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PROCESSES OF HYDROGENATING NITRILES

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This invention relates to processes of hydrogenating nitriles, and it comprises processes wherein relatively high molecular weight aliphatic nitriles, such as those obtained from, and corresponding to, the fatty acids, are hydrogenated in the presence of small quantities of water; it further comprises processes wherein such nitriles are hydrogenated in the presence of small quantities of alkaline-reacting materials, such as caustic soda, alkali metal soap, and the like.

The high molecular weight primary aliphatic amines have recently become commercially important. Amines having six or more carbon atoms, for example, octadecylamine, can be used in many industrial relations. They are splendid flotation agents in certain processes of separating ores.

Use of these amines industrially has been hampered in the past because of difficulties in preparing them in commercially satisfactory yields. The classical textbook process, for example, gives a yield of only about 50% of primary amines from the corresponding nitriles, and this is not high enough. The percentage yield should be increased to at least 60% or 70% for the process to be of technical interest.

When an aliphatic nitrile is hydrogenated by the customary procedure the reaction may take a number of different courses. The nitrile may first hydrogenate to an imine which in turn may undergo polymerization, or form secondary amines, or result in other complex reaction products. The simple introduction of hydrogen gas into a nitrile in the presence of a hydrogenation catalyst does not mean that the course of the reaction shall yield primary amines only.

We have further investigated the hydrogenation of aliphatic nitriles having at least six carbon atoms and we have discovered ways by which the yield of primary amine can be markedly increased.

The process of the present invention is based upon our discovery that when water is present during the hydrogenation there is a markedly less tendency for the formation of undesired by-products, and the yield of primary aliphatic amine increases over that obtained in the absence of added moisture. We have further discovered that when the hydrogenation is conducted under alkaline conditions the yield is still further increased. Apparently the added moisture results in the formation of free hydroxyl ions. Proof of this can be shown by the fact that hydrogenation in the presence of added ammonia

alone does not give as high yields as hydrogenation in the presence of water alone, or mixtures of water and ammonia. We are aware that it is old to hydrogenate nitriles in the presence of added ammonia.

In one instance we have ascertained that sodium ethylate also functions to improve the yield but we are not prepared to explain the behaviour of sodium ethylate, except upon the theory that the sodium ethylate dissociates to give an ethoxy radical analogous to an ordinary hydroxyl radical.

The present application, however, is devoted to hydrogenation in the presence of moisture as a first condition, together with hydrogenation in the presence of moisture and added alkali as an improvement thereon.

We shall now describe our invention in greater detail with reference to the hydrogenation of fatty acid nitriles derived from common fats or fatty acids. These nitriles can be prepared by processes hitherto described in the patented art. Such processes include, for example, reacting ammonia with heated fatty acids derived from fats or fatty oils by splitting, or with heated triglycerides, or with synthetic fatty acids prepared by oxidizing hydrocarbons.

In each of the examples for which we shall give specific details, 110 pounds of the fatty acid nitriles are measured into a mixing tank, a Raney nickel catalyst containing approximately 1400 to 1600 grams nickel then added, and the mixture transferred to a hydrogenator. The hydrogenator is first freed of air by the repeated admittance and release of hydrogen, and the charge therein then heated to the reaction temperature, namely about 130° to 140° C. This is the customary condition for hydrogenating nitriles by conventional methods.

During the hydrogenation hydrogen is introduced under a pressure of about 200 pounds per square inch and the hydrogenation continued until the hydrogen absorption rate falls to about 2 cubic feet in five minutes. In some instances, as we shall describe, ammonia is also introduced and the ammonia pressure built up to about 50 pounds per square inch.

At the conclusion of the hydrogenation the reaction product is distilled up to 166° C. under 0.5 mm. of mercury, the distillate dissolved in alcohol and distilled water, and titrated with one-half normal hydrochloric acid for determining its content of primary amines.

In the past, the hydrogenation of fatty acid nitriles has been performed substantially in ac-

cordance with the above. The yield of primary amine by such method never exceeds 50% and is usually much less. Secondary amines and complex amine polymerization products are obtained. This conventional method is occasionally modified by passing in ammonia gas during the hydrogenation but yields of primary amine remain low, never exceeding 50%.

As stated, in our invention we modify the conventional hydrogenation procedure by hydrogenating in the presence of moisture and alkaline-reacting materials. These added agents are admixed with the nitriles prior to admission of hydrogen thereto. Advantageously the added water or alkali is admixed with the nitrile when the nickel catalyst is incorporated in the batch.

Thus, when we admix about 1 to 2 parts by weight of water with each 110 parts by weight of cotton seed fatty acid nitriles and then hydrogenate at 130°-140° C., as described above, the reaction product contains 60% primary amines, 6% unreacted nitriles and 33% of residue. When water is added as just described, and, in addition, ammonia gas is also blown into the hydrogenator during the process, the yield of primary amine increases to 70.3%, the nitriles amount to 6.9% and the residue is reduced to 22.8%. In this case the total hydrogenation time for 110 pounds of nitriles is about 95-110 minutes.

