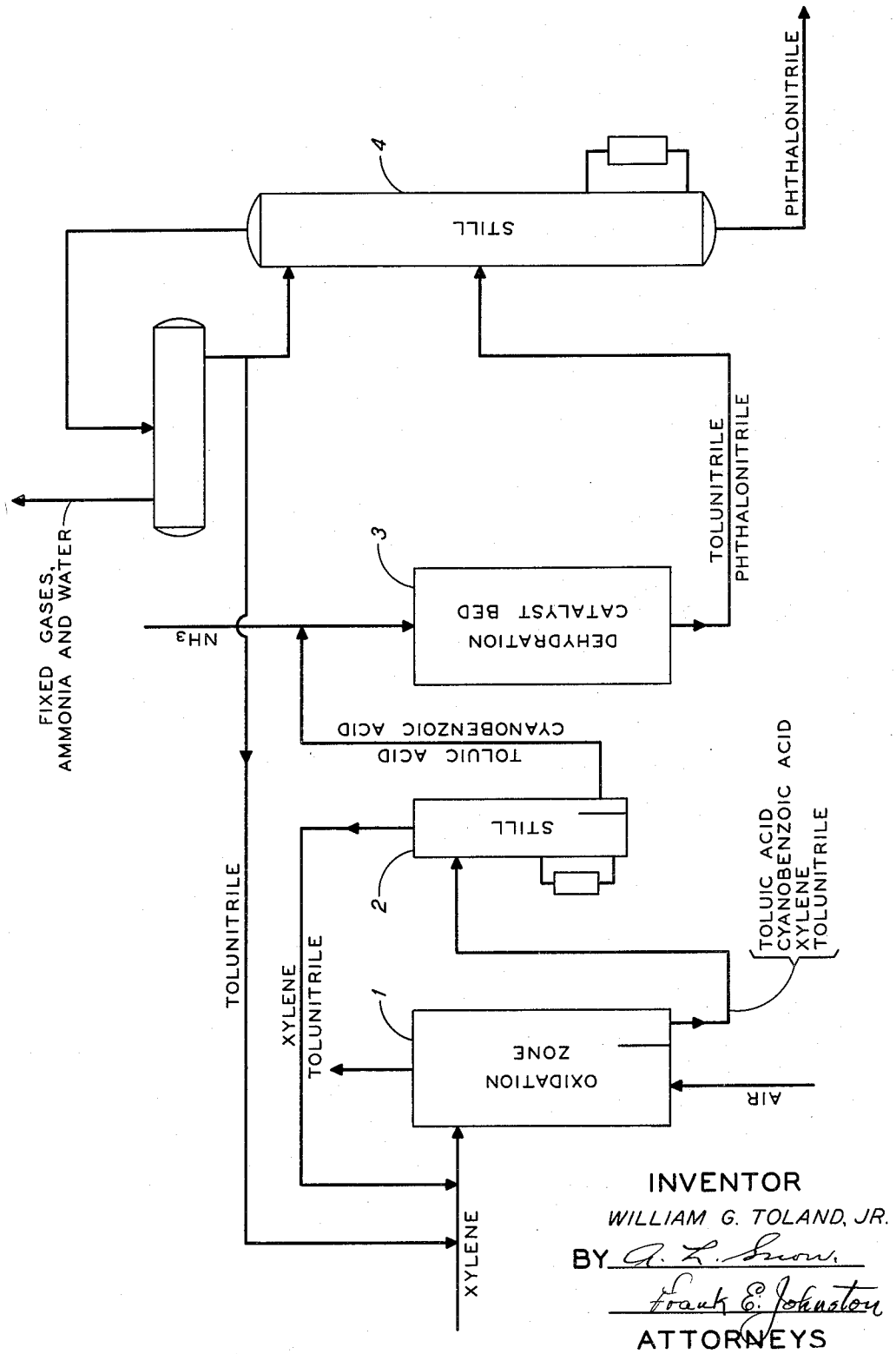
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PRODUCTION OF AROMATIC NITRILES

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PRODUCTION OF AROMATIC NITRILES

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This invention relates to a process for the production of nitriles. More particularly, it relates to a process for producting aromatic nitriles, especially the phthalonitriles.

