plants prefer to dilute with inert oils to reduce the rate of reaction.

ASPHALT EMULSIONS

Large amounts of tall oil are used to make asphalt emulsions. It appears preferable to rosin and other cheap fatty acids for asphalt emulsions of certain specifications.

RUBBER CHEMICALS

Tall oil is being used for softening or curing rubber, replacing stearic acid, cotton seed fatty acids, or hydrogenated fish oils in these processes.

Since the production of tall oil in this country is less than ten years old many promising applications have not yet emerged from the laboratory.

The Preparation and Properties of High Molecular Weight Primary Amines*

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ANY derivative which is classed as a commercial derivative must have useful properties. These are always a function of the chemical and physical properties of the compound in question. In addition to the requirement that the compound or group of compounds be useful, they must also be available in substantial amounts at reasonable prices. This requires that the raw material from which such compounds are prepared must be readily available and that their synthesis from this material be by a commercially practical procedure. In any discussion of fatty acid derivatives it should be borne in mind that the fatty acids fulfill the first of these requirements in that the raw material exists in extremely large quantities. The problem, therefore, of preparing fatty acid derivatives which have commercial significance is to synthesize compounds which have useful properties from the fatty acids by processes which are commercially feasible and practical.

The question of the utilization of fatty acids for the preparation of derivatives which show commerical promise is fundamentally the same as that encountered in any field where one is attempting to utilize a starting material which exists in enormous amounts. Numerous compounds are prepared and their physical and chemical properties studied. From this group of compounds prepared in the laboratory a certain few will appear to possess interesting properties and to have possible commercial applications. A more intensive study is then made of the preparation and properties of such compounds with the view to placing them within the price range of commercial acceptability.

Generally speaking, all fatty acid derivatives have some properties in common which properties have and will continue to influence both research and commercial developments in this field. These properties result from the presence of the long hydrocarbon chain of the fatty acid. The combination of a long hydrocarbon chain attached to a polar group or groups brings about a unique surface chemistry, adsorption phenomena, plasticizing properties, and various other effects which characterize these compounds. The influence of this long chain is illustrated by the difference in properties of sodium acetate and sodium stearate. The long chain imparts to solutions of sodium stearate surface properties, properties of emulsification, etc., which are essentially absent in sodium acetate.

In the time allowed to this talk it is impossible to discuss many of the fatty derivatives. The high molecular weight amines are interesting products which can be prepared from the fatty acids and I wish to discuss briefly their method of preparation, general physical and chemical properties, some of their simple derivatives, and their indicated uses.

The most satisfactory method for the preparation of high molecular weight amines is by the hydrogenation of the corresponding nitriles. Nitriles are formed by passing ammonia gas into a fatty acid held at a temperature somewhat below its boiling point. The mechanism of the reaction is probably represented by the following series of equilibrium.

Figure 1

Equilibria Involved in Nitrile Formation.

$$RCOOH + NH_3 \rightleftarrows RCOONH_4$$

$$RCOONH_4 \rightarrow RC(=O)NH_2 + H_2O$$

$$2RC(=O)NH_2 \rightleftarrows RCN + RCOOH$$

When ammonia is passed into the system continuously this cycle is repeated until the fatty acids are quantitatively converted into nitriles.

The mechanism of the catalytic hydrogenation of nitriles to amines is somewhat complex. The overall reaction is represented as follows:

$$RCN + 2H_2 \rightarrow RCH_2NH_2$$

A high yield of primary amines and a low percentage of secondary amines and other products is desirable. The hydrogenation probably proceeds in stages and a high yield of primary amines requires a very careful selection of the conditions of hydrogenation.

The simplest explanation for the formation of secondary amines is that two molecules of primary amine lose one molecule of ammonia according to the following reaction:

$$2RNH_2 \rightarrow R_2NH + NH_3$$

However, secondary amines may be formed as a primary hydrogenation product under certain conditions. The following equation (see "Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts" by Homer Adkins, Page 53) illustrates one possible mechanism for the formation of secondary amines.

