Protective Compositions Based on Modified Colza Oil Refining Products against Carbon Steel Atmospheric Corrosion

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Abstract
IE(\%) of CORP (with AN of 7.8 and 3.5., and modified with Zn powder, MGr or MCNT) used as coatings against CS atmospheric corrosion has been investigated. The studies were carried out by gravimetry and PSP methods. CORP composition was: phosphatides, hydrated oil and SF. IE(\%) effect of CO coatings with the investigated compositions on CS corrosion kinetic parameters was estimated in a 0.5 M NaCl solution. Zn powder (50 wt.\%) addition to CORP increased their IE(\%) up to 80-86\%. In this case, the coatings IE(\%), at an anodic E of -0.2 V, reached 93-99\%. The addition of MGr or MCNT to CORP modified by Zn powder had mostly a negative effect on IE(\%).

Keywords: anticorrosive composition, low-EA CO, MGr powders and Zn.

Introduction*
CORP utilization is of certain interest for the corrosion inhibition of agricultural machinery stored in open areas and under sheds. In this way, it is possible to solve simultaneously three problems: obtaining edible oil, disposing of waste and preserving the oil during temporary storage. Previous studies have shown high CORP IE(\%) in neutral environments without surface-active ions. On the contrary, aggressive media with Cl-ions sometimes stimulate steel electrochemical corrosion [1]. Such effect takes place if the steel is covered by the mixture of low-EA CO refining products. Obviously, it is necessary to modify the protective compositions by means of various additives. In the present work, the effect of CORP modified by Zn powder, MGr and MCNT on St3 CS CR and kinetic parameters was estimated in neutral NaCl media. To date, numerous works have attempted to utilize plant products for mitigating steel corrosion in various media. Although plant extracts are sometimes used to form protective coatings on metals [2, 3], they are more often introduced into corrosive environments as metal corrosion inhibitors [4, 5].

* The abbreviations and symbols definition lists are in pages 476-477.
Experimental
For the experiments, unrefined CO was used. CO treatment with softened water (10 wt.%), by vigorous stirring, for 3 h, at 50-60 ºC, led to the formation of an emulsion, which stratified upon standing during a day. Its lower layer was an aqueous dispersion containing P, mucus, scraps of cellular tissue, etc. The upper layer was treated by HO with concentrated H₃PO₄ (0.05 wt.% CO), for removing non-hydratable P forms. The resulting oil had an AN of 7.8 mg KOH (CO of AN = 7.8). Then, HO was neutralized with a NaOH solution (15 wt.%), by vigorous stirring, for 3 h, at 60-70 ºC, in order to remove free fatty acids.

After SF precipitation and separation, the oil was sequentially washed with water and a C₆H₈O₇ solution (10 wt.%), by vigorous stirring, at 90-95 ºC, for extracting residues.

AN of the resulting oil was 3.5 mg KOH. Then, CO of AN = 3.5 was dried at 90-95 ºC, and intensively stirred, in order to remove the traces of moisture [6, 7].

CORP (P, HO, CO of AN = 7.8, SF and CO of AN = 3.5) were used as coatings for inhibiting St3 CS atmospheric corrosion. The compositions were modified by adding 50 wt.% Zn powder or 50 wt.% Zn powder + 0.1 wt.% MGr or MCNT (Table 1).

Table 1. Corrosion inhibitors compositions.

<table>
<thead>
<tr>
<th>P + Zn powder</th>
<th>HO + Zn powder</th>
<th>CO of AN = 7.8 SF</th>
<th>CO of AN = 3.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>P + Zn powder</td>
<td>HO + Zn powder</td>
<td>CO + Zn powder</td>
<td>SF + Zn powder</td>
</tr>
<tr>
<td>+ MGr</td>
<td></td>
<td>MGr</td>
<td>+ MGr</td>
</tr>
<tr>
<td>+ Zn powder</td>
<td>HO + Zn powder</td>
<td>CO + Zn powder +</td>
<td>SF + Zn powder</td>
</tr>
<tr>
<td>+ MCNT</td>
<td></td>
<td>MCNT</td>
<td>+ MCNT</td>
</tr>
</tbody>
</table>

