Screening of individual organic compounds as chamber corrosion inhibitors


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Abstract

The effect of chamber treatment in the vapors of nitrogen-containing bases, benzothiazole and triazole derivatives, as well as carboxylic acids on the corrosion resistance of zinc, steel, copper, brass, aluminum and magnesium alloys under periodic moisture condensation conditions was studied. Corrosion screening showed that carboxylic acids with branched hydrocarbon chains are promising compounds for the creation of efficient chamber corrosion inhibitors (CIN) for zinc and aluminum alloys. However, their use is unacceptable for the chamber treatment of items containing copper, brass and magnesium parts. Octadecylamine demonstrates high efficiency in the protection of steel and copper items. It is essential that it also inhibits to some extent the corrosion of the other materials studied. This allows us to consider this compound as a basis for creating versatile mixed CINs. Lauric acid, which provides more than a tenfold inhibition of corrosion initiation on all the materials studied, except for the aluminum alloy, may be yet another potential component for versatile CINs. However, the protective properties of this CIN are quite pronounced even on this alloy. Altax, which proved itself as a contact inhibitor of these materials, is promising for the chamber protection of items made of copper and its alloys.

Keywords: zinc, steel, copper, brass, aluminum, magnesium, atmospheric corrosion, corrosion inhibitors, chamber corrosion inhibitors.

Introduction

The modern production of metal products is a complex, often multi-stage process that involves mechanical and chemical treatment of semi-finished items. Individual operations should ideally be performed sequentially without long interruptions. However, in practice, storage and/or transportation of items from one production site to another are almost inevitable [1, 2]. This creates a risk of metal corrosion. According to [3], metal items may be stored without preservation for 0.5 to 4 hours during the production process, depending on the previous operation. If storage is performed for a longer time, it is necessary to take measures for the interoperational protection of items from corrosion.
The anticorrosion protection of ready-made metal items for the period of their transportation and storage presents a separate problem.

A set of measures for the anticorrosion protection of semi-finished and finished metal items for the period of their transportation and storage is commonly referred to as temporary protection. One of its most common and convenient methods involves the vapor-phase protection with inhibitors [4–8]. It usually involves the use of organic compounds with high vapor pressures under normal conditions (≥10⁻⁵ mmHg), the so-called volatile inhibitors (VCIs) [4]. Their use is justified if it is possible to seal the space enclosing the items to be protected. As VCIs evaporate, they saturate the space to be protected with vapors, reach the metal surface and are adsorbed on it to form surface films that protect the items from atmospheric corrosion. If the airtightness of the space is broken, the VCI concentration in the atmosphere decreases, so it desorbs from the metal surface and escapes. After some time, this process can result in corrosion initiation.

The requirement for the airtightness of the space being protected is lifted if vapor-phase inhibitors of another type, namely, chamber inhibitors (CIN), are utilized. They are applied by short-term treatment of metal items in a closed space (chamber) with vapors of low-volatile organic inhibitors at elevated temperatures [9–15]. During the treatment, stable adsorption films are formed on the metal surface, which protect an item from atmospheric corrosion for a long period of time after it is removed from the chamber.

Both individual compounds or their mixtures can be used as CINs. The use of mixed CINs has advantages reported elsewhere [11, 15]. However, from the practical point of view, one-component CINs should not be excluded from consideration, either. In addition, data on their protective ability are necessary to create efficient mixed CINs [15].

The purpose of this work was to perform a screening study of the efficiency of individual organic compounds as CINs for various metals.

Materials and Methods

The protective properties of individual CINs were estimated in relation to the following materials: Ts1 zinc, St3 steel, M1 copper, L63 brass, aluminum alloy AMg6 and magnesium alloy MA8M. The studies employed rectangular samples with dimensions of 50×30×2 mm, with a hole for mounting in chambers and test cells. Before chamber treatment (CT), they were cleaned on abrasive wheels of P240–P1000 grades (grain sizes 63–14 μm) and degreased with acetone. Further, the samples were mounted on special polymer hooks in 0.6 L airtight glass cells (chambers) containing 0.5 g of a CIN sample or without a CIN (background experiments) and underwent heat treatment.

The following compounds were used as the CINs:

- nitrogen-containing bases (octadecylamine, diphenylguanidine, polyethylene polyamine, hexamethylenetetramine);
- benzothiazole derivatives (Captax and Altax);
• triazoles with various structures (1,2,4-triazole, 3-aminotriazole, 4-aminotriazole, benzotriazole, tolyltriazole, 5-chlorobenzotriazole);
• carboxylic (lauric, tridecanoic, stearic, oleic, linolenic, 2-ethylhexanoic, neodecanoic) acids.