In one specific embodiment of the invention a mixture of xylenes and tolunitriles is intimately contacted in liquid phase with a free oxygen-containing gas at a temperature in the range from 200° F. to 400° F. in an oxidation zone to produce a mixture of toluic acids and cyanobenzoic acids. The acids are reacted with ammonia at a temperature in the range from about 500° F. to 1000° F. to produce phthalonitriles and tolunitriles. The phthalonitriles are recovered as a process product and the tolunitriles are returned to the oxidation zone with further quantities of xylene.

The oxidation step may be conducted in the presence of a catalyst if desired. Oil-soluble compounds of multivalent metals which are capable of interchanging their valence structure at reaction temperatures are useful in the process. Oil-soluble compounds of cobalt, manganese, chromium, nickel, and lead are all effective catalysts in the process, the cobalt compounds being preferred. Cobalt toluate and cobalt naphthenate at low concentrations, usually in the range from 0.001 to 0.05% by weight of the metal based on the total weight of the reaction mixture, are especially effective catalysts.

Alkyl cyanobenzenes, such as the tolunitriles, can be oxidized in liquid phase with a free oxygen-containing gas in the presence or absence of catalysts of the type described at temperatures in the range from 300° F. to 500° F. to produce cyanobenzoic acids. At 300° F. the reaction proceeds so slowly that very long reaction times would be required in order to obtain an appreciable yield of cyanobenzoic acid. At temperatures above about 375° F., the reaction is very much more rapid and temperatures near this level would be necessary in any practical conversion of alkyl cyanobenzenes to cyanobenzoic acids. The oxidation of alkyl benzenes in liquid phase with a free oxygene-containing gas proceeds at a satisfactory rate at temperatures well below 300° F., for example, at 260° F. It has been found that when a mixture of an alkyl benzene, such as ethyl benzene, a xylene, a trimethyl benzene, methyl ethyl benzene, diethyl benzene, cymenes and other alkyl benzenes containing preferably not more than 3 carbon atoms in each alkyl group, with an alkyl cyanobenzene, such as tolunitrile, is contacted in liquid phase with a free oxygen-containing gas, both the alkyl benzene and the alkyl cyanobenzene are readily oxidized at temperatures below 300° F., for example in the range 200–300° F., at which temperatures the alkyl cyanobenzene alone would be for all practical purposes inert. The mixture of alkyl cyanobenzene and alkyl benzene should have a substantial alkyl benzene content. At least 5% by volume of the alkyl benzene should be employed and preferably a larger amount 20 to 50 volume per cent is present. The ability to bring about the oxidation of alkyl cyanobenzenes at lower temperatures in this

manner results in higher yields of cyanobenzoic acid at any given conversion level, smaller amounts of the alkyl cyanobenzene being consumed in side-reactions which yield undesired products.

The reaction product produced in the oxidation step of the process contains a benzene carboxylic acid, such as benzoic acid, toluic acid, or other alkyl benzoic acids, and a cyanobenzoic acid. These acids are separated from the unconverted portion of the feed and reacted with ammonia to convert the carboxyl radicals to nitrile radicals. If desired, the acids can be separated from each other, the cyanobenzoic acid can be retained as a product and the alkyl benzene acid reacted with ammonia to produce an alkyl cyanobenzene which is returned to the oxidation zone. Conversion of the acids to nitriles can be accomplished non-catalytically by intimately contacting ammonia with the acids at temperatures from about 500° F. to 1000 F. In the reaction an acid such as toluic acid is converted to tolunitrile and the cyanobenzoic acids are converted to phthalonitriles. When this reaction is conducted without a catalyst, the acids are preferably subjected to a sufficient pressure to maintain them in liquid phase and ammonia gas is mixed into the molten acids. This operation can be performed in a still, from which water can be removed as formed to drive the reaction to completion.

