Hexadecylamines were derived from palmitic acid, which was converted into nitrile followed by catalytic hydrogenation of nitrile to amines. These amines were used as principal agents of corrosion inhibitions. In the present report the synthetic work is mainly given.
Studies on Corrosion Inhibitors* (I)

(Received Nov. 26, 1992)

Seiichi FUJII**

Abstract

Hexadecylamines were derived from palmitic acid, which was converted into nitrile followed by catalytic hydrogenation of nitrile to amines. These amines were used as principal agents of corrosion inhibitions. In the present report the synthetic work is mainly given.

I. Introduction

In this country the use of natural gas has been developed for the last ten years. But corrosion of gas-well steel-pipes by the salted water flowing up with natural gas, has become urgent problems to be overcome if more exploitation is to be made. In Niigata city in the worst cases the wells have been destroyed by corrosion within a half year. We are therefore going to make a study of corrosion inhibitors of cationic surface-active agents, such as higher fatty amines, which can be so adsorbed by metallic surfaces to give them a water-repellent, organophilic character. But few data for the higher fatty amines have so far been reported. So we now regard with a great deal of interests these amines with long chain alkyl groups. Moreover, amines derived from natural fatty acids, so far as our experiments go, seem more effective as principal agents of corrosion inhibition than ones derived from the higher alcohols. Such important amines are Hexadecylamines and Octadecylamines that have been synthesised in our laboratory.

II. Synthesis of Hexadecylamines

Hexadecylamines are derived from palmitic acid converting it into nitrile which, in turn, is followed by catalytic hydrogenation to amines, according to the following equations.

$$\text{C}_{16}\text{H}_{31}\text{COOH} + \text{SOCl}_2 \xrightarrow{60^\circ C} \text{C}_{16}\text{H}_{31}\text{COCl} + \text{SO}_2 + \text{HCl} \quad (1)$$

$$\text{C}_{16}\text{H}_{31}\text{COCl} + 2\text{NH}_3 \xrightarrow{0^\circ C \text{ in aq.}} \text{C}_{16}\text{H}_{31}\text{CONH}_2 + \text{NH}_4\text{Cl} \quad (2)$$

$$\text{C}_{16}\text{H}_{31}\text{CONH}_2 \xrightarrow{\text{heat} \text{ P}_2\text{O}_5} \text{C}_{16}\text{H}_{31}\text{C} = \text{N} \quad (3)$$

$$\text{C}_{16}\text{H}_{31}\text{C} = \text{N} + 2\text{H}_2 \xrightarrow{160^\circ C \text{ 150 atm. catalyst}} \text{C}_{16}\text{H}_{31}\text{CH}_3\text{NH}_2 \quad (4)$$

* The Summary of this report and one following is given by the author in "Corrosion Engineering Digest" vol. 1, No. 6, p. 398 published by Japan Scientific Council 97th. Committee.

** Dr. Sci., Prof. at Keio University.

For these reactions few descriptions have hitherto been given. So, here we are going to say something about these reactions before describing corrosion inhibitors, which is the subject of this paper.

The reaction (1) is easily carried out yielding 80% or more of the chloride so long as conditions are favorable. Too low reaction-temperature, too short reaction time lead to less yields. Especially shortage of thionylchloride in the process of the reaction, which is caused by its escape out of the reaction-vessel together with such evolving gases as hydrochloric acid or sulphur dioxide, lead to less yields. In consequence, non-reacted acid and formed acid chloride are secondarily condensed to palmitic acid anhydride, while evolving hydrochloric acid, when they are heated for the fractional vacuum distillation to isolate the acid chloride, as shown by the following equation (5).

\[
\text{C}_{15}\text{H}_{31}\text{COOH} + \text{C}_{15}\text{H}_{31}\text{COCI} \rightarrow \text{HCl} + \text{C}_{15}\text{H}_{31}\text{CO}^+ \quad (5)
\]

The residue obtained after distilling off the acid chloride is dissolved in benzene. From this benzene solution free palmitic acid is excluded by washing it with a diluted sodium carbonate solution. After drying the benzene solution, acid anhydride \(^2\) is recrystallized and then identified. Since our objective in our purpose lies in obtaining palmitic acid amide, we are not necessarily frustrated as it is obtainable by precipitating itself by introducing ammonia into the benzene solution. And then palmitic acid is successfully converted to palmitic acid amide with a good yield.

Palmitic acid chloride reacts with ammonia in an aqueous media at 0-5° C. to produce acid amide quantitatively. The reaction-temperature must be kept below 5° C. so as for amide not to hydrolyse.

