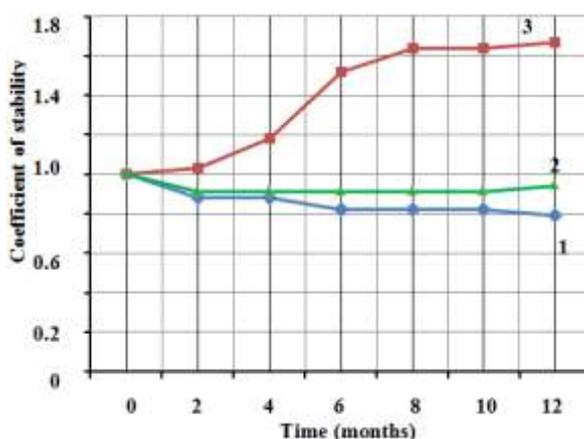


Figure 9. Depending of chemical resistance of LEM-coverings on oxide-contained additives: 1- without adding, 2- 2% of additives, 3- 7% of additives

When water penetrates to the interphase surface of the ebonite coating, the adhesion decreases, but is then restored after some time. For example, if the adhesion is decreased fast enough (within a few hours) the adhesion will be restored after a few weeks, or months. Testing found that once samples coated with the ebonite coating were completely dry, the adhesion fully returned to its original strength.

Thermoadhesiogrammes of adhesives prepared by the method "heating-cooling" exhibit an extreme temperature adhesion dependence. For temperatures below the critical range (140-144°C - about the melting point of sulfur) the curves display hysteresis, whereas for higher temperatures the curves appear close. The calculated value of energy activation for the process of adhesive bond breaking, when the coating is removed, is 97 kJ/mole [4].

The thermoadhesiogrammes of the joint "metal-ebonite coating" obtained in heating-cooling mode, show the extreme nature of adhesion depending on the temperature (Figure 10). At temperatures below the critical strongly pronounced hysteresis is manifested whereas in above the critical area the curves are almost identical [7].

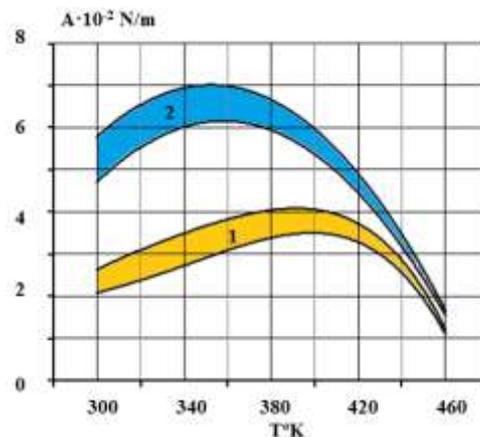


Figure 10. Thermoadhesiogrammes ebonite coverings based on NMPB (1) and mixture NMPB with SKDNN in the ratio 1:1 (2)

In many cases ebonite coating are intended to protect the inner surface of cylindrical apparatus. In this connection we consider the system in the form of a hollow circular cylinder with an ebonite coating on the inner surface taking into account the characteristic properties of the polymer at the interface with the metal (Figure 11), [7].

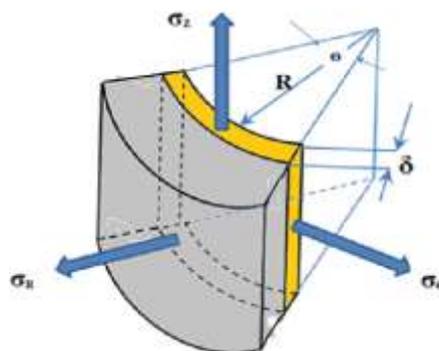


Figure 11. Ring sample of metal cylinder with inner ebonite covering

Calculation's results of the internal stresses distribution in a circular sample ($R = 11$ cm) with an ebonite coating are presented in Table 15, [7].

Table 15. Subsurface stresses into ring metal simples with inner ebonite covering

δ mm	Temperature °C	Subsurface stresses (10^5Pa)		
		σ_R	σ_Θ	σ_Z
1	70	-1.51	-84.5	
2	48	-1.10	-58.2	-59.4
3	28	-1.90	-32.4	-34.0

It should be noted that the layer of ebonite coating is compressed. Because of this in defect places of the coating may be a phenomenon reminding the local buckling, resulting in delamination of the structure.

