Protective efficiency of oil compositions with Cortec VpCI-368D

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Abstract

The protection of metals by coatings based on compositions of a number of petroleum oils with Cortec VpCI-368D has been studied by gravimetric and electrochemical methods. Cortec VpCI-368D is a blend of organic solvent with volatile inhibitor. Oil compositions with Cortec VpCI-368D are well wetted with water (contact angles less than 90°), they themselves spread over the steel surface (contact angles 1–3°), displacing water layers, and are characterized by low surface tension. The work of adhesion of the compositions studied was calculated. Wetting the coatings with water promotes the penetration of an aqueous medium through the pores in them to the metal surface and the formation of an ionic double electric layer there, as a result of which it becomes possible to carry out electrochemical measurements. The protective efficiency of the composition of industrial oil I-20A and Cortec VpCI-368D (5–10 wt%) was estimated on the basis of polarization curves at a short-term exposure of a steel electrode with coating in a 0.5 M NaCl solution ($Z=97\text{--}98\%$). Compositions of petroleum oils with Cortec VpCI-368D (5–10 wt%) showed the high protective efficiency in relation to carbon steel in a thermal moisture chamber (97–100%) and natural conditions (80–94%). These compositions are most effective in relation to brass L-62 ($Z=70\text{--}80\%$) in a chloride-containing neutral solution at an exposure of 456 h; their use for protecting copper is impractical, since the protective effect does not exceed 40%. Only compositions with commercial oil I-20A ($Z=67\%$) are reasonable in these conditions in relation to carbon steel. Consumption of Cortec VCI-368D for coating deposition at 20 and 70°C was calculated.

Keywords: oil compositions, protective effectiveness, atmospheric corrosion, chloride solution, field tests, thermal moisture chamber.

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Introduction

Various oil compositions [1–5] are widely used for temporary anticorrosive protection of equipment against atmospheric corrosion. Interest in application of volatile corrosion

inhibitors for these purposes, the use of which is limited by the need to create closed spaces [6–9], has also grown in recent years. The combination of contact corrosion inhibitors with volatile components is undoubtedly relevant and modern if it will slow down corrosion processes, especially in places of defects on the metal surface, and enhance the protective properties of the compositions.

Cortec Corporation, USA (on the territory of Russia and the CIS countries, the official representative is the company LLC “CORTEC RUS”) offers a composition of an organic solvent with a volatile inhibitor (30%) Cortec VpCI-368D for temporary protection against atmospheric corrosion. Long-term (up to 5 years) protection of ferrous and non-ferrous metals against corrosion under the open sky is predicted. The composition forms a translucent, waxy, self-tightening film that can be removed with common solvents or an alkaline cleaner.

The purpose of this work is to study a protection of carbon steel, copper and brass against atmospheric corrosion by means of petroleum oil compositions with Cortec VpCI-368D.

Experimental technique

Industrial (I-20A), transformer (TKp), commercial motor (M10G2k) and waste motor (WMO) oils were used as a solvent-support in oil compositions.

The concentration of Cortec VpCI-368D in the oil compositions was 3–10 wt%.

The studies were carried out on samples of carbon steel St3 with a composition, wt%: C 0.20; Mn 0.51; Si 0.15; P 0.04; S 0.05; Cr 0.32; Ni 0.21; Cu 0.23; Fe 98.29; copper M2: Al≤0.002; Zn≤0.005; Mn≤0.01; Cr≤0.05; Si≤0.01; Zr≤0.05; Cu 99.7; two-phase (α+β) brass L62: Zn 22.5; Mn 2.9; Fe 2.0; Al 4.1; Cu is the rest.

The oil composition coatings were deposited by immersion of the samples into the bath containing the composition at 20°C for 10 seconds. After that, the samples were kept in a suspended state at room temperature to drain the excess oil composition and to form a protective film. The thickness of the formed film (μm) was evaluated gravimetrically, assuming the layer to be uniform, according to the formula:

$$h = \frac{\Delta m \cdot 10^6}{S \cdot \rho}$$

where Δm is the change in the mass of the sample due to the formation of the coating, kg; S is the surface area, m²; ρ is the density of the preservation material, kg/m³.

Corrosion tests were carried out in a 0.5 M NaCl solution (GOST 9.042-75), a thermal moisture chamber G-4 (GOST 9.054-75), and in natural conditions. The corrosion rate was calculated from the weight loss of the samples and by extrapolating the Tafel sections of the polarization curves to the corrosion potential.