The CT temperatures were 100°C for zinc, 120°C for steel, 100°C for copper, 120°C for brass, and 120°C and 150°C for aluminum and magnesium alloys, respectively. The CT time was 1 h.

After chamber treatment, the samples were removed from the chambers, kept for 24 h in air, and subjected to corrosion tests. To do so, samples were mounted in corrosion cells that had the same design as the cells (chambers). Distilled water (100 mL) heated to 40°C was poured onto the bottom of each cell. The distance between the lower edge of the sample and water was 15–20 mm. After that, the cells were placed in a heating cabinet heated to 40°C. This temperature was kept for 7 h, after which the heating was turned off for 17 h. The temperature in the cells dropped to 25°C, and abundant water condensation occurred on the surface of the samples. The samples were examined every 30 minutes during the first 6 hours of the experiment, then once an hour until the end of the first day of the experiment, once every 4 hours during the second to fifth days, and twice a day thereafter. The efficiency of the CINs was estimated by the time until the appearance of the first corrosion damage on the metals.

Results and Discussion

Metal samples that were not subjected to chamber treatment quickly began to corrode under conditions of intense moisture condensation. Corrosion in the form of gray spots on zinc and a reddish deposit on steel was detected after 1 hour from the beginning of the test. Copper and brass were more resistant: corrosion damage (black spots) appeared on them after 4 and 2 hours, respectively, from the beginning of the tests. The aluminum alloy showed a sufficiently high corrosion resistance under the conditions of this experiment. The first corrosion damage (black dots) became visible on it after 240 hours of exposure under periodic moisture condensation conditions. Already after 30 minutes from the start of the experiments, corrosion damage in the form of black spots was observed on the surface of magnesium samples.

Heat treatment of samples without a CIN at the temperatures that are optimal for the metals did not result in an increase in the corrosion resistance of the materials studied or to a change in the corrosion pattern.

**Zinc (Ts1 grade)**

The adsorption films of all the compounds studied that were formed upon CT inhibited the initiation of zinc corrosion to some extent. However, the protective aftereffect (PAE) of the

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1In accordance with [9–15], these are optimal temperatures for the CT of the metals studied.
CINs (see Table 1) changed by almost 3 orders of magnitude (from 3 to 1680 hours), depending on the CIN nature.

**Table 1.** Protective aftereffect of CINs of various nature under conditions of periodic moisture condensation.

<table>
<thead>
<tr>
<th>CIN</th>
<th>Time (hours) until the first corrosion damage appeared on:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ts1</td>
</tr>
<tr>
<td>–</td>
<td>1</td>
</tr>
<tr>
<td>Octadecylamine</td>
<td>4</td>
</tr>
<tr>
<td>Diphenylguanidine</td>
<td>2</td>
</tr>
<tr>
<td>Polyethylenepolyamine</td>
<td>12</td>
</tr>
<tr>
<td>Hexamethylenetetramine</td>
<td>5</td>
</tr>
<tr>
<td>Captax</td>
<td>4</td>
</tr>
<tr>
<td>Altax</td>
<td>2</td>
</tr>
<tr>
<td>1,2,4-Triazole</td>
<td>3</td>
</tr>
<tr>
<td>3-Aminotriazole</td>
<td>3</td>
</tr>
<tr>
<td>4-Aminotriazole</td>
<td>3</td>
</tr>
<tr>
<td>1,2,3-Benzotriazole</td>
<td>8</td>
</tr>
<tr>
<td>Tolyltriazole</td>
<td>3</td>
</tr>
<tr>
<td>5-Chlorobenzotriazole</td>
<td>4</td>
</tr>
<tr>
<td>Lauric acid</td>
<td>24</td>
</tr>
<tr>
<td>Tridecanoic acid</td>
<td>48</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>24</td>
</tr>
<tr>
<td>Oleic acid</td>
<td>12</td>
</tr>
<tr>
<td>Linolenic acid</td>
<td>12</td>
</tr>
<tr>
<td>2-Ethylhexanoic acid</td>
<td>1680</td>
</tr>
<tr>
<td>Neodecanoic acid</td>
<td>1632</td>
</tr>
</tbody>
</table>

*Note: Corrosion defects already appear during chamber treatment.*

The nitrogen-containing bases studied did not prove to be efficient CINs of zinc corrosion. However, the most efficient compound, namely polyethylenepolyamine, slowed down the initiation of corrosion of this metal 12-fold.

