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| Author           | 藤井, 晴一 (Fujii, Seiichi)<br>荒牧, 国次 (Aramaki, Kunitsugu)  |
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## Studies on Corrosion Inhibitors ( II )

(Received November 25, 1953)

Seichi FUJII\*

Kunitsugu ARAMAKI\*\*

### Abstract

In the former report,<sup>1)</sup> higher fatty amines were prepared by catalytic hydrogenation of nitrile derived from corresponding acid amide converting them from acid. As principal agents for corrosion inhibition, products by the reactions between amines and higher fatty acids have been found best. In the present report, corrosion-tests have been made under various conditions using various derivatives of these amines. And the most effective rust inhibitors were found to be the products by the reactions between 1 mol. of n-hexadecylamine and 3 mols. of linolenic acid, or between 1 mol. of di-n-hexadecylamine and 2 mols. of linolenic acid. And moreover, they can resist corrosion not only when used in acidic solutions but when in alkaline salting water.

(I) Too little is known how amines function as rust inhibitors.<sup>2)3)</sup> But such amines as having lower molecular weights<sup>4)</sup> than pentylamines are effective as rust inhibitors only when they are used in acidic solutions.<sup>5)</sup> These amines of lower molecular weights can not resist when they are employed in sea water.

Those higher fatty amines we have been studied, can resist both in acid and in neutral<sup>6)</sup> or alkaline solutions.<sup>7)</sup>

Surface-active agents have hydrophile parts and hydrophobic parts. In water, salts of above amines dissociate as  $(RNH_3)^+ X^-$  while metallic surfaces ( or other negatively charged surfaces ) adsorb the surface-active amines locating them with the nitrogen-atom, which is carrying the positive charge, and the lipophile groups are left extending outward to give hydrophobic surfaces. Thus, iron-surfaces, treated with solution of salts of such amines, resist corrosion by giving repellent surfaces to water. And also, iron-surfaces are covered with repellent film to water which will be more easily coated with rust

\* 藤井晴一 Dr. sci., Professor at Keio university.

\*\* 荒牧国次 Student of Master Course.

1) S. Fujii, This Proceedings 4, 55

2) Breston, Ind. Eng. Chem. 44, 1755 (1952)

3) W. Zisman, Ind. Eng. Chem. 45, 1406 (1953)

4) Mann, Trans. Electrochem. Soc. 69, 115 (1936)

5) Mann, Laurer, Hultin, Ind. Eng. Chem. 28, 59, 1048 (1936)

6) S. Fujii, Corrosion Eng. Jap. 1, 398 (1952)

7) S. Fujii, K. Aramaki, Corrosion Eng. Jap. 2, 230 (1953)

preventive oil. From these standpoints we have examined many products of reactions between amines and acids. And more effective inhibitors can be prepared from reactions between hexadecylamines and several acids. But because these inhibitors are so slightly soluble, most effective results can be obtained when they are duly dispersed. For this purpose linseed oil solution of these products and small amounts of emulsifiers can serve more effectively as rust inhibitors.

(II) Many preliminary corrosion tests suggest that these amines are more effective for rust inhibition when they are the quaternary ammonium salts or amine-salts, and most effective ones are obtainable using such inhibitors which are prepared by the reaction at about 130° C between 1 mol. of amine and 2 or 3 mols. of acid. For these phenomena we have yet been unable to clarify why they might be, but as an example, following corrosion tests with inhibitors prepared by the reactions between 1 mol of amine and some mols. of linolenic acid show that rust inhibitions are duly exhibited when mol. ratio of primary amine to acid are laid at 1:3 and secondary amine at 1:2, respectively.

Table 1. Reduction in Corrosivity of Salted Water When treated with 5 p. p. m. of the Inhibitors prepared by the Reaction between 1 mol. of Mono-n- or di-n-Hexadecylamine and Some mols. of Linolenic Acid

| Mol. ratio          |                  | Penetration |
|---------------------|------------------|-------------|
| Amine               | : Linolenic acid | mm/yr.      |
| n-hexadecylamine    |                  |             |
| 1                   | : 1              | 0.0460      |
| 1                   | : 2              | 0.0204      |
| 1                   | : 3              | 0.00582     |
| di-n-hexadecylamine |                  |             |
| 1                   | : 1              | 0.00978     |
| 1                   | : 2              | 0.00507     |
| Blank test          |                  | 0.126       |

To examine how and what sorts of acids affect higher alkyl amine inhibitors, corrosion tests have been made in artificial sea water<sup>8)</sup> at room temperature.