The recalculation of the corrosion rate from electrical units to mass units was carried out according to the formula:

$$K = \gamma i_{\text{cor}},$$

where K is the corrosion rate, $\text{g}/(\text{m}^2 \cdot \text{h})$, i_{cor} is the corrosion current, A/m^2 ; γ is the electrochemical equivalent of iron, taking into account its transition to solution (oxidation) in the form of Fe^{2+} ($\text{g}/\text{A} \cdot \text{h}$).

The protective effectiveness of the compositions was evaluated by the formula:

$$Z = \frac{K_0 - K}{K_0} \cdot 100\%,$$

where K_0 and K are metal corrosion rates in the absence and presence of a film of the oil composition, respectively.

Potentiodynamic polarization measurements at a potential sweep rate of 0.66 mV/s were carried out in 0.5 M NaCl solution in an electrochemical cell made of Pyrex glass with anodic and cathodic spaces separated by a thin section using an IPC-Pro MF potentiostat. The reference electrode was a saturated aqueous silver/silver chloride, the auxiliary electrode was smooth platinum. The working electrode was reinforced with a mandrel made of ED-5 epoxy resin hardened with polyethylene polyamine. Potentials were recalculated according to normal hydrogen electrode.

The contact angles of wetting (θ) of the oil compositions were determined using the EASYDROP device and by the calculation method [10]. The values of surface tension (σ) were obtained by the method of ring tearing on a Du-Nui device, and the value of the work of adhesion (W_a) was calculated according to the formula:

$$W_a = \sigma(1 + \cos \theta)$$

Results and Discussion

The quality of wetting and spreading of the compositions over the metal surface affects the appearance, continuity, adhesive strength and protective ability of coatings.

The values of the contact angles (θ_1) of wetting of the oil compositions under study with water, obtained using the EASYDROP device, do not exceed 90° (Table 1), therefore, water actively wets the investigated coatings. The rapid spreading of the oil compositions drops themselves over the St3 steel surface did not allow determining their contact angles (θ_2) using the EASYDROP device; therefore, a calculation method was used [10].

The maximum contact angles (θ_1 and θ_2) were obtained for compositions based on WMO, however, the difference in values for compositions based on other oils is insignificant (Table 1). The θ_2 values of the compositions are much lower than the corresponding values for distilled water (77°); therefore, all the studied oil compositions should effectively displace the surface phase water layers.

The values of surface tension (σ) and work of adhesion (W_a) of different oil compositions are close to each other and tend to decrease slightly with increasing concentration of Cortec VpCI-368D (Table 1).

Table 1. Contact angles of wetting of the Cortec VpCI-368 D oil compositions with water (θ_1) and steel with oil compositions (θ_2), surface tension and work of adhesion of the compositions.

Oil	Cortec VpCI-368 D concentration, wt%	θ_1 , deg.	θ_2 , deg.	σ (l/g), (mN/m)	W_a , (mN/m)
TKp	3	61	0.95	20.79	41.51
	5	62	0.72	20.04	40.08
	7	56	0.70	20.35	40.70
	10	56	0.70	20.35	40.70
I-20A	3	54	1.35	17.33	34.66
	5	56	1.36	17.23	34.46
	7	52	1.10	16.55	33.10
	10	49	1.11	16.66	33.32
M10G2k	3	73	1.12	19.63	39.26
	5	63	1.18	19.90	39.72
	7	76	1.28	18.94	37.86
	10	70	1.27	18.89	37.76
WMO	3	79	3.10	25.79	51.58
	5	78	3.00	20.04	40.08
	7	72	2.84	18.85	37.70
	10	70	1.76	18.73	37.46

Although the oil compositions are capable to displace the phase water layers on the metal surface, nevertheless, the wetting of the oil coatings with water promotes the penetration of the aqueous medium through the pores in them to the metal surface and the formation of an ionic double electric layer there, as a result of which it becomes possible to carry out electrochemical measurements [3, 4]. The protective efficacy of oil formulations is due to the adsorption of inhibitors contained in them on the metal surface.

Electrochemical studies make it possible to give an express assessment of the protective properties of the studied oil compositions. The polarization curves of a steel electrode coated with the compositions based on I-20A oil measured after a 15-minute exposure in a 0.5 M NaCl solution are shown in Figure 1.

Figure 1. Polarization curves of St3 steel coated with protective compositions in 0.5 M NaCl solution: 1 – no coating, 2 – I-20A; (3–7) I-20A with Cortec VpCI-368 D, mass. %: 3 – 100; 4 – 3; 5 – 5; 6 – 7; 7 – 10.

