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New Conservation Materials on the Base of Colza Oil for the Steel Protection against Atmospheric Corrosion

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Abstract

Protective efficiency of the composition on the base of low erucic colza oil has been studied against the carbon steel corrosion in the salt solution (3 % NaCl), thermo-moisture chamber and the natural conditions. The following compositions have been used:

1. Colza oil (CO) and its components without the inhibiting additives;
2. CO with the synthetic fat acids bottoms (SFAB) additive (1–10 wt.%);
3. CO with the anticorrosion additive IFHAN 29-A (20 wt.%);
4. CO with zinc micro powder filler (50 wt.%);
5. CO with Zn micro powder (50 wt.%) and micro graphite (≤ 1 wt.%);
6. CO with Zn micro powder (50 wt.%) and multiwalled carbon nano tubes (≤ 1 wt.%).

The corrosion tests, electrochemical measurements have been conducted. Moisture absorption by the investigated compositions, their adhesion and cohesion with respect to steel surface were estimated.

Protective coatings of CO and its components are not effective in the presence of the chloride ions, but provide the 90 % protective efficiency in natural conditions. The compositions with SFAB and IFHAN 29-A show the protective effect equal to 40–50 % in chloride media and 99 % in a thermo-moisture chamber and natural conditions. The presence of Zn powder in the compositions allows to reach a high protective effect (up to 99 %) irrespective of the nature of the solvent-support (colza oil or its components). Addition of the multiwalled carbon nano tubes decreases the protective effect of the compositions.

Keywords

Colza oil; steel; protection; atmospheric corrosion.

Introduction

Hydrophobic materials are traditionally used for the engineering protection against atmospheric corrosion [1]. They complicate water diffusion causing electrochemical corrosion of metals. Such materials are prepared on the mineral oils basis, in which the corrosion inhibitors are put. In this paper the study of conservation materials has been carried out on the phytogenous oil basis. The choice of the solvent has been determined by a number of the factors. Among them is the cost of petroleum, which steadily rises, increasing the engineering preservation expenses for the agricultural manufacturers. The other aspect of the problem is the availability of oils to their direct manufacturers. An ecological aspect of the engineering preservation is also of great importance, because one of the most dangerous soil pollutants is the petroleum. Colza oil has better tribochemical properties than mineral oils and the high ability for biodegradation [2]. So, colza oil decomposes up to 98 % for 7 days without causing new ecotoxicity. The rest decomposes for next 14 days [3]. For the same periods the mineral oils decompose up to 25 and 45 % respectively. But at the same time a number of the additives presented in them come into soil and their behavior is unknown and unpredictable. It is possible to use the product obtained immediately after extraction of phytogenous raw material without any additional processing. The food-unfit oil would be a perfect solvent-support for the conservation materials.

The aim of the present work is to investigate the protective efficiency of low erucic colza oil, its compositions with the synthetic fat acids bottoms (SFAB) additive (1–10 wt.%); the anticorrosion additive IFHAN-29 A (20 wt.%), zinc micro powder filler (50 wt. %), zinc micro powder filler (50 wt. %) + + micro graphite (≤ 1 wt.%) with reference to carbon steel in the conditions of atmospheric corrosion and in the 0.5 M NaCl solution.

Experiment

Acid number of unrefined low erucic colza oil is 61.8 mg KOH / 1 g; peroxide number is 3.6 (% J_2). Primary acids in the composition of used low erucic colza oil are, wt.%: linoleic (46.0), oleic (15.5), arachidonic (8.7), palmitic (6.9). stearic (3.0), docosadiene (1.6), eicotriene (1.4), palmiticoleic (1.3), behenic (0.9), erucic (0.1).

The treatment of the unrefined colza oil with water at 50–60 °C gives phospholipids and hydrated oil.

Corrosion tests of the carbon steel samples (St3) covered with the film of unrefined low erucic colza oil (UCO), its composition with IFHAN-29 A, and other fillers phospholipids or hydrated oil were made in 0.5 M NaCl solution for 14 days, in the apparatus for heat and moisture treatment (one cycle includes exposure for 8 h at 40 °C and 100 % relative humidity and for 16 h at gradual cooling to room temperature in the switched off and closed reactor) for 30 days and in an open site in the conditions of the industrial atmosphere for 6 months. The protective action (Z, %) is calculated according to formula

$$Z = (K_0 - K_i) \cdot 100 / K_0,$$

where K_0 and K_i are the corrosion rates of unprotected and protected by the oil composition film steel samples, respectively.

