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PROTECTIVE PROPERTIES AND SPECTRAL ANALYSIS OF NITROGEN- AND OXYGEN-CONTAINING CORROSION INHIBITORS FOR OIL EQUIPMENT

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Abstract. The protective properties of six corrosion inhibitors based on imidazolines, amides, amines and esters have been determined using gravimetric and potentiometric methods. The effect of inhibitor solvent on the protective properties has been examined. The dependence of inhibitor protective effect upon the content of nitrogen and functional groups has been determined. The most effective inhibitors have been chosen and their IR-spectra have been shown.

Keywords: corrosion, corrosion inhibitors, carbazole, imidazoline, amides, amines, protective effect.

1. Introduction

The corrosion rate of metal constructions in technological media of various oil-refining processes is sufficiently high from the standpoint of industrial safety. In this connection good fettle of equipment is constantly controlled and methods of decrease of aggressive medium influence on the metal are applied.

The experience of corrosion control shows that inhibitors application is the simplest and relatively cheap protection method for the technological equipment.

In most cases the inhibitors used in oil refinery are polar or semi-polar organic compounds, molecules of which consist of hydrocarbon radical connected with the functional group. The group contains nitrogen, oxygen, sulphur, and other atoms. Nitrogen-containing compounds are the inhibitors which have been most widely used for a long time with success. The world output involves amides (diamides), amines, imidazoline bases and their mixtures as the basis of the majority of modern corrosion inhibitors.

The ways of corrosion reduction for the equipment of oil primary processing have been shown in [1]. The internal and external corrosion factors affect the effectiveness of corrosion inhibitors. The solubility of inhibitor active basis, low-temperature properties of the inhibitors, corrosion medium acidity, inhibitor concentration and others are the main factors. The equipment material corrodes [2], thus the material composition is also among the main factors. Under the real conditions these factors may interact between each other complicating the establishment of mechanism of inhibitor action and design of inhibitor protection.

The investigations of solubilizing ability and low-temperature properties of nitrogen- and oxygen-containing compounds are represented in [3]. On the basis of the mentioned investigations some compounds were chosen for the following experiments (see below).

Corrosion inhibitors must satisfy a series of requirements: to provide the maximum protective effect at low concentration; to be technological (not to violate the normal technological regime of the plant, not to deteriorate the products quality and activity of the secondary processes catalysts); to be economic, stable for oxidation and reduction; to have non-toxic effect on staff; and not to endanger the environment.

Since the production of corrosion inhibitors for petroleum industry is absent in Ukraine it is vital to identify compounds which may be produced by the Ukrainian plants as high-effective corrosion inhibitors.

The aim of this work is to examine the anticorrosive properties of nitrogen- and oxygen-containing compounds using gravimetric analysis and to establish the mechanism of their protective effect using potentiometric analysis. Also it is necessary to confirm the chemical composition of the chosen compounds by spectral analysis and to select the best ones for the further investigations.

2. Experimental

2.1. Investigation Objects

On the basis of solubility data [2] we chose the following corrosion inhibitors: carbazolines based on stearic acid ST-4 (1-(5-amino-3-azapentyl)-(2-heptadecynile)imidazoline) with the nitrogen content of 14.2 mas % and SD (1-(2-aminoethyl)-(2-heptadecyl)imidazoline with the nitrogen content of 12 mas %; carbazolines based on oleic acid OD-3 (1-(2-aminoethyl)-2-(8-heptadecynile)imidazoline) with the nitrogen content of 12 mas % and OT-2 (1-(2-diethanolaminoethyl)-2-(8-heptadecynile)imidazoline) with the nitrogen content of 9.6 mas %; cation-active fat R-1 (*N,N*-substituted amides and esters of colza oil acids) with the nitrogen content of 6 mas %. The inhibitor Dodigen-481 (produced by Clariant, Switzerland) on the basis of polyaminenaphthenic acids amides was chosen for the comparison. The nitrogen content in it is 14 mas %.

2.2. Gravimetric Investigations

Gravimetric investigations were carried out studying the protective effect of 50% solutions of investigated compounds in toluene, solvent naphtha, hexane solvent P-1 65/75 and jet fuel TS-1 (JF). The experiments were carried out using artificial corrosive media prepared by the standard procedure as well as by the procedures developed by the authors. The steel plates made of steel St20 with the total area of 30 cm² were used as control samples.