Such fatty acids as with branched alkyl chain are not so effective as non-branched<sup>9)</sup>. Table 2 shows that acids with straight carbon chains of C<sub>8</sub> to C<sub>12</sub> carbon atoms are more effective than those with lower or higher straight carbon chains.

Table 2.<sup>†</sup> Effects of Saturated Fatty Acids upon n-Hexadecylamine Inhibitors

| Acid          | Penetration mm/yr. |
|---------------|--------------------|
| Acetic acid   | 0.0132             |
| Butyric acid  | 0.0147             |
| Caprylic acid | 0.0081             |
| Capric acid   | 0.0101             |
| Lauric acid   | 0.00912            |
| Palmitic acid | 0.0192             |
| Stearic acid  | 0.0202             |
| Blank test    | 0.0705             |

8) N. N. Subow, "Oceanographical Tables" pp. 208 (1931) Moscow

9) C. C. Nathan, Corrosion 9, 199 (1953)

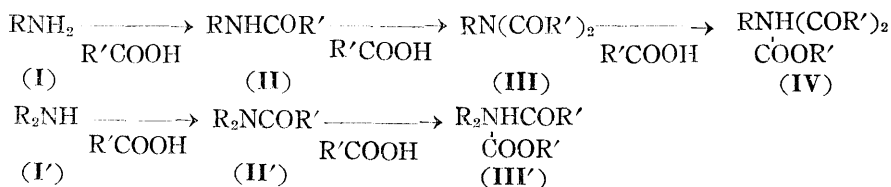
These results may depend on the affinity of acids for water. In the inhibitor-molecule, the hydrophile group unbalances the hydrophobic group. So, lower or higher fatty acids can not bring themselves into proper correlation with the amines. To correspond higher acids with the amines, longer chain alkyl groups of acids may have unsaturated linkages which have hydrophile properties. Several inhibitors which are prepared by combining with unsaturated commercial higher fatty acids (Table 3) have been tested for rust inhibitors.

Table 3 Corrosion Effects in Inhibitors by the Reactions between n-Hexadecylamine and Several Unsaturated Fatty Acids

| Acid           | Penetration mm/yr. |
|----------------|--------------------|
| Stearic acid   | 0.0228             |
| Oleic acid     | 0.0157             |
| Linolenic acid | 0.0142             |
| Blank test     | 0.108              |

As the results of the tests, the products by the reactions between 1 mol. of amine and 2 or 3 mols. of linolenic acid can resist corrosion as well as the products with C<sub>8</sub> to C<sub>12</sub> straight chain saturated fatty acids. Double bonds which may absorb oxygen dissolved in the corrosive solution (which is one of factors of corrosion) give more favorable influence for corrosion inhibition to some extents. And among such C<sub>18</sub> straight chain fatty acids as with double bonds linolenic acid which have three double bonds give the best influence to the inhibitors.

The most effective rust inhibitors consist of 1 mol. of primary amine and 3 mols. of linolenic acid or of 1 mol. of secondary amine and 2 mols. of linolenic acid. But these inhibitors are always prepared by heating them together at about 130°C. for 30 minutes or more, and non-heated products are not so effective. For these reasons we have such conceptions about these reactions as illustrated in following equations:



The above equations have not been determined, but the behavior of these inhibitors seems to indicate definite compounds. Definite products are given by the hydrolysis of the so-prepared inhibitors above mentioned and they give definite melting points. If our conceptions are not imaginary, the last mol. of linolenic acid is reacted to form salts of the compound III (or II'). And these salts are markedly surface-active<sup>10)</sup> and can be used as rust inhibitors<sup>11)</sup>.

When these inhibitors are dispersed in stronger acid solutions, the anion R'COO<sup>-</sup> are substituted by the stronger acid anion (as an example, Cl<sup>-</sup> in HCl solution). These results are to be shown by Figures 3 and 2. In Figure 3, the inhibitor A is obtained

10) Moilliet, Collie, "Surface Activity", London (1951) pp. 326

11) L. Piatti, Werks. u. Korr. 4. 153 (1953)

by making salt of the compound III with acetic acid and B with hydrochloric acid.

Chloride of the compound III is more effective for rust inhibition in acetic acid solution than acetate of the compound III. In acid solution the inhibitor B is more polarized than the inhibitor A, so the B is more strongly adsorbed by negatively charged surfaces.

In Figure 2. the inhibitor A is obtained by making salt of the compound III with linolenic acid, B with hydrochloric acid and C is also obtained by making salt of the compound II' with linolenic acid. For the same reason, in sea water B is more strongly adsorbed than A.