The reaction of ammonia with the acids produced in the oxidation step can also be conducted in the presence of a dehydration catalyst. Suitable catalysts for this reaction include alumina, silica, thoria, titania, and mixtures of these oxides such as silica-alumina, thoria-alumina, and the like. When a dehydration catalyst is employed in the reaction, the acids and ammonia are contacted with the catalyst at temperatures in the range from about 600° F. to about 1000° F. The acids and ammonia are ordinarily passed downwardly through a bed of the dehydration catalyst. At the reaction temperature the acids will ordinarily be in mixed phase and contact with the catalyst will be made at approximately atmospheric pressure. Higher pressures may be employed to increase the concentration of ammonia in the reaction zone and to maintain substantially all of the acids in liquid phase during the reaction.

Following the reaction with ammonia, the reaction product is distilled, the di-nitriles being recovered as a kettle product, and the alkyl cyanobenzenes being recovered as an overhead fraction which is desirably returned to the oxidation zone together with further quantities of the alkyl benzene.

An arrangement of apparatus and process flow suitable for the practice of the invention is diagrammatically illustrated in the appended drawing. Xylene and tolunitrile are introduced into oxidation zone 1 which is maintained at a temperature usually in the range from 230° F. to 300° F. The oxidation zone is held under a sufficient pressure to keep the xylene in liquid phase. A free oxygen-containing gas, which may be air, air enriched with oxygen or oxygen itself, is passed into the lower portion of the oxidation zone. Intimate contact between the free oxygen-containing gas and the feed may be obtained by the use of packing, bubble plates, or mechanical agitation. The residue of the free oxygen-containing gas is withdrawn from the upper portion of the oxidation zone and is preferably passed through a condenser to recover xylene and tolunitrile vapors contained therein. The reaction product mixture is continuously withdrawn from the lower portion of the oxidation zone from a baffled area therein. The reaction product mixture contains toluic acid, cyanobenzoic acid, and unconverted xylene and tolunitrile. This mixture is passed into still 2 where it is flashed at a still bottom

temperature of about 425° to 475° F. to remove unconverted xylene and tolunitrile overhead for recycle to the oxidation zone. The bottoms from still 2, consisting essentially of toluic acid and cyanobenzoic acid, are passed together with ammonia into reaction zone 3 which is packed with granular alumina. Reaction zone 3 is maintained at a temperature in the range 600 to 1000° F., more desirably at 700 to 900° F. In reaction zone 3 toluic acid is converted to tolunitrile and cyanobenzoic acid is converted to phthalonitrile. The reaction product withdrawn from reaction zone 3 is passed into still 4 which is operated at a bottoms temperature in the neighborhood of 525° F. Tolunitrile and any unconverted toluic acid are removed overhead and recycled to the oxidation zone. Excess ammonia contained in the effluent from reaction zone 3 is removed in the overhead from still 4 together with any fixed gases produced in the reaction. The ammonia and fixed gases are bled from the reflux drum, the ammonia is separated and returned to reaction zone 3. Phthalonitriles are removed from the bottom of still 4 as a net reaction product. They may be purified if desired by recrystallization from suitable solvents such as the lower alcohols, or by distillation. If the reaction is conducted noncatalytically, reaction zone 3 may be a simple still. Ammonia is passed into the bottom of the still to contact the acids and water is continuously removed overhead.

A particularly desirable feed to the oxidation zone is a mixture of one or more xylene isomers with one or more tolunitrile isomers. For example, terephthalonitrile may be produced by feeding a mixture of para-xylene and para-tolunitrile to the oxidation zone. Isophthalonitrile can be produced by feeding a mixture of meta-xylene and meta-tolunitrile to the oxidation zone. Commercial xylenes containing the three isomers may be used as a starting material. In starting up, the xylene alone is fed to the oxidation zone and oxidized to toluic acid which is reacted with ammonia to produce tolunitriles, which are then returned to the oxidation zone together with additional quantities of xylene. When the xylene feed is derived from a petroleum source, i. e., a xylene-rich fraction of catalytically reformed naphtha, the xylene feed may contain up to about 10% ethyl benzene and an apreciable proportion of paraffins. The ethyl benzene will be oxidized to acetophenone and benzoic acid, the latter being converted to benzonitrile, and still 4 can be modified to recover benzonitrile as the overhead and the tolunitriles for recycle as a side cut. The overhead of still 2 can be treated to remove paraffins and acetophenone before recycle, or a portion of the overhead can be rejected to prevent paraffin and/or acetophenone buildup in the oxidizer.

