Optimization of the composition of anticorrosion additives for protection of ferrous and non-ferrous metals

Optimalizace složení aditiv pro protikorozi ochranu železných a neželezných kovů

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It is well known that nitrated petroleum products are effectively used as anticorrosion additives in various types of fuels and lubricants. Due to processes of nitration and oxidation, the products obtained by us possess anodic and shielding properties of corrosion inhibitors for both ferrous and non-ferrous metals. Their protective ability is enhanced as a result of intramolecular interactions. Their particular implementations in different petroleum products are related both to the molecular weight and the group hydrocarbon composition of the raw material. The addition of the compounds obtained, which contain amine and amide group, the cathode properties of the inhibitors are also improved. The concentration limits at which the anodic, shielding and cathodic inhibitors to obtain maximal protective effect were determined. A technique for production of conservation and work-conservation oils containing this complex corrosion inhibitor was developed.

Nitrované ropné produkty jsou využívány jako antikorozi aditiva v různých typech paliv a maziv. Díky procesům nitrace a oxidace námi připravené produkty disponují anodickým a adsorpčním inhibičním mechanismem na železných i neželezných kovech. Jejich ochranný účinek je zvýšen mezimolekulovými interakcemi. Konkrétní využití různých ropných produktů je spojeno s molekulovou hmotností a složením uhlovodíkových skupin surového materiálu. Přídavkem látek obsahujících amino či amido skupinu je vylepšen i katodický mechanismus inhibice. Bylo stanoveno koncentrační rozmezí maximální účinnosti inhibitorů z hlediska inhibice anodické, katodické i adsorpční. Byl vytvořen postup výroby konzervačních olejů s obsahem navržených inhibitorů.

INTRODUCTION

A main task of modern oil-refining industry is to produce various lubricants with enhanced performance properties. This problem is to be solved within existing refineries, using modern technology, considering maximum economy and rational utilization of the raw materials and energy resources. Since the production of petroleum products amounts to millions of tons per annum, the problem with their quality and the resources is more and more important [1-4].

In modern oil-refining, motor oils properties are improved by using high-index base oils in which the corresponding compositions and additives are introduced to obtain commercial oils of good properties. For this reason, the production of highly effective additives turned out to be the key for the production of high quality lubricating oils [1-4].

The studies carried out were aimed at the preparation of polyfunctional additives on the basis of petroleum raw materials of certain structure-group composition which were expected to improve a number of performance characteristics of the most widely used lubricants [5-12]. The nitrated oils are known for their protection effect on ferrous metals [5,7,13-16]. In this respect, the effects of the different functional groups and different topology of the compounds present which form the protective film on the metal surface is not well clarified [1-4].

EXPERIMENTAL

Studies were carried out to establish the adsorption-chemisorption properties of mixtures composed of various hydrocarbons obtained from nitrated and oxidized oil fractions.

The protective mechanism of various kinds of compounds is studied by a complex of electrochemical methods [13, 14]. They provide information on the insulation ensured by the different products:

- Schematic diagrams of the devices used (Figures 1 and 2).
- Determination of the relative polarity of inhibition (RPI). Plated of standard dimensions (45×35×3 mm) were immersed in 0.5 M NaCl solution and then polarized by an external source. With the products studied, first one plate (anode) was protected, then anode and cathode simultaneously, and finally – plates without protection were tested. The conditions were: voltage 20 V, temperature 20°C, experiment duration 6 h, electrolyte – distilled water or 3% NaCl solution.

For the anode inhibitors studied, i.e. products donors of electrons, the RPI was calculated by the formula (%):

$$\text{RPI} = 100 - \frac{A_f - A_p}{A_f - K_p} \cdot 100$$

For cathode inhibitors, i.e. acceptors of electrons:

$$\text{RPI} = 100 - \frac{A_f - K_p}{A_f - A_p} \cdot 100$$

where: A_f - mass loss of the plate without protection; K_p - mass loss of the plate with protected cathode; A_p - mass loss of the plate with protected anode.

To determine the properties of the inhibited oils, the relative ohmic resistance (ROR) and relative polarization resistance (RPR) were calculated by the formulae:

$$\text{ROR} = 100 - \frac{R_{\Omega,1}}{R_{\Omega,2}} \cdot 100 \quad \text{RPR} = 100 - \frac{R_{\text{pol},1}}{R_{\text{pol},2}} \cdot 100$$

where: $R_{\Omega,1}$ and $R_{\text{pol},1}$ - ohmic and polarization resistances of clean plates; $R_{\Omega,2}$ and $R_{\text{pol},2}$ - ohmic and polarization resistances of plates protected with the products studied.

