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[54] PROCESS FOR REFINING AMINES

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[58] **Field of Search** .... 260/583 N

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[57] ABSTRACT

Long chain alkyl amines produced from petrochemical methods are refined by treatment with 0.01 to 5 % by weight of a borohydride compound to eliminate the tendency to form colored compounds when further converted to amine salts.

9 Claims, No Drawings

PROCESS FOR REFINING AMINES

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for refining amines. More precisely, it relates to a process comprising refining aliphatic amines by treating them with borohydride compounds, and thereby preventing colorization of amine salts, quaternary ammonium salts or aminebetaine derived from the refined amines.

2. Description of the Prior Art

Long-chain alkyl amines have heretofore been produced from a starting material derived from natural animal or vegetable oils. But recently, following the development of the petrochemical industry, they are produced from an intermediate raw material derived from petroleum products, particularly low polymers of ethylene such as materials well known in the art as α-olefins and Ziegler alcohols.

Long-chain alkyl amines are widely used as cationic surfactants and as ampholytic surfactants such as amine salts, quaternary ammonium salts, or alkyl betaine, or they are converted to known useful long-chain alkylamine oxides.

However, when preparing these surfactants, sometimes the products are undesirably colored yellow or pale red. Colorization is marked when the surfactants are derived from long-chain alkyl amines obtained from ethylene low polymers or derived from alkylamine mixtures containing said long-chain alkylamines as a constituent, and the commercial value of the products are reduced greatly.

SUMMARY OF THE INVENTION

We have discovered that the foregoing disadvantage can be overcome by treating the amines with a special class of reducing agents. We have discovered that hydrogenated boron compounds are superior in their effects, and in their safety and stability in an aqueous solution as a reducing agent for such amines. The present invention is an economic and simple industrial process for obtaining purified alkyl amines which are not apt to color during subsequent salt-forming reactions.

The present invention provides an improved process for refining aliphatic amines by treating said amines with hydrogenated boron compounds.

The invention is a method of refining aliphatic hydrocarbon amines having at least one alkyl group of 9 to 22 carbon atoms attached to the amino nitrogen, said amines being derived from polymerized ethylene by known methods and having a tendency to form colored amine salts, which comprises suppressing said tendency by reacting said aliphatic amine with 0.01 to 5% by weight based on the amine of a borohydride compound selected from the group consisting of an alkali metal borohydride, amine borohydrides, quaternary ammonium borohydrides and mixtures thereof, and recovering refined aliphatic amine from the reaction mixture.

The amine material to which the refining process of the invention can be applied are generally aliphatic primary, secondary and tertiary amines, and mixtures of such amines. The amines have the formulas RNH_2, $RR'NH$ and $RR'R''N$, wherein R is alkyl having from 9 to 22 carbon atoms, preferably 10 to 18 carbon atoms, especially lauryl, and wherein R' and R'' are alkyls having 1 to 22 carbon atoms, preferably 1 to 6 carbon atoms, especially methyl and ethyl. In many instances, the amine material is a mixture of primary, secondary or tertiary amines in which R has various values within the range of carbon atom number for R set forth above. The amine material can be a mixture of primary and/or secondary and/or tertiary amines. As amine materials with which the process of the invention is particularly effective, there are enumerated amine materials derived from ethylene low polymers such as α-olefins and Ziegler alcohols or amine mixtures containing said amines as a constituent. These amine materials derived from ethylene low polymers have the tendency of forming undesired color substances when converted to amine salts, quaternary ammonium salts and/or betaines, apparently owing to a minor amount of impurities therein. Examples of such amines and their preparation are described in (1) M. T. Atwood, JAOCS. 40, 64 (1963); (2) T. Clarke et al., JAOCS. 41, 78 (1964); (3) Onyx Corp. U.S. Pat. No. 3,471,562 (Oct. 7, 1969); and (4) Sun Chemical Corp. U.S. Pat. No. 3,401,203 (Sept. 10, 1968).

As the boron hydride, there can be employed an alkali metal salt of boron hydride such as sodium borohydride, potassium borohydride and lithium borohydride, an amine salt of boron hydride, a quaternary-ammonium salt of boron hydride and mixtures thereof.

The boron hydrides can be added in the form of dry powder or in alkaline aqueous solution. The amount of boron hydride to be added is dependent on the kind of amine to be treated, the process by which it was manufactured, and its properties. The amount of boron hydride used should be kept as low as possible in order to minimize expense, but the use of an excess amount of boron hydride does not cause any adverse effect. Generally, the boron hydride compound is added in an amount from about 0.01 to about 5% by weight, based on the weight of the starting amine material, preferably from 0.05 to 2% by weight.

