Preservative materials based on vegetable oils for steel protection against atmospheric corrosion. I. Colza oil

V.I. Vigdorovich,[1] L.E. Tsygankova,[2] E.D. Tanygina,[2] A.Yu. Tanygin[1] and N.V. Shel[3]

[1]All-Russian Scientific Research Institute of Use of Machinery and Oil Products, Novo-Rubezhnyi per., 28, Tambov, 392022, Russian Federation
[2]Derzhavin State University, ul. Internatsyonalnaya, 33, Tambov, 392000, Russian Federation
[3]Tambov State Technical University, ul. Sovetskaya, 106, Tambov, 392000, Russian Federation
E-mail: vits21@mail.ru

Abstract

The protective efficiency of a formulation based on low erucic colza oil against carbon steel corrosion in salt solution (0.5 M NaCl), in a thermal moisture chamber and under natural conditions has been studied. The following formulations have been used: (1) colza oil (CO) without inhibiting additives; (2) CO with addition (1–10 wt.%) of synthetic fat acids bottoms (SFAB); and (3) CO with the IFHAN-29A anticorrosion additive (20 wt.%). Corrosion tests and electrochemical measurements have been conducted. Protective CO coatings are not efficient in the presence of chloride ions but provide a high protective efficiency under natural conditions.

Key words: *colza oil, steel, protection, atmospheric corrosion.*

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Introduction

Hydrophobic materials are traditionally used for equipment protection against atmospheric corrosion [1]. They hinder water diffusion that causes the electrochemical corrosion of metals. Such materials are prepared on the basis of mineral oils with addition of corrosion inhibitors [2–5]. In this paper we have studied preservative materials based on a phytogenous oil. The choice of the solvent was caused by a number of circumstances, including the cost of petroleum, which varies continuously, increasing the cost of equipment preservation for agricultural manufacturers. The other aspect of the problem is the value of oils for deep oil processing. An ecological aspect of equipment preservation is also of great importance, because petroleum is one of the most hazardous soil pollutants. Colza oil has better tribochemical properties than mineral oils and a high ability for biodegradation [6]. In fact, colza oil decomposes for up to 98% in 7 days without formation of new ecotoxic products. The rest decomposes within the next 14 days [7]. In the same periods of time, mineral oils decompose for up to 25 and 45%, respectively. At the same time, a number of additives they contain penetrate into soil and their behavior is unknown and unpredictable. It is possible to use a product obtained at once after extraction of phytogenous raw material without any additional processing. The food-unfit oil would be a perfect solvent-support for the preservative materials.

The purpose of this work is to study the protective efficiency of low erucic colza oil, its formulations with a synthetic fat acids bottoms (SFAB) additive (1–10 wt.%), and the IFHAN-29A anti-corrosive additive (20 wt.%) toward carbon steel under atmospheric corrosion conditions and in 0.5 M NaCl solution.

Experimental

The acid number of unrefined low erucic colza oil is 61.8 mg KOH/1 g and the peroxide number is 3.6 (% J_2). The content of primary acids in the formulation of the low erucic colza oil used 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).

Corrosion tests of carbon steel samples (St3) covered with a film of unrefined low erucic colza oil (UCO), its formulation with IFHAN-29A, and SFAB were carried out in 0.5 M NaCl solution for 14 days, in an apparatus for heat and moisture treatment (one cycle includes exposure for 8 h at 40°C and 100% relative humidity and for 16 h with gradual cooling to room temperature in the closed reactor that has been turned off) for 30 days, and in an open site under industrial atmosphere conditions for 6 months. The protective effect (Z, %) was calculated according to the formula:

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

where K_0 and K_i are the corrosion rates of unprotected steel samples and those protected by a film of an oil based formulation, respectively.

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

Potentiostatic polarization measurements on carbon steel were carried out in aerated 0.5 M NaCl solution on horizontal electrodes reinforced into epoxy resin and coated by a film of the protective formulation (thickness 20–40 microns). A three-electrode electrochemical cell (“Pyrex” glass) with divided anodic and cathodic spaces equipped with a saturated silver/silver chloride reference electrode and a smooth platinum auxiliary electrode were used. The potentials were converted to the normal hydrogen scale.

Results and discussion

Colza oil itself, without additives, does not render any significant protective effect in 0.5 M NaCl solution. Addition of 2.5 wt.% SFAB to colza oil stimulates steel corrosion. However, a further increase in the SFAB content slows down corrosion, and the protective effect reaches a significant value at 15–20 wt.% SFAB in the colza oil formulation (Table 1).

Table 1. The concentration dependence of carbon steel corrosion rate (*K*) and the protective action (*Z*) of colza oil formulations with SFAB in 0.5 M NaCl solution.