Ohmic resistance and capacity presents Figure 2. The coefficient of corrosion inhibition (C_i) was calculated as the ratio between the corrosion without and in presence of the corresponding additive. The determination of the corrosion rate was based on its correlation with the polarization resistance and is carried out using corrosion meters. The protection degree was assessed by the damaged plate surface vs. its total area (%). In order to determine the protection effect of different anticorrosion oil compositions, tests were carried out by the following standard methods:

- Bulgarian State Standard (BDS) 14353-77. Determining the protection ability against aggressive gases and vapours in a chamber "Aggressive medium" (7 days and nights, 33°C, 100% humidity). Conditions are created periodically for the formation of a certain amount of sulphur dioxide.

Fig. 1. Scheme for measuring the polarization and ohmic resistance of the electrolyte tested products (E_1 and E_2 – electrodes protected with products studied; E_0 – auxiliary electrode; P_1 and P_2 – relays; T_1 – T_4 – trembler; R – resistor). Obr. 1. Schéma měření polarizačního odporu a odporu elektrolytu (E_1 a E_2 – pracovní elektrody; E_0 – protielektroda; P_1 a P_2 – relé; T_1 až T_4 – spínače; R – odpor)

Fig. 2. Scheme for measuring the capacity and resistance of the products studied (R_1 and R_2 – constant resistors; R – variable resistor; C – variable capacitor; O – oscilloscope; G – AC generator; R_x and C_x – resistance and capacity of cells under test)

Obr. 2. Schéma měření kapacity a odporu korozních produktů (R_1 a R_2 – konstantní odpory; C – variabilní kondenzátor; O – osciloskop; G – generátor střídavého proudu; R_x a C_x – odpor a kapacita testovaných poločlánků)

- BDS 14354-77. Determining the protection stability against salts in a "Salty fog" chamber (10 days and nights, 80°C, 100% humidity) by periodically creating conditions for the formation of fog from a 5% aqueous solution of sodium chloride.
- BDS 14355-77. Determining the protection stability against humid heat-climate regime in a "Humidity" chamber (7 hours per each 24 hours for a period of 12 days and nights) at changing temperature and moving moist air in the chamber.
- BDS 14558-77. Determining the protection ability against condensation water in a "Condensation water" chamber (7 days and nights, 30°C, 100% humidity).

RESULTS AND DISCUSSION

It is well known that the nitrocompounds are anticorrosion additives of donor character towards the protected metal [13, 14]. The information about their electronic and geometry characteristics is important for the elucidation of the relationship structure – activity.

In the research performed, the criterion for the efficiency of the corresponding compound was chosen to be the corrosion inhibition coefficient value (C_i), which shows the decrease of corrosion in the presence of the corresponding additive in comparison with the control sample.

- The inhibition effect decreases in the following order: primary > secondary > tertiary [5-9,13,14];
- The lengthening of the hydrocarbon chain causes an increase of the C_i [5-9,13,14];
- The branching out of the chain decreases the inhibition effect. The influence of cycloparaffin and arylene substituents is the strongest [5-9,13,14].

The action of the corrosion inhibitors is connected with the formation of a protective layer over the metal surface. Different mechanisms are proposed describing this process [15]. One of the most widely adopted ones is that of the chemical model where the inhibitor forms a donor-acceptor bond with a metal ion from the surface. In the case of nitrocompounds, the formation of chemiadsorptive complexes is a result of an interaction between $-\text{NO}_2$ group and the metal surfaces.

The similarity in geometry and charge distribution between the most and the less active compounds from the corresponding group shows that the chain length influences only the solubility of the additive in mineral oil. The different activities depend on some properties of the molecule as a whole, and the mutual molecule orientation in the chemiadsorptive layer is connected with them [5-9,13,14].

Good relationship is observed in the case of the nitrocompounds with straight chain and alkyl branches. The presence of arene and cycloalkane substituents

destroys the established correlation. In this case, the three-dimensional factor comes into action which disturbs the regular arrangement of the inhibitor molecules in the protective film. The situation with the tertiary nitrocompounds is similar [5-9,13,14].

The electrochemical studies [1-22] were carried out to find the adsorption and chemisorptions properties of mixtures composed of different hydrocarbons and obtained from nitrated oil fractions. The most suitable ratios for two- and multi-component mixtures are presented in Table 1.

From the data on the capacity and ohmic resistance, information is obtained on the insulating action exerted on the metal surfaces.

The ohmic insulation of the metal surfaces shows the ability of the film formed on them to ensure protection from corrosion activity and penetration of water vapour or water. The strongest protective properties will have the products with the highest ohmic resistance and the lowest capacity measured [13, 14].

The nitro groups which determine the polarity of the molecules orient themselves towards to the metal. As a whole, this group is characterized with highly negative static induction effect despite that the positive charge of the nitrogen atom is partially compensated by the negative nuclei of the oxygen atoms. Nevertheless, its polarity is high enough to induce chemisorption interactions with the metals by the formation of the protective layer.