If a small amount of alkali is added to the starting amine material together with the boron hydride compound, the effect of the boron hydride compound is greatly enhanced and the properties of the amines are further improved. The alkali is preferably water-soluble and is added in an amount up to 50%, preferably in the range of 0.1 to 10%, based on the weight of the starting amine materials. As the alkali, it is preferred to use sodium hydroxide, potassium hydroxide and sodium carbonate. The amount thereof to be added is not critical. The boron hydride compound is effective even if no alkali at all is added.

The preferred mode of performance of this invention consists of treating the starting amine material with boron hydride compound in an amount of from about 0.01 to about 5% by weight, based on the weight of the amine, in the presence of an alkali.

A specific preferred process according to this invention comprises placing the starting amine material, boron hydride compound and an aqueous solution of caustic alkali in a reactor, and agitating the mixture for several (about 2 to about 10) hours at about 50° to 70°C. It will be understood, however, that the treating temperature and the treating time are not critical.

The present invention is carried out usually in a homogeneous or non-homogeneous phase of amine and water, but if necessary, alcohol such as methanol, ethanol or isopropanol can be added.

The presence of inorganic salts in the starting amine material, such as sodium chloride, sodium bromide, and potassium chloride, does not inhibit the desired effect of the boron hydride compound. Therefore, it is possible to employ as a starting amine material, a tertiary amine produced by reaction of an alkyl halide and a primary or secondary amine in the presence of an excess of alkali, followed by treatment of the resultant tertiary amine in place as it is, not isolated, with the boron hydride compound. This is an effective and simple process.

When the amine treated according to the process of this invention is isolated and converted to an amine salt, quaternary ammonium salt or amine betaine, by a known process, there is obtained a practically colorless product. Thus the colorization that occurs when an untreated product is similarly converted, is avoided by treating the amine material by the process of this invention. The amine material treated according to the process of this invention and the above-described compounds obtained from that amine material are quite similar to the corresponding products obtained from untreated amine material in the features of chemical analysis, physical properties and chemical activity, but they are remarkably free of colorization.

The effect of the boron hydride compounds in this invention is unexpected and unique. It cannot be obtained with other reducing agents such as sodium sulfite, hydrosulfite, hydrazine and hypophosphorous acid.

The invention is further described by reference to the following illustrative and non-limiting Examples.

EXAMPLE 1

Lauryl alcohol consisting of 70 wt. % Ziegler alcohol and 30 wt. % coconut alcohol was converted to the corresponding chloride, and the lauryl dimethylamine produced from the chloride in known manner was employed as the starting amine material. To a mixture of 115 grams of said lauryl dimethylamine, 100 grams of water and 12 grams of isopropyl alcohol, there were added 2 grams of caustic soda and 390 mg. of sodium borohydride. The mixture was agitated at 50°–60°C for 2 hours. After the end of this period, the product was allowed to separate into phases, and the upper layer, i.e., the amine layer, was washed with 100 ml of warm water twice to obtain refined lauryl dimethylamine. The analytical values of the lauryl dimethylamine were as follows:

Untreated starting material:	total amine value:	250.9
	tertiary amine value:	249.7
Treated product:	total amine value:	250.7
	tertiary amine value:	248.2

To 55 gram samples of each of said treated and untreated amine, there were added 100 grams of water and 101 grams of 3N hydrochloric acid, and the mixtures were agitated at 50° – 60°C for 2 hours. Then, the degree of colorization of 25% aqueous solutions of the produced lauryl dimethylamine hydrochlorides was observed. The hydrochloride of the untreated amine material was pale red, while the hydrochloride of the amine material treated with boron hydride compound according to this invention was colorless. The percent transmission of the respective hydrochlorides was determined, based on that of distilled water as being 100%, by a colorimeter at a wave length of 500$m\mu$. The percent transmission was 89.5% with the hydrochloride of the untreated amine, whereas hydrochloride of the treated amine product of this invention had a percent transmission of 94.8%.

The treated and untreated tertiary amines were each reacted with benzylchloride by a conventional process to produce a 50% aqueous solution of lauryl benzyl dimethylammonium chloride. The product obtained using the untreated tertiary amine was pale red at pH lower than 5, whereas the product obtained from the tertiary amine which had been treated with boron hydride was colorless.

EXAMPLE 2

The same conditions as in Example 1 were employed except that the amount of sodium borohydride was reduced to 100 mg. The lauryl dimethylamine hydrochloride obtained by a conventional process as in Example 1 was colorless and had a percent transmission of 93.6%. (The percent transmission was determined by the method used in Example 1. This applies also in the following examples.)

EXAMPLE 3

The same conditions as in Example 1 were employed except that there was used 550 mg. of potassium borohydride instead of sodium borohydride. The hydrochloride obtained by a conventional process as in Example 1 was colorless and had a percent transmission of 93.8%.

