

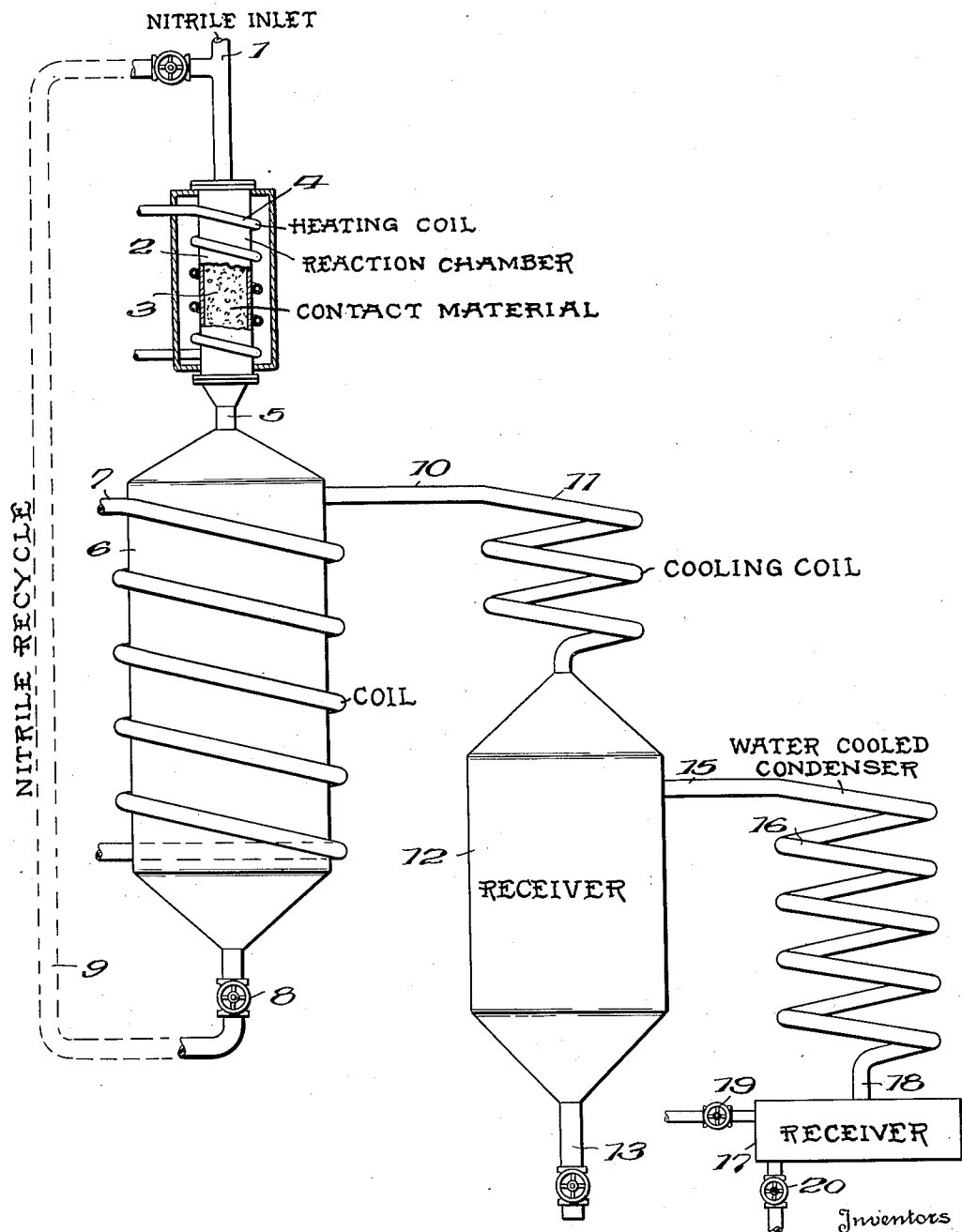
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PROCESS OF PREPARING NITRILES

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PROCESS OF PREPARING NITRILES

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This invention relates to processes of pyrolytically treating higher fatty acid nitriles and it comprises processes wherein higher fatty acid nitriles are "cracked" while in the vapor state, and at substantially atmospheric pressure, to yield nitriles of lower molecular weight.

Higher fatty acids such as stearic and palmitic are extremely abundant and cheap materials. They are, of course, common constituents in the form of glycerides in animal and vegetable oils and fats. Hitherto attempts to "crack" these fatty acids whereby fatty acids of lower molecular weight are formed have met with little or no success. This is largely because the carboxyl groups of the fatty acids readily break down. They are not heat resistant and attempts to prepare lower fatty acids by pyrolytically treating higher fatty acids have resulted in the formation of ketones, gums, resins, tars, and polymerized products of little or no utility. Nevertheless, any process by which the relatively long hydrocarbon chain in higher fatty acids can be "cracked" to give products of lower molecular weight is of considerable economic interest. Whereas the higher fatty acids, such as stearic, command rather low prices, products of lower molecular weight command quite high prices.