The high values of the relative ohmic and polarization resistances account for the formation of this film.

The synergetic effect observed for some of the properties was found to differ depending on the concentration due to intermolecular interactions. The most stable film on the protected surface which was expected to exert the strongest protection had the following composition: 75% alkane-cycloalkane and 25% single ring arene hydrocarbons; 98% alkane-cycloalkane and 2% two cycle-ring arene hydrocarbons; 99.5% alkane-cycloalkane hydrocarbons and 0.5% tar-asphalt substances. The poly cycle-ring arene hydrocarbons have negative effect on the protective characteristics of the alkane-cycloalkane structures.

The most active adsorption-chemisorption interactions which provide for the formation of most stable films onto the protected surfaces occurred by combining mixtures of 72-75% alkane-cycloalkane hydrocarbons, about 25% single cycle-ring arenes, up to 2% two cycle-ring arenes and about 0.5% tar-asphalt substances. The synergetic effect was observed at these concentrations. If the system contained more than 2% two cycle-ring arene hydrocarbons, the protective film density deteriorated and the values of the electrochemical properties were worse. Any amount of poly cycle-ring arene hydrocarbons is unwanted since it strongly affects the density and the strength of the film formed.

Tab. 1. Electrochemical properties of mixtures of nitration hydrocarbons: alkanes – cycloalkanes (AC), monocyclic arenes (MCA), dicyclic arenes (DCA), polycyclic arenes (PCA), tar-asphalt products (TAP) obtained from the middle boiling oil fraction (MBOF) / *Elektrochemické vlastnosti nitrovaných uhlovodíkových směsí: alkany-cykloalkany (AC), monocyklické areny (MCA), dicyklické areny (DCA), polycyklické areny (PCA), tér-asfaltové produkty (TAP) připravené ze středně vroucích frakcí ropy (MBOF)*

MIXTURE COMPOSITION					PARAMETERS					
					Ohmic resistance	Capacity	Relative polarity of inhibition	Relative polarization resistance	Relative ohmic resistance	Coefficient of inhibition
					Ω	mF	%	%	%	C_i
Binary mixtures										
100% (AC)					182	1.7	60	76	58	3.1
90% (AC) + 10% (MCA)					187	1.6	64	79	59	3.3
75% (AC) + 25% (MCA)					201	1.0	85	89	69	3.8
30% (AC) + 70% (MCA)					181	1.6	69	74	63	3.2
98% (AC) + 2 % (DCA)					185	1.4	62	79	59	3.2
90% (AC) + 10 % (DCA)					168	2.2	54	68	56	2.8
30% (AC) + 70 % (DCA)					145	3.0	49	57	52	2.2
99,8% (AC) + 0,2% (PCA)					180	1.8	58	74	56	3.0
99% (AC) + 1% (PCA)					165	2.7	51	66	50	2.6
90% (AC) + 10% (PCA)					150	4.2	47	62	48	2.4
99,9% (AC)+ 0.1% (TAP)					185	1.6	63	80	60	3.2
99,5% (AC)+ 0.5% (TAP)					202	1.2	74	90	70	3.9
99% (AC)+ 1% (TAP)					199	1.6	62	82	67	3.5
Multicomponent mixtures										
AC	MCA	DCA	PCA	TAP						
75	25				201	1.0	85	89	69	3.8
74	25	1			203	0.9	88	95	70	4.0
73	25	2			205	1.0	90	94	66	3.9
72	25	3			183	1.5	87	92	64	3.7
75	24	1			196	1.8	80	90	60	3.5
72.5	25	2	0.5		185	2.0	77	85	56	3.1
72.5	25	2		0.5	208	1.8	79	87	59	3.3
72	25	2	0.5	0.5	188	2.4	75	76	52	3.2

The results from the studies on the adsorption-chemisorptions properties of the individual types of compounds obtained from the interaction of hydrocarbons of different homologous series with nitrogen acid are presented in Table 2.

It was found that the relative polarity depends on the concentration and type of the individual substances in the solution [5-9].

The alkene-cyanoallene hydrocarbons gradually increase solution polarity with the increase of their concentration to reach the highest value in pure substance. For arene hydrocarbons, maxima in the relative polarity were observed indicating for the highest concentration above which they are engaged in intermolecular interactions. This reduced their polarity. With the increase of the molecular weight and the number of arene rings in the hydrocarbon chain, these interactions can occur at lower concentrations. The influence of arene hydrocarbons on this phenomenon was confirmed also for resinated products since it is well known that their structures take

part in the compositions of resin-asphaltous substances. They show maximum of the relative polarity at lower concentrations in the solution [5-9].

Nitrocompounds have higher values of the relative polarity compared to the oxidized hydrocarbons. [5-9].

