Protective properties of oil compositions modified with Cortec VpCI-369

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Abstract. This paper investigated the effectiveness of anticorrosive protection of a number of metals by means of compositions based on petroleum oils modified with the Cortec VpCI-369 composition (Cortec Corporation, USA). The work of adhesion of the studied compositions and their wetting with water were determined. The contributions of individual components of the protective system to the total effectiveness in a chloride solution are estimated using the method of polarization resistance. Oil compositions with Cortec VpCI-369 (3-10 wt.%) show high protective efficiency when applied to structural carbon steel tested in a thermal moisture chamber (98-100%) and under normal conditions (86-96%). In a chloride-containing neutral solution with an exposure time of 456 h, these compositions are effective against the effect of copper and brass.

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

1. Introduction
Corrosion of metals is a thermodynamically determined process. So, inhibitory corrosion protection is always relevant. The capabilities of oil compositions for protecting machinery and equipment from atmospheric corrosion are widely known [1-5]. Recently, there has been much research on the use of volatile corrosion inhibitors (VCIs) for these purposes, despite their somewhat limited area of application [6-9]. Possible synergy of using a composite of volatile and oil products makes it attractive. The line of protective materials made by Cortec Corporation, USA (the official representative is KORTEK RUS LLC in Russia and CIS). Cortec also makes compositions containing both oil and volatile components. One of these is Cortec VpCI-369, which contains 5% VOC in oil. The manufacturers predict long-term (up to 5 years) protection of ferrous and non-ferrous metals from atmospheric corrosion using this material in undiluted form or use as an anti-corrosion additive in low concentrations in petroleum oils and greases. The original composition forms a translucent self-tightening film removable with conventional solvents. The gradual replacement of metal structures with composite ones is partial solution of the problem of corrosion resistance. However, composite structural are much more expensive, rendering the replacement economically ineffective in a number of cases [10, 11].

The purpose of this work is to study the protective properties of compositions based on petroleum oils modified by Cortec VpCI-369. Industrial (I-20A), commercial motor (M10G2k) and waste (MMO) oils were used as petroleum oils. The concentration of Cortec VpCI-369 in the oil compositions was 3-10 wt. %. The studies were carried out on specimens of carbon structural steel (St3 grade) 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 - rest.
To deposit the coating, the specimens were immersed in a conservation bath for 10 seconds. After that, they were left in air in a suspended vertical position for 1 day to drain the excess oil composition and form a protective film. The thickness of the formed film (μm) was evaluated gravimetrically, assuming the layer to be uniform, using the formula

\[ h = \frac{\Delta m \cdot 10^6}{S \cdot \rho}, \]  

where \( \Delta m \) is the change in specimen weight due to coating formation, kg; \( S \) is the surface area, m²; \( \rho \) is the conservation material density, 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 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 using the formula:

\[ K = \gamma i_{corr}, \]  

where \( K \) is the corrosion rate, g/(m²h), \( i_{corr} \) is the corrosion current, A/m²; \( \gamma \) is the metal electrochemical equivalent.

The protective efficacy of the compositions is given by:

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

where \( K_0 \) and \( K \) are the metal corrosion rate without and with the oil coating, respectively.

Polarization measurements were carried out using an IPC-ProMF potentiostat in a potentiodynamic mode with a potential sweep rate of 0.66 mV/s in an electrochemical cell made of Pyrex glass with an anode and cathode spaces separated by a thin section. The reference electrode is saturated aqueous silver chloride, the auxiliary electrode is smooth platinum. The working electrode is reinforced in a mandrel made of ED-5 epoxy resin hardened with polyethylene polyamine. The potentials have been recalculated.

Using the method of linear polarization resistance, the partial contributions of the components of protective oil compositions to the total protective effect were determined according to the method described in [12]. The studies were carried out using an "Expert-004" corrosion meter capable of measuring the instantaneous corrosion rate at any time.

The contact angles of wetting (θ) of the oil compositions were determined using the EASYDROP device (KRUSS, Germany) and by the calculation method [13]. 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 (Wa) was calculated by the formula:

\[ W_a = \sigma (1 + \cos \theta) \]  