In the Ralston, U. S. Patent 1,991,955 there are described processes whereby higher fatty acids can be heat treated to give products of lower molecular weight and of greatly increased usefulness in the arts. In that process the fatty acid, or its alkyl esters, is heated in the presence of a dehydrating catalyst and in the presence of ammonia or an alkyl amine. That process is based on the discovery that ammonia and amines act as protective agents in preventing the decomposition of the fatty acids to tars, resins and polymerized products. In the process of the patent it is believed that higher fatty acid nitriles are first formed and that these subsequently decompose or "crack" to yield nitriles of lower molecular weight in the presence of the catalyst and the ammonia. Doubtless, the reactions during the heating occur simultaneously or substantially so and it is an observable fact that if no ammonia or alkyl amines be present the heat treatment leads to the formation of many undesirable products. Hence, when starting with higher fatty acids of their esters it is necessary that such "protective" materials be present.

In that process, nitriles of higher fatty acids which are a part of the reaction products formed are occasionally recycled. At all times there is in the reaction zone a mixture undergoing treat-

ment containing fatty acids, fatty acid esters and fatty acid nitriles. In the absence of ammonia or other protective agents, large quantities of tars and polymerized products, which eventually lead to coke formation in the catalyst, invariably result. Accordingly, it was believed that at all times protective gases must be present and this is actually the case when any free fatty acid or fatty acid ester is present in the reaction zone.

However, we have now discovered that protective gases are not necessary when the reaction mixture undergoing cracking is substantially free of fatty acids or esters. It is these fatty acids and esters alone which lead to the formation of tars and polymerized products. We have discovered that the higher fatty acid nitriles alone can be cracked or pyrolyzed to give commercial yields of lower molecular weight nitriles without requiring the presence of ammonia or an amine during the pyrolysis. This is something which is indeed surprising because it could not be predicted that the nitrile or —CN group would show such marked stability toward heating. Ordinarily, it would be expected that decomposition would take a course resulting in the formation of considerable quantities of ammonia and possibly hydrocyanic acid.

The present invention therefore simplifies methods of making lower molecular weight nitriles from higher fatty acid nitriles in that the process can be broadly divided into two steps, the first of which consists in making the higher fatty acid nitriles by well-known ways, and then the pyrolysis of these nitriles while in fairly pure form. Better yields of desired products can be obtained and the reaction can be controlled nicely. The present invention is therefore concerned with processes of cracking higher fatty acid nitriles.

In the practice of the present invention, we can treat any of the higher fatty acid nitriles, namely those having at least six carbon atoms, but we generally start with the nitriles of higher fatty acids having from ten to eighteen carbon atoms. Stearo- and palmito-nitrile can be easily and inexpensively prepared from the abundant stearic and palmitic acids and these nitriles can be pyrolytically treated to give nitriles of very much lower weight and of much greater utility. These lower nitriles can be readily hydrolyzed to carboxylic acids, they can be reduced to amines by hydrogenation, and they thus are substances of wide usefulness as starting materials in organic synthesis. In themselves, they are good insecticides and doubtless many other uses will be found for them.

In its broadest aspects, then, our invention

consists in vaporizing a higher fatty acid nitrile, passing the vapors, at substantially atmospheric pressure, through a cracking zone, and condensing reaction products. Any unreacted nitrile can be recycled to the reaction or cracking zone and the lower boiling nitriles can be fractionated into nitriles of rather narrow boiling range. Concurrently with the formation of the lower nitriles considerable quantities of hydrocarbons are formed and these, too, can be fractionated into hydrocarbons of narrow boiling range. Advantageously the nitrile vapors in the reaction zone are brought into contact with a contact material such as pumice, silica gel, or simply baffles to obtain better heat transference to and through the reaction zone. Alternatively, the reaction chamber can contain a dehydrating catalyst such as aluminum oxide or others described in the Ralston Patent 1,991,955. These are metal oxide catalysts such as the oxides of thorium, osmium, and iron.

We do not wish to be limited to the pyrolysis of any particular higher fatty acid nitrile. All of them, including nitriles of the unsaturated fatty acids can be used. Thus, we can start with nitriles of the following fatty acids: caprylic, capric, lauric, myristic, palmitic and stearic or higher acids such as behenic. We can also use unsaturated higher fatty acid nitriles such as those obtained from oleic acid and linoleic acid. Generally, however, we start with the nitriles of palmitic and stearic acid since these acids are abundant and cheap and can be readily converted to their corresponding nitriles. We shall, therefore, describe our invention specifically with reference to the cracking of these substances, it being understood, however, that other higher fatty acid nitriles can be used.