It is well known that the substances having the highest polarities in a solution and less engaged in intermolecular interactions tend to orient faster on boundary surfaces between different phases. Thus, they form a mechanical barrier averting the access of other substances [13,14,16].

The strongest synergism was observed when primary nitrocompounds were combined with carboxyl derivatives. Good protective properties exhibited also the mixtures composed of primary and secondary nitrocompounds. The tertiary nitrocompounds disturb the protection film density since the hydrocarbon carcass of their macromolecules is highly branched [5-9] and does not facilitate regular and tight packing of the protective film. The addition of tar-asphalt products to

them resulted in certain film densification due to their plasticity and adhesion but this cannot guarantee very stable performance characteristics. For ternary mixtures where the synergism of the individual nitrocompounds was also confirmed, the presence of tar products was found to be decisive. Tar product fill-in the interspaces due to their strong polarity and mobility [5-9]. This effect was proved also by the substitution of tertiary nitrocompounds with tar-asphalt products in both three- and four-component mixtures.

The strongest polar substances of the oil solution (the primary nitrocompounds) are the most likely to be the first orienting on the metal surface. These with lower polarity, like secondary nitro- and carboxyl compounds, form a second layer which fills the probable gaps between the regularly arranged molecules of the first layer. The tar-asphalt products lay over the two layers already formed to finalize the protective layer packing onto the metal surface.

Tab. 2. Electrochemical properties of mixtures of primary (PNC), secondary (SNC), tertiary (TNC) nitrocompounds, carboxylic compounds (CC) and tar-asphalt products (TAP), obtained by nitration of the hydrocarbons from medium boiling oil fraction (MBOF) / *Elektrochemické vlastnosti směsí primárních (PNC), sekundárních (SNC), terciárních (TNC) nitrosloúčenin, karboxylových sloučenin (CC) a tér-asfaltové produkty (TAP) připravené nitrací ze středně vroucích frakcí ropy (MBOF)*

MIXTURE COMPOSITION					PARAMETERS					
TAP	TNC	CC	PNC	SNC	Ohmic resistance	Capacity	Relative polarity of inhibition	Relative polarization resistance	Relative ohmic resistance	Coefficient of inhibition
					Ω	mF	%	%	%	C_i
nitration alkanes – cycloalkanes										
+	+				113	2.5	37.9	48.5	49.6	2.16
		+	+		140	1.6	64.3	78.3	56.2	2.96
			+	+	138	2.0	59.4	68.2	54.2	2.60
+		+	+		195	1.4	68.2	81.6	60.2	3.35
	+	+	+		141	1.9	60.4	72.9	54.2	2.72
+			+	+	131	2.0	53.4	70.7	55.9	2.79
		+	+	+	134	1.8	61.7	76.2	57.2	2.96
	+		+	+	125	2.3	55.4	68.9	52.3	2.49
+		+	+	+	190	1.6	62.9	78.4	58.8	3.27
+	+	+	+	+	182	1.7	60	76	58	3.10
nitration monocyclic arenes										
+	+				101	2.9	34.8	38.6	51.9	1.58
		+	+		137	1.9	61.6	66.8	52.6	2.33
			+	+	131	2.3	57.3	57.1	49.2	2.02
+		+	+		186	1.7	65.8	70.8	58.3	2.74
	+	+	+		133	2.2	57.9	61.9	51.9	2.11
+			+	+	119	2.2	51.6	58.8	49.7	2.13
		+	+	+	123	2.0	58.8	67.2	50.1	2.33
	+		+	+	117	2.6	52.7	57.3	48.2	1.90
+		+	+	+	183	1.9	60.6	67.6	52.6	2.68
+	+	+	+	+	170	2.1	58	65	50	2.5
nitration resin products										
+	+				90	4.6	20.4	26.9	48.1	1.69
		+	+		128	3.7	44.7	56.8	54.1	2.48
			+	+	115	3.1	37.4	45.9	51.3	2.16
+		+	+		180	2.5	48.8	62.2	57.9	2.88
	+	+	+		120	2.8	41.7	51.4	53.3	2.58
+			+	+	110	3.0	34.7	49.1	53.8	2.29
		+	+	+	112	2.7	40.9	56.8	56.1	2.40
	+		+	+	107	3.2	34.7	47.6	50.7	1.97
+		+	+	+	171	3.0	42.8	59.6	56.1	2.65
+	+	+	+	+	160	3.7	42	55	57	2.6

The densest packing was observed with primary nitrocompounds of alkane-cycloalkane and single cycle-ring arene hydrocarbons.

Their optimal concentrations were studied, especially in combinations with tertiary nitrocompounds which are produced at the highest rate by the treatment of petroleum hydrocarbons with nitric acid. The amounts of different hydrocarbon groups were contemplated with the statistically established limits within which are their contents in the initial petroleum fractions. The mixtures causing the most significant changes in the protection characteristics are shown in Table 3.