EXAMPLE 4

Lauryl dimethylamine, produced by the reaction of lauryl bromide prepared by the radical addition reaction of dodecene with hydrogen bromide and dimethylamine, was treated with sodium borohydride under the same conditions as in Example 1. The 25% aqueous solution of lauryl dimethylamine hydrochloride prepared from the treated amine was colorless and the percent transmission thereof was 94.0%. The corresponding hydrochloride of the untreated amine was pale red, and the percent transmission thereof was 86.8%.

From the treated and untreated amines, lauryl benzyl dimethylammonium chorides were prepared by a conventional process. The chloride derived from the amine treated with sodium borohydride was colorless, whereas the chloride derived from the untreated amine was pale red at pH less than 3.

EXAMPLE 5

Lauryl amine, produced by the reaction of lauryl bromide used in Example 4 and ammonia, was treated with sodium borohydride under the same conditions as in Example 1, and then a 25% aqueous solution of lauryl amine hydrochloride was prepared by a conventional process. The solution was colorless. The lauryl amine hydrochloride prepared from the untreated amine was slightly red.

EXAMPLE 6

From the lauryl bromide used in Example 4 and dimethylamine, lauryl dimethylamine was prepared in the presence of an excess of caustic soda by a conventional process. 112 mg. of sodium borohydride were added to 152 grams of the unrefined crude amine reaction product, and the mixture was treated at 50° – 70°C for 2 hours. Then, a 25% aqueous solution of lauryl dimethylamine hydrochloride was prepared by a conventional process as in Example 1. It was colorless and the percent transmission thereof was 94.0%.

COMPARISON EXAMPLE

The unrefined lauryl dimethyamine used in Example 1 was treated with the reducing agents listed in Table 1, instead of boron hydride compounds. The treating conditions were the same as in Example 1. The tertiary amines treated with the reducing agents were converted to the hydrochlorides by a conventional process as in Example 1, and the degree of colorization was determined. The results are shown in Table 1.

Table 1

Reducing Agent	Charged Amount (based on the wt% of amine)	Hydrochlorides	
		% Transmission	color
Sodium sulfite	5.5%	88.8%	Pale red
Sodium hydrosulfite	9.1	88.5	Pale red
Hydrazine	2.2	90.0	Pale red
Hypophosphorous acid	2.9	91.0	Slightly red
Untreated	—	85.2	Pale red

As seen in Table 1, there was found a slight improvement effect in each case, in comparison with the untreated material. But in each case the improvement was greatly inferior to that of the product treated with boron hydride.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for refining aliphatic hydrocarbon amines having at least one alkyl group of 9 to 22 carbon atoms attached to the amino nitrogen, said amines being derived from polymerized ethylene and containing impurities which form coloring substances when the amines are converted to amine salts, which comprises the steps of: reacting said amine with

A. from 0.01 to 5 percent by weight, based on said amine, of a borohydride substance selected from the group consisting of alkali metal borohydrides, amine borohydrides, quaternary ammonium borohydrides and mixtures thereof, and

B. up to 50 percent by weight, based on said aliphatic amine, of an alkali,

and recovering from the reaction mixture a refined aliphatic amine which is not apt to color during salt-forming reactions.

2. A method according to claim **1** in which said amine is selected from the group consisting of compounds of the formulas RNH, RR'NH and RR'R''H and mixtures thereof, wherein R is alkyl having 9 to 22 carbon atoms, and wherein R' and R'' are alkyls having 1 to 22 carbon atoms.

3. A method according to claim **2** wherein R is alkyl having 10 to 18 carbon atoms and R' and R'' are alkyls having 1 to 6 carbon atoms.

4. A method according to claim **2** wherein R is lauryl and R' and R'' are methyl or ethyl.

5. A method according to claim **3** in which said borohydride substance is selected from the group consisting of sodium borohydride, potassium borohydride and lithium borohydride.

6. A method according to claim **5** in which the amount of said borohydride substance is from 0.05 to 2 percent by weight, based on said amine.

7. A method according to claim **6** in which said alkali is selected from the group consisting of sodium hydroxide, potassium hydroxide and sodium carbonate, and the amount of said alkali is from 0.1 to 10 percent by weight, based on said amine.

8. A method according to claim **7** in which said amine, said borohydride substance and an aqueous solution of said alkali are placed in a reactor and are mixed therein, at about 50° to 70°C, for from 2 to 10 hours, and the refined amine is recovered by allowing the liquid reaction mixture to separate into layers and the layer containing the refined amine is removed from the remainder of the reaction mixture.

9. A method according to claim **1** in which the reaction is carried out in water.

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