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	0.010	77
20	686	0.001	98

Potentiostatic polarization curves (Figure 1) allowed us to determine the corrosion potential E_{cor}, corrosion current i_{corr}, the Tafel slopes of anodic and cathodic polarization curves (b_a, b_c), the protective effect (Z_{cor}) based on corrosion current i_{corr}, and the protective effect of steel anodic ionization Z_a at a potential of –0.10 V (Table 2).

Barrier coatings with similar thickness (10–16 μm) were formed to eliminate the effect of thickness on the protective effect in 0.5 M NaCl solution.

Colza oil without any additives shifts the corrosion potential of carbon steel (E_{cor}) by 0.1 V in the positive direction. 2.5 wt.% of SFAB magnifies this effect, but a further growth in the SFAB concentration steadily reduces E_{cor}. Evidently, SFAB is an anodic inhibitor, similarly to compounds based on mineral oils that are usually used as the support solvent for SFAB.

The corrosion current of carbon steel under coatings of colza oil and its formulations decreases more than 2.5-fold. This effect practically does not depend on the SFAB concentration. The formulation with 5 wt.% of SFAB is an exception. A similar situation occurs in the case of the protective effect determined from corrosion current. Z_{cor} depends on the additive concentration and does not exceed 65–72%. It should be noted that the Z_{corr} values of colza oil and its formulations with SFAB (C_{SFAB} = 2.5–10 wt.%) determined by electrochemical measurements are significantly higher, whereas for the formulation with 20 wt.% of SFAB it is lower than that determined from corrosion tests in the same medium. Possibly, the discrepancy in this case is determined by different coatings thickness (in particular, 16 and 688 μm).

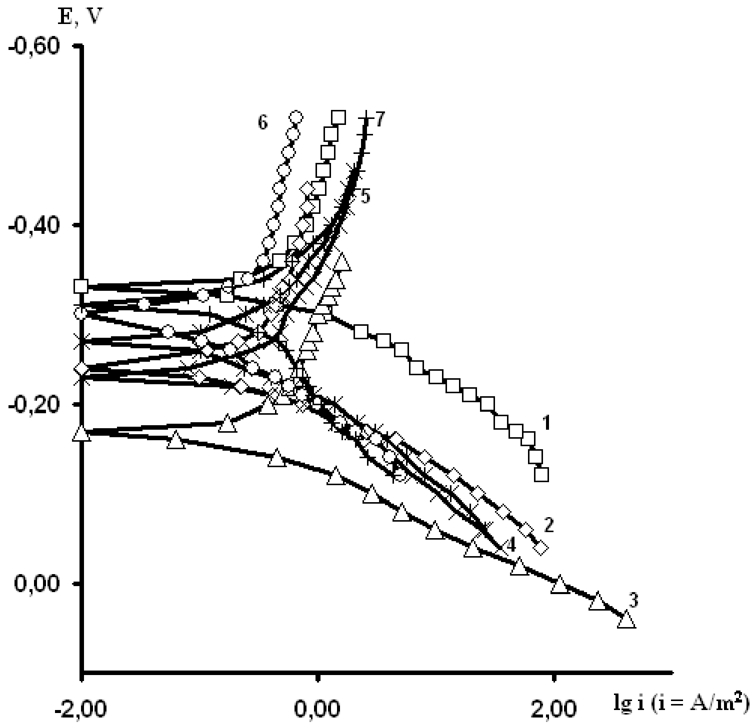

Figure 1. Carbon steel polarization curves in 0.5 M NaCl solution without (*1*) and under colza oil coating (*2*) and its formulations containing, wt.% SFAB: *3* – 2.5; *4* – 5; 5 – 10; *6* – 15; *7* – 20.

Table 2. Protective effect of coatings based on colza oil and SFAB according to data of polarization curves in 0.5 M NaCl solution.

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

The Tafel slope of the anodic polarization curve decreases significantly in the case of coatings of colza oil and its formulations with 5 wt.% of SFAB, compared to unprotected steel, and increases for formulations containing 20 wt.% of SFAB. The anodic protective action at a fixed potential of –0.10 V exceeds 90 percent and reaches its peak value under the protective coating with 20 wt.% of SFAB. The Z_a in this case is similar to the value determined from the corrosion tests. The anodic protective effect of colza oil and its formulations with SFAB (C = 2.5–15 wt.%) is higher than Z determined from corrosion tests.

The Tafel slope coefficient of the cathodic polarization curve decreases in the presence of a colza oil coating compared to unprotected steel. Addition of 2.5 wt.% of the additive increases this effect.