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

Experimental studies have shown that the values of contact angles (θ₁) of oil compositions based on CortecVpCI-369 applied to the surface of St3 steel do not exceed 90° with water (Table 1); therefore, water actively wets the investigated coatings. The rapid spreading of drops of the oil compositions themselves on steel St3 did not allow determining their contact angles of wetting (θ₂) using the EASYDROP device; therefore, the calculation method was used [13]. The largest contact angles (θ₁ and θ₂) are typical for compositions based on MMO, however, the difference in values with compositions based on other oils is insignificant. The θ₂ 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. Analysis of the values of surface tension (σ) and work of adhesion (Wa) of oil compositions shows (table 1) that they are close to each other and tend to decrease slightly with increasing concentration of CortecVpCI-369.
Table 1. Contact angles of wetting of oil compositions. CortecVpCI-369 with water ($\theta_1$) and steel with oil compositions ($\theta_2$), surface tension and the work of adhesion of the compositions

| Oil     | $C_{\text{Cortec}}$ wt. % | $\theta_1$ | $\theta_2$ | $\sigma$ (mN/m) | $W_a$ (mN/m) |
|---------|--------------------------|------------|------------|-----------------|--------------|
| I-20A   | 3                        | 47         | 1.71       | 20.55           | 41.10        |
|         | 5                        | 45         | 1.72       | 20.98           | 41.96        |
|         | 7                        | 46         | 1.56       | 19.83           | 39.66        |
|         | 10                       | 48         | 1.29       | 19.48           | 37.19        |
| M10G2k  | 3                        | 57         | 1.89       | 20.42           | 40.84        |
|         | 5                        | 74         | 1.90       | 17.86           | 35.72        |
|         | 7                        | 57         | 2.30       | 17.05           | 34.10        |
|         | 10                       | 55         | 1.45       | 17.61           | 35.22        |
| MMO     | 3                        | 67         | 1.85       | 24.11           | 48.22        |
|         | 5                        | 70         | 1.88       | 21.55           | 43.90        |
|         | 7                        | 65         | 2.00       | 19.11           | 38.22        |
|         | 10                       | 66         | 1.30       | 19.73           | 39.46        |

Although the oil compositions are capable of displacing the phase water layers from the metal surface, nevertheless, the wetting of the coatings with water promotes the penetration of the aqueous medium through the pores in them to the metal surface and the formation of a double ionic electric layer there. Thus, it becomes possible to carry out electrochemical measurements [3, 4]. The protective effectiveness of oil compositions is due to the adsorption of inhibitors they contain on the metal surface.

An express assessment of the protective properties of the investigated oil compositions can be done with electrochemical studies. For example, Figure 1 shows the polarization curves of a steel electrode coated with compositions based on I-20A in a 0.5 M NaCl solution, measured after a 15-minute exposure. The corrosion potential ($E_{\text{cor}}$) of the steel electrode in the without a coating is -0.37 V, the corrosion current density ($i_{\text{cor}}$) is 5.01 A/m². The slope of the Tafel section of the anodic polarization curve is close to 60 mV (Table 2), corresponding to the value of 2.3 RT/F, which is typical for anodic ionization of iron in chloride media without passivation. After applying a film of fresh I-20A oil, $E_{\text{cor}}$ retains its previous value, and $i_{\text{cor}}$ decreases to 2.10 A/m². The anodic curves practically coincide, 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 CortecVpCI-369 shifts $E_{\text{cor}}$ in the positive direction, significantly reduces metal corrosion currents and, accordingly, increases the protective effectiveness of the coating (Figure 1, table 2). In this case, a slowdown of the anodic process is observed, which is especially significant in the presence of 5–10% additive. The cathode curves show a rapid transition to the limiting oxygen current.

The presence of a film of undiluted Cortec VpCI-369 on the electrode provides a protective effect of 90%. The protective efficiency of oil compositions with 3 and 5% Cortec VpCI-369 additive is lower, and at a concentration of 7 and 10%, on the contrary, it is higher (99%).
Figure 1. Polarization curves on grade St3 steel coated with protective compositions in 0.5 M NaCl:
1 - absent, 2 - VpCl-369; 3 - I-20A; 4 - I-20A + 3% VpCl-369; 5 - I-20A + 5% VpCl-369;
6 - I-20A + 7% VpCl-369; 7 - I-20A + 10% VpCl-369

Table 2. Protective properties of oil compositions based on I-20 A and Cortec VpCl-369 on St3 steel

| Coating composition          | $E_{corr}$, V | $I_{corr}$, A/m$^2$ | $b_{corr}$, V | $Z$, % |
|------------------------------|---------------|---------------------|---------------|-------|
| No coating                   | 0.37          | 5.01                | 0.06          | -     |
| I-20A                        | 0.37          | 2.15                | 0.06          | 57    |
| VpCl-369                     | 0.23          | 0.50                | 0.03          | 90    |
| 3% VpCl-369 in I-20A         | 0.29          | 0.82                | 0.04          | 84    |
| 5% VpCl-369 in I-20A         | 0.10          | 1.26                | 0.03          | 75    |
| 7% VpCl-369 in I-20A         | 0.05          | 0.05                | 0.02          | 99    |
| 10% VpCl-369 in I-20A        | -0.01         | 0.01                | 0.01          | 99    |