On the appended single sheet of drawing, we have illustrated one convenient form of apparatus for practicing our process. In the drawing, a reaction chamber 2 is provided with heating coils 4 and advantageously contains contact material 3 such as pumice, silica gel, baffles, or dehydrating catalysts as described above. An inlet for nitriles is provided at 1 and products flowing from the reaction chamber issue by way of 5 and flow to receiver 6 advantageously provided with a heating coil 7. The receiver has an outlet 8 and a nitrile recycle line 9 for returning any unreacted nitrile to the reaction zone. The receiver is also provided with an outlet 10 leading to a cooling coil or condenser 11 which is in turn connected to a second receiver 12 provided with an outlet 13 and an outlet 15. Outlet 15 communicates with a water-cooled condenser 16 discharging into a third receiver 17 by way of line 18. Any non-condensable material collected in 17 can be drawn off through outlet 19 and final products collected in 17 can be withdrawn therefrom through line 20. The series of receivers 6, 12 and 17 together with condensers 11 and 16 constitutes a sort of fractionating device for roughly separating products of the reaction.

As stated, the catalyst in chamber 2, when a catalyst is used, is generally aluminum oxide but other metallic oxides such as those of thorium, titanium and zirconium can be used. These catalysts are well known dehydrating catalysts and they function very well in our process. Advantageously, the catalyst can be supported on an inert material such as pumice in ways well known, and we do not, therefore, describe any particular way of preparing the catalyst. Since these catalysts are customarily classified as de-

hydrating catalysts, we so define them in the appended claims. We do not, however, need to use a contact material or catalyst. The reaction products are substantially the same both with and without a catalyst but use of the catalyst tends to increase the reaction rate somewhat and thus permits us to operate at somewhat lower temperatures. Although we ordinarily use a catalyst we are not obliged to do so.

We shall now describe our invention with particular reference to the cracking of stearonitrile. This material can be prepared from stearic acid in ways well known and it has a boiling point of about 360° C. at atmospheric pressure. We first volatilize the stearonitrile advantageously in a still and pass the vapors, at substantially atmospheric pressure, through inlet 1 into the reaction chamber. The chamber is best maintained at a temperature of about 550° C. When starting with about 500 parts by weight of stearonitrile we advantageously feed the vapors thereof to the chamber at a rate of about 100 parts per hour. In a single pass through the chamber with the time of contact therein, not exceeding about 60 seconds, the product recovered in receiver 6 is a light greenish colored liquid of rather pleasing odor and amounts to about 90% of the quantity of stearonitrile fed to the catalyst. The product has a boiling range of from 50° to about 360° C. and analysis shows that it contains various lower molecular weight nitriles both saturated and unsaturated and also quantities of hydrocarbons. By fractional distillation we can separate the mixture into its constituents and we find that it contains valeronitrile, capronitrile, caprylonitrile, caprinitrile, and others.

In another example we fill the reaction chamber with granular aluminum oxide and pass stearonitrile vapors therethrough. If the temperature be kept at 550° C. the rate of flow can be increased to about 150 parts per hour with a shorter time of contact. If the rate of flow be kept at 100 parts per hour as in the preceding example, the temperature can be reduced to about 425°-475° C.

Under the above conditions, we do not make use of the heating coil surrounding receiver 6. We can, however, operate the apparatus shown in the drawing in such a way that only the higher boiling material, mostly unreacted stearonitrile, is collected in receiver 6, the desired product being distilled out of the mixture in receiver 6 and fractionally condensed in condensers 11 and 16. This is especially advantageous when we wish to increase the flow of stearonitrile vapors to the reaction zone. When this happens, a considerable quantity, as much as 25%, of the stearonitrile goes through the reaction chamber unchanged and collects in receiver 6. By maintaining the receiver at about 270° C. by means of the heating coil 7, desirable products pass through the receiver while still in the vapor state and fractionally condense in 11 and 16. In this case the stearonitrile in receiver 6 is advantageously recycled to the reaction zone by way of line 9. A typical boiling point analysis of the products obtained is as follows: From 1000 parts of stearonitrile fed to the reaction zone, we obtain a total condensate of about 750 parts. The remainder is non-condensable gas leaving the gas outlet 19. Fractionation of the 750 parts gives the following cuts:

Fraction 1—25 percent boiling range 40° C.-100° C.

Fraction 2—35 percent boiling range 100° C.—175° C.

Fraction 3—25 percent boiling range 175° C.—275° C.