Adhesion strength of the “metal-ebonite coating” system does not significantly change under electric field below the ultimate tension. The decreasing in adhesion takes place only in the zone corresponding to the critical temperature. In this situation, there is a threshold of the field tension; its value depends on the sign of the potential applied to the coating and the coated material.

Electrochemical Protection Properties of Ebonite Coating

The results of electrochemical studies are in good agreement with measurements of adhesive strength. Coatings with high adhesion are characterized by the high protective properties. Increase of polybutadien’s viscosity in the system "metal-ebonite coating" tends to decrease the current of passivation resulting in increase of anticorrosion effect. Introduction in NMPB based ebonite compositions polymers with functional hydroxyl and carboxyl containing groups improves both the adhesion and protective properties of the coatings.

Oligomers with oxygen-containing functional groups can be considered as surfactants capable to chemisorption interaction with the active centers of a metal surface. In response to chemisorption of surfactant-oligomers electric fields which arise in this area produce passive regions (Figure.12) [7].

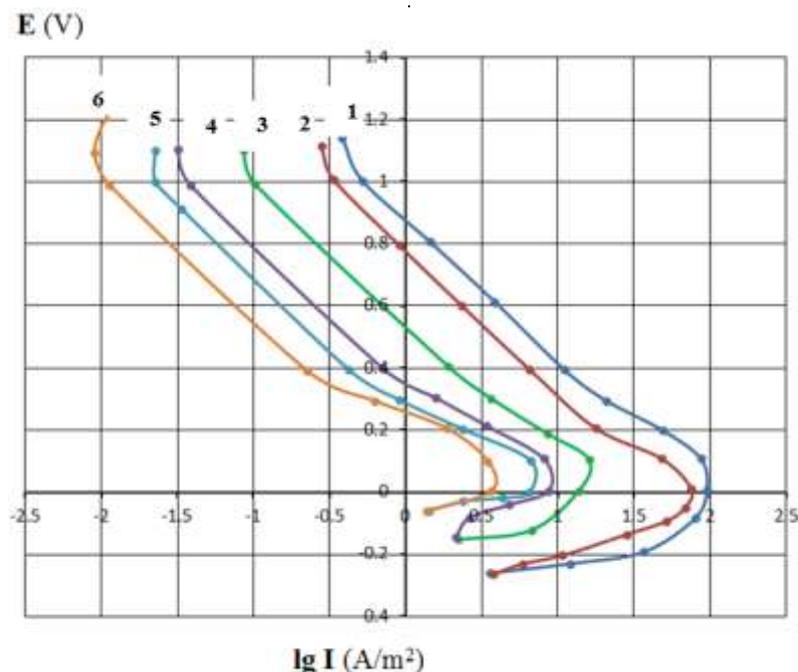


Figure 12. Curves of anode polarization of the low –alloyed steel with ebonite coating based on NPBM oligodiene . **1-** no modifiers; **2-6** with modifiers containing following groups: **2-** 1.17% OH; **3-** 2.8%COOH; **4-** 2.3%COOH; **5-** 1.4%OH; **6-** 1.5%OH in 0.1M H_2SO_4

Kind of vulcanizing system and the degree of ebonite coating vulcanization effect on its electrochemical protective properties. Figure 13 [7] demonstrates the dependence of the frequency dispersion coefficient K_0 of the anodic polarization (Figure 12) on exposure time ebonite coating based on oligobutadiene NMPB with thickness $\pm 250 \pm 20 \mu\text{m}$ vulcanized at temperature 150°C (coating №1)⁵ и 100°C (coating №2)⁶ in a few corrosive environments.