By their composition the prepared corrosion media are close to those technological corrosive media occurred in reflux reservoirs of the plants of oil primary and secondary processing, as well as during oil transportation. The temperature conditions are typical for the mentioned processes. Taking into account the high corrosiveness of the medium and the previous results, the inhibitor consumption was 200 g/t of corrosive medium. To reduce the error of inhibitor batching, it was introduced as 5% solution in the studied solvents. The composition of

aqueous phases and experimental conditions are represented in Table 1.

The quantitative estimation of inhibitor protective effect (at definite concentration) on the corrosion process rate is characterized by a protection degree Z. It was determined using the procedure described in [5]. The accuracy of the results was achieved by the calculation of average value from three experiments.

The laboratory plant by means of which the inhibitor protective effect is studied was developed by the authors (Fig. 1). The process temperature was controlled to be within the given range. The medium homogeneity was provided by definite rotation speed of magnetic stirrer.

2.3. Potentiometric Investigations

Polarization investigations were carried out using Solatron 1286 Electrochemical interface and Solatron SI 1255 HF Frequency Response Analyzer in the medium containing 0.098M HCl and 0.226M 1-butanol. The experiments were carried out with 50 ppm of the inhibitor and without it. The comparative electrode was calomel electrode equilibrium with the solution. The platinum gauze ($D = 0.1$ mm) was used as intermediate electrode. It was concentrically placed around Luggine capillary over the sample. The geometrical area of the surface was ≈ 70 cm².

The used material was commercial Armco iron (Fe, other elements, wt %: C 0.031; Mn 0.12; Si 0.01; P 0.008; S 0.015; Cr 0.01; Ni 0.01; Cu 0.02 and Al 0.03) in the form of rolled plate (thickness 1 mm). The geometrical area of the sample surface was 0.2715 ± 0.0037 cm². The exposed surface was grinded, polished and degreased by acetone. We used 5 plates for every inhibitor. The procedure of the tests was as following: 1. The vessel was filled by corrosive medium with or without inhibitor. 2. After 1-2 min the corrosion potential was recorded. 3. The cathodic galvanostatic polarization was taken under current density of 1 mA/cm² (30 s). 4. The dependence of potentiodynamic polarization on the current density was determined with the rate of 1 mV/s from -1 to +5 mA/cm² with the subsequent return to -0.2 mA/m². (The investigations were carried out in the laboratory of Physical Chemistry Institute of the Polish Academy of Sciences, Warsaw, Poland).

Table 1

Composition of aqueous phases (AP) used for the investigations and experimental conditions

Medium number	Composition of corrosive media AP						Experimental conditions			
	NH ₄ Cl	HCl	NaCl	MgCl ₂ ·6H ₂ O	H ₂ S	Ca(HSO ₄) ₂ ·2H ₂ O	CaCl ₂	JFl:cor.med. ratio	T, K	Time, h
1	1 %		1 %		0.06 %			1:2	343 ± 2	2
2			163 g/l	17 g/l		0.14 g/l	34 g/l	2:1*	$343 \pm 2^*$	2*
3		0.1N						1:2	$293 \pm 2^{**}$	2

Notes: * experimental conditions correspond to the patent [4]; ** the temperature corresponds to the temperature of oil production

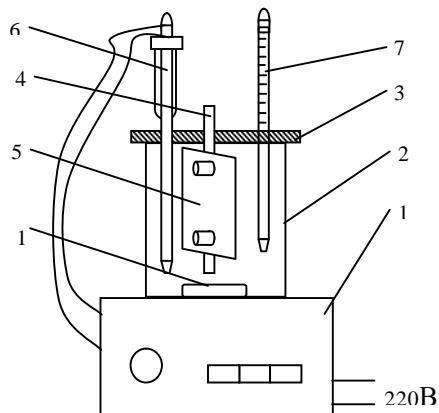


Fig. 1. Laboratory plant for the investigation of inhibitors anticorrosive effect:
magnetic stirrer (1); beaker (2); Teflon lid (3); glass rod (4); steel plate (5); contact thermometer
with temperature control (6) and thermometer (7)

2.4. Spectral Investigations

On the basis of the investigations concerning protective properties of the studied compounds the most effective inhibitors were selected. The spectral investigations were carried out to prove their chemical compositions. Nicolet Magna 560 infrared spectroscope was used. Kbr was used as a filler. The inhibitor was added to the filler, the mixture was homogenized and so called "pellets" were formed. They were placed inside the spectroscope using which the data were taken.