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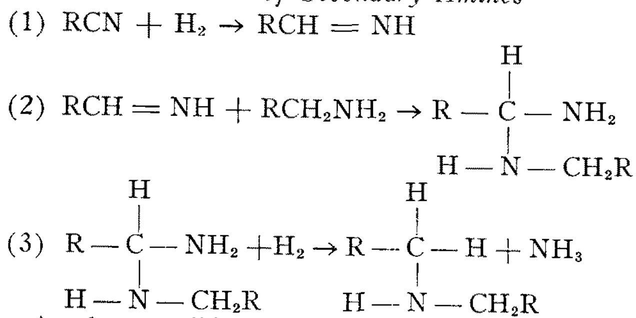
Figure 2

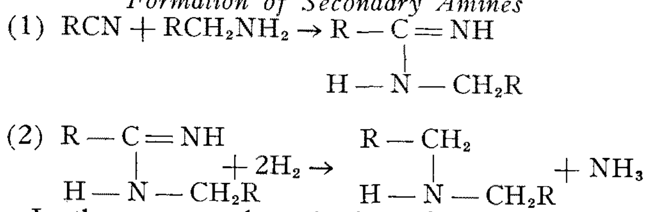
Formation of Secondary Amines



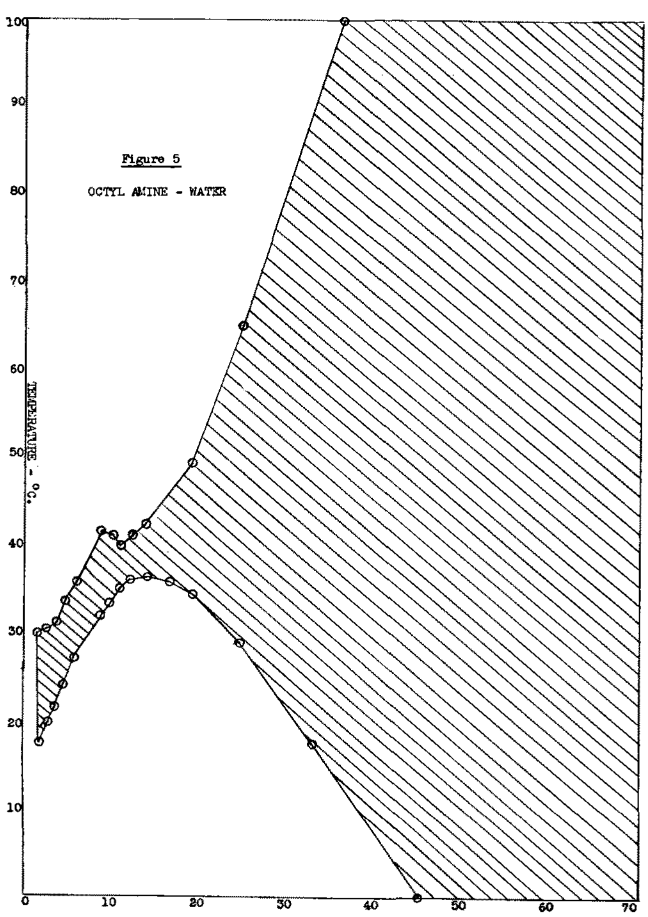
Another possible mechanism for the formation of secondary amines involves the reaction of one nitrile molecule with one molecule of primary amine to form a compound which upon hydrogenation loses ammonia and is converted directly to the secondary amine. This is represented by the following equations:

Figure 3

Formation of Secondary Amines



In these proposed mechanisms for the formation of secondary amines it is evident that ammonia is one of the final products. If the hydrogenation is conducted, therefore, in the .presence of a high partial pressures of ammonia the formation of secondary amines will be retarded.



The high molecular weight primary amines are either high boiling liquids or low melting solids. The amines from six to eighteen carbon atoms can be vacuum distilled without undergoing decomposition. The boiling points of the primary amines from six to eighteen carbon atoms are shown in the following table:

Table 1

Boiling Points of Primary Amines.