Figure 2 shows the time history of the instantaneous corrosion rate in 0.5 M NaCl solution of the grade St3 steel with and without coatings. The time history of obtained by the method of polarization resistance. Without a coating, the corrosion rate at the initial stage of exposure to the environment decreases with time due to the formation of a solid-phase oxide film on the metal surface, then increases, apparently due to a change in its structure upon absorption of moisture by the film, and reaches a plateau, obviously, upon saturation of the film with moisture (figure 2, curve 1).
If point A1 on curve 1 in Figure 2 is taken as the origin of the corrosion process, the corrosion rate at time $\tau_{A1}$ is denoted by $K_{A1}$, then the values of the protective efficiency of the solid-phase oxide film at times $\tau_{B1}$, $\tau_{C1}$, and $\tau_{D1}$ can be calculated by the formulas:

$$Z_{B1} = \frac{(K_{A1} - K_{B1})}{K_{A1}}$$

$$Z_{C1} = \frac{(K_{A1} - K_{C1})}{K_{A1}}$$

$$Z_{D1} = \frac{(K_{A1} - K_{D1})}{K_{A1}}$$

If in section A1B1 the corrosion rate changes rapidly with time, then in section C1D1 near C1 the value of $dK/d\tau$ is significantly reduced, or tends to zero altogether, when a stationary state near D1 is reached. Thus, a solid-phase film is characterized by a well-defined value of the protective effect $Z_{D1}$.

The application of films of the studied oils to the surface of corrosive steel leads to a decrease in the corrosion rate (Figure 2, curves 2-4) and, accordingly, an increase in the protective effect of the "solid-phase film-oil" system. In such a bimodal defense system, there are two components that have a protective effect. The protective efficiency of the first of them (solid-phase oxide film) was estimated from the data of curve 1 in Figure 2. We assume that the contribution of the solid-phase film remains unchanged in the presence of oil.

Let us estimate the oil content $Z_i$ by denoting $Z_{i,m}$ at time intervals $\tau_{B}$, $\tau_{C}$ and $\tau_{D}$.

$$Z_{B,m} = \frac{(K_{B1} - K_{B2})}{K_{A1}}$$

$$Z_{C,m} = \frac{(K_{C1} - K_{C2})}{K_{A1}}$$

$$Z_{D,m} = \frac{(K_{D1} - K_{D2})}{K_{A1}}$$

The total effect of the protective system at the corresponding time from the beginning of the process is equal to:

$$Z_{\Sigma, B} = Z_B + Z_{B,m}$$

$$Z_{\Sigma, C} = Z_C + Z_{C,m}$$

$$Z_{\Sigma, D} = Z_D + Z_{D,m}$$
where $Z_B$, $Z_C$ and $Z_D$ is the protective effect of the solid-phase film (an oxide film in our case). The data obtained for the considered oils are reflected in Table 3, from which it follows that the contribution of the oil to the protective efficiency increases with time, and the contribution of the solid-phase film decreases.

Table 3. Protective efficiency of the bimodal system "solid-phase film-oil", according to Figure 2

| Oil       | Protective effectiveness ($Z$), % |
|-----------|----------------------------------|
|           | $Z_{B1}$ | $Z_{C1}$ | $Z_{D1}$ | $Z_{B,M}$ | $Z_{C,M}$ | $Z_{D,M}$ | $Z_{Σ,B}$ | $Z_{Σ,C}$ | $Z_{Σ,D}$ |
| MMO       | 34.1     | 24.8     | 21.7     | 41.0      | 60.8      | 62.7      | 75.1      | 85.6      | 84.4      |
| M10G2K    | 34.1     | 24.8     | 21.7     | 50.0      | 62.5      | 64.6      | 84.1      | 87.3      | 86.3      |
| I-20A     | 34.1     | 24.8     | 21.7     | 44.2      | 57.3      | 58.1      | 78.3      | 82.1      | 79.8      |

Now consider coatings with compositions based on oils with Cortec VpCI-369 additives. We accept the additivity of the action of all components of the defense system. Three components will contribute to the total protective effect: solid-phase film (TPF), uninhibited oil (UO) and inhibitor in the composition of Cortec VpCI-369 (IC).

$$Z_{Σ} = Z_{TPF} + Z_{UO} + Z_{IC}$$ (14)

Let us consider corrosion rate time history using the example of the inhibitor oil I-20A (Fig. 3). The addition of Cortec VpCI-369 to I-20A reduces the corrosion rate and, accordingly, increases the protective effectiveness of the oil composition. However, the maximum value of the protective effect is observed at a 3% concentration of Cortec VpCI-369, an increase to 5-10% corresponds to a lower $Z$ value, although higher than in the presence of a film of individual oil. It is possible that with an increase in the concentration of Cortec VpCI-369, structural changes occur in the films of the compositions, which contribute to an increase in the corrosion rate.