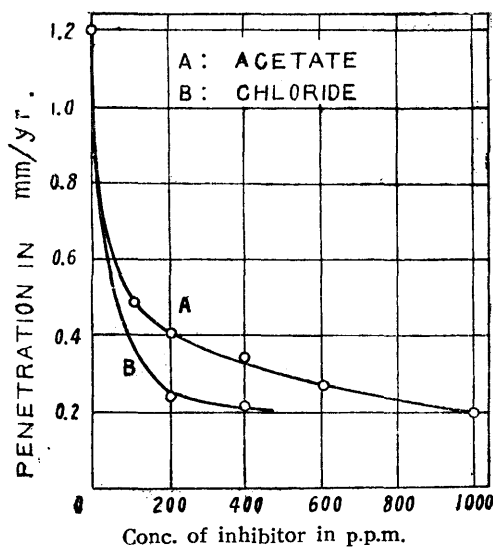


Fig. 2. Penetration in 10% Acetic Acid Solution treated with Inhibitors at Room Temperature

(III). Corrosion tests: The same sized mild steel test-pieces ( as illustrated in Figure 1 ) after polishing and weighing, are separately dipped in flasks containing corrosive solutions treated with various concentrations of inhibitors solved in linseed oil. After corrosion tests, each test-pieces are polished with care and weighed. Corrosion losses during the tests are determined by differences between both weighings.

Expt. 1 (Table. 1) For this experiment, inhibitors are prepared by the reactions at about 130° C. between 1 mol. of n-hexadecylamine or di-n-hexadecylamine and 1~3 mols. of linolenic acid. Concentrations of these

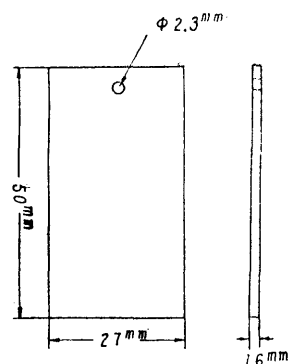


Fig. 1. Test Piece

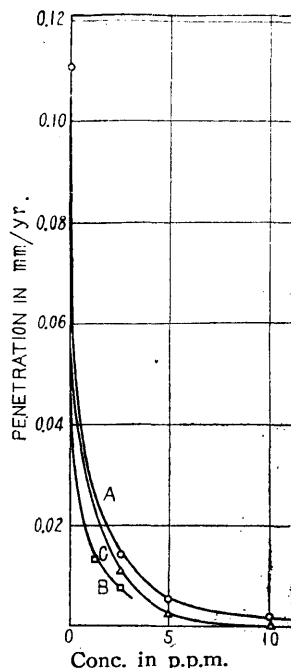
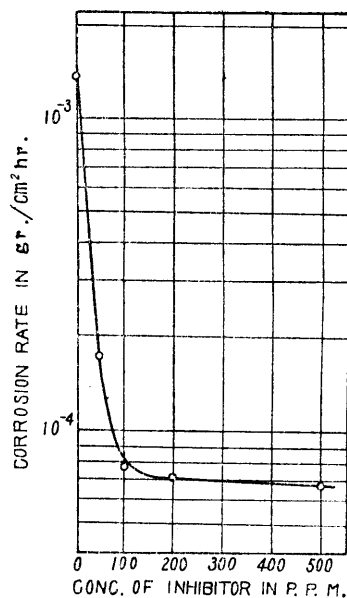


Fig. 3. Penetration in Artificial Sea water treated with Inhibitors at Room Temp.

inhibitors in solutions are 5 p. p. m.\* in each. n-Hexadecylamine—3 mols. of linolenic acid or di-n-hexadecylamine—2 mols. of linolenic acid inhibitor are both found best by 72 hrs. dipping tests at room temp. in artificial sea water. **Expt. 2.** (Table.2) For this experiment, inhibitors are prepared by the reactions at about 130°C. between 1 mol. of n-hexadecylamine and 3 mols. of saturated fatty acids such as acetic (C<sub>2</sub>), butyric (C<sub>4</sub>), caprylic (C<sub>8</sub>), capric (C<sub>10</sub>), lauric (C<sub>12</sub>), palmitic (C<sub>16</sub>) and stearic (C<sub>18</sub>) acid. Concentrations of these inhibitors in solutions are 20 p. p. m. in each. n-hexadecylamine—C<sub>8</sub>~C<sub>12</sub> fatty acid inhibitors are found best by 72 hrs. dipping tests at room temp. in artificial sea water. **Expt. 3.** (Table III) Inhibitors are prepared by the reaction at about 130° C. between 1 mol. of n-hexadecylamine and 3 mols. of unsaturated fatty acid such as oleic and linolenic acid. Concentrations of these inhibitors in solutions are 20 p. p. m. in each. n-hexadecylamine—linolenic acid inhibitor is found best by 72 hrs. dipping test at room temp. in artificial sea water. **Expt. 4.** (Figure 3) Inhibitors used in various concentrations are as follows; A: Acetic acid salt of the products (the compound III) of the reaction between n-hexadecylamine and linolenic acid.