3. Results and Discussion

3.1. Gravimetric Investigations

Gravimetric investigations in the medium 1 (Fig. 2) show that the best protective effect has cation-active fat R-1 with the nitrogen content of 6 %. Its effect is commensurable with the protective effect of Dodigen-481 (the nitrogen content is 14 %). It should be noted that the mentioned inhibitors show the highest protection degree (86–89 %) in toluene and solvent naphtha. The value is by 5–15 % higher than that in *n*-alkane solvents.

The solutions of alkylimidazoline derivatives based on unsaturated oleic acid OD-3 and OT-2 with the nitrogen content of 12 and 9.6 %, respectively, also have sufficiently high protection degree (82–87 %) in toluene and solvent naphtha.

The solutions of alkylimidazoline derivatives with saturated alkyl chain SD and ST-4 (the nitrogen content is 12 and 14.2 %, respectively) have a relatively low protective degree (66–69 %) in aromatic solvents.

The following corrosion medium was medium 2 (Fig. 3). The conditions were chosen in accordance with the patent [4].

The alkylimidazolines derivatives based on oleic acid show the best protective effect in toluene and solvent naphtha. The protective effect of carbazoline OT-2 is 98 %. It is even higher than that of Dodigen-481 (92–93 %). The cation-active fat R-1 also shows the high protective effect (92–93 %), which is commensurable with the effect of the import analogue. The alkylimidazoline derivatives based on stearic acid have the low protective effect, the same as in the previous case.

The protective effects of inhibitors under the low-temperature hydrochloric corrosion in the model corrosion medium 3 are shown in Fig. 4. The total protective effect reduces due to the high acidity of the medium, however the highest effect is observed in toluene and solvent naphtha. Among all investigated inhibitors the R-1 has the highest effect (88–90 %). Imidazoline derivatives based on oleic acid show somewhat lower effect (76–85 %, depending on the solvent). The lowest effect (53–60 %) is observed for imidazolines based on stearic acid. ST-4 carbazoline in the oil solvent Nephrase P-1 65/75 practically does not protect the steel surface due to its bad solubility.

Since the highest protective effect is observed in aromatic solvents, we studied the protection degree of the investigated inhibitors in different corrosion media (Fig. 5). The protective effects were determined under the conditions represented in [4].

While comparing the results one can see that the highest protective effect for every inhibitor is observed in the medium 2. It is the medium which is maximally close to the medium in reflux reservoirs of the rectifying column. The experimental temperature conditions correspond to the vapor condensation temperature in the condensers. Under the experimental conditions the best data are observed for inhibitors OT-2 and R-1.

Fig. 6 shows the dependence of inhibitors protection degree on the nitrogen content. The data of protective effects obtained under the experimental conditions as per patent [4] were taken for the comparison.

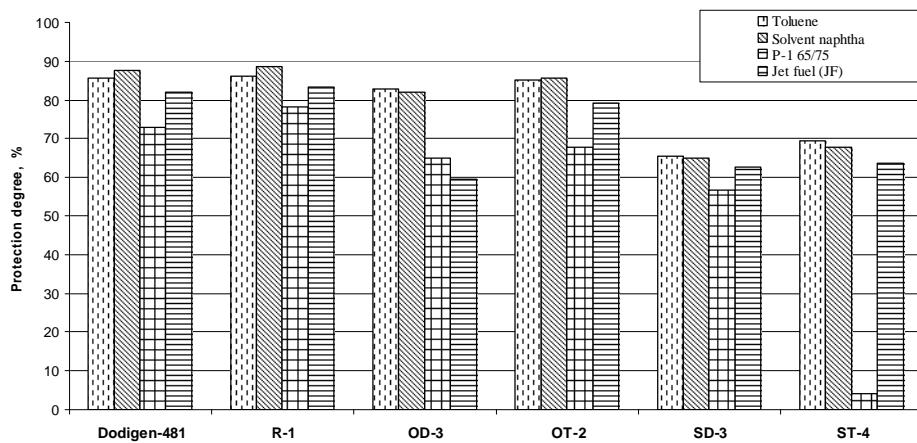


Fig. 2. The protective effect of corrosion inhibitors in different solvents in the corrosion medium 1