Zn powder (99.9 %), with the fractional composition of μm/wt.% 2-5 ~ 96, 5...10-4 and 10...20-0.01, was used. MGr, with the fractional composition of μm/wt.% > 88-0.9, 80...70-7, 70...56-71, 56...40-15.7 and below 40-5.5, was employed. MCNT were produced by catalytic pyrolysis of a propane-butane mixture, at 600-650 ºC, on Ni/Mg [8]. MCNT had the following initial parameters: outer diameter of 10-20 nm; content of amorphous carbon of 0.3-0.5 wt %; specific gravimetric surface area not smaller than 144 m²/g⁻¹; average pore volume of 0.22 nm³; and average effective pore size of 7 nm. MCNT were activated at 107 ºC, in an aqueous solution of concentrated HNO₃ and H₂SO₄, in a 1:3 volume ratio. MCNT disperse composition was investigated by DLS (PCS), using a Photocor-FC correlator (UK).

The corrosion tests were conducted on St3 CS with the composition (wt.%): C (0.2); Mn (0.5); Si (0.15); P (0.04); S (0.05); Cr (0.30); Ni (0.20); Cu (0.20); and Fe (98.36). The samples with the size of 70 × 30 × 3 mm were used for corrosion testing by the gravimetric method. The CO coatings were deposited by immersion of the samples into the bath containing the composition shown in Table 1, at 20 ºC, for 15-20 min. Then, the samples were kept in a suspended state, for a day, at room T, in order to drain the excess composition and allow the formation of a protective film. The film thickness the was gravimetrically estimated, assuming that the coating was uniform. After the corrosion tests completion, the samples were cleaned from films and corrosion products, degreased, dried and weighed. The corrosion IE(%) was determined by the formula:
\[ IE(\%) = \frac{K_0 - K_c}{K_0} \cdot 100 \]  

where \(K_0\) and \(K_c\) are CR of uncoated and coated CS, respectively. The duration of the experiment in 0.5 M NaCl was 336 h, at room T.

Stationary PSP measurements, with a E step of 20 mV, were carried out in a three-electrode cell made of Pyrex glass, with separated anode and cathode spaces, at room T, with natural aeration. E values were measured relative to a saturated Ag-AgCl RE, and converted to the standard H\(_2\) scale. The WE was St3 CS, with a horizontal working surface area of 0.5 cm\(^2\), and it was reinforced into a mandrel made of epoxy resin ED-5, with a polyethylene polyamine hardener. The WE was polished without pastes, degreased with acetone and dried with filter paper. The AE was smooth Pt. A protective film of the test composition, with a thickness equal to 20±5 µm, was formed on the electrode surface, after 15 min. The BGE was 0.5 M NaCl. IE\(_{a}(\%)\) (at anodic E of -0.20 V) and IEE\(_{corr}(\%)\) (at E\(_{corr}\)) were estimated from PSP measurements, according to formula (A).

**Results and discussion**

In a 0.5 M NaCl solution, corrosion tests on St3 CS covered by films of the low-EA CORP showed that their IE(%) did not exceed 45 %, and increased as shown in Table 2 and row 1:

\[
IE(\%) \ (CO \ (AN = 7.8)) < IE(\%) \ (P) < IE(\%) \ (HO) \\
< IE(\%) \ (SF) < IE(\%) \ (CO \ (AN = 3.5))
\]  

(1)

Introduction of 50 wt.% Zn powder into the low-EA CORP resulted in an appreciable increase in their IE(%). Moreover, Zn evened out IE(%) of different CORP components. This was probably caused by Zn more dominant role in the inhibition of CS electrochemical corrosion than that of surfactants-CORP constituents adsorbed onto the metal surface (Table 2).