B: Hydrochloric acid salt of the products (the compound III) of the reaction between n-hexadecylamine and linolenic acid. This corrosion test is conducted at room temp. for 20 hrs. in 10% acetic acid solution. Complete inhibition is more difficult in organic acid solution than in mineral acid solution. The reason may be that organic acid is more penetrating than mineral acid. **Expt. 5.** (Figure 2) Three inhibitors are used. A: Linolenic acid salt (the compound IV) of the product by the reaction between 1 mol. of n-hexadecylamine and 2 mols. of linolenic acid. B: Hydrochloric acid salt of the product (the compound III) by the reaction between 1 mol. of n-hexadecylamine and 2 mols. of linolenic acid. C: Linolenic acid salt (the compound III') of the product by the reaction between 1 mol. of di-n-hexadecylamine and 1 mol. of linolenic acid. Dipping tests for various concentrations are conducted with above inhibitors at room temp. for 72 hrs. in artificial sea water. **Expt. 6.** (Figure 4) The inhibitor is B of **Expt. 5.** Dipping tests are conducted at elevated temp. in 5% HCl—solution for 6 hrs.

Complete inhibition requires 500 p. p. m. or more of the inhibitor. **Expt. 7.** (Figure 5) In 5% H<sub>2</sub>SO<sub>4</sub>



Conc. of inhibitor in p.p.m.  
**Fig. 4.** Reduction in Corrosivity of 5% HCl Solution at 60°C.

\* p.p.m. : part per million.

solution, tests are conducted employing the inhibitor A of Expt. 5. in various concentrations at room temp. for 20 hrs.

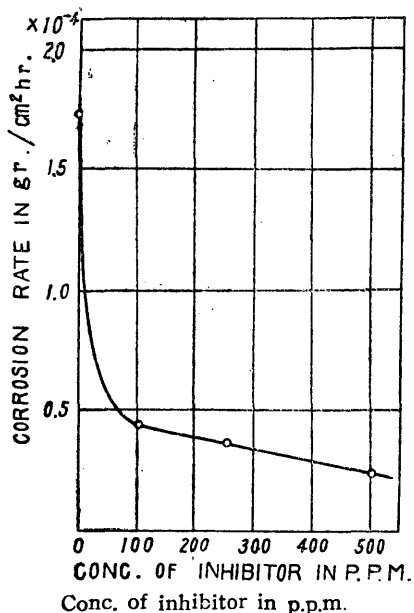


Fig. 5. Corrosion Test in 5% H<sub>2</sub>SO<sub>4</sub> Solution Inhibited at Room Temperature

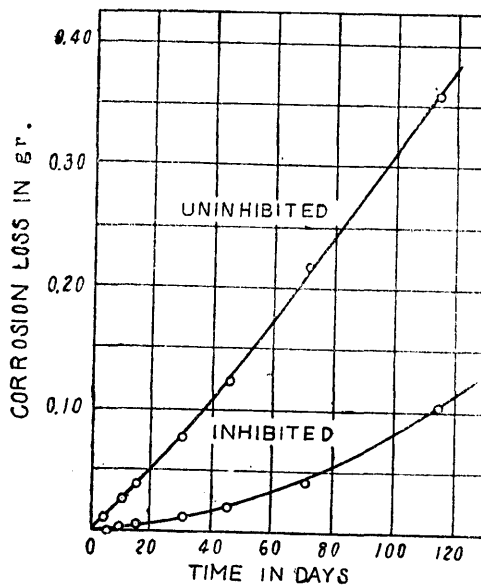


Fig. 6 Corrosion Losses in Artificial Sea Water during Treatment with the Inhibitor at Room Temp.

**Expt. 8.** (Figure 6) In salt water long period tests are conducted at room temp. with the inhibitor A of Expt. 5. 20 p. p. m. of the inhibitor is mixed in salt water at the beginning of these tests. After 114 day-dipping, 71% of corrosion losses are found eliminated. Test pieces used in this experiment are the same as illustrated in Fig. 1.