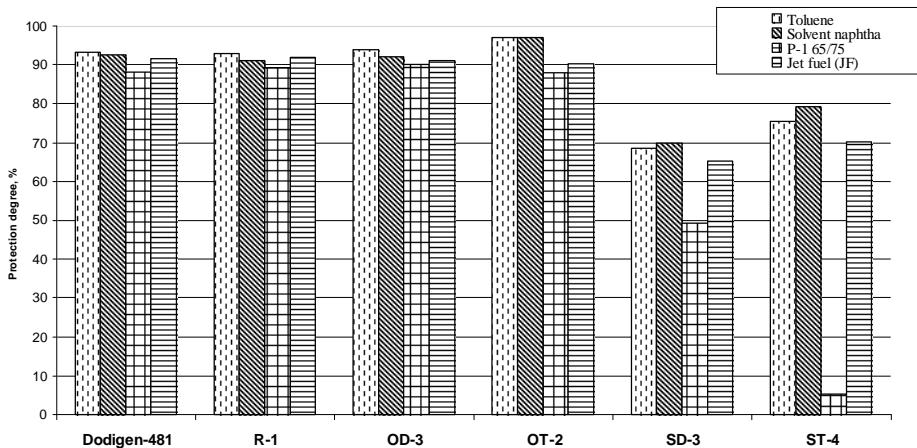


Fig. 3. The protective effect of corrosion inhibitors in different solvents in the corrosion medium 2

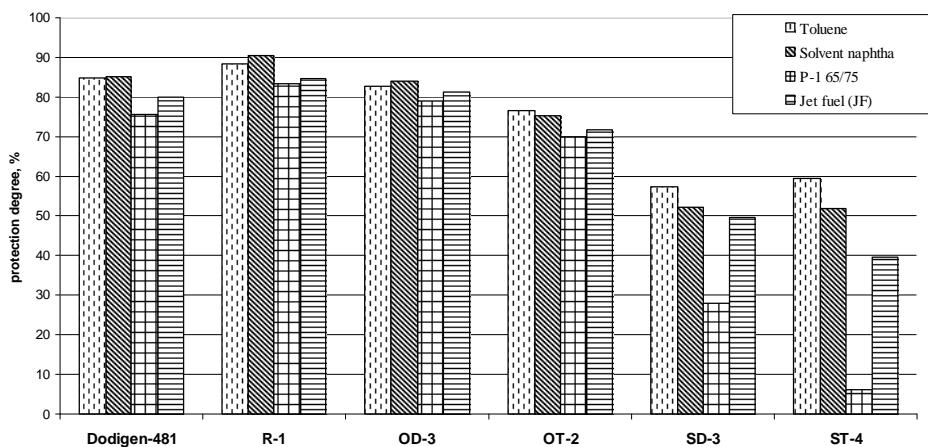


Fig. 4. The protective effect of corrosion inhibitors in different solvents in the corrosion medium 3

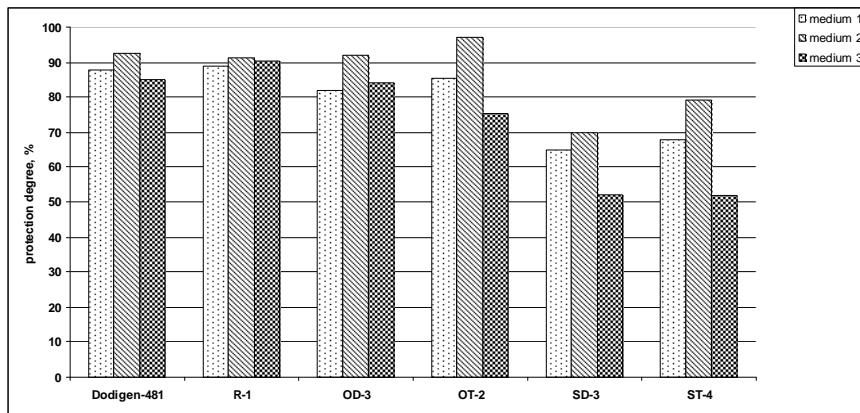


Fig. 5. The protective effect of corrosion inhibitors soluble in solvent naphtha in different corrosion media