**Table 2.** Relationship between the nature of the protective films and their corrosion IE(%) in a 0.5 M NaCl solution.

<table>
<thead>
<tr>
<th>Initial CORP</th>
<th>Film thickness of 20±5 µm</th>
<th>IE(%) of additives with initial composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Absent</td>
<td>Zn</td>
</tr>
<tr>
<td>HO</td>
<td>29</td>
<td>88</td>
</tr>
<tr>
<td>CO (AN = 7.8)</td>
<td>24</td>
<td>86</td>
</tr>
<tr>
<td>P</td>
<td>27</td>
<td>77</td>
</tr>
<tr>
<td>SF</td>
<td>33</td>
<td>78</td>
</tr>
<tr>
<td>CO (AN = 3.5)</td>
<td>45</td>
<td>83</td>
</tr>
</tbody>
</table>

The addition of MGr to Zn-filled low-EA CORP coatings further decreased Zn powder C, thus reducing equipment conservation costs, while the use of activated MCNT allowed assessing the effect of the filler dispersion on IE(%).

Corrosion tests on CS covered by low-EA CORP films filled with Zn showed that their IE(%) with MGr powder addition was practically absent (Table 2). Moreover, in some cases, there was even a slight reduction in the IE(%) of some CORP.
The effect of MCNT addition to low-EA CORP films filled with Zn, at C of 0.1 wt.%, on the corrosion tests of coated CS samples, is illustrated in Table 2. MCNT dispersion composition was determined by PCS (Fig. 1).

**Figure 1.** MCNT particle size distribution. R is the average radius of particles.

Fig. 1 shows that this system has bimodal distribution. The first peak corresponds to particles with a size close to 320 nm. The second peak corresponds to particles with a cross-section of \( \sim 10^3 \) nm. Large particles are nanoobjects conglomerates. They were MCNT stochastically rolled up into agglomerates.

MCNT addition to CORP containing Zn powder, in 50 wt.% C, did not increase the corrosion IE(%), and even led to its decrease. Thus, although the modification of coatings based on CORP by Zn powder was very effective, the introduction of MCNT particles of various natures and degrees of dispersion was impractical.

This conclusion was verified by PSP studies on the electrochemical corrosion kinetics of CS covered with the appropriate coatings (Figs. 2-5). \( \beta_a, \beta_c, E_{\text{corr}}, i_{\text{corr}}, \) IE(%)\text{corr} and IE(%)\text{a}, at \( E_a = -0.20 \) V, are shown in Tables 3-6.

**Figure 2.** PSP curves obtained on CS: 1- uncovered; covered with CORP films of 2 - HO; 3 - CO of AN = 7.8; 4 - P; 5 - SF; and 6 - CO of AN = 3.5.
Table 3. CORP coatings IE(%) and their effect on the kinetic parameters of CS in a 0.5 M NaCl solution.

<table>
<thead>
<tr>
<th>Coatings composition</th>
<th>$E_{\text{corr}}$ V</th>
<th>$i_{\text{corr}}$ A/m²</th>
<th>$\beta_a$ V</th>
<th>$i_a$ A/m²</th>
<th>$i_{\text{lim}}$ A/m²</th>
<th>$\text{IE(%)}_{E_a=-0.20}$</th>
<th>$\text{IE(%)}_{E_a=-0.20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncovered steel</td>
<td>-0.41</td>
<td>0.010</td>
<td>0.030</td>
<td>0.070</td>
<td>1.320</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HO</td>
<td>-0.27</td>
<td>0.006</td>
<td>0.040</td>
<td>0.100</td>
<td>0.130</td>
<td>0.040</td>
<td>37</td>
</tr>
<tr>
<td>CO of AN = 7.8</td>
<td>-0.31</td>
<td>0.009</td>
<td>0.040</td>
<td>0.150</td>
<td>0.480</td>
<td>0.050</td>
<td>37</td>
</tr>
<tr>
<td>P</td>
<td>-0.29</td>
<td>0.006</td>
<td>0.040</td>
<td>0.120</td>
<td>0.230</td>
<td>0.060</td>
<td>37</td>
</tr>
<tr>
<td>SF</td>
<td>-0.33</td>
<td>0.006</td>
<td>0.050</td>
<td>0.180</td>
<td>0.500</td>
<td>0.040</td>
<td>37</td>
</tr>
<tr>
<td>CO of AN = 3.5</td>
<td>-0.41</td>
<td>0.004</td>
<td>0.060</td>
<td>0.020</td>
<td>1.200</td>
<td>0.040</td>
<td>60</td>
</tr>
</tbody>
</table>