It can be seen that every decrease of tertiary nitrocompounds content had positive effect on the characteristics determining the strength of the protective layer. The decrease of the contents of all the other polar substances (carboxylic, primary and secondary nitrocompounds) had negative effect of the properties of the protective film.

Considering the results obtained from these studies, the following optimal concentrations of the individual substances were derived, by which the protective effect was found to be the strongest: primary nitrocompounds

Tab. 3. Electrochemical properties of mixtures of primary (PNC), secondary (SNC), tertiary (TNC) nitrocompounds, carboxylic compounds (CC) and tar-asphalt products (TAP), obtained by nitration of mineral oil (MO) and nitration of hydrocarbons isolated from medium boiling (MBOF) / *Elektrochemické vlastnosti směsí primárních (PNC), sekundárních (SNC), terciárních (TNC) nitrosloúčenin, karboxylových sloučenin (CC) a tér-asfaltové produkty (TAP) připravené nitrací minerálních olejů a uhlovodíků izolovaných ze středně vroucích frakcí ropy (MBOF)*

MIXTURE COMPOSITION					PARAMETERS					
TAP	TNC	CC	PNC	SNC	Ohmic resistance	Capacity	Relative polarity of inhibition	Relative polarization resistance	Relative ohmic resistance	Coefficient of inhibition
%					Ω	mF	%	%	%	C_i
nitration mineral oil										
1	59	16	12	12	200	2.1	79.4	96.9	73.7	4.48
3	58	16	11	12	197	2.6	76.2	92.4	70.5	4.17
3	63	16	6	12	189	3.2	66.1	86.9	65.7	3.75
3	60	16	11	10	211	1.1	87.1	102.8	80.5	5.15
3	62	16	11	8	210	1.3	86.7	102.6	80.3	5.13
3	62	12	11	12	205	1.5	83.4	99.8	78.1	4.81
5	56	16	11	12	197	2.7	76.4	92.7	70.8	4.20
nitration alkanes – cycloalkanes										
1	59	16	12	12	191	1.8	63.7	79.5	64.7	3.40
3	58	16	11	12	194	1.5	65.8	81.7	66.8	3.79
3	63	16	6	12	183	2.4	60.2	78.5	63.3	3.22
3	60	16	11	10	178	2.6	58.1	73.8	58.4	2.75
3	62	16	11	8	188	1.9	62.2	78.3	62.9	3.08
3	62	12	11	12	183	2.2	60.9	76.7	61.3	3.07
5	56	16	11	12	175	2.8	56.6	72.7	56.2	2.63
nitration monocyclic arenes										
1	59	16	12	12	160	2.8	49.8	61.7	38.6	1.54
3	58	16	11	12	157	2.9	47.2	60.3	35.5	1.43
3	63	16	6	12	177	2.2	65.1	78.4	57.4	2.40
3	60	16	11	10	174	2.1	61.4	75.3	54.5	2.24
3	62	16	11	8	175	2.0	63.3	76.7	56.4	2.33
3	62	12	11	12	178	1.9	66.6	80.4	60.1	2.54
5	56	16	11	12	180	1.7	68.3	82.9	63.2	2.61
nitration resin products										
1	59	16	12	12	192	2.1	45.7	68.7	67.4	2.94
3	58	16	11	12	179	3.5	31.7	55.8	48.9	1.38
3	63	16	6	12	189	2.4	42.7	65.5	63.7	2.60
3	60	16	11	10	187	2.6	40.5	63.7	61.3	2.34
3	62	16	11	8	186	2.7	39.7	62.5	59.6	2.21
3	62	12	11	12	190	2.3	43.1	66.8	65.3	2.77
5	56	16	11	12	178	3.6	30.5	54.7	47.4	1.22

– not less than 6%, secondary nitrocompounds more than 8%, tar-asphalt products up to 3%, the smallest possible content of tertiary nitrocompounds and carboxylic compounds – more than 8%.

The studies carried out so far [5,7-11] showed that the conditions for the interaction between mineral oils with concentrated nitric acid should be selected so as the concentrations of oxidized products was the smallest possible. In this case, it appears to be economically unreasonable to isolate the oxidized products and dose them at certain ratios to obtain compositions ensuring the preparation of compositions with the strongest protective properties [23-32]. Furthermore, these products are usually hardly soluble in oils and adding them to commercial products would deteriorate a number of their properties [5,7-11].

Besides, the fractions containing resinated and carboxylic acids have polar properties corresponding to the screening inhibitors of corrosion [13,14]. The fractions containing nitrated hydrocarbons show properties characteristic for corrosion inhibitors of anodic properties which form strong chemisorption compounds on the protected metal surfaces.