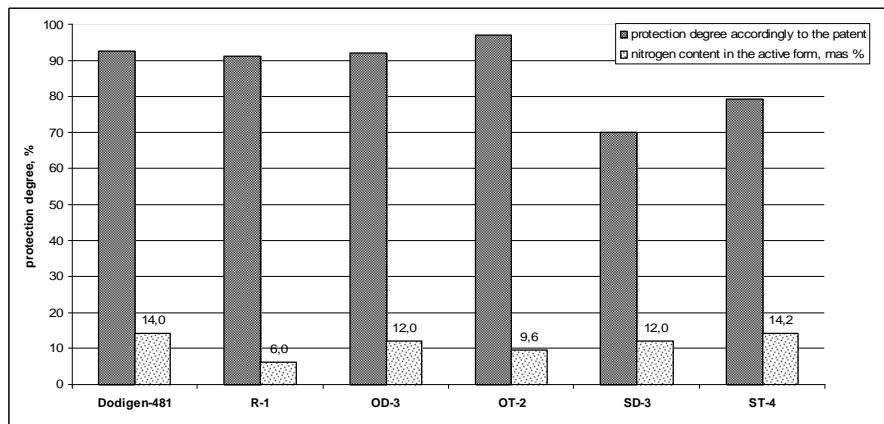


Fig. 6. Dependence of inhibitors protective effect on the nitrogen content

The oxyethylized carbazoline OT-2 with 9.6 % of nitrogen has the highest protective effect, *i.e.* the value is higher than that of the compounds with higher nitrogen content. This fact is in disagreement with the general opinion that the inhibitor's protective effect depends upon the nitrogen content (*i.e.* the higher nitrogen content, the higher protective effect). Thus Dodigen-481 (the nitrogen content is 14 %) protects 92.6 % of the surface and ST-4 (the nitrogen content is 14.2 %) – only 79.3 % of the surface. The sufficiently high protective effect is observed for cation-active fat R-1 with the nitrogen content of 6.0 %.

Thus the protective effect does not depend on the nitrogen content in the inhibitor (see Fig. 5). If we analyze the structure of the investigated compounds given in [3] we can see that the highest effect is observed for those compounds with oxygen-containing groups. The presence of the mentioned groups in carbazoline OT-2, cation-active fat R-1 and Dodigen-481 and the absence of oxygen-containing groups in carbazolines ST-4 and SD confirm the above assumption.

3.2. Potentiometric Investigations

To examine the mechanism of inhibitors action we selected carbazoline OT-2, cation-active fat R-1 and Dodigen-481. Carbazoline SD was selected due to the technological simplicity of its production. Fig. 7 represents the polarization curves of Armco iron with and without inhibitors.

Potentiometric investigations show that compounds adsorption over the iron surface decreases the rate of redox reaction, as well as affects the reaction limitative stages. The change of curves slope testifies to this fact. The shift of the corrosion potential toward positive values, *i.e.* the decrease of anode current relative to cathode current, indicates the predominant inhibition of oxidation reactions. It means that all compounds may be attributed to the inhibitors of anode type. However carbazoline OT-2 and cation-active fat R-1 also change the mechanism of cathode reaction, although to a lesser degree. That is why they may be attributed to the inhibitors of mixed action. Actually, it is difficult to stop corrosion owing to the

retardation of only one reaction – anode or cathode [6]. Therefore, the inhibitors of mixed action would have

higher protective effect compared with other investigated compounds.