CORP, excluding CO of AN = 3.5, shifted CS $E_{\text{corr}}$ to the anodic region, in the order:

$$E_{\text{corr}}(\text{HO}) > E_{\text{corr}}(\text{P}) > E_{\text{corr}}(\text{CO of AN = 7.8}) > E_{\text{corr}}(\text{SF})$$

$$> E_{\text{corr}}(\text{uncovered CS}) = E_{\text{corr}}(\text{CO of AN = 3.5})$$

(2)

The $i_{\text{corr}}$ of St3 CS covered by these films increased in the order:

$$i_{\text{corr}}(\text{uncovered CS}) \approx i_{\text{corr}}(\text{CO of AN = 7.8}) > i_{\text{corr}}(\text{P, HO and SF}) > i_{\text{corr}}(\text{CO of AN = 3.5})$$

(3)

$\beta_a$ polarization curves coefficient, measured on CS St3 covered by the films, increased in the order (Fig. 2):

$$\beta_a(\text{CO of AN = 3.5}) > \beta_a(\text{SF}) > \beta_a(\text{P}) \approx \beta_a(\text{CO of AN = 7.8})$$

$$\approx \beta_a(\text{HO}) > \beta_a(\text{uncovered CS})$$

(4)

The $i_a$ of St3 CS without and with the protective coatings and their IE(\%)$_{a}$, at the $E_a$ of -0.20 V, increased according rows (5) and (6), respectively:

$$i_a(\text{uncovered CS}) > i_a(\text{CO of AN = 3.5}) > i_a(\text{SF})$$

$$> i_a(\text{CO of AN = 7.8}) > i_a(\text{P}) > i_a(\text{HO})$$

(5)

$$\text{IE(\%)}(\text{HO}) > \text{IE(\%)}(\text{P}) > \text{IE(\%)}(\text{CO of AN = 7.8, SF})$$

$$> \text{IE(\%)}(\text{CO of AN = 3.5})$$

(6)

The considered materials (except CO of AN = 3.5) suppressed CS St3 cathodic process, with the change in $\beta_c$ coefficient according to the order:

$$\beta_c(\text{SF}) > \beta_c(\text{CO of AN = 7.8}) > \beta_c(\text{P}) > \beta_c(\text{HO})$$

$$> \beta_c(\text{uncovered CS}) > \beta_c(\text{CO of AN = 3.5})$$

(7)

The cathodic polarization curves are characterized by a limit current ($i_{\text{lim}}$), which increased in the order (8):

$$i_{\text{lim}}(\text{uncovered CS}) = i_{\text{lim}}(\text{P}) > i_{\text{lim}}(\text{CO of AN = 7.8})$$

$$> i_{\text{lim}}(\text{CO of AN = 3.5; SF; HO})$$

(8)

IE(\%) at $E_{\text{corr}}$ was maximum for CO coating of AN = 3.5 and minimum for CO coating of AN = 7.8, which is consistent with the corrosion tests data in a 0.5 M NaCl solution (Tables 2 and 3).
Zn powder addition to protective coatings levels out row (2), and significantly increases CS $E_{\text{corr}}$ with CO of AN = 3.5+ Zn and SF + Zn coatings (Fig. 3), row (9):

$$E_{\text{corr}} \text{(uncovered CS)} < E_{\text{corr}} \text{(HO + Zn)} \approx E_{\text{corr}} \text{(CO of AN = 7.8 + Zn; P + Zn)}$$

and

$$E_{\text{corr}} \text{(CO of AN = 3.5 + Zn)} < E_{\text{corr}} \text{(SF + Zn)}$$

(9)

Figure 3. PSP curves obtained on CS: 1- uncovered; covered with CORP films modified with 2- HO + Zn; 3- CO of AN = 7.8 + Zn; 4- P+ Zn; 5- SF + Zn; and 6- CO of AN = 3.5 + Zn.