The corrosion potential (E_{cor}) of a steel electrode in the absence of a coating is -0.37 V, the corrosion current density (i_{cor}) is 5.01 A/m². The slope of the Tafel section of the anodic polarization curve is close to 56 mV (Table 2), which corresponds to the value of $2.3RT/F$ typical of anodic ionization of iron in chloride media in the absence of passivation. E_{cor} retains the same value after applying a film of fresh I-20A oil, and i_{cor} decreases to 2.14 A/m². The anodic curves practically coincide in both cases, and the cathodic process on the electrode with the I-20A film is inhibited. The protective efficiency of such a coating (Z) is 57% . The oil composition with Cortec VpCI-368D significantly reduces corrosion currents and, accordingly, increases the protective effectiveness of the coating (Figure 1, Table 2). At the same time, a slowdown of the anodic process is observed, especially significant in the presence of 5–10% additive. A quick transition to the limiting oxygen current is observed on the cathodic curves.

Table 2. Protective properties of the compositions based on I-20A and Cortec VCI-368D applied to St3 steel.

Coating composition	$-E_{\text{cor}}$, V	I_{cor} , A/m ²	b_c , V	b_a , V	Z, %
Absent	0.37	5.01	0.102	0.056	–
I-20A	0.37	2.10	0.155	0.065	57
VCI-368D	0.17	0.63	0.090	0.043	87
3% VCI-368D in I-20A	0.32	0.54	0.272	0.034	89
5% VCI-368D in I-20A	0.18	0.13	0.195	0.034	98
7% VCI-368D in I-20A	0.30	0.10	0.384	0.026	98
10% VCI-368D in I-20A	0.16	0.17	0.160	0.035	97

Coating with a 3 wt% Cortec VCI-368D composition exhibits almost the same protective effect as a coating with an individual Cortec VCI-368D. The protective effectiveness of compositions with 5–10% additive to I-20A reaches 97–98%.

Protective compositions based on all studied oils containing 5–10 mass. % Cortec VCI-368D are characterized by a Z value of the order of 97–100% during accelerated (960 hours) corrosion tests in a thermal moisture chamber G-4 (Table 3). The lowest Z values (97–98%) are typical for compositions based on I-20A oil. Obviously, this is due to the lowest value of the work of adhesion of these compositions in comparison with the rest.

Table 3. Results of corrosion tests of steel samples with oil coatings in a thermal moisture chamber G-4 at an exposure of 960 hours.

Oil	Cortec VpCI-368 D concentration, wt%	Coating thickness, μm	K, g/(m ² h)	Z, %
TKp	Control	0	0.1225	–
	0	11	0.1086	20
	3	13	0.0085	93
	5	13	0.0002	99
	10	14	0.0002	99
I-20A	Control	0	0.1225	–
	0	13	0.0448	63
	3	14	0.0106	91
	5	14	0.0023	98
	7	15	0.0023	98
	10	15	0.0015	99

Oil	Cortec VpCI-368 D concentration, wt%	Coating thickness, μm	K , $\text{g}/(\text{m}^2\text{h})$	Z , %
M10G2k	Control	0	0.1225	–
	0	15	0.0502	59
	3	15	0.0072	94
	5	16	0.0002	99
	10	17	0.0001	~100
	Control	0	0.1225	–
WMO	0	17	0.0282	77
	3	18	0.0024	98
	5	19	0.0001	~100
	10	21	0.0001	~100
	Control	0	0.1225	–

Gravimetric corrosion tests of steel samples covered by the oil compositions were also carried out in a 0.5 M NaCl solution with a duration of 456 hours (Table 4). The protective efficiency of the oil compositions with such a long exposure in a chloride solution turned out to be noticeably lower than in a thermal moisture chamber and in a chloride solution with short-term exposure (according to the polarization curves). The reason, obviously, is in the aggressive action of Cl^- - ions, which are absent during tests in a thermal moisture chamber and did not fully manifest themselves when the samples were kept in the solution for a short time. Compositions of I-20A oil with a concentration of additive equal to 5–10% are more effective than compositions based on other oils.

Table 4. Results of gravimetric corrosion tests in a 0.5 M NaCl solution at an exposure of 456 hours.

Oil	Cortec VpCI-368 D concentration, wt%	Steel St3		Copper M2		Brass L62	
		$K \cdot 10^{-3}$, $\text{g}/(\text{m}^2\text{h})$	Z , %	$K \cdot 10^{-3}$, $\text{g}/(\text{m}^2\text{h})$	Z , %	$K \cdot 10^{-3}$, $\text{g}/(\text{m}^2\text{h})$	Z , %
I-20A	Control	122.9	–	30.0	–	30.0	–
	0	98.0	20	20.0	33	26.4	12
	3	86.0	30	20.0	33	6.0	80
	5	40.6	67	18.0	40	9.0	70
	7	40.6	67	18.0	40	9.0	70
	10	40.6	67	18.0	40	14.1	53