IFHAN-29 A is a product of interaction between tall pitch and higher aliphatic amines in the presence of special catalyst produced in A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of the Russian Academy of Sciences. Protective films have been deposited on the steel samples by their immersion in the protective composition for 30 min. with subsequent hanging in the vertical position for a day in the open air. A thickness of the coating was calculated on data gravimetrical measurements with assumption of the uniform film. The size of the samples was $70 \times 30 \times 3$ mm for the tests in the NaCl solution and the apparatus for heat and moisture treatment and $150 \times 50 \times 3$ mm for the tests in an open site.

The carbon steel polarization potentiostatic measurements have been carried out in the 0,5 M NaCl aerated solution on the horizontal electrode reinforced in epoxy resin and covered by the protective composition film (thickness 20–40 μm).The three-electrode electrochemical cell (glass "Pyrex") with the divided anodic and cathodic spaces has been used. The reference electrode was saturated silver, silver-chloride, auxiliary one- smooth platinum. The potentials have been converted to the normal hydrogen scale.

Results and discussion

The colza oil itself without additives does not render any significant protective effect in the 0.5 M NaCl solution. The insertion of 2.5 wt.% SFAB into colza oil stimulates the steel corrosion. But the further increase in the SFAB content is characterized by the corrosion retardation and at the 15 – 20 wt.% SFAB in the colza oil composition the protective effect reaches a significant value (Table 1).

The potentiostatic polarization curves (Fig. 1) have allowed to determine the corrosion potential E_{cor}, the corrosion current i_{corr}, the Tafel slope coefficients of the anodic and cathodic polarization curves (b_a, b_c), protective effect (Z_{cor}) by the corrosion current i_{corr}, protective effect of the anodic ionization of steel Z_a at the potential equal to 0.10 V (Table 2).

Table 1

The concentration dependence of the carbonaceous steel corrosion rate (*K*) and the protective action (*Z*) of the colza oil compositions with SFAB

C_{SFAB}, wt.%	$h_{coating}$, μm	K, g/(m^2·h)	Z, %
0	24	0,041	6
2,5	29	0,063	Stimulation
5	39	0,039	10
10	62	0,036	18
15	180	0,0100	77
20	686	0,001	98

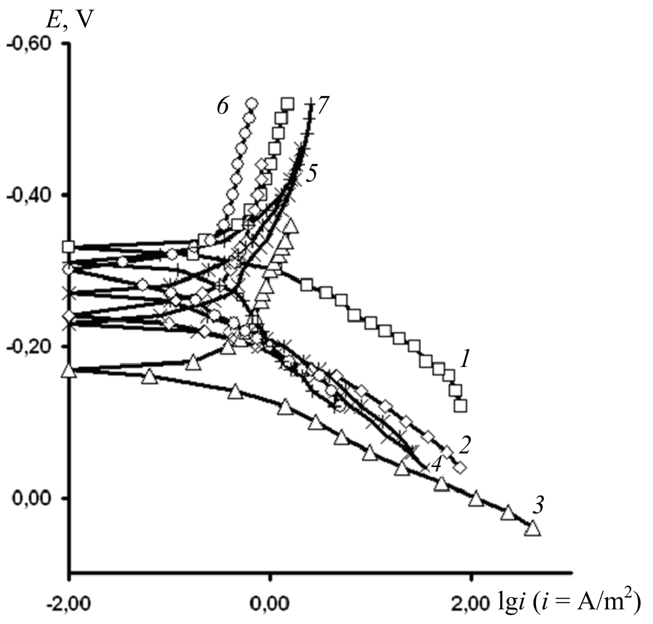

Fig. 1. The carbon steel polarization curves in 0,5 M NaCl solution without (*1*) and under colza oil coating (*2*) and its compositions, wt.% SFAB:
3 – 2,5; *4* – 5; *5* – 10; *6* – 15; *7* – 20

The similar thickness (10–16 μm) barrier coatings were formed to eliminate its influence in the 0.5 M NaCl solution.