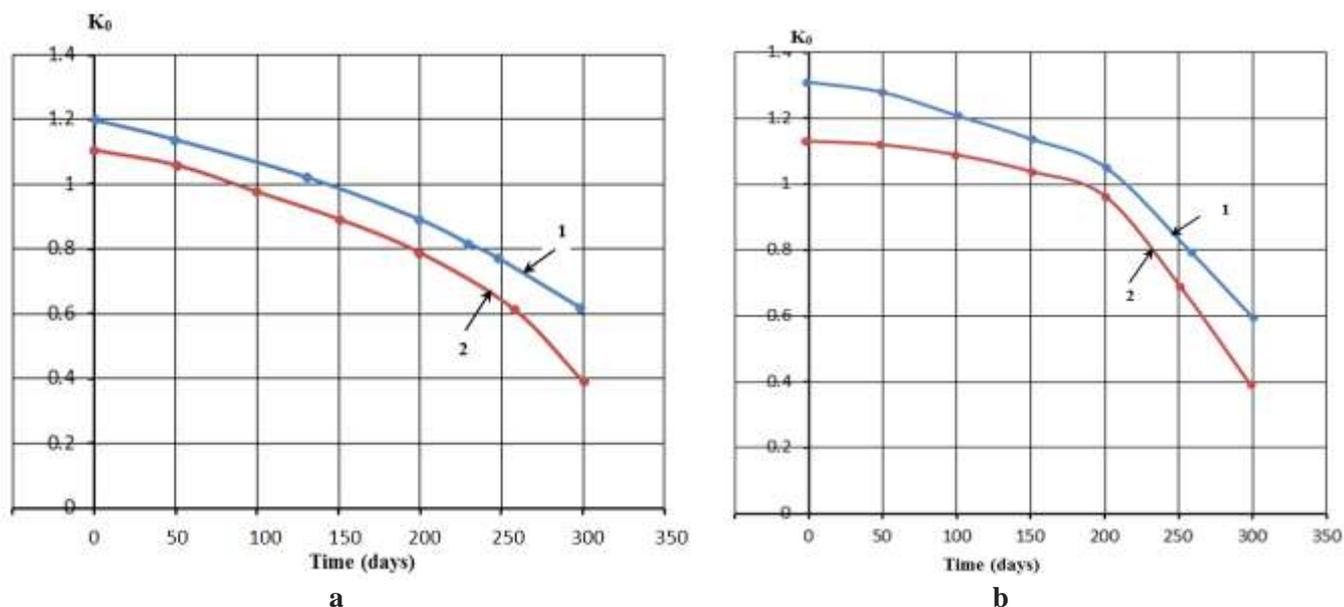


Figure 13. Dependence of the frequency dispersion coefficient K_0 of the anodic polarization (Figure 12) on exposure time ebonite coating in a- 30% solution of sulfuric acid; b- 30% solution of hydrochloric acid. 1- sulfur vulcanized coating at 150°C ; 2- sulfur and Ethyl Zimate ® vulcanized coating at 100°C

One can see that designer useful life ($K_0=1$) of the first coating is about 180 days exposition in solutions of hydrochloric and sulfuric acids whereas for second coating we have less than 130 days in 30% solution of sulfuric acid but more 200 days in 30% solution of hydrochloric acid. Therefore at the deeper vulcanization (150°C) dependence of kind of corrosive environment on the diffusive permeability of vulcanizate is less noticeable than for the low-temperature curing at a temperature of 100°C .

TECHNOLOGICAL PROCESS OF MANUFACTURE AND PROPERTIES OF EBONITE MIXTURES

The principal application characteristics of ebonite coatings, prepared from liquid non-solution compositions based on 1,4-cis oligobutadiene of the hydrocarbon structure are presented in Table 16 [4].

Schematic diagram of manufacturing of the liquid ebonite mixtures are shown in Figure 14, [7].

One-pot composition

One-pot ebonite compositions do not contain solvents and are produced on a basis of the low-viscosity oligobutadienes, therefore they are safe during storage and use. A feature of these compositions is that all the ingredients are in one heterogeneous system.

As the bond matrix of the ebonite compositions ES-100_T and GES-1, was used oligobutadiene SKDNN (Table 17), [7].

⁵ Structure of composition (mass parts): NMPB -100, sulfur- 30, Kaptax-3, carbon black-20;

⁶ Structure of composition (mass parts): NMPB -100, sulfur- 30, Ethyl Zimate ® -103, carbon black-20

Double-pot composition

Double-pot compositions consist of an elastomer binder (basis) and the vulcanizer (paste). Basis of the double-pot compositions GES-2, GES-3 and GES-04M is butadiene and nitrile butadiene oligomer. Low-viscosity oligobutadiene is used as vulcanizer paste. Technological and operation properties of the double-pot compositions and coatings are presented in Table 18 [7].