The $i_{\text{corr}}$ values of CS coated with the films of original low-EA CORP (Table 3, row (3)), and their analogs modified by Zn powder (Table 4, row (10), are comparable, although their positions are different:

$$i_{\text{corr}} \text{(CO of AN = 7.8 + Zn)} > i_{\text{corr}} \text{(uncovered CS)} \approx i_{\text{corr}} \text{(SF + Zn)} > i_{\text{corr}} \text{(CO of AN = 3.5 + Zn)} > i_{\text{corr}} \text{(HO + Zn)} \approx i_{\text{corr}} \text{(P + Zn)}$$

(10)

Table 4. IE(%) of low-EA CORP coatings modified with Zn powder, and their effect on CS kinetic parameters in a 0.5 M NaCl solution.

<table>
<thead>
<tr>
<th>Coatings composition</th>
<th>$E_{\text{corr}}$ V</th>
<th>$i_{\text{corr}}$ A/m$^2$</th>
<th>$\beta_a$ V</th>
<th>$\beta_c$ A/m$^2$</th>
<th>$i_{\text{lim}}$ A/m$^2$</th>
<th>$\text{IE}_{\text{corr}}$ (%)</th>
<th>$\text{IE}_{\text{a}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncovered CS</td>
<td>-0.41</td>
<td>0.010</td>
<td>0.030</td>
<td>0.070</td>
<td>1.320</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HO + Zn</td>
<td>-0.30</td>
<td>0.003</td>
<td>0.070</td>
<td>0.130</td>
<td>0.060</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>CO of AN = 7.8 + Zn</td>
<td>-0.29</td>
<td>0.016</td>
<td>0.080</td>
<td>0.450</td>
<td>0.160</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>P + Zn</td>
<td>-0.29</td>
<td>0.004</td>
<td>0.080</td>
<td>0.100</td>
<td>0.050</td>
<td>-</td>
<td>60</td>
</tr>
<tr>
<td>SF + Zn</td>
<td>-0.21</td>
<td>0.010</td>
<td>0.050</td>
<td>0.250</td>
<td>0.020</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>CO of AN = 3.5 + Zn</td>
<td>-0.27</td>
<td>0.008</td>
<td>0.070</td>
<td>0.120</td>
<td>0.090</td>
<td>0.030</td>
<td>20</td>
</tr>
</tbody>
</table>

$\beta_a$ polarization curves coefficient of CS covered by CORP films filled with Zn increased by more of dozens mV than those of the corresponding original low-EA CORP (Table 4). The highest $\text{IE}_{\text{a}}(\%)$ was provided by P + Zn and CO of AN = 7.8 + Zn coatings (row (11)):

$$\beta_a \text{(P + Zn)} \approx \beta_a \text{(CO of AN = 7.8 + Zn)} > \beta_a \text{(CO of AN = 3.5 + Zn)}$$

$$\approx \beta_a \text{(HO + Zn)} > \beta_a \text{(SF + Zn)} > \beta_a \text{(uncovered CS)}$$

(11)

The $i_a$ of CS coated by CORP filled with Zn and, therefore, the coatings $\text{IE}_{\text{a}}(\%)$, at $E_a = -0.20$ V, varied according to rows (12) and (13), respectively:
Moreover, $i_a$ of CS coated by CORP filled with Zn powder was noticeably lower than that without it (Tables 3 and 4). Rows (5) and (12) also differ markedly from each other. Thus, in row (12), minimum $i_a$ and maximum $\text{IE}_{\text{a}}(\%)$ (row (13), at $E = -0.20 \text{ V}$, correspond to CS covered by SF + Zn and, in (5) and (6), to the HO coating.