For this reason, the studies were aimed at the preparation of mixtures of petroleum fractions nitrated with nitric acid and oxidized paraffin which have proved their anodic and shielding properties [5,7-14]. Parallel investigations were carried out also with the often used in practices stearic acid [5,7-12,27]. The hydrocarbon radical present in this acid ensures its full solubility in oils and oil compounds and it was not expected to have negative effect on the regular arrangement of the protective layer molecules [5,7-11].

For mixtures optimization, samples containing nitrated mineral oil fractions and shielding products were prepared (Fig. 3).

The coexistence of nitrated and oxidized hydrocarbons results in synergism of the anti-corrosion action. The gradual increase of the amount of the shielding component up to 18% lead to enhancement of the protective properties of the mixtures obtained. More intense was found to be the protective properties enhancement when the oxidized products concentration increased to 6.8%, above which the protection degree increased gradually to 22%. Above this concentration, certain effect of mixtures anti-corrosion properties began to exert the shielding and water-resistant properties of the oxidized products. Since their inhibiting effect was weak, the resultant protection effectiveness of the mixtures decreased. Their high acidity number affected the total acidity of the mixtures and, hence, the standard properties of the products incorporating them. These considerations, as well as the results obtained, determined the optimal concentrations of the oxidized products added to the anodic inhibitors to be in the range 8-10 %.

Samples of nitrated initial raw materials containing different amounts of the product studied were prepared. Their protective ability was studied by the present method (Fig. 4).

It was confirmed that the optimal amounts of oxidized products at which the strongest protective effect was registered was from 8 to 10%. The protective ability of the different inhibitors depends basically on the hydrocarbon composition of the initial material.

Fig. 3. Protective capacity of mixtures containing nitration with nitric acid MO and MBOF with stearic acid and oxidized residual paraffin [* Steel 10 (BDS) $\approx$ Steel 040 A10, Steel 1010 (AISI, SAE, ASTM)].

Obr. 3. Ochranná účinnost směsí obsahujících nitrované minerální oleje a středně vroucí frakce ropy s kyselinou stearovou a zbytkovým oxidovaným parafínem

Fig. 4. Protective capacity of mixtures containing calcium salts of nitration with nitric acid MBOF and MO, with residual oxidized paraffin and stearic acid [* Steel 10 (BDS) $\approx$ Steel 040 A10, Steel 1010 (AISI, SAE, ASTM)].

Obr. 4. Ochranná účinnost směsí obsahujících vápenaté soli nitrovaných minerálních olejů a středně vroucí frakce ropy s kyselinou stearovou a zbytkovým oxidovaným parafínem

The products obtained from mineral oil (MO) possessed slightly better anti-corrosion properties than these containing middle-boiling oil fractions (MBOF).

When calcium salts are used, inhibitors of enhanced properties were obtained.

Probably, the synergism in the protective effect between the shielding component and the nitrated mineral oil (MO) was much more pronounced. Their basic advantage is the absence of polycyclic-ring arene hydrocarbons in their composition.

The combination of the donor with protective properties of corrosion inhibitors gave better results. The shielding component ensures rapid initial removal of water from the protected surface by keeping it within the conservation material [13,14]. The inhibitor obtained from nitrated oil fraction is adsorbed onto the surface freed from water. The present studies proved that it contained compounds of chemisorptions donor properties.

To form chemisorption films onto both negatively and positively charged regions of the protected metal surface, the inhibitor should contain components with acceptor properties beside these with donor-shielding ones [13,14].

The preparation of a complex oil-soluble corrosion inhibitor is related with the establishment of the optimal content of each individual component without impairing their stability in the solution but obtaining the highest possible effect of protection. For this purpose, it is necessary to determine the suitable concentration at which the inhibitor of anodic-shielding properties (ASI), as well as the possibility to replace the imported inhibitors used now for the production of conservation oils according to the Bulgarian State Standard (BDS 14357 and

BDS 15021). Thus, the anodic-shielding inhibitors which showed the strongest protective ability according to previous studies were added in concentrations 1-10% to the basic non-inhibited petroleum fraction from which conservation oil is produced. The samples were subjected to tests by a complex of standard methods providing various atmospheric conditions in chambers - BDS 14354, BDS 14353, BDS 14558, BDS 14355. The data are presented in Table 4.

It was found that the use of ASI in concentrations up to 5% could replace the commercial inhibitor NA-SUL BSB used now for the production of conservation oils. The results obtained allowed widening the studies towards possible replacement of the practically widely used inhibitor of the series AKOR for the production of work-conservation oils. Tests were carried out with transmission fluid TM-5/90EP to which, besides the additives required for the corresponding viscosity class and performance level, 1-10% of the ASI obtained were added (Tab. 5).