5 Residue—15 percent boiling range 275° C.—360° C.

Fraction 1 is mostly saturated and unsaturated nitriles containing 5 and 6 carbon atoms with low boiling saturated and unsaturated hydrocarbons.

10 Fraction 2 is mostly saturated and unsaturated nitriles containing 6 and 7 carbon atoms with saturated and unsaturated hydrocarbons.

15 Fraction 3 is mostly saturated and unsaturated nitriles containing 7, 8, 9, 10, 11, 12 carbon atoms with high boiling saturated and unsaturated hydrocarbons. The residue is saturated and unsaturated nitriles containing 12, 13, 14, 15, 16, 17 carbon atoms with saturated and unsaturated hydrocarbons and unchanged stearonitrile.

20 In a similar way we can start with mixtures of various higher fatty acid nitriles. Thus, for instance, we can start with a mixture of palmitonitrile and stearonitrile and we can start with a mixture of nitriles obtained from lard fatty acids and also with unsaturated nitriles such as oleonitrile.

25 In the foregoing example we have referred specifically to a temperature of about 550° C. This seems to be the most desirable temperature for heating nitriles having from 14 to 18 carbon atoms, but we can operate at temperatures somewhat lower and somewhat higher. Thus, for instance we can operate at temperatures as high as 900° C., although considerably lower yields of lower molecular weight nitriles are obtained. The cracking temperature seems to be from about 400° C. to 800 or 900° C. The minimum is generally about 400° C. It will, however, be obvious that the particular temperature used for a particular nitrile will vary from that used for another nitrile and therefore we do not wish to limit ourselves specifically in this respect. In the appended claims we have accordingly defined the temperature as a cracking temperature. And in the appended claims the language "higher fatty acid nitrile" is intended to cover nitriles having 6 or more carbon atoms.

30 As described above, in the present invention we operate at pressures which are substantially atmospheric. These pressures are of the order of 15 pounds per square inch although it is to be understood that minor variations therefrom are intended to be covered in the appended claims. We can, for instance, force vapors of higher fatty acid nitriles into and through the reaction chamber at a moderate pump pressure, of the order of 20 pounds per square inch, and we can increase the rate of flow of vapors through the reaction chamber by operating under moderately reduced pressures, of the order of 10 pounds per square inch. In our copending application, Serial Number 9,660, filed March 6, 1935, we have specifically described and claimed processes of cracking higher fatty acid nitriles at substantially elevated pressures, of the order of 150 pounds per square inch or higher.

35 Having thus described our invention what we claim is:

1. The pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile hav-

ing at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed.

2. The process as in claim 1 wherein the higher fatty acid nitrile is stearonitrile.

3. The process as in claim 1 wherein the temperature is about 550° C.

4. The process as in claim 1 wherein the cracking zone contains a contact material.

5. The pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed and then condensing reaction products.

6. The pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed, and separately condensing unreacted higher fatty acid nitrile and lower molecular weight nitriles.

7. The pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed, separately condensing higher fatty acid nitrile and lower molecular weight nitriles and returning the condensed higher fatty acid nitrile to the cracking zone.

8. The catalytic pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone containing a solid dehydrating catalyst maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed.

9. The process as in claim 8 wherein the catalyst is aluminum oxide.

10. The process as in claim 8 wherein the higher fatty acid nitrile is chosen from the group consisting of palmitonitrile, stearonitrile, and lard fatty acid nitriles.

11. The process as in claim 8 wherein the temperature is about 550° C.

12. The catalytic pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone containing a solid dehydrating catalyst maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed and then condensing reaction products.

13. The catalytic pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone containing a solid dehydrating catalyst maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the

said higher fatty acid nitrile are formed and separately condensing unreacted higher fatty acid nitrile and lower molecular weight nitriles.

14. The catalytic pyrolysis of higher fatty acid nitriles which comprises introducing into a cracking zone containing a solid dehydrating catalyst maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed, separately condensing unreacted higher fatty acid nitrile and lower molecular weight nitriles and returning the condensed higher fatty acid nitrile to the cracking zone.

15. The catalytic pyrolysis of higher fatty acid nitriles which comprises introducing into a crack-

ing zone containing a solid dehydrating catalyst maintained at a cracking temperature a vaporized mixture consisting substantially wholly of at least one vaporized higher fatty acid nitrile having at least six carbon atoms whereby nitriles having a molecular weight lower than that of the said higher fatty acid nitrile are formed and fractionally condensing reaction products.

16. The pyrolysis of higher fatty acid nitriles which comprises heating a higher fatty acid nitrile having at least six carbon atoms at a cracking temperature at substantially atmospheric pressure in the absence of ammonia and its alkyl and aryl derivatives.

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