$$\text{IE}_{\text{a}}(\%) (\text{SF} + \text{Zn}) > \text{IE}_{\text{a}}(\%) (\text{HO} + \text{Zn}) \approx \text{IE}_{\text{a}}(\%) (\text{P} + \text{Zn}) > \text{IE}_{\text{a}}(\%) (\text{CO of AN} = 7.8 + \text{Zn})$$

The differentiation in $\text{IE}_{\text{a}}(\%)$, which depends on CORP nature, was smoothed out with Zn powder addition, as in the corrosion tests with 0.5 M NaCl (Tables 2-3). Zn powder addition to the coatings was accompanied by an increase in $\beta_c$, while all coatings on the CS surface (row (14), Table 4), in contrast to row (7), suppressed cathodic $\text{O}_2$ reduction:

$$\beta_c (\text{CO of AN} = 7.8 + \text{Zn}) > \beta_c (\text{SF} + \text{Zn}) > \beta_c (\text{HO} + \text{Zn}) \approx \beta_c (\text{P} + \text{Zn}) > \beta_c (\text{uncovered CS})$$

Cathodic $i_{\text{lim}}$ order of CS was (row (15)):

- CO of AN = 3.5 + Zn coating > uncovered CS > CO of AN = 3.5 + Zn coating

Zn powder presence in the coatings differentiated their $\text{IEE}_{\text{corr}}(\%)$ (Table 4). CO of AN = 7.8 + Zn coating stimulated CS electrochemical corrosion, apparently due to the high content of free carboxylic acids (row (16)).

$$\text{IEE}_{\text{corr}}(\%) (\text{HO} + \text{Zn}) > \text{IEE}_{\text{corr}}(\%) (\text{SF} + \text{Zn}) > \text{IEE}_{\text{corr}}(\%) (\text{CO of AN} = 3.5 + \text{Zn}) > \text{IEE}_{\text{corr}}(\%) (\text{P} + \text{Zn})$$

MGr particles in CORP coatings filled with Zn prevented CS $E_{\text{corr}}$ shift to the anodic region (row 17). This effect was most pronounced in the SF + Zn + MGr coating (Table 5 and Fig. 4), where $E_{\text{corr}}$ value is comparable to those in Table 4.

$$E_{\text{corr}} (\text{uncovered CS}) < E_{\text{corr}} (\text{HO} + \text{Zn} + \text{MGr}) < E_{\text{corr}} (\text{CO of AN} = 7.8 + \text{Zn} + \text{MGr}, \text{P} + \text{Zn} + \text{MGr}) < E_{\text{corr}} (\text{CO of AN} = 3.5 + \text{Zn} + \text{MGr}) < E_{\text{corr}} (\text{SF} + \text{Zn} + \text{MGr})$$

### Table 5. IE(%) of low-EA CORP coatings modified with Zn powder and MGr, and their effect on CS kinetic parameters in a 0.5 M NaCl solution.

<table>
<thead>
<tr>
<th>Coating composition</th>
<th>$E_{\text{corr}}$ V</th>
<th>$i_{\text{corr}}$ A/m²</th>
<th>$\mu_a$ V</th>
<th>$\beta_a$ V</th>
<th>$i_a$ A/m²</th>
<th>$E_a = -0.20$ V</th>
<th>$i_{\text{lim}}$ A/m²</th>
<th>$\text{IEE}_{\text{corr}}(%)$</th>
<th>$\text{IE}_{\text{a}}(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncovered CS</td>
<td>-0.41</td>
<td>0.010</td>
<td>0.030</td>
<td>0.070</td>
<td>1.318</td>
<td>0.057</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>HO + Zn + MGr</td>
<td>-0.27</td>
<td>0.030</td>
<td>0.060</td>
<td>0.190</td>
<td>0.316</td>
<td>-</td>
<td>76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO of AN = 7.8 + Zn + MGr</td>
<td>-0.25</td>
<td>0.040</td>
<td>0.060</td>
<td>0.240</td>
<td>0.282</td>
<td>0.250</td>
<td>Stim.* 79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P + Zn + MGr</td>
<td>-0.25</td>
<td>0.030</td>
<td>0.040</td>
<td>0.050</td>
<td>0.398</td>
<td>-</td>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF + Zn + MGr</td>
<td>-0.18</td>
<td>0.040</td>
<td>0.010</td>
<td>0.160</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO of AN = 3.5 + Zn + MGr</td>
<td>-0.23</td>
<td>0.030</td>
<td>0.060</td>
<td>0.070</td>
<td>0.100</td>
<td>0.250</td>
<td>93</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*stimulation
The $i_{corr}$ of CS covered by CORP, modified by Zn and MGr, was higher than that of the unprotected CS (Table 5), i.e., there was a stimulation of CS corrosion ($IEE_{corr}$(%) < 0).