The colza oil without any addition shifts the carbon steel corrosion potential (E_{cor}) by 0.1 V in the positive direction. The 2.5 wt.% of the SFAB magnifies this effect, but the further growth of the SFAB concentration steadily reduces E_{cor}. Evidently, the SFAB is the anodic action inhibitor, as in the case of the compounds based on the mineral oils, which are usually used as the solvent-support for the SFAB.

The carbon steel corrosion current under the colza oil and its compositions coatings decreases by more than 2.5 times. This effect practically does not depend on the SFAB concentration. The exception is the composition with the 5 wt.% of the SFAB. A similar situation occurs in the case of the protective effect by the corrosion current. Z_{cor} depends on the addition concentration and does not exceed 65–72 %. It must be noted that the Z_{corr} of the colza oil and its compositions with the SFAB (C_{SFAB} = 2,5–10 wt.%) determined by the electrochemical measures is significant higher and for the composition with 20 wt.% of the SFAB is lower than by the corrosion tests in the same medium.

Possibly in that case the discrepancy is determined by the various coatings thickness (particularly 16 and 688 μm).

The Tafel slope coefficient of the anodic polarization curve decreases significantly in the case of colza oil and its compositions with 5 wt.% of the SFAB coatings compared to the unprotected steel and increases for the compositions with 20 wt.% of the SFAB. The anodic protective action by the fixed potential –0,10 V tops 90 percent and reaches its peak value under the protective coating with 20 wt.% of the SFAB. The Z_a at that is similar to such a value determined by the corrosion tests. The anodic protective effect of the colza oil and its compositions with the SFAB (C = 2.5–15 wt.%) is higher than Z determined by the corrosion tests.

The Tafel slope coefficient of the cathode polarization curve decreases under the coating of the colza oil compared to the unprotected steel. The insertion of the 2.5 wt.% of the additive increases this effect.

The carbon steel polarization potentiostatic measurements have been carried out after the coatings' washing-off to estimate their degradation under the precipitation. These tests allow to make assumptions, by the implicit data, about water absorbing, adhesion and water permeability of the protective coatings. The washing-off during one minute has been made by the lamellar flow of the distilled water with the flow velocity 1l/min. The results of polarization potentiostatic measurements are presented in the Table 3 and in the Fig. 2.

As it can be seen from Table 3, the protective coatings' adhesion is high. The carbon steel corrosion currents under the proper coatings increase in most cases after the films' washing-off. The protective effect determined by the anodic polarization curves reduces to zero in the case of the colza oil film and virtually does not change if the coatings contain the

Table 2

Protective effect of the coatings based on the colza oil and SFAB according to data of the polarization curves

Coating	$h_{coating}$, μm	E_{cor}, V	b_a, V	Z_{cor}, %	Z_a, %
Without coating	–	–0,34	0,063	–	–
Colza oil	12	–0,23	0,056	63	92
Colza oil + 2,5 % SFAB	16	–0,17	0,026	65	98
Colza oil + 5 % SFAB	16	–0,25	0,056	37	90
Colza oil + 10 % SFAB	16	–0,27	0,063	68	97
Colza oil + 15 % SFAB	16	–0,27	0,083	72	97
Colza oil + 20 % SFAB	11	–0,31	0,100	72	98

SFAB. The washing-off basically does not influence the protective effect determined by the corrosion currents measures. The Tafel slope coefficients of the anodic polarization curves decrease significantly for the proper compositions.

The data of the corrosion tests in the apparatus for heat and moisture treatment (hydrostat) show high protective effect of used coatings (Table 4), but at the same time *Z* value depends on neither a film composition nor a film thickness.

Table 3

The washing-off influence of electrochemical corrosion kinetics on the carbon steel under the coatings based on the colza oil (the coating thickness is 10–20 μm)

Coating	E_{corr}, V	b_a, V	Z_{corr}, %	Z_a, %
Colza oil	–0.29	0.063	65	0
Colza oil + 2.5 % SFAB	–0.19	0.035	99	98
Colza oil + 5 % SFAB	–0.36	0.039	99	60
Colza oil + 10 % SFAB	–0.29	0.029	98	98
Colza oil + 15 % SFAB	–0.43	0.056	98	94
Colza oil + 20 % SFAB	–0.19	0.063	75	98

Application of the oxidized colza oil kept in the not compact closed package for two years lowers the protective effect of its coating in the hydrostat to 71 %. However, an insertion of IFHAN-29 A (20 %) into oxidized colza oil heightens *Z* value up to 97 %. But the protective effect basically does not change because of the insertion of the additive into fresh colza oil. Thus, it is worth to insert IFHAN-29 A only into oxidized colza oil, when these conservation materials are used for the protection of equipment and spare parts indoors, including non-heated indoor environments.