Benzothiazoles proved to have low efficiency against zinc CT. Altax and Captax inhibited the initiation of metal corrosion 2- and 4-fold, respectively.
The majority of the triazoles studied provided complete metal protection for 3 hours. Only in the case of chlorobenzotriazole and benzotriazole, the protective aftereffect (PAE) slightly exceeded this value and amounted to 4 and 8 hours, respectively.

Carboxylic acids are more efficient chamber inhibitors for zinc. However, within this series of compounds, the PAE varied over a very wide range, from 12 hours for oleic and linolenic acids to 1632 and 1680 hours for neodecanoic and 2-ethylhexanoic acids, respectively. The set of the compounds studied does not allow us to reliably identify the laws according to which the structure of the hydrocarbon chain in carboxylic acids affects their efficiency as CINs for zinc corrosion. Nevertheless, it can be noted that the maximum zinc protection was provided by carboxylic acids with branched hydrocarbon chains.

It is significant that in the majority of experiments, the CT of zinc changed the corrosion mode from general to pitting corrosion. Only Altax and Captax did not affect the type of corrosion damage.

Steel (St3 grade)

Mild steel is a more difficult material for chamber protection than zinc. Of organic nitrogen-containing amine bases, octadecylamine was the most efficient CIN for steel corrosion. It increased the time until the appearance of the first corrosion damage 129-fold. The other compounds of this group were significantly inferior to it in protective ability, as they provided complete protection of the metal for a period ranging from 2 h (urotropine) to 10 h (diphenylguanidine).

Captax and Altax did not affect the corrosion resistance of steel. In both cases, corrosion appeared on the samples after 1 hour of exposure to corrosive conditions.

All the triazole derivatives studied had approximately the same protective effect, namely, 3–4 hours.

Lauric acid had the largest effect among the carboxylic acids. It provided complete steel protection for 72 hours. 2-Ethylhexanoic acid was noticeably inferior to lauric acid, namely, 12 hours of complete protection. Stearic acid did not affect the corrosion resistance of steel. The other acids inhibited corrosion initiation 2- to 4-fold.

Like in the case of zinc, the CINs studied changed the corrosion mode from general to pitting corrosion.

Copper (M1 grade)

Many of the compounds studied proved to be promising CINs for M1 copper.

Of the nitrogen-containing bases studied, octadecylamine had the best protective effect and completely suppressed corrosion for 1080 hours. The rest of the compounds of this group were noticeably less efficient. Nevertheless, urotropine inhibited corrosion initiation by about a factor of 2, while diphenylguanidine, by a factor of 47. Polyethylenepolyamine not only failed to show protective properties, but even stimulated corrosion already during the CT. It may be assumed that this is due to its thermal destruction accompanied by release of ammonia that is corrosive toward copper.
Captax decreased the corrosion resistance of copper. Already after 2 hours of exposure to corrosive conditions, the samples tarnished noticeably and became almost black after 24 hours. It is noteworthy that the surface film obtained in the vapors of its dimer, \( i.e. \), Altax, had rather a long PAE of 192 hours.

Triazole derivatives showed high efficiency of copper protection. Of these, benzotriazole had the maximum protective effect, as it provided complete protection of the metal for 960 hours. The other compounds of this group were noticeably inferior to benzotriazole. Nevertheless, even 4-aminotriazole, which was the least efficient, inhibited the onset of corrosion on the samples 42-fold.

Of carboxylic acids, the adsorption films of lauric acid (1272 h) and stearic acid (845 h) showed the maximum PAE. It is noteworthy that the results of tests of lauric and tridecanoic acids whose hydrocarbon chain lengths differ by only one atom differ strikingly. Unsaturated aliphatic acids with the same chain length as stearic acid were noticeably less efficient. Oleic acid (one double bond) and linolenic acid (3 double bonds) prevented copper corrosion for 24 and 50 hours, respectively. Treatment in vapors of 2-ethylhexanoic and neodecanoic acids led to strong etching of the metal and formation of a green coating on the surface of the samples already during the CT.

All the CINs studied, except for the above-mentioned 2-ethylhexanoic and neodecanoic acids, changed the copper corrosion mode from general to pitting corrosion.

**Brass (L63 grade)**

All the compounds studied, except for stearic, ethylhexanoic, and neodecanoic acids, inhibited the corrosion of brass to some extent. However, in general, the efficiency of brass chamber protection was lower than that of copper.

Of the nitrogen-containing bases, diphenylguanidine and urotropine were the most efficient and provided alloy protection for 48 hours. Octadecylamine, which is one of the best CINs for copper and steel, increased the lifetime of brass to only 4 hours. Treatment of brass in polyethylene polyamine vapors, like in the case of copper, led to the appearance of corrosion on the metal already during the CT.