![Figure 4. PSP curves obtained on CS: 1 - uncovered; coated with: 2- HO + Zn + MGr; 3- CO of AN = 7.8 + Zn + MGr; 4 - P + Zn + MGr; 5- SF + Zn + MGr; 6- CO of AN = 3.5 + Zn + MGr.]

$\beta_a$ polarization curves coefficients decreased in the row (18), approaching to those of the unmodified CORP (Tables 3 and 5), thus reducing the effect of Zn powder addition (Tables 4 and 5):

$\beta_a$(CO of AN = 3.5 + Zn + MGr, SF + Zn + MGr),
$\beta_a$(CO of AN = 7.8 + Zn + MGr) > $\beta_a$(P + Zn + MGr)
$\approx \beta_a$(uncovered CS) > $\beta_a$(HO + Zn + MGr)     (18)

MGr addition to CORP coatings filled with Zn increased sharply $i_a$. $IE_a$(%) of CO coatings filled with Zn + MGr was markedly lower than that of similar Zn compositions (Tables 4 and 5), with the exception of SF + Zn + MGr coating. $IE_a$(%) decreased in row (19):

$IE_a$(%) (CO of AN = 3.5 + Zn + MGr) >
$IE_a$(%) (CO of AN = 7.8 + Zn + MGr)
$\approx IE_a$(%) (HO + Zn + MGr) > $IE_a$(%) (P + Zn + MGr)     (19)

The coarse-grained MGr particles introduced into the Zn-filled coatings interchanged $\beta_c$(HO + Zn + MGr) and $\beta_c$(P + Zn + MGr) in the row (14), preserving the tendency for decrease in this value, in rows (14) and (20), and in the values shown by Tables 4 and 5:

$\beta_c$(CO of AN = 7.8 + Zn + MGr) > $\beta_c$(HO + Zn + MGr) >
$\beta_c$(SF + Zn + MGr) > $\beta_c$(CO of AN = 3.5 + Zn + MGr; P + Zn + MGr)     (20)

The cathodic $i_{lim}$ took place on CS covered by CO of AN = 3.5 + Zn + MGr and CO of AN = 7.8 + Zn + MGr coatings, whereby,

$i_{lim}$ (uncovered CS) > $i_{lim}$ CO A.N = 3.5 + Zn + MGr
and CO A.N = 7.8 + Zn + MGr     (21)
MCNT addition to CORP coatings filled with Zn had a negative effect on $\text{IEE}_{\text{corr}}(\%)$. Thus, if $\text{IEE}_{\text{corr}}(\%) < 0$ and $\text{IE}_a(\%) < 0$, $i_{\text{corr}}$ and $i_a$ values increase. $\beta_a$ polarization curves coefficients changed insignificantly, but those of $\beta_c$ decreased sharply (Fig. 5 and Table 6).

**Figure 5.** PSP curves obtained on CS: 1- uncovered; covered with: 2- HO + Zn + MCNT; 3- P + Zn + MCNT; 4- SF + Zn + MCNT; 5- CO of AN = 3.5 + Zn + MCNT.

**Table 6.** IE(%) of CORP coatings modified by Zn powder and MCNT, and their effect on CS kinetic parameters in a 0.5 M NaCl solution.

