

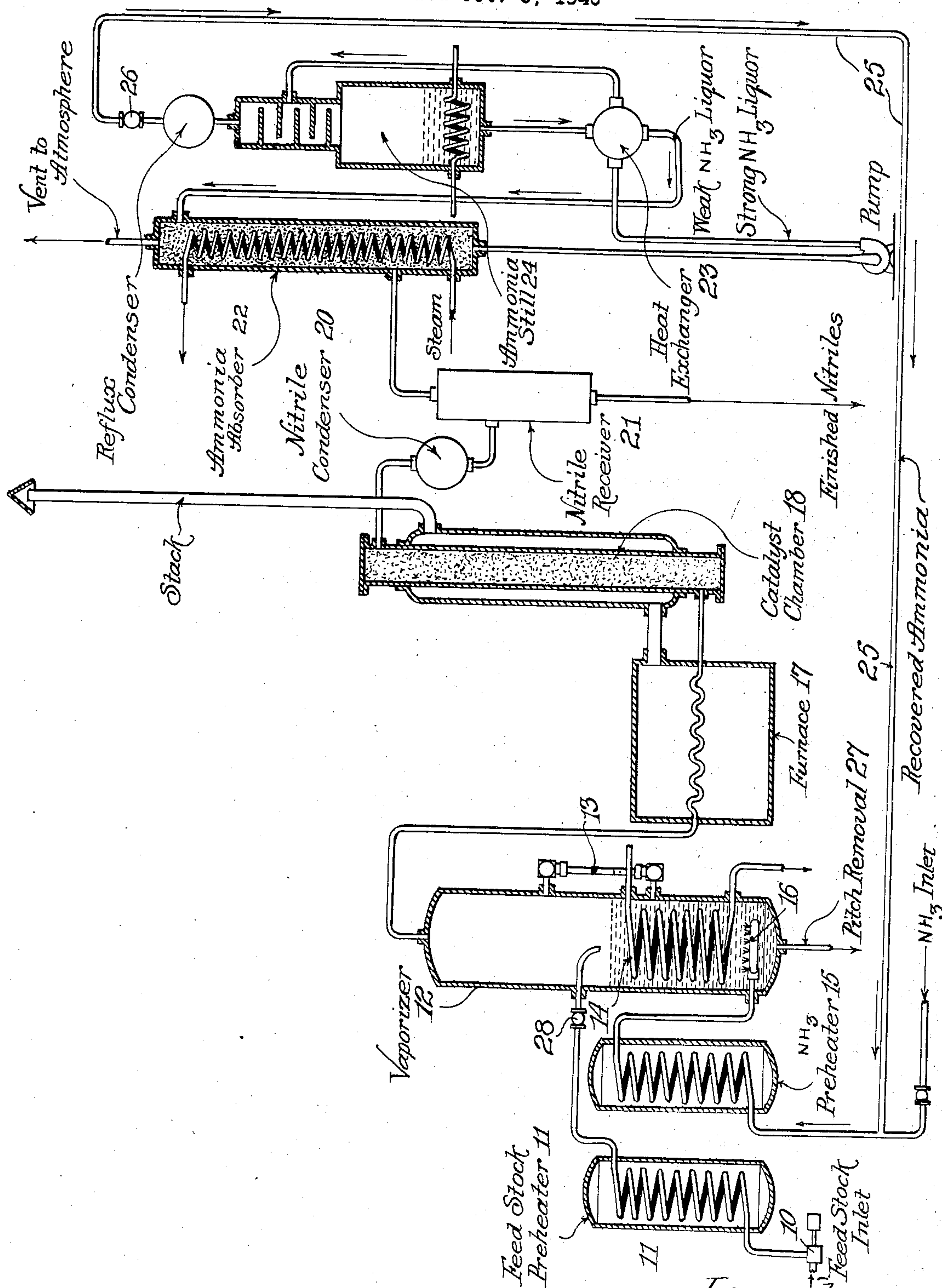
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PROCESS OF PREPARING NITRILES

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## PROCESS OF PREPARING NITRILES

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This invention relates to the manufacture of nitriles, particularly nitriles having long chain hydrocarbon radicals, by the reaction of fatty acids or their esters with ammonia.