Polarization potentiostatic measurements on carbon steel were carried out after washing-off the coatings in order to estimate their degradation under atmospheric precipitations. These tests allow us to make assumptions based on implicit data about water absorption, adhesion and water permeability of the protective coatings. The coating was washed off for one minute by a lamellar flow of distilled water with a flow velocity of 1 L/min. The results of polarization potentiostatic measurements are presented in Table 3 and in Figure 2.

Table 3. Effect of washing-off on the carbon steel electrochemical corrosion kinetics under coatings based on colza oil (coating thickness 10–20 μm) in 0.5 M NaCl solution.

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

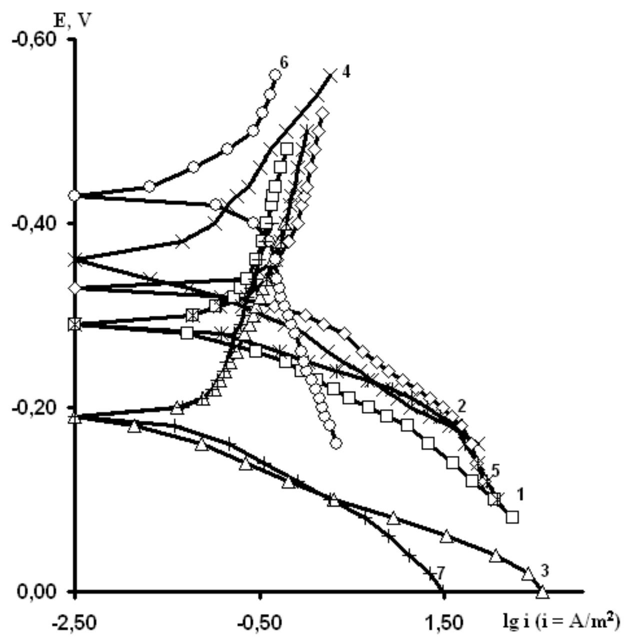

Figure 2. Carbon steel polarization curves in 0.5 M NaCl solution under coatings of colza oil and its formulations after coating wash-off: *1* – without coating, *2* – colza oil, *3* – colza oil + 2.5% SFAB, *4* – colza oil + 5% SFAB, *5* – colza oil + 10% SFAB, *6* – colza oil + 15% SFAB, *7* – colza oil + 20% SFAB.

As shown in Table 3, the adhesion of the protective coatings is high. The carbon steel corrosion currents under the proper coatings increase in most cases after the film wash-off. The protective effect determined from anodic polarization curves decreases to zero in the case of a colza oil film and virtually does not change if the coatings contain SFAB. Washing-off basically does not influence the protective effect determined from corrosion currents measurements. The Tafel slopes of anodic polarization curves decrease significantly in the presence of formulations containing 2.5–10 wt.% SFAB.

The data of the corrosion tests in the apparatus for heat and moisture treatment ("hydrostat") show high a protective effect of the coatings used (Table 4), but at the same time the *Z* value does not depend on either the film composition or the film thickness.

Table 4. Protective effect (*Z*, %) of the protective formulations used for carbon steel in a hydrostat.

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

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

Application of oxidized colza oil kept for two years in an unsealed package lowers the protective effect of its coating in the hydrostat to 71%. However, addition of IFHAN-29A (20%) into oxidized colza oil increases *Z* to 97%. However, the protective effect basically does not change upon addition of the additive into fresh colza oil. Thus, it is worthwhile to add IFHAN-29A only to oxidized colza oil, if these preservative 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 a sufficiently high protective effect of unrefined colza oil and its formulation with IFHAN-29A and SFAB, which increases with an increase in the test duration (Table 5). After 6 months of the experiment, all the formulations show the same protective effect (99%). Thus, it is inexpedient to add IFHAN-29A and SFAB to colza oil for protection of equipment in the open site (industrial atmosphere).

Table 5. Protective effect (*Z*, %) of the protective formulations used for carbon steel in the open site ((industrial atmosphere).

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

The presence of Zn powder in the formulations allows one to reach a high protective effect (up to 99%) [8–10] irrespective of the nature of the support solvent (colza oil or its components). Addition of multiwalled carbon nano tubes decreases the protective effect of the formulations [9].

Conclusion

Protective materials based on unrefined low erucic colza oil, its formulations with IFHAN-29A and SFAB show a high protective effect for carbon steel corrosion, namely, 98–99% in a hydrostat and 99% in an open site after 6 months exposure. However, these preservative materials are inefficient in neutral solutions containing chloride ions. Their use in such media required addition of special components to increase the protective action.

It is expedient to add IFHAN-29A (20 wt.%) only to oxidized colza oil where these preservative materials are used for protection of equipment and spare parts indoors, including non-heated indoor environments.

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