APPLICATIONS OF EBONITE COATINGS

With superior chemical resistance and functionality, LEM can replace the conventional, even-surface rubber sheet linings found in a multitude of products and industries and is commercially available in thicknesses of 2.5 to 4.0 mm. It can be easily applied using such simple coating techniques as brushing, rolling, spraying, flooding or dipping.

Before application a vulcanized paste is introduced into the composition to give preliminary curing to the LEM-layer in air at 20 - 25°C, which results in forming a rubber-like vulcanizate.

Unlike the traditional multi-layered rubber sheets or liquid rubberizing compounds, LEM is most efficient in protecting the intricate shaped and perforated parts of pumps, fans, centrifuge rotors, small diameter pipes and outlets, shut-off and control valves, stirrers and many other complex parts. As a break-through product, LEM offers a flexibility not found in its traditional predecessors (Figure 15),[8]

Table 16. Properties of ebonite coatings prepared from oligobutadiene

No.	Parameter	Units	Value
Liquid Composition			
1	Color :	Yellow-gray, White, Black	
2	Viscosity	Pa·sec	80 to 280
3	Method of Coating :	Brushing, Spraying, Dipping	
4	Condition of vulcanization (without pressure)		
	<ul style="list-style-type: none"> • heat carrier • temperature 	°C	Hot dry air 100 to 150
5	LEM consumption per 1mm of coating thickness	Kg/m ²	0.9 to 1.0
Coating after vulcanization			
1	Volumetric shrinkage	%	3.2-4.5
2	Tensile strength	MPa	20-32
3	Shore hardness ("D")		55-60
4	Impact strength	N·m	>50
5	Adhesion strength to steel substrate by tear test	MPa	20-32
6	Strength of the contact with the metal:		
	<ul style="list-style-type: none"> • with Steel-3. at breaking • with aluminum, at stripping away 	MPa	8-10
		N/m	175-400
7	Thermal expansion at heating to 130°C	%	1.5-2
8	Thermal stability of the adhesive coating	°C	120-130
9	Diffusion coefficient	sq.m/s	(0.7-4.8)E-14
10	Cyclic stability (up to exfoliation) temperature cycle from -20°C to 100°C		90
11	Electrical stability "heating-cooling" regime [(+20)-(+100)-(-20)°C]	MV/m	10-27
`	Chemical stability of coatings (maximal concentration):		
	a. in acids:		
	<ul style="list-style-type: none"> • nitric • sulfuric 		10 (to 20 °C)
			70 (to 20 °C)
			50 (to 60 °C)
	<ul style="list-style-type: none"> • hydrochloric • fluoric • acethyc • phosphoric 		35 (to 20 °C)
			40 (to 20 °C)
			50 (to 20 °C)
			80 (to 20 °C)
	b. `in salt solutions:		
	<ul style="list-style-type: none"> • Al/Zn sulfate • Na/Ca chloride • K/Na dichromate 	%	20 (to 60 °C)
			10 (to 60 °C)
c. in alkalis:			
<ul style="list-style-type: none"> • Na/K hydroxide 	%	40 (to 20 °C)	
d. in organic media:			
<ul style="list-style-type: none"> • acetone • benzene • ethanol, butanol • oils 		to 20 °C	
		to 60 °C	
12	Estimated delay of exploitation of coatings (2mm thickness) in 30% - sulfuric and hydrochloric acids, at 20°C	years	4.1-5.3