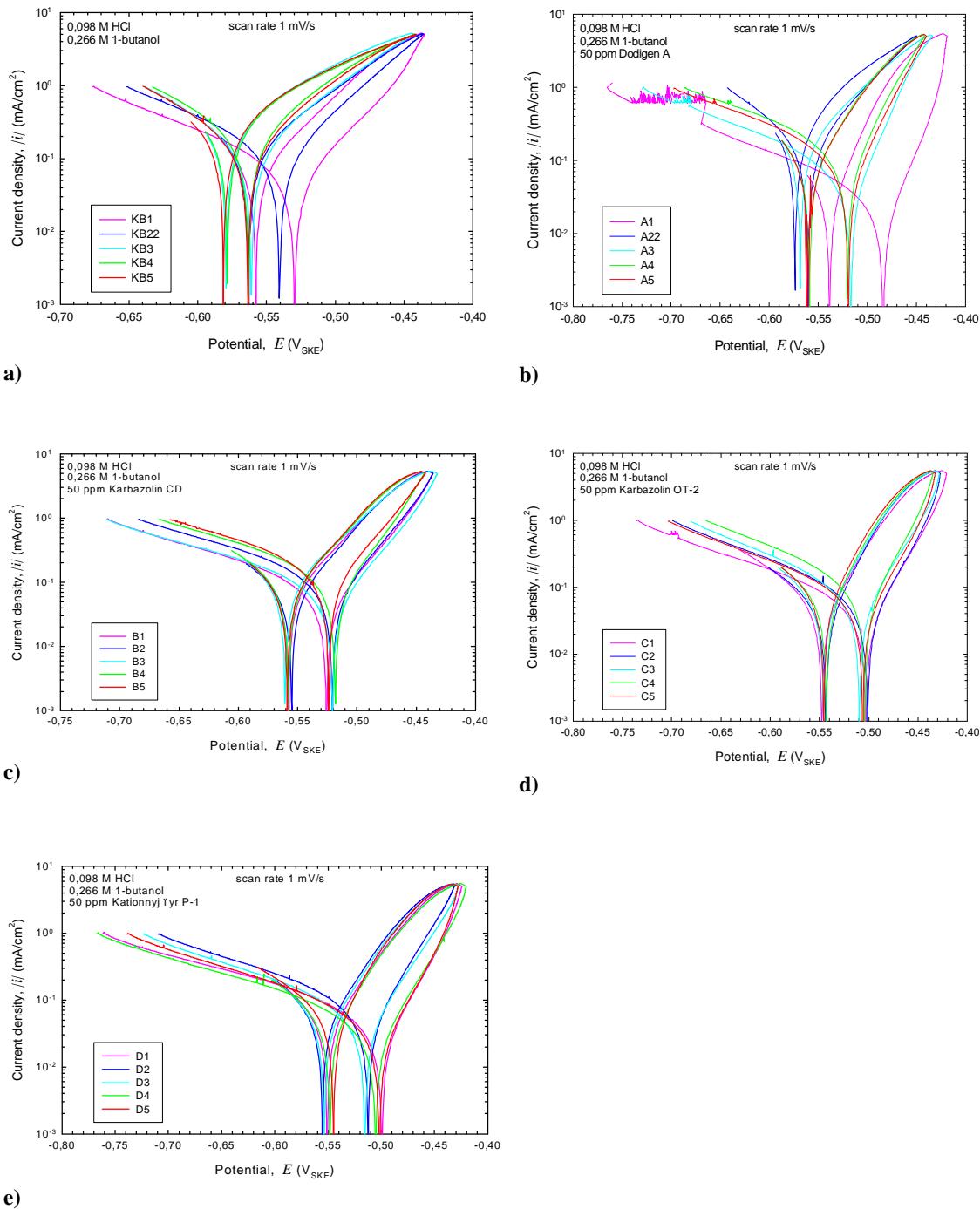


Fig. 7. Potentiometric polarization curves of Armco iron: without inhibitor (a); with Dodige-481 (b); with carbazoline SD (c); with carbazoline OT-2 (d) and with cation-active fat R-1 (e)

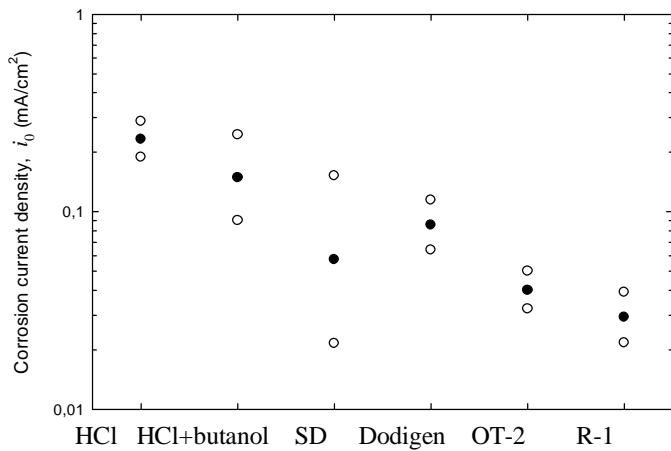


Fig. 8. Corrosion current density: maximum and minimum values (blanc points); average values (filled points)