Amide is easily dehydrated to nitrile with dehydrating agents such as phosphorpentaoxide. But it is difficult to dehydrate and hydrogenate amide to amines directly in an autoclave with dehydration and hydrogenation catalysts. Various catalysts have been repeatedly used, but in vain. Only when hydrogenated in dioxane as a solvent of amide on the contact of Adkins catalyst \(^3\) under the conditions of about 200 atms. at 250°C., 68% amines of the theory are obtained. (Table 1. Ex. No.4). The reason why amide cannot be directly converted into amines except on these particular conditions, is probably due to the association through hydrogen-bonding as illustrated as follows:

\[
\text{H}_2\text{N} - \text{C} = \text{O} \cdots \text{H} - \text{NH} - \text{C} = \text{O} \cdots \text{H} - \text{NH} -
\]

\[
\text{C}_{15}\text{H}_{31} \quad \text{C}_{15}\text{H}_{31}
\]

According to Wojcik's spectroscopic studies \(^4\) of amide, it is monomeric in the dilute dioxane solution. So it may be that they are hydrogenated to amines only

---

2) Halde, Ripper, & Zadeck; Ber. 57B, 103(1924)
3) H. Adkins; "Reaction of Hydrogen" P.22 (1937)
4) B. Wojcik; Jour. Chem. Soc. 56, 2416 (1934)
Studies on Corrosion Inhibitors

in dioxane. This monomeric amide has been identified by infra-red spectroscopic studies on the lower amides in 1947. H. Adkins explained about the solvent that he made use in the hydrogenation of laurylic acid amide under the conditions of 200-300 atms. at 250-265°C. as dispersers of water formed by the dehydration.

Table 1. Dehydration and hydrogenation of palmitic acid amide on the contact of Cu-Cr-Ba-oxide Catalysts.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>40</td>
<td>0</td>
<td>170</td>
<td>1</td>
<td>106</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>30</td>
<td>50</td>
<td>250</td>
<td>0.7</td>
<td>198</td>
<td>primary</td>
<td>27</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>20</td>
<td>0</td>
<td>256</td>
<td>*</td>
<td>186</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>20</td>
<td>35</td>
<td>255</td>
<td>1.2</td>
<td>194</td>
<td>primary</td>
<td>68</td>
</tr>
<tr>
<td>* 5</td>
<td>4.5</td>
<td>30</td>
<td>50</td>
<td>260</td>
<td>2</td>
<td>188</td>
<td>–</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>4.5</td>
<td>30</td>
<td>50</td>
<td>260</td>
<td>2.5</td>
<td>155</td>
<td>–</td>
<td>0</td>
</tr>
</tbody>
</table>

* Dioxane contained water.

To avoid these difficulties, amines are to be prepared beforehand by the contact hydrogenation of nitrile under pressures.

Purified palmitonitrile is hydrogenated to n-Hexadecyl-amine, on the contact of Raney Nickel under 165 atms. at 115°C. or on that of Cu-Cr-Ba-oxide catalyst under 165 atms. at 165°C. And under the best conditions of these hydrogenation, the main parts of hydrogenated products are primary amine and only 1% secondary amine (Table 2 Ex. No.3). But when reaction pressures are below 100 atms or when they fall while hydrogenating, secondary amine predominates. (Table 2. Ex No.6). From these facts the same may be concluded as that mentioned by Adkins in his paper concerning hydrogenation of nitriles of the lower molecular weights. When reaction pressures are kept over 100 atms. while the reaction is under way, alkylidene imine formed as an intermediate in the stepwise hydrogenation of nitrile (shown by the Equation (6)) is converted into primary amine according to the equation (7). But when pressures drop below 100 atms., imine is coupled with previously formed primary amine more rapidly than when hydrogenated to primary amine, and after deammonating the condensed products, secondary amine is obtained as shown by the equation (8). Tertiary amine we have not yet purely obtained.

$$\text{C}_{15}\text{H}_{31}\text{C} = \text{N} + \text{H}_2 \longrightarrow \text{C}_{15}\text{H}_{31}\text{CH} = \text{NH} \quad (6)$$

$$\text{C}_{15}\text{H}_{31}\text{CH} = \text{NH} + \text{H}_2 \longrightarrow \text{C}_{15}\text{H}_{31}\text{CH}_2\text{NH}_2 \quad (7)$$

6) H. Adkins: ibid. p.112
Exp. no.3.; Hydrogen were charged twice to keep pressures over 100 atms.

**Experimetal Parts**

(1) \[ \text{C}_{15}\text{H}_{31}\text{COOH} + \text{SOCl}_2 \rightarrow \text{C}_{15}\text{H}_{31}\text{COCl} + \text{SO}_2 + \text{ACl} \]

1. Mol. palmitic acid and 1.5~2.0 Mol. thionyl-chloride are mixed together in a round flask and heated on the water bath with an effective condenser until the evolution of gases cease. The clear liquid is distilled in vacuo and the fraction boiling at 184-160°C/8m.m. Hg. collected. The residue, after distilling off palmitic acid chloride, is mainly palmitic acid anhydride.

**Table 3. Chlorination of palmitic acid**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>60</td>
<td>3.5</td>
<td>0</td>
<td>45 (86)</td>
</tr>
<tr>
<td>2</td>
<td>813</td>
<td>570</td>
<td>55-60</td>
<td>8.5</td>
<td>157</td>
<td>442 (63)</td>
</tr>
</tbody>
</table>

(2) \[ \text{C}_{15}\text{H}_{31}\text{COCl} + 2\text{NH}_3 \rightarrow \text{C}_{15}\text{H}_{31}\text{CONH}_2 + \text{NH}_4\text{Cl} \]

Excess of 28% aqueous ammonia is cooled to 0°C. in a freezing mixture. Stir
whilst cooling to produce amide. Add palmitic acid chloride slowly to this, and if the temperature rises above 5°C, a few lumps of ice are added. After the reaction is over, suspending amide is quickly filtered and dried. Recrystallize from alcohol. Pure amide melts at above 98°C. The best yields 96% of the theory.