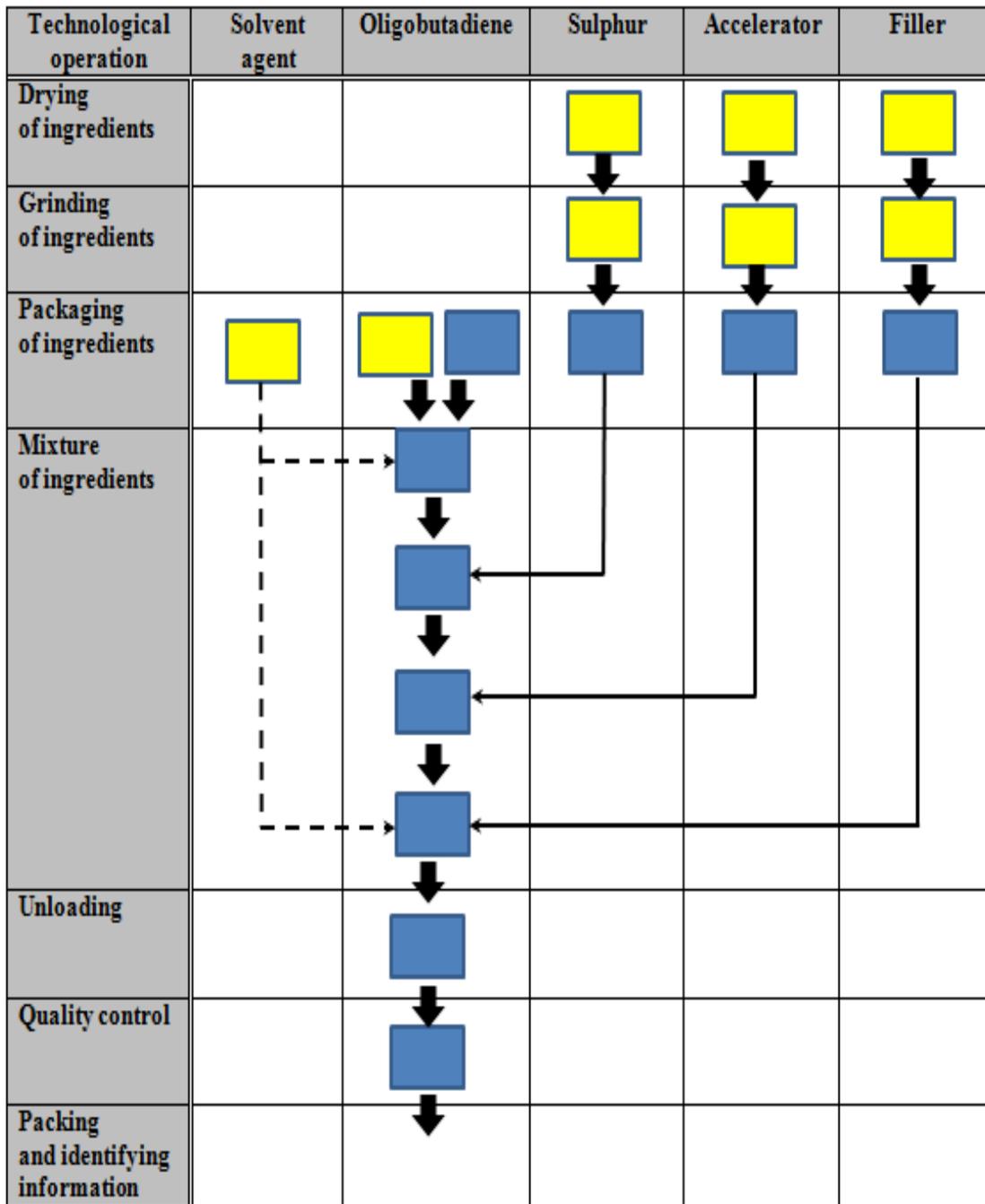


Figure 14. Schematic diagram of manufacturing of the liquid ebonite mixtures

Table 17. Composition and properties of rubber ebonite mixtures and coatings

Factor	Composition	
	GES-1	ES-100t
Formulation of the mixture, mass parts		
SKDNN	100	
Sulhur	30	
Carbonate	20	
Thiuram	-	5
Zink oxide	-	
Technological properties		
Surface appearance	Homogeneous viscosity liquids, black color	
Viscosity (75% solution in toluene at 20°C), sec	50	45
Temperature of vulcanization, °C	150	100
Time of vulcanization, hours:		
• Intermedia coat	2	5
• Last coat	8	25
Material consumption at application of one layer, kg/m ²	0.4	0.38
Physical-mechanical properties		
Rupture resistance	26.0	12.5
Adhesion strength with steel substrate, MPa, (no less)	8.0	8.2