Amine	Boiling Point
Hexyl	129.5-131.0
Heptyl	154.5-155.9
Octyl	178-179
Nonyl	107-108.5 at 38.5 mm.
Decyl	114.5-116 at 25 mm.
Undecyl	129.5-130.5 at 25 mm.
Dodecyl	78-81 at 1 mm.
Tridecyl	101.0-102.0 at 1 mm.
Tetradecyl	97-100 at 1 mm.
Pentadecyl	107-110 at 1 mm.
Hexadecyl	117-122 at 1 mm.
Heptadecyl	128-130 at 0.5-1 mm.
Octadecyl	172-173 at 2.5 mm.

The solubility of the high molecular weight amines in water decreases very rapidly with increase in the chain length. The solubility of hexyl amine at room temperature is greater than 0.9% and less than 1.68% whereas the solubility of dodecyl amine is less than 0.2%.

The binary systems of aliphatic amines with water offer an interesting study. We have made observations upon a number of these systems and although this work is by no means completed, some mention of it may be in order at this time.

Samples were prepared by weighing a definite amount of an aliphatic amine and water into a glass tube. The tube was then sealed and the sample of known amine and water content immersed in a water bath. The tubes were attached by means of clamps to a metal rod in such a manner that the amine-water mixture was kept in constant agitation. The temperature of the bath was then raised slowly and visual observations recorded. Figure 5 shows the results obtained when various mixtures of octyl amine and water were studied. This figure shows the range of miscibility of octyl amine and water as a function of the molecular compositions of the mixture and the temperature. The shaded areas represent the region of complete miscibility.

It will be noted that water is much more soluble in octyl amine than octyl amine is in water. It is also apparent that the solubility of octyl amine goes through a maximum and minimum as the temperature increases. The rather peculiar solvent behavior in the compositions containing small amounts of amine suggests that we may be dealing with an octyl amine hydrate, the stability of which is a function of the temperature.

As the molecular weight of the amine increases the temperature area over which amine-water mixtures containing less than twenty molecular percent of amine is miscible decreases very rapidly. Figure 6 shows the system decyl amine-water as a function of the composition and the temperature. A comparison of Figure 5 with Figure 6 shows that octyl amine is soluble in water over a greater temperature range than decyl amine and also that water is not soluble in decyl amine over as great a temperature range as water in octyl amine.

Table 2

Solubility of Dodecyl Amine Acetate in Water

Composition (grams dodecyl amine acetate per 1000 grams H_2O)	Temperature at which mixture becomes homogeneous °C.
0.1476	31.5
0.3670	1.0
0.5747	-12.0
1.1240	35.0
2.7441	33.0
4.9404	25.5
12.4271	1.0
24.4991	1.0
49.2612	1.0
144.824	1.0

Since the amines are basic they form salts with acids, most of which salts are appreciably soluble in water. The salts of the high molecular weight amines have a solubility in water which suggests hydration. This behavior in water can be somewhat correlated to the behavior of the soaps of the high molecular weight fatty acids. We have studied the amine salt-water systems for a number of acetates and hydrochlorides and some observations on the acetates can be given at this time.

Hexyl amine acetate is completely miscible with water. The solubility of the amine acetates decreases very rapidly as the molecular weight increases. Table 2 shows the temperatures at which compositions containing various percentages of dodecyl amine acetate and water become homogeneous. The results were obtained by sealing the mixtures in glass tubes and rotating the tubes in a water bath as previously described for the amine-water systems. The compositions are reported as grams of dodecyl amine acetate per one thousand grams of water.

These results indicate a very peculiar solubility behavior for this compound. When the amount of dodecyl amine acetate is increased the temperature at which the mixture becomes homogeneous first goes to a minimum, then a maximum and then another minimum where it becomes constant. It is possible that these results may be explained by hydration of the amine acetate.

The solubility of tetradecyl amine acetate is shown in Table 3.