It was found that the presence of ASI in concentrations higher than 5% imparted worse protection properties compared to the reference inhibitor only under the conditions defined in BDS 14558 and better protection for all the other tests. To overcome this drawback, it was not necessary to increase the suggested ASI concentration but studies must be carried out to increase its efficiency by adding an inhibitor with cathodic properties (CI). The most suitable products for this purpose appear to be these obtained from stearic acid and carbamide (CI-1) or ethylenediamine (CI-2) in concentrations 0.5, 0.7, 1.0, 1.2, 1.5%. The data on their anticorrosion effectiveness are presented in Table 6.

Tab. 4. Protective capacity of conservation oil inhibited with an anode-shielding inhibitor (ASI), representing calcium salt of nitration MO + 8% stearic acid (ASI - 2) / *Ochranná účinnost konzervačního oleje inhibovaného anodickým inhibitorem, reprezentovaným vápenatou solí nitrovaného minerálního oleje a 8% kyseliny stearové (ASI-2)*

Type of inhibited oil: conservation oil +	Corrosion tests on BDS				
	14354 (g/m ²)	14353 (mg "AM")	14358 (g/m ²)	14355	
				Steel 08 kp* № of cycles	Copper bal
+ 1% ASI-2	133,6	2850	13.0	7	1
+ 3% ASI-2	66,2	1980	9.5	11	1
+ 4% ASI-2	57,4	1460	5.5	12	1
+ 5% ASI-2	55,5	1040	4.0	over 12	1
+ 6% ASI-2	53,0	1060	4.1	over 12	1
+ 7% ASI-2	56,1	1560	3.8	over 12	1
+ 10% ASI-2	55,0	1500	3.7	over 12	1
+ 1.5% NA-SUL BSB	55,5	1060	1.8	over 12	1
Without inhibitor	278.9	3960	15.9	3	3

* Steel 08 kp (BDS) $\approx$ Steel A 622 (AISI, SAE, ASTM)

Tab. 5. Protective capacity of the transmission oil (TM-5/90EP), inhibited by ASI-2 / *Ochranná účinnost transmisního oleje (TM-5/90EP), inhibovaného ASI-2*

Type of inhibited oil: TM-5/90EP + ...	Corrosion tests on BDS				
	14354 (g/m ²)	14353 (mg "AM")	14358 (g/m ²)	14355	
				Steel 08 kp* № of cycles	Copper bal
+ 1% ASI-2	175.36	3763.2	6.7923	3	1
+ 3% ASI-2	99.72	2939.5	4.7771	10	1
+ 4% ASI-2	72.41	2824.3	3.9026	12	1
+ 5% ASI-2	56.85	2609.2	3.8873	over 12	1
+ 6% ASI-2	55.95	2601.5	3.3512	over 12	1
+ 7% ASI-2	55.39	2592.8	2.5768	over 12	1
+ 10% ASI-2	55.06	2585.7	1.0014	over 12	1
+ 10% AKOR	64.02	2704.7	0.9987	11	1
Without inhibitor	291.78	4675.4	12.6472	2	2

* Steel 08 kp (BDS) $\approx$ Steel A 622 (AISI, SAE, ASTM)

Tab. 6. Protective capacity of the transmission oil (TM-5/90EP), inhibited by ASI-2 and CI / *Ochranná účinnost transmisního oleje (TM-5/90EP), inhibovaného ASI-2 a CI*

Type of inhibited oil: TM-5/90EP + ...	Corrosion tests on BDS				
	14354 (g/m ²)	14353 (mg "AM")	14358 (g/m ²)	14355	
				Steel 08 kp* № of cycles	Copper bal
5% ASI-2 + 0.5% CI-1	70.15	2794	1.7458	9	2
5% ASI-2 + 0.7% CI-1	61.72	2685	0.9944	11	2
5% ASI-2 + 1.0% CI-1	50.48	2038	0.8932	over 12	1
5% ASI-2 + 1.2% CI-1	47.29	2030	0.8138	over 12	1
5% ASI-2 + 1.5% CI-1	65.13	2087	1.0594	11	2
5% ASI-2 + 0.5% CI-2	72.47	2834	2.6334	10	1
5% ASI-2 + 0.7% CI-2	65.72	2712	1.0025	over 12	1
5% ASI-2 + 1.0% CI-2	66.37	2479	0.8173	over 12	1
5% ASI-2 + 1.2% CI-2	55.92	2637	0.9654	over 12	1
5% ASI-2 + 1.5% CI-2	70.36	2670	1.2314	10	2
10% AKOR	64.02	2704.8	0.9987	11	1

* Steel 08 kp (BDS) $\approx$ Steel A 622 (AISI, SAE, ASTM)

The results obtained showed that the most suitable combination of ASI and CI at which maximal protection properties are provided, equal or better than the reference used, can be obtained by mixing 5% with 1% of the corresponding inhibitors. The characteristics of these compositions (Tab. 7) showed that a complex corrosion inhibitor (CCI) having acceptor, donor and shielding properties was obtained. With this inhibitor, transmission oils with improved work-conservation properties can be produced.