![Figure 3. Instantaneous corrosion rate time history of the St3 grade steel without a coating (1) and with coatings I-20A with Cortec VpCI-369 with concentration, wt. %: 2 – 0; 3 - 3; 4 – 5; 5 – 7; 6 – 10](image)

Table 4 shows data on the partial contributions of the components of the protective system to the total protective effect of the inhibitor industrial oil. The results indicate that the contribution of the oil prevails over the contribution of the solid-phase film and the contribution of the inhibitor. The contribution of
the inhibitor at 3 and 5% concentration changes insignificantly over time, at 7 it decreases, at 10% it turns out to be lower than at lower concentrations.

It also follows from Table 4 that the highest protective effect is observed at 3% additive content in I-20A, in contrast to the data obtained by the method of polarization curves, where the most effective were coatings containing 7 and 10% Cortec VpCl-369. The difference is obviously due to the different duration of the experiments.

In addition to electrochemical tests, gravimetric tests were carried out in a thermal moisture chamber G-4 for 960 hours. According to the data obtained (table 5), protective compositions with 5 to 10 mass. % Cortec VpCl-369 based on all tested oils almost completely protects the steel surface (Z = 99-100%). At a 3% addition of Cortec VpCl-369, the protective effect in M10G2k oil is slightly lower than in other oils, apparently due to the lower work of adhesion (Table 1).

According to the results of gravimetric corrosion tests of coated steel samples with a duration of 456 hours in a 0.5 M NaCl solution (Table 3), the protective effectiveness of oil compositions is noticeably lower than in a thermal moisture chamber and in a chloride solution with short-term exposure (according...
to polarization curves). The reason, obviously, lies 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 solution for a short time. The most effective compositions are based on MMO with an additive concentration of 5-10%. Similar results are observed for coatings based on I-20A.

The protective efficiency of oil I-20A compositions with Cortec VpCl-369 in a 0.5 M NaCl solution was investigated, in addition to steel, in relation to copper M2 and brass L62 with a duration of 456 hours. The results obtained (table 6) indicate that the investigated compositions more effectively protect these metals than steel. The highest results were obtained on L62 brass at a Cortec VpCl-369 concentration of 3 and 5 wt% (Z = 99%).

Table 6. Results of gravimetric corrosion tests of copper and brass in a 0.5 M NaCl solution at an exposure of 456 hours

| Coating composition | -E_{corr}, V | I_{corr}, A/m² | Z, % | -E_{corr}, V | I_{corr}, A/m² | Z, % |
|---------------------|-------------|----------------|------|-------------|----------------|------|
| No coating          | 0.008       | 0.0250         |      | 0.01        | 0.020          |      |
| I-20A               | -0.009      | 0.0141         | 44   | -0.03       | 0.012          | 40   |
| VpCl-369            | -0.035      | 0.0001         | 99   | 0           | 0.00002        | 99   |
| 3% VpCl-369 in I-20A| -0.290      | 0.0008         | 97   | 0           | 0.00002        | 99   |
| 5% VpCl-369 in I-20A| -0.145      | 0.0027         | 90   | 0           | 0.00006        | 99   |
| 7% VpCl-369 in I-20A| -0.135      | 0.0038         | 85   | -0.010      | 0.0022         | 89   |
| 10% VpCl-369 in I-20A| -0.120      | 0.0063         | 75   | -0.015      | 0.0060         | 70   |

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 full-scale bench tests (Fig. 4, Table 7), in which compositions based on M10G2k and MMO oils exhibit the best protective effect.

![Figure 4. Appearance of structural steel specimens after 2-month tests](image)

Table 7. Results of two-month (September-October 2020) field-bench tests of St3 samples coated with oil compositions with Cortec VpCl-369

| Concentration | I-20A | M10G2K |
|---------------|-------|--------|
| Cortec VpCl-369, Wt. % | K, g/(m²h) | Z, % | K, g/(m²h) | Z, % | K, g/(m²h) | Z, % |
| 0             | 0.00325 | 35     | 0.0265 | 47     | 0.00250 | 50     |
| 3             | 0.00070 | 86     | 0.00030 | 94     | 0.00018 | 93     |
| 5             | 0.00039 | 88     | 0.00030 | 94     | 0.00030 | 94     |
| 10            | 0.00040 | 92     | 0.00025 | 95     | 0.00002 | 96     |

Control specimen | 0.0050

2. Conclusion
Metal coatings with compositions based on petroleum oils and Cortec VpCI-369, containing 5% of a volatile inhibitor in oil, exhibit a high protective effect against carbon steel when tested in a thermal moisture chamber (98-100%) and natural conditions (86-96%). In a chloride-containing neutral solution, when exposed for 456 h, compositions based on I-20A are effective in relation to steel, but to a much greater extent in relation to copper and brass.

Using the method of linear polarization resistance, the contributions of individual components of the protective system to their integral efficiency in a chloride solution are estimated.

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