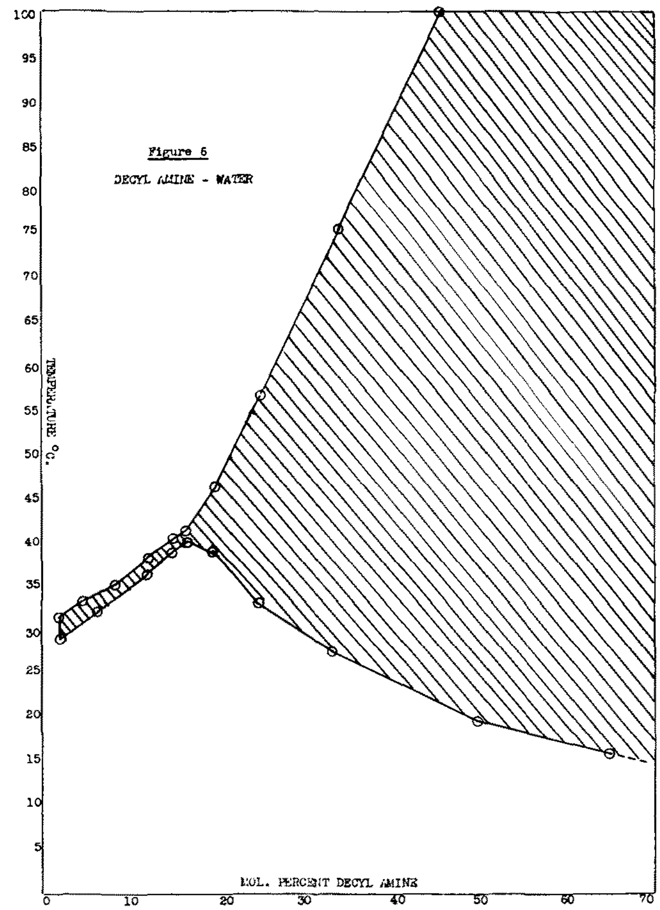
Table 3

Solubility of Tetradecyl Amine Acetate in Water

Composition (grams tetradecyl amine acetate per 1000 grams H_2O)	Temperature at which mixture becomes homogeneous °C.
0.2281	54.0
0.5190	54.0
1.3080	49.5
2.4825	49.5
4.9925	38.5
11.539	33.5
25.065	13.2
54.587	13.2
141.284	13.2

The temperature at which the mixtures become homogeneous decreases with increasing content of tetradecyl amine. It then becomes constant over a wide range of concentration.

High molecular weight amines have a number of uses and some brief comments can be made upon them at this time. The amine salts are excellent wetting agents and can be used to increase the penetration



of dyes and in many other cases where wetting agents stable in acid solutions are required. Several of their derivatives show superior detergent action. The amines and their salts also show promise as emulsifying agents.

The salts of the high molecular weight amines are used as flotation agents particularly for the separation of silica from ores.

The high molecular weight amines and their salts are strongly bactericidal and their solutions can be used as sterilizing mediums. A nine thousandth molar solution of tetradecyl amine acetate in water kills S. aureus after fifteen minutes contact and E. coli after ten minutes contact.

Some of the amines possess high insecticidal values and their kerosene solutions can be used as fly sprays or for the extermination of other insect pests.

A rather novel and interesting use of high molecular weight amines is for the clarification of turbid waters. A concentration of approximately ten parts per million of dodecyl amine acetate produces flocculation of the suspended particles in turbid waters so that a clear water is obtained after filtration whereas without the addition of the amine salt the turbidity of the water is not materially reduced by repeated filtration.

In conclusion, it may be said that high molecular weight amines are extremely interesting both from the viewpoint of their physical chemistry and their commercial possibilities.

The speaker wishes to acknowledge at this time the work of Drs. H. J. Harwood and W. O. Pool who collaborated upon the preparation and hydrogenation of the nitriles, of Dr. E. J. Hoffman who determined the solubilities, and of Mr. W. M. Selby who prepared the compounds used in these tests.