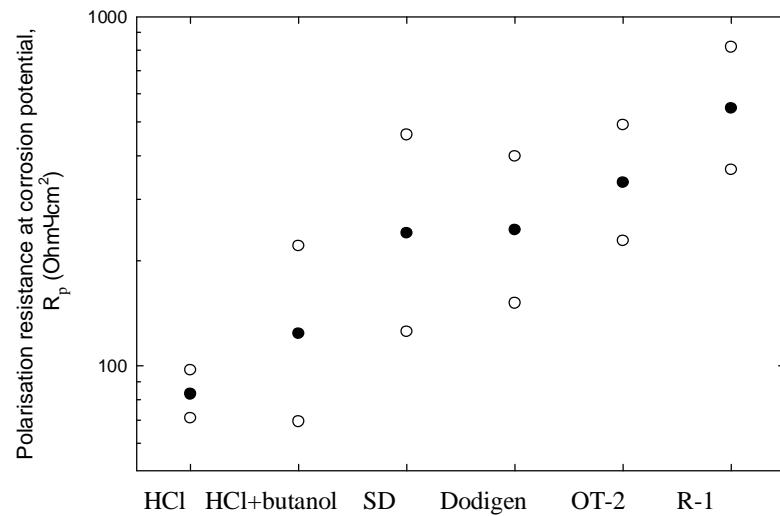


Fig. 9. Polarization resistance: maximum and minimum values (blanc points); average values (filled points)

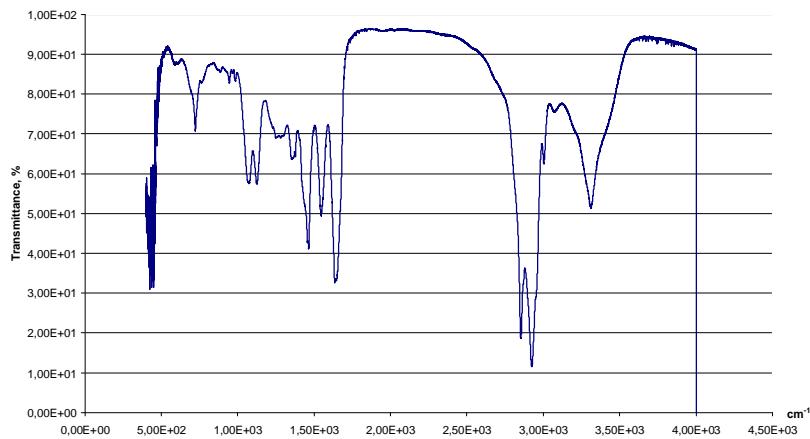


Fig. 10. IR-spectrum of carbazoline OT-2

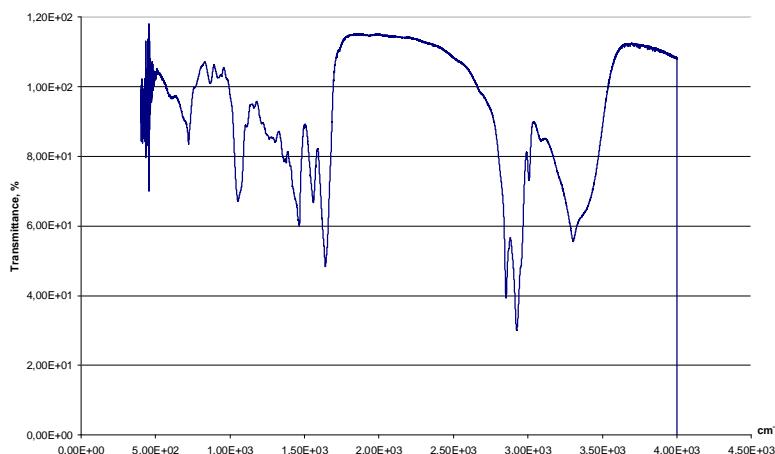


Fig. 11. IR-spectrum of cation-active fat R-1

To compare the protective effect of different inhibitors the values of corrosion current density in different media with and without inhibitors are shown in Fig. 8. Blanc experiments were carried out in the medium containing 0.1M HCl and 0.098M HCl + 0.266M 1-butanol. For all types of inhibitors we observe the considerable decrease of the current density compared with the density in non-inhibited media. But the least values are observed for OT-2 and R-1. It means that they have a better protective effect compared with the other inhibitors.

The dynamics of polarization resistance change for the iron electrode is shown in Fig. 9. The increase of polarization resistance due to the formation of inhibitor protective layer over the electrode surface is observed for all investigated compounds. The maximum value corresponds to the inhibitors R-1 and OT-2.

On the basis of the obtained results we selected carbazoline OT-2 and cation-active fat R-1 to prove their composition conformity with the formulae. The data of spectral analysis of OT-2 and R-1 are represented in Figs. 10 and 11, respectively.