The effectiveness of CCI was studied to find possibilities to use the combined inhibitor for preparation of work-conservation motor oils - M6W8C₂/D₁; M10D₂/E₁;

M16D₂/E₁. The results obtained from these studies are presented in Table 8.

With the optimal composition and concentration determined, the complex corrosion inhibitor suggested showed better protective properties than these of the one used now (AKOR). Among the two inhibitors suggested, more effective appeared to be CCI-2A. The physicochemical analyses showed that the work-conservation oils containing these inhibitors fully comply with the requirements of BDS. The optimal concentration of the inhibitors in the oil is 6%. They also have higher sensibility than the reference used which is introduced in concentration of 10% for the production of this type of motor oils.

Tab. 7. Physicochemical parameters of combined corrosion inhibitor (CCI) / Fyzikálně-chemické parametry kombinovaných korozních inhibitorů (CCI)

PARAMETERS		VALUE	
		CCI – 2A (5%ASI-2 + 1%CI-1)	CCI – 2B (5%ASI-2 + 1%CI-2)
Colour		Brown viscous liquid	
Density at 20°C, kg/m ³		900	880
Kinematic viscosity at 100°C, mm ² /s		24	20
Flash point (open cup), °C		194	190
Pour point, °C		0	2
Content of water-soluble acids and alkalis, %		missing	missing
Mechanical impurities, %		missing	missing
Solubility in oil, %		completely	completely
Water, %		0.003	0.003
Calcium, %		2.2	1.8
Permittivity (0.1 M solution in benzene)		2.80	2.72
* Electrical properties of donors and acceptors, mV		+110	+102
* Relative polarization resistance, %		83	74.2
* Relative ohmic resistance, %		85	82.5
* Displacement of water, mm	d ₁	101	78
	d ₂	101	86
	d ₃	101	87

* Tests were performed in 5% solution of MO

Tab. 8. Protective capacity of work-conservation oils inhibited by CCI-2A and CCI-2B / Ochranná účinnost konzervačních olejů inhibovaných CCI-2A a CCI-2B

Type of inhibited oil	Corrosion tests on BDS				
	14354 (g/m ²)	14353 (mg "AM")	14358 (g/m ²)	14355	
				Steel 08 kp* № of cycles	Copper bal
M6W8C ₂ /D ₁ + 6% CCI-2A	41.25	2078	0.0653	over 24	0
M6W8C ₂ /D ₁ + 6% CCI-2B	42.34	2264	0.0830	over 12	1
M6W8C ₂ /D ₁ + 10% AKOR	46.14	2381	0.3542	12	1
M10D ₂ /E ₁ + 6% CCI-2A	21.37	1329	0.0875	over 24	0
M10D ₂ /E ₁ + 6% CCI-2B	25.64	1570	0.1098	over 12	1
M10D ₂ /E ₁ + 10% AKOR	47.48	1725	0.4455	over 12	1
M16D ₂ /E ₁ + 6% CCI-2A	42.51	2031	0.0618	over 12	0
M16D ₂ /E ₁ + 6% CCI-2B	47.01	2144	0.0758	over 12	1
M16D ₂ /E ₁ + 10% AKOR	47.36	2486	0.3472	12	1

* Steel 08 kp (BDS) ≡ Steel A 622 (AISI, SAE, ASTM)

CONCLUSIONS

The most active adsorption-chemisorption interactions ensuring the formation of a stable film onto the protected surfaces take place by the combination of mixtures of alkane-cycloalkane hydrocarbons, single cycle-ring arenes, two cycle-ring arenes and tar-asphalt substances. Their protective effect results from synergetic action. Any content of poly cycle-ring arene hydrocarbons is unwanted since it deteriorates the density and the strength of the film obtained.

The strongest synergetic effect was observed when primary nitro-compounds were combined with carboxylic derivatives. Good protection properties showed also mixtures of primary and secondary nitro-compounds. Any reduction of ternary nitro-compounds content has positive effect on the characteristics stipulating the strength of the protective film.

The co-presence of nitrated and oxidized hydrocarbons results in synergetic anticorrosion action.

To form chemisorption film both on negatively and positively charged regions of the metal surface, components with acceptor properties should be added to the inhibitor besides these with donor-shielding properties.

The physicochemical analyses showed that the work-conservation motor oils containing the inhibitors suggested by us fully comply with the requirements of BDS.

The additives prepared have surfactant properties and improve a number of properties of the motor oils to which they are added.

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