Table 18 Properties of two-pot ebonite compositions and coverings

Composition	Technological properties			Operation properties	
	Method of application	Thickness of one-layer coating, mm	Mode of vulcanization °C · hour	Rupture resistance, MPa	Adhesion strength with steel substrate, MPa
GES-2	by brush	0.4-0.7	150·4÷5	26	9.8
GES-3	by applicator	0.8-1.5	150·3÷4	28	10.4
GES-4M	by brush or by applicator	0.3-0.5	150·4.5÷5	35-42	10.0



Figure 15. Examples of application of rubber covering

The recommended areas of application are given on the Table 19.

Table 19. The recommended area of LEM application

Area of industry	Protective equipment	Aggressive medium	Working temperature °C	Full time of testing in the working conditions
Chemical Industry				
<ul style="list-style-type: none"> • Linings made from LEM will protect the intricate surfaces of filtered centrifuges, ventilators and air ducts cleaning systems from blended acids solutions, vapors of HCl, HF, salt solutions and oxides of nitrogen, chlorine and bromine. • Parts coated with LEM are operating in oxalic acid working conditions up to 95° -100° C. • LEM will effectively protect vacuum pumps from vapors of HCl and scrubbers from NiCl₂. • Sheet-steel cylinders of gas collectors coated with LEM will find protection from H₂S and vapors of HF 				
Chemical reagents	Filtered centrifuges	Master solutions	30	18
	Ventilators	Vapors of HCl, HF and oxides of nitrogen		24
	Ventilators and air ducts	Vapors of HCl, salt solutions, oxides of nitrogen and chlorine-bromine		21
	Drying effects	Oxalic acid	95-100	16
	Vacuum pump	Vapors of HCl	30	24
	Scrubber	NiCl ₂		12
	Cryolite	Sheet-steel cylinders of gas collectors	H ₂ S and vapors of HF	48-54
Fertilizers	Picke pipeline	Solution of KOH and NaOH	80-90	24
Synthetic rubber	Mixing tank	H ₂ SO ₄	80	16
Refrigerant	Bottom boxes	Vapors of HF	60-70	11
Agricultural industry	Tanks	Solution of KOH and NaOH, liquid complex fertilizers	20-30	24
Automobile industry	Bottom of cars	Chloride salts, sea water, big abrasive attack	(-40)- (+45)	
Marine	Variety of applications	Corrosive salts		

CONCLUSION

Following the results obtained from conducting experimental studies on vulcanization processes for oligobutadienes. It was found the most effective bonding material for non-solution compositions to Ebonite coatings which display excellent properties in durability and adhesion. Ebonite coatings may be applied to prepared surfaces by conventional methods used in lacquer-paint coating technology which decreases significantly the time needed for rubberizing of complex-profile or perforated techniques.

REFERENCES

1. Harper C.A. (Ed.), *Handbook of Plastics, Elastomers and Composites*, New York, NY., 1996
2. Weismantel G.E. (Ed.) *Paint Handbook*, New York, NY.,1981
3. Figovsky O., Blank N., Liquid Ebonite Mixtures for Anticorrosive Coverings , *NACE International; Italia Section / Associazione Italiana di Metallurgia by NACE International Italia Section*, Monza; 1995 pp.93-596
4. Pushkarev Y., Figovsky O., Protective Vulcanizate Coatings on the Base of Oligobutadiene, *Anti- Corrosion Methods and Materials*, vol.46, no.4, 1999, pp.261-267
5. Pushkarev Y., Figovsky O., Protective Vulcanizate Coatings on the Base of Oligobutadiene without Functional Groups, *Corrosion Reviews*, vol.14, no.7, 1999, pp.33-46
6. Figovsky O., Liquid Solventless Synthetic-Rubber –Based Composition, *US Patent 7,989,541 B2, 2011*
7. Pushskarev Y., Ebonite Compositions and Covering Based on Oligobutadienes, *Burun Kniga, Kharkov, 2012* ,pages 172 (in Russian)
8. <http://www.helyx.ru/antikorroziynaya-zaschita/gummirovanie/>