The corrosion tests in an open site for 3 and 6 months show sufficiently high protective effect of unrefined colza oil and its composition with IFHAN-29 A and SFAB increasing with an increase of the test duration (Table 5). After the 6 months of the experiment all the compositions show the same protective effect (99 %). Thus, it is inexpedient to insert IFHAN-29 A and SFAB into colza oil for the protection of equipment in the open site (industrial atmosphere).

The presence of Zn powder in the compositions allows to reach a high protective effect (up to 99 %) [4–6] independently from a nature of the solvent-support (colza oil or its components). The addition of the multiwalled carbon nano tubes decreases the protective effect of the compositions [5].

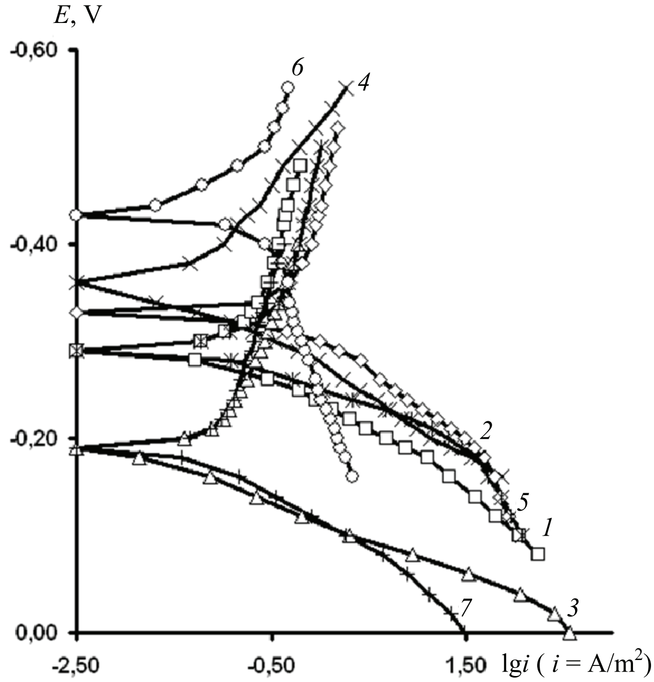

Fig. 2. The carbon steel polarization curves in 0.5 M NaCl solution under colza oil and its composition coatings after coatings' washing-off:
1 – without coating; *2* – colza oil; *3* – colza oil + 2,5% SFAB; *4* – colza oil + 5% SFAB; *5* – colza oil + 10% SFAB; *6* – colza oil + 15% SFAB; *7* – colza oil + 20% SFAB

Table 4

Protective effect (*Z*, %) of used protective compositions with reference to carbon steel in the hydrostat

Protective coating	Thickness of protective film, μm	*Z*, %
Unrefined colza oil (UCO)*	31/29	99/71
UCO + IFHAN-29 A (20 %)*	32 / 29	98/97
Colza oil + 20 % SFAB	1750	~100

*numerator – data for the fresh UCO; denominator – data for the oxidized UCO.

Table 5

Protective effect (*Z*, %) of used protective compositions with respect to carbon steel in the open site ((industrial atmosphere)

Coating	*Z*, % at the test duration, month	
	3	6
Unrefined colza oil (UCO)	96	99
UCO + IFHAN-29 A (20 %)	93	99
UCO + SFAB (10–20 %)	93	99

Conclusion

Protective materials on the base of unrefined low erucic colza oil, its compositions with IFHAN-29 A and SFAB show high protective effect with reference to carbon steel corrosion in the hydrostat equal to 98–99 % and in an open site after 6 months exposition – 99 %. But these conservation materials are ineffective in the neutral solutions containing chloride ions. Their use in such media demands an insertion of special additives which would increase the protective action.

It is worth inserting IFHAN-29 A additive (20 wt.%) only into oxidized colza oil, when these conservation materials are used for the protection of equipment and spare parts indoors, including non-heated indoor environments.

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