Oil	Cortec VpCI-368 D concentration, wt%	Steel St3		Copper M2		Brass L62	
		$K \cdot 10^{-3}$, g/(m ² h)	Z, %	$K \cdot 10^{-3}$, g/(m ² h)	Z, %	$K \cdot 10^{-3}$, g/(m ² h)	Z, %
M10G2k	0	73.0	40	21.0	30	13.5	55
	5	65.1	47	21.0	29	9.0	70
	10	70.0	43	21.3	29	10.5	65
WMO	0	59.0	52	19.8	34	12.6	58
	5	90.9	26	19.8	34	9.0	70
	10	86.0	30	19.5	35	7.0	75

The protective efficacy of oil compositions with Cortec VCI-368D was investigated, in addition to steel, in relation to copper M2 and brass L62 in 0.5 M NaCl solution (Table 4). In the case of brass, the values of the protective effectiveness are higher than for copper and steel. For copper, the investigated compositions are generally not effective in a chloride-containing medium, since the protective effect does not exceed 40%.

The high protective efficiency of the investigated compositions with respect to steel, observed during tests in a thermal moisture chamber G-4, is confirmed by the results of two-month tests in an open site (Table 5). The best protective effect is shown by the compositions based on the WMO and M10G2k oils.

Table 5. Results of two-month (September–October 2020) tests of St3 samples coated with the oil compositions in an open site.

Cortec VpCI-368 D concentration, wt%	I-20A		M10G2k		WMO	
	K , g/(m ² h)	Z, %	K , g/(m ² h)	Z, %	K , g/(m ² h)	Z, %
0	0.00325	35	0.00265	47	0.00250	50
3	0.00075	85	0.00035	93	0.00040	92
5	0.00065	87	0.00030	94	0.01260	93
10	0.00055	89	0.00030	94	0.01260	93
Control	0.0050					

Determination of the theoretical consumption of the oil compositions was carried out by gravimetric method based on obtaining a single-layer coating of a given thickness without taking into account of irrecoverable losses (Table 6). For all the oil compositions (OC) at a concentration of 5–10 wt% Cortec VCI-368D its consumption does not exceed 1 g/m². Moreover, a formation of the coating at an elevated temperature (70°C) helps to reduce the consumption of the additive.

Table 6. Theoretical consumption of Cortec VpCI-368D for coating deposition at 20 and 70°C.

Oil	Concentration		Temperature of coating deposition, °C	OC density, kg/m ³	Coating thickness <i>h</i> , μm	Theoretical consumption	
	Oil, wt%	Cortec VpCI-368 D, wt%				OC, kg/m ²	Cortec VpCI-368 D, g/m ²
I-20A	100	–	20	890	19.1	0.017	0
			70		5.1	0.004	0
	95	5	20	878	20.2	0.018	0.9
			70		14.6	0.013	0.7
	90	10	20	876	20.6	0.018	0.9
			70		16.3	0.014	0.7
M10G2k	100	–	20	884	19.5	0.017	0
			70		6.0	0.005	0
	95	5	20	887	19.9	0.018	0.9
			70		10.6	0.010	0.5
	90	10	20	893	21.0	0.019	1.0
			70		11.0	0.010	0.5
WMO	100	–	20	866	20.3	0.017	0
			70		8.5	0.007	0
	95	5	20	869	23.5	0.015	0.8
			70		11.4	0.010	0.5
	90	10	20	871	17.9	0.015	0.8
			70		12.8	0.010	0.5

Conclusion

The protective performance of metal coatings based on the petroleum oils (I-20A, TKp, M10G2k and WMO) and Cortec VpCI-368D, a mixture of an organic solvent with a volatile inhibitor, has been investigated. The oil compositions with Cortec VpCI-368D are well wetted with water, they themselves spread over the steel surface, displacing water layers, and are characterized by low surface tension.

The protective efficiency of the composition of industrial oil I-20A and Cortec VpCI-368D (5–10%) at a short-term exposure of a coated steel electrode in a 0.5 M NaCl solution ($Z=97\text{--}98\%$) was estimated on the basis of polarization curves.

Compositions of the petroleum oils with Cortec VpCI-368D (5–10 wt%) show high protective efficiency in relation to carbon steel in a thermal moisture chamber and in natural conditions. These compositions are most effective in relation to L62 brass in a chloride-containing neutral solution; it is impractical to use them to protect copper, since the protective effect does not exceed 40%. In relation to carbon steel in these conditions, only compositions with commercial oil I-20A are advisable.

Consumption of Cortec VCI-368D for coating deposition at 20 and 70°C was calculated.

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