Table 4. Amidation of Palmitic acid chloride

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Palmitic acid chloride grs.</th>
<th>28% Ammonia water c.c.</th>
<th>Reaction temp.°C.</th>
<th>Reaction time hrs.</th>
<th>Palmitic acid amide grs. (M.pt.)</th>
<th>Yield % of the theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>94</td>
<td>200</td>
<td>0-10</td>
<td>0.5</td>
<td>58 (96°)</td>
<td>71</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>300</td>
<td>0-5</td>
<td>0.5</td>
<td>44 (99°)</td>
<td>90</td>
<td></td>
</tr>
</tbody>
</table>

(3) \( \text{C}_{15}\text{H}_{31}\text{CONH}_2 + \text{heat} \rightarrow \text{C}_{15}\text{H}_{31}\text{CN} \)

Amide, dully dried up, and phosphor-pentaoxide are equimolecularly mixed in a Cleisen distilling flask. The mixture is gently warmed until it becomes liquidified. Then by vacuum distillation, palmitonitrile boiling at 164~168°C/mm.m.Hg. are collected.

Table 5. Dehydration of Palmitic acid amide

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Palmitic acid amide</th>
<th>( \text{P}_2\text{O}_5 )</th>
<th>Palmitonitrile grs</th>
<th>Yield % of the theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50 grs</td>
<td>30 grs</td>
<td>30 grs</td>
<td>64</td>
</tr>
<tr>
<td>2</td>
<td>45</td>
<td>30</td>
<td>36</td>
<td>82</td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>30</td>
<td>27</td>
<td>66</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
<td>30</td>
<td>32</td>
<td>69</td>
</tr>
<tr>
<td>5</td>
<td>115</td>
<td>60</td>
<td>93</td>
<td>87</td>
</tr>
</tbody>
</table>

(4) \( \text{C}_{15}\text{H}_{31}\text{CN} + 2\text{H}_2 \rightarrow \text{C}_{15}\text{H}_{36}\text{CH}_4\text{NH}_2 \)  

In an autoclave palmitonitrile and Cu-Cr-Ba-oxide catalyst which are 5~8% to the weights of nitrile are mixed. Then under the conditions of 150 atm. at 150-165°C, it is hydrogenated. n-Hexadecylamine is mainly obtained when pressures are kept over 120 atm. But when pressures fall below 100 atm., secondary amine increases and primary amine decreases, as discussed before.

\( \text{C}_{15}\text{H}_{31}\text{CONH}_2 + 2\text{H}_2 \rightarrow \text{C}_{15}\text{H}_{36}\text{CH}_4\text{NH}_2 \)

Amide dissolved in Dioxane is dehydrated and hydrogenated on the contact of
Cu-Cr-Ba oxide catalyst amounting 15—20wt. % of amide under the conditions of about 200 atm. at 600°C.

III. Corrosion Inhibitors

Metallic surfaces or other negatively charged surfaces adsorb the surface-active amines such as Hexadecylamines, (or Octadecylamines) whose synthesis have been described above. Such surfaces hold the positive surface-active ions whilst water is negatively charged. These ions, in locating themselves with the nitrogens which is carrying the positive charge at the adsorbing surfaces, leave their hydrocarbon radical C_{16}H_{33} (or C_{18}H_{37}) extending outward to give organophilic surfaces. Thus iron-surfaces treated with solution of hexadecylamines, resist corrosion and are more easily coated with rust-preventive oil which serves as well as solvents of hexadecylamines.

So, we have made various experiments to examine what sorts of compounds modified with these amines act as corrosion-inhibitors. But more detailed report on the subject will be made in the next paper. It will show, in a word, that condensed products of 1 Mol. of n-hexadecylamine with 2 Mol. of the unsaturated higher fatty acids with 2 or 3 double bonds, or with 1 Mol. of anhydrides of the higher fatty acids have been found best as corrosion-inhibitors of natural gas-well pipings.

And, when iron-surfaces are treated with diluted hydrochloric acid solution, for an example, to avoid troubles caused by scale, small amounts of hexadecylamines, if present in the solution, resist acid corrosion of iron-surfaces. For an example when iron-test pieces of same size were dipped in a large amount of 10% hydrochloric acid solution, following results as shown in Table 6 were obtained.

<table>
<thead>
<tr>
<th>Amounts of Hexadecylamines</th>
<th>0</th>
<th>250 p.p.m.*</th>
<th>500 p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loses</td>
<td>302 mg.</td>
<td>9.5 mg.</td>
<td>5.8 mg.</td>
</tr>
</tbody>
</table>

Table 6. Loses by acid corrosion after 24 hrs. room-temp dipping.

* parts per micron.