The comparison between hydrogenating in the presence of ammonia, and in the presence or absence of water is striking; the addition of small amounts of water increases the yield to 70%, a percentage improvement of 140%. This appears to be attributable to the alkaline conditions created by the ammonia and water used together.

Instead of imparting alkalinity by ammonia we can use caustic soda to even greater advantage, or we can use ammonia and caustic soda together.

For example, when we add about 1 to 2 parts by weight of water and 0.1 part by weight of caustic soda, for each 110 parts of nitriles and maintain an ammonia pressure of about 50 pounds per square inch, the primary amine yield is 79.9%, the nitriles are 6.8% and the residue drops to 13.4%.

We shall now give similar comparative data for the hydrogenation of crude palm oil fatty acid nitriles derived from palm oil fatty acids. Here again the hydrogenation conditions are substantially the same, namely 110 parts of nitriles, a hydrogenation pressure of 200 pounds per square inch, a temperature of about 130° to 140° C. and water or other addition agents added prior to transferring the mixture to the hydrogenator.

When about 1 to 2 parts by weight of water for each 110 parts of nitriles is used with an ammonia pressure of 50 pounds per square inch, the yield of primary amines is 71%, the nitriles amount to 10% and the residue is 9.9%. With water alone (no ammonia) the yield is 64.9% of primary amines with 11.2% of nitriles and 24% of residue.

The yield of primary amines increases to 77.4% when about 0.5 part by weight of caustic soda for each 110 parts of nitriles is added, together with water and ammonia. When caustic soda and water alone are used, no ammonia being introduced, and the amount of caustic soda being approximately 0.1 to 0.5 part by weight the yield of primary amines is from 75% to 78%, the unreacted nitriles amount to 9% to 6%; and the

residue is about 15% to 16% of the reaction product.

When alkalis are used to increase the yield enough alkali should be present to react with any free fatty acids in the nitriles, together with a slight excess thereof. We have ascertained that improvement in yield is not due only to the absence of free fatty acids in the nitriles during hydrogenation. There must be additional alkali present over that required for neutralization.

Although, in the above examples we have described the use of caustic soda specifically, we have found that other alkalies, such as caustic potash, will also work. The alkali metal soaps are effective since in the presence of water they appear to dissociate.

It is to be understood that our invention is directed to improving the yield of primary aliphatic amines from their corresponding nitriles hydrogenating in the presence of water, or water and alkaline-reacting substances. The temperature during hydrogenation can vary in accordance with variations hitherto used in the prior art. Instead of admixing water with the nitrile prior to hydrogenation we can introduce water vapor along with the hydrogen or ammonia as the hydrogenation proceeds. But we find it more convenient to simply admix the water with the nitrile at the time of adding the catalyst. We claim no novelty for any particular catalyst since any of those used for the hydrogenation of nitriles can be used in our process. During the hydrogenation the mixture is continuously agitated for best results, also in accordance with prior art processes. Hydrogenation is, of course, continued until substantially the theoretical quantity of hydrogen gas is absorbed, or the rate of absorption decreases to but slight quantities over long periods of time, as described above.

Since our process is useful in hydrogenating nitriles of six or more carbon atoms regardless of the source thereof, we broadly so claim our invention in the appended claims. In the examples given above the nitrile starting materials are mixtures of nitriles having at least six carbon atoms and including nitriles of eighteen carbon atoms. Nitriles of even higher molecular weight can be hydrogenated in accordance with our process. Fish oil fatty acid nitriles can be converted to amines having as high as twenty two or more carbon atoms.

Having thus described our invention, what we claim is:

1. The process of preparing aliphatic amines having at least six carbon atoms which comprises catalytically hydrogenating a liquid mixture composed of the corresponding fatty acid nitrile in the presence of an aqueous solution of an alkaline-reacting material in sufficient quantity to maintain free hydroxyl ions in the mixture.

2. The process of preparing primary aliphatic amines having at least six carbon atoms which comprises catalytically hydrogenating a liquid mixture composed of the corresponding fatty acid nitrile in the presence of an aqueous solution of ammonia.

3. The process of preparing primary aliphatic amines having at least six carbon atoms which comprises catalytically hydrogenating a liquid mixture composed of the corresponding fatty acid nitrile in the presence of an aqueous solution of an alkali metal hydroxide.

4. The process of preparing primary aliphatic amines having at least six carbon atoms which comprises catalytically hydrogenating a liquid

mixture composed of the corresponding fatty acid nitrile in the presence of an aqueous solution of caustic soda.

5. The process of preparing primary aliphatic amines having at least six carbon atoms which comprises catalytically hydrogenating a liquid mixture composed of the corresponding fatty acid nitrile in the presence of an aqueous solution of caustic soda and ammonia.

6. The process as in claim 1 wherein the fatty acid nitrile is chosen from the group consisting of palm oil fatty acid nitriles and cotton seed oil fatty acid nitriles.

7. The process as in claim 2 wherein the fatty acid nitrile is chosen from the group consisting of palm oil fatty acid nitriles and cottonseed oil fatty acid nitriles.

8. The process as in claim 3 wherein the fatty acid nitrile is chosen from the group consisting of palm oil fatty acid nitriles and cottonseed oil fatty acid nitriles.

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