Though such nitriles are useful in many applications, they have not in the past come into great commercial importance largely because of difficulties in their manufacture. Several methods have heretofore been available for their preparation. One method involves the heating of alkyl iodides with potassium cyanide, but this method is of academic interest only because of the difficulty in preparation of the alkyl iodide.

Another method which has heretofore been tried involves the vaporizing of the fatty acids and passing the fatty acid vapors along with ammonia over a dehydrating catalyst. This method is difficult to accomplish in large scale operation because of the breakdown of the acids as they are heated to the temperature necessary for reaction over the catalyst. Such breakdown causes excessive coking of the heating apparatus and affects the quality of the nitriles produced.

A method is disclosed in Ralston et al. United States Patent No. 2,061,314 which has many important advantages. In this method the reaction is conducted in liquid phase, a catalyst being employed for the prevention of clogging by soaps, low boiling acids, etc. As disclosed in this patent, the nitriles are withdrawn from the reaction chamber after the conversion is completed. An important advantage is that in this process objectionable decomposition is largely avoided.

In some respects, the present invention is an improvement of the method disclosed in Ralston 2,061,314. One of the important objects of this invention is to provide a method which retains the advantages of the Ralston method but which is continuous in operation and which is more adaptable to large scale commercial operation. Another object is to provide a method which utilizes low grade stocks in the production of nitriles of a good grade with a minimum of difficulty in operation. More specifically it is desired to provide a method permitting easy removal of any pitch or other material which cannot be volatilized without decomposition or polymerization and which may be included in the charging stock being used.

The invention will best be understood with reference to the following detailed description taken with the accompanying drawing, in which the figure given represents schematically one type of apparatus which may be used in practicing the improved process.

As shown in the drawing, the feed stock containing fatty acids or their esters is fed continuously by feed pump 10 into a preheater 11 where it is heated to a temperature preferably above 400° F. but below the boiling points of the acids in the material. Specifically we attempt to maintain the temperature of the fatty substance leaving the preheater at about 550° F., especially when using stocks containing a substantial proportion of stearic acid. The preheater may advantageously be of the type employing as a heating medium, a vapor having a condensation temperature below the vaporization temperature of the fatty acids of the feed stock, but other types of heaters may be used.

From the preheater the stock is discharged continuously, in liquid form, through control valve 28 into the vaporizing chamber 12. This chamber may be of any suitable construction and preferably should be equipped with a sight gauge 13, by means of which the liquid within the chamber may be maintained at a desired level. The heating coil 14 is included in the embodiment shown, and this serves to supply the heat necessary for continuous vaporization from the liquid body.

Suitably, anhydrous ammonia is preheated in preheater 15 to a temperature preferably in the neighborhood of 550° F. and is continuously introduced in gaseous form into the lower portion of the liquid fatty substance in vaporizer 12 by means of the distributor 16. The gaseous ammonia is thus intimately admixed into the fatty substance during the time the substance remains in liquid state. It is essential that the liquid acid substance and the ammonia remain in contact until the initial reaction takes place, and in controlling the conditions to accomplish this the heat supplied through coil 14 and the quantity of preheated stock being introduced into chamber 12 are so regulated that the liquid acid stock remains in contact with the ammonia for a period of time, preferably averaging in excess of 45 minutes. Thus with a greater amount of heat supplied through coil 14 it is necessary to discharge acid stock into the vaporizer at a more rapid rate so that the liquid body within the chamber will not be destroyed through more rapid vaporization or the time of contact between the liquid acid substance and the ammonia be decreased to the point where reaction is avoided. In the specific operation from which the accompanying diagram was drawn, the proper input of commercial stearic acid into the vaporizer was found to be about 50 pounds per hour.