The analysis of IR-spectrum of carbazoline OT-2 (Fig. 10) confirms the presence of imidazoline ring in the compound. The absorption bands at 1550, 1650 and 3320 cm^{-1} testify to this fact. The presence of methyl group in alkane chains is confirmed by the absorption bands at 1370, 1470 and 2860 cm^{-1} ; methylene groups in alkane chains – at 725, 948, 2930 and 3090 cm^{-1} ; ethylene group in alkenes – at 608, 1650 and 3010 cm^{-1} ; primary alcohol groups – at 1080, 1130, 1470 and 3320 cm^{-1} ; and tertiary amine group – at 1050 and 1250 cm^{-1} [7, 8].

The analysis of IR-spectrum of R-1 (Fig. 11) confirms the presence of disubstituted amides. The absorption bands at 1640 and 3310 cm^{-1} indicates this fact.

The presence of primary alcohol groups is confirmed by the absorption bands at 1310, 1400 and 3310 cm^{-1} ; secondary alcohol groups – at 1310, 1400 and 3310 cm^{-1} ; secondary amines – at 1560 and 3310 cm^{-1} ; amide groups – at 1560 and 3310 cm^{-1} . The absorption bands at 725, 1400, 1470, 2860 and 2930 cm^{-1} indicates the presence of methylene groups in alkane and alkene chains; at 1060 and 1470 cm^{-1} – the presence of ethyl groups; at 1060 and 1560 cm^{-1} – the presence of secondary amines; at 1310, 1400 and 2930 cm^{-1} – the presence of carbonic acids radicals; at 1310, 1640 and 3010 cm^{-1} – the presence of ethylene groups; and at 1470 cm^{-1} – the presence of *n*-propyl group.

The obtained spectra of carbazoline OT-2 and cation-active fat R-1 prove the conformity with the given formulae.

4. Conclusions

1. The highest protective effect has been established for the corrosion inhibitors soluble in aromatic solvents.
2. At the same nitrogen content the highest protective effect is observed for imidazolines based on unsaturated oleic acid. The effect of carbazolines OD-3 and OT-2 is within the range from 76 to 98 % in aromatic solvents. Moreover, they have better low-temperature properties. The solutions of alkylimidazoline derivatives with saturated alkyl chain SD and ST-4 (based on stearic acid) have relatively low protection degree (from 39 to 80 %) in a majority of corrosion media.
3. The protective effect of imidazolines based on unsaturated oleic acids is higher in the presence of amine and hydroxyl groups.
4. The inhibitors with amide and amine groups, as well as esters have a better protective effect. Thus, the

inhibitor R-1 obtained on the basis of colza oil has the protective effect 89–92 %.

5. Potentiometric investigations confirm the results of gravimetric studies, viz. R-1 and OT-2 are the best inhibitors with the lowest corrosion current and the highest corrosion resistance. By the mechanism of their action they are attributed to the inhibitors of anode action. The mechanism of cathode reaction is changed by them to a lesser degree.

6. The protective effect depends not only upon the nitrogen content but it is determined by the structure to which nitrogen belongs, as well as by the structure and hydrophobic property of hydrocarbon radical, which is a part of inhibitor molecule.

7. The obtained results show that the effectiveness of the best inhibitors OT-2 and R-1 is commensurable and sometimes is higher than that of import analogue Dodigen-481. Since the mentioned commercial compounds have another appropriation, we patented them as corrosion inhibitors [9, 10]. These compounds will be used for the further investigations.

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ДОСЛІДЖЕННЯ ЗАХИСНИХ ВЛАСТИВОСТЕЙ ТА СПЕКТРАЛЬНИЙ АНАЛІЗ НІТРОГЕН- ТА ОКСИГЕНВМІСНИХ ІНГІБІТОРІВ КОРОЗІЇ НАФТОВОГО ОБЛАДНАННЯ

Анотація. Гравіметричними та потенціометричними методами визначено захисні властивості шести інгібіторів корозії на базі імідазолінів, амідів, амінів та естерів. Досліджено вплив розчинника інгібітора на його захисні властивості. Встановлено залежність захисного ефекту інгібітора від вмісту нітрогену та функціональних груп. Вибрано найбільш ефективні інгібітори і наведено їх I^{C} -спектри.

Ключові слова: корозія, інгібітори корозії, карбозолін, імідазоліни, аміди, аміни, захисний ефект.