<table>
<thead>
<tr>
<th>Coating composition</th>
<th>$E_{\text{corr}}$ V</th>
<th>$i_{\text{corr}}$ A/m²</th>
<th>$\beta_a$ V</th>
<th>$\beta_c$ V</th>
<th>$i_a$ A/m²</th>
<th>$i_{\text{lim}}$ A/m²</th>
<th>$\text{IEE}_{\text{corr}}(%)$</th>
<th>$\text{IE}_a(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>uncovered CS</td>
<td>0.41</td>
<td>0.010</td>
<td>0.033</td>
<td>0.07</td>
<td>0.320</td>
<td>0.057</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HO + Zn + MCNT</td>
<td>0.24</td>
<td>0.200</td>
<td>0.070</td>
<td>0.06</td>
<td>17.780</td>
<td>-</td>
<td>Stim.*</td>
<td>Stim.</td>
</tr>
<tr>
<td>P + Zn + MCNT</td>
<td>0.27</td>
<td>0.070</td>
<td>0.060</td>
<td>0.08</td>
<td>7.080</td>
<td>-</td>
<td>Stim.</td>
<td>Stim.</td>
</tr>
<tr>
<td>S + Zn + MCNT</td>
<td>0.29</td>
<td>0.040</td>
<td>0.060</td>
<td>0.05</td>
<td>50.120</td>
<td>-</td>
<td>Stim.</td>
<td>Stim.</td>
</tr>
<tr>
<td>CO of AN = 3.5 + Zn + MCNT</td>
<td>0.56</td>
<td>0.060</td>
<td>0.050</td>
<td>0.08</td>
<td>-</td>
<td>-</td>
<td>Stim.</td>
<td>-</td>
</tr>
</tbody>
</table>

*stimulation

**Conclusions**

- Low-EA CORP IE(%), without and with modifying Zn powder, MGr and MCNT, has been studied on CS corrosion in a 0.5 M NaCl solution.
- It has been shown that Zn powder (50 wt.%) addition to CORP made possible for it to achieve an IE(%) of 80-86 % in 0.5 M NaCl, which was probably due to its protective effect.
- The effect of the protective coatings on CS corrosion kinetic parameters in 0.5 M NaCl was estimated.
- MGr powders or MCNT addition to CORP modified by Zn powder had, in most cases, a negative effect on the coatings IE(%) and on CS corrosion kinetic parameters.
- CORP coatings filled with Zn are promising as protective materials for temporary storage of machinery and spare parts under a shelter, in open areas and in unheated premises.
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Authors’ contributions
V. I. Vigdorovich: conceptualized the study methodology; curated data; performed formal analyses; wrote the paper. E. D. Tanygina: performed the analyses; curated data. A. Yu Tanygin: collected data; made stationary PSP measurements. A. A. Uryadnikov: collected the corrosion tests data. L. E. Tsygankova: validated data; wrote the paper.

Abbreviations
AE: auxiliary electrode
AgCl: silver chloride
AN: acid number
BGE: background electrolyte
C₆H₈O₇: citric acid
C: concentration
CORP: colza oil refining products
CR: corrosion rate
CS: carbon steel
DLS: dynamic light scattering
E: potential
Eₐ: anodic potential
EA: erucic acid
Ecorr: corrosion potential
H₃PO₄: phosphoric acid
HO: hydrated oil
i: current density
iₐ: anodic current density
iₐ: cathodic current density
i_corr: corrosion current density
IE(%): inhibition efficiency
IEa(%): anodic inhibition efficiency
IEEcorr(%): inhibition efficiency at corrosion potential
i_lim: limit current density
KHO: potassium hydroxide
MCNT: multiwalled carbon nanotubes
MGr: micrographite
MZn: microzinc
NaCl: sodium chloride
P: phosphatides
PCS: photon correlation spectroscopy
PSP: potentiostatic polarization
**RE**: reference electrode

**SF**: soap flakes

**T**: temperature

**WE**: working electrode

**Symbols definition**

- \( \beta_a \): anodic Tafel slope
- \( \beta_c \): cathodic Tafel slope

**References**