We have found that a satisfactory balance can be obtained when the internal temperature of vaporizer 12 and of the vapors contained therein is less than 700° F. and preferably about 590° F. The vapors issuing from the vaporizer, being below the desired temperature for reaction in the presence of catalyst, may be passed, as shown in the drawing, through the tube heater 17 where they are heated preferably to about 750° F. to 800° F. The heater 17 illustrated is fired by gas, but other means for heating the vapors as they pass continuously therethrough may be used. The vapors thus heated pass through catalyst chamber 18 which contains activated aluminum oxide or other suitable dehydrating catalyst.

The vapors leaving catalyst chamber 18 are substantially condensed in condenser 20 and the mixture passes into separator 21 where the nitriles and water are separated from excess ammonia.

The excess ammonia is desirably recovered and recycled for further use in the process. In this procedure the ammonia gas passes into the scrubber 22 where a descending stream of cold weak ammonia solution absorbs the ammonia, the non-condensable gases being vented to the atmosphere. The relatively strong ammonia solution from the base of the scrubber is pumped through heat exchanger 23 and to the ammonia still 24 which utilizes pressure to release gaseous ammonia. The ammonia thus obtained may be passed through line 25 and regulating valve 26 back to the preheater 15. It is understood that the use of the ammonia recovery system here employed, while useful, is not essential to the operation of our improved method of nitrile manufacture.

The reactions involved in the conversion of the fatty acid substance to nitriles are believed to include the following chemical changes:

1.  $\text{RCOOH} + \text{NH}_3 \rightleftharpoons \text{RCOONH}_4$
2.  $\text{RCOONH}_4 \rightleftharpoons \text{RCONH}_2 + \text{H}_2\text{O}$
3.  $2\text{RCONH}_2 \rightarrow \text{RCN} + \text{RCOOH} + \text{NH}_3$

Thus, it appears that the fatty acids are first converted to amides which in turn break down to form nitriles and further acids. Water and ammonia are given off in the changes taking place, the ammonia being useful for reaction with further acids.

In the present process, the series of changes which result in the formation of nitriles begins with the contact between liquid acids and ammonia in the vaporization chamber. A part of the acids are at this stage converted through amides to nitriles so that the vapors issuing from the fatty acid body have a substantial nitrile content. This conversion appears to be aided by the fact that nitriles vaporize at about 35° F. lower than the corresponding acids. In addition to nitriles, the vapors issuing from the liquid fatty acid body contain also amides and fatty acids as well as water vapor and ammonia.

The vapors containing the reaction products are heated and passed through the catalyst chamber, and in this procedure there is further breakdown of amides to nitriles and reaction by any remaining fatty acids in vapor phase with ammonia, to complete the conversion of the fatty acid stock to nitriles. By operating this improved method, it is possible to obtain a pure nitrile product which contains as low as about .2% of uncombined acids.

As before mentioned, the improved process per-

mits a wide variation in the feed stock which may be used. Usually we start with mixed fatty acids which have been obtained by hydrolyzing fat or oil with the Twitchell or autoclave process, however, we can use to advantage commercially pure acids, such as caprylic, capric, lauric, myristic, palmitic, stearic, oleic, linoleic, and others of the higher fatty acids. We also can use hydrogenated acids, and alkyl esters of the acids, or the fats themselves. The procedure and temperatures heretofore given with particular reference to fatty acids will usually be found to apply in cases where the alkyl esters or the fats are used as charging material.

Our process is advantageous in the case of feed stock which contains non-volatile, non-convertible materials or materials which readily decompose or polymerize before vaporization. Such materials do not pass off from the vaporization chamber but accumulate in the bottom portion where they may be periodically removed through the draw-off line 27.

Though we find it generally satisfactory to operate the improved method with only atmospheric pressure in the vaporization chamber, it will be found advantageous in some instances to employ pressures above atmospheric at this point of the process. This is especially true in the case of the lower chain length acids since the pressure aids in maintaining the liquid body while permitting the temperature of the body to be high enough for initial reaction with ammonia.