Captax and Altax provided brass protection for 168 hours. These are the best results among the set of CINs studied. It is noteworthy that at the same time, Captax demonstrated weak protection of copper and zinc, \( i.e., \) the main brass components.

Triazole and its derivatives, except for tolyltriazole and chlorobenzotriazole, increased the corrosion resistance of brass by a factor of 2.5–5 compared to the background. Tolyltriazole and chlorobenzotriazole extended the metal protection time to 48 and 72 hours, respectively.

Among the carboxylic acids, lauric acid provided the maximum PAE on brass, namely, 72 hours. Like in the case of copper, the protective properties of tridecanoic acid, which has a similar structure, are lower by an order of magnitude. Oleic and linolenic acids did not prove to be efficient CINs. In the presence of the other acids, corrosion damage appeared on brass during the CT. In the case of stearic acid, reddening of the samples occurred, which is
characteristic of brass dezincification, while in the case of ethylhexanoic and neodecanoic acids, greenish corrosion products appeared.

All compounds that inhibited the initiation of corrosion also favored its localization.

**Aluminum alloy (AMg6)**

AMg6 is a more complex object for chamber protection compared to the other metals considered in this paper.

The adsorption films formed in the vapors of octadecylamine, diphenylguanidine, or urotropine slightly increased the corrosion resistance of the alloy. CT in the presence of polyethylene polyamine resulted in an almost 1.5-fold decrease in the total protection time compared to the background sample.

The adsorption films formed in Captax or Altax vapors behaved similarly to those formed on M1 copper. Captax reduced the corrosion resistance of the alloy, while in contrast, its dimer (Altax) increased it slightly.

Chamber treatment in the vapors of triazole derivatives did not affect the resistance of the aluminum alloy under the experimental conditions.

Of the compounds studied, carboxylic acids had the best protective properties toward AMg6. High results were demonstrated by ethylhexanoic and neodecanoic acids that prevented the alloy corrosion for 1200 and 792 hours, respectively. A significantly lower protective effect was shown by CT in the vapors of oleic acid (576 h) and lauric acid (432 h). Stearic, linolenic, and tridecanoic acids had an insignificant effect on the onset of alloy corrosion.

The CINs studied did not affect the point-like character of the first corrosion damage of the aluminum alloy.

**Magnesium alloy (MA8M)**

Despite the very low corrosion resistance of the magnesium alloy, it was characterized by higher protection factors than AMg6.

Nitrogen-containing bases inhibited the corrosion initiation 6-fold (urotropin) or 48-fold (polyethylene polyamine).

Treatment in the vapors of Captax and Altax increased the time of complete alloy protection by a factor of 6 and 8, respectively.

Triazoles are weak CINs for MA8M. Among them, chlorobenzotriazole showed the best PAE. The incubation time of corrosion on the samples treated by this compound was 9 h.

Carboxylic acids with non-branched hydrocarbon chains possessed the highest protective properties among the compounds of the classes studied. The maximum PAE was provided by treatment of the alloy in lauric acid vapors. The adsorption films of stearic and oleic acids provided complete protection of magnesium for 27 and 36 hours, respectively. Linolenic acid was significantly inferior to them (7 h). Like in the case of copper and brass, the PAE of tridecanoic acid (3 h) was significantly smaller than that of lauric acid with a
similar structure. Ethylhexanoic and neodecanoic acids cause continuous corrosion of MA8M during the CT.

The CINs studied did not affect the character of the first corrosion defects of the aluminum alloy.

Conclusions

The results of our experiments showed that carboxylic acids with branched hydrocarbon chains are promising compounds for the creation of efficient CINs for zinc and aluminum alloys. It can be assumed that 2-ethylhexanoic and neodecanoic acids would also provide protection of galvanized steels whose corrosion resistance under atmospheric conditions is determined by zinc. It should be borne in mind that these compounds are unacceptable for the CT of items containing copper, brass and magnesium parts.

Octadecylamine demonstrates high efficiency in the protection of steel and copper items. It is essential that it also inhibits to some extent the corrosion of the other materials studied. This allows us to consider this compound as a basis for creating versatile mixed CINs.

Lauric acid, which provides more than a tenfold inhibition of corrosion initiation on all the materials studied, except for the aluminum alloy, may be yet another potential component for versatile CINs. However, the protective properties of this CIN are quite pronounced even on the Al alloy.

Altax, which is known to be a contact inhibitor of these materials, is promising for the chamber protection of items made of copper and its alloys.

References


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