Though in the foregoing description special operation and specific operating conditions have been referred to at many points, such references are not to be taken in a limiting sense but only for clearness of explanation, it being expected that such factors may be varied widely according to the feed stock used, the equipment available, etc.

What we claim as new and desire to secure by Letters Patent is:

1. In the conversion of fatty acid substances chosen from the group consisting of fatty acids and esters thereof to the corresponding nitriles, the steps which comprise admixing ammonia with a body of the fatty acid substance in liquid phase in a heated liquid phase conversion zone, feeding fatty acid substance and ammonia to said zone, continuously withdrawing a vapor mixture from said zone, the vapor mixture containing nitriles formed in said liquid phase conversion zone, together with fatty acids, amides, and ammonia, passing said vapor mixture to a heated vapor phase conversion zone containing a dehydrating catalyst to convert fatty acids and amides in said vapors to nitriles while in the presence of said vaporized nitriles which have been vaporized from the liquid phase conversion zone, and condensing nitriles leaving said vapor phase conversion zone, all of the nitriles formed in said liquid phase conversion zone being vaporized therefrom and the vapors thereof subsequently condensed.

2. In the conversion of fatty acid substances chosen from the group consisting of fatty acids and esters thereof to the corresponding nitriles, the steps which comprise admixing ammonia with a body of the fatty acid substance in liquid phase in a heated liquid phase conversion zone, feeding preheated fatty acid substance and ammonia to said zone, continuously withdrawing a vapor mixture from said zone, the vapor mixture containing nitriles formed in said liquid phase conversion zone, together with fatty acids,



amides, and ammonia, passing said vapor mixture to a heated vapor phase conversion zone containing a dehydrating catalyst to convert fatty acids and amides in said vapors to nitriles while in the presence of said vaporized nitriles which have been vaporized from the liquid phase conversion zone, and condensing nitriles leaving said vapor phase conversion zone, all of the nitriles formed in said liquid phase conversion zone being vaporized therefrom and the vapors thereof subsequently condensed.

3. In the conversion of fatty acid substances chosen from the group consisting of fatty acids and esters thereof to the corresponding nitriles, the steps which comprise admixing ammonia with a body of the fatty acid substance in liquid phase in a heated liquid phase conversion zone, feeding fatty acid substance and ammonia to said zone, continuously withdrawing a vapor mixture from said zone, the vapor mixture containing nitriles formed in said liquid phase conversion zone, together with fatty acids, amides, and ammonia, raising the temperature of said vapor mixture, passing said vapor mixture to a heated vapor phase conversion zone containing a dehydrating catalyst to convert acids and amides in said vapors to nitriles while in the presence of said vaporized nitriles which have been vaporized from the liquid phase conversion zone, and condensing nitriles leaving said vapor phase con-

version zone, all of the nitriles formed in said liquid phase conversion zone being vaporized therefrom and the vapors thereof subsequently condensed.

4. In the conversion of fatty acid substances chosen from the group consisting of fatty acids and esters thereof to the corresponding nitriles, the steps which comprise admixing ammonia with a body of the fatty acid substance in liquid phase in a heated liquid phase conversion zone, feeding preheated fatty acid substance and ammonia to said zone, continuously withdrawing a vapor mixture from said zone, the vapor mixture containing nitriles formed in said liquid phase conversion zone, together with fatty acids, amides, and ammonia, raising the temperature of said vapor mixture, passing said vapor mixture to a heated vapor phase conversion zone containing a dehydrating catalyst to convert fatty acids and amides in said vapors to nitriles while in the presence of said vaporized nitriles which have been vaporized from the liquid phase conversion zone, and condensing nitriles leaving said vapor phase conversion zone, all of the nitriles formed in said liquid phase conversion zone being vaporized therefrom and the vapors thereof subsequently condensed.

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