Small amounts of phthalic acids are ordinarily produce in the oxidation zone and converted to phthalonitriles in reaction zone 3. Their formation occasions no difficulty in the process.

The following examples illustrate the operation of the process of the invention.

Example 1

A mixture of equimolar parts of para-xylene and paratolunitrile were charged to a mechanically stirred oxidation vessel (turbomixer) fitted with a water separator and reflux condenser. The mixture was heated to a temperature of 260° F. and under atmospheric pressure. Air was passed through the mixture while maintaining the temperature at 260° F. After air had been passed through the reaction mixture for 3 hours, the flow of air was discontinued, the products cooled, and removed. The reaction mixture was fractionally distilled to separate unconverted xylene and tolunitrile from toluic acid and cyanobenzoic acid. Xylene and tolunitrile conversions were approximately 30% and 25%, respectively. The acids were charged to a still and heated to reflux temperature—approximately 530° F. Ammonia was passed into the still, and excess ammonia and water formed were removed overhead until reaction ceased, the cessation being indicated by no further water formation.

The reaction product was a mixture of terephthalonitrile and tolunitrile. The tolunitrile was separated from the terephthalonitrile by fractional distillation.

Example 2

Example 1 was repeated, using .005% by weight of cobalt naphthenate as the catalyst in the oxidation step and using granular alumina to catalyze the reaction between the oxidation reaction product and ammonia. Acid yields in the oxidation step were appreciably higher. Reaction of the acids with ammonia produced terephthalonitrile and tolunitrile as in Example 1.

Example 3

A mixture of xylenes and tolunitriles was oxidized in liquid phase in a pressure oxidation vessel fitted with a heater, a jet inlet, a water separator, a reflux condenser and a pressure controller. The xylene feed was a xylene-rich fraction recovered from catalytically reformed naphtha and contained 21.7% para-xylene, 51.3% meta-xylene, 11.4% ethyl benzene, 13.6% ortho-xylene and 2% paraffins. 1000 g. of this xylene feed and 500 g. of mixed tolunitriles were charged to the oxidation vessel. Cobalt naphthenate was added to the charge in amount sufficient to give the feed mixture a cobalt content of 0.01% by weight. The oxidation vessel was heated to 350° F. and the pressure was regulated to 100 p. s. i. g. Air was passed through the feed mixture at the rate of 20 cubic feet per hour for a period of 1½ hours. The oxidation vessel was cooled and the reaction products were transferred to a still having a 3 foot column packed with glass helices. A first fraction boiling up to 300° F. and consisting principally of unreacted xylenes was removed overhead. A second fraction boiling up to 400° F. and containing principally acetophenone and ortho-tolunitrile was removed overhead. A third fraction boiling up to 428° F., consisting principally of meta-tolunitrile and para-tolunitrile, was removed overhead and combined with the recovered xylenes for recycle to the oxidation zone. The distillation was interrupted at this point and gaseous ammonia was introduced into the still bottom which was maintained at 500° F. Ammonia introduction was continued until water ceased to be evolved from the reaction mixture. The reaction product of ammonia and the still bottoms were distilled to remove tolunitriles formed by reaction of ammonia with toluic acids overhead. This fraction was added to the stream for recycle. 246 g. of still bottoms containing upward of 75% of phthalic di-nitriles were recovered. Sublimation of the bottoms yielded white crystals of di-nitriles.

Example 4

500 g. of ethyl benzene and 200 g. of para-tolunitrile were charged to a turbomixer fitted with a stirrer, an air inlet, a water separator and a reflux condenser. This mixture was heated to 265° F. and air was passed through the mixture at the rate of 1.5 cubic feet per hour for 4 hours. 19 cc. of water were recovered in the water separator.

The reaction products were steam stripped. An organic layer was recovered overhead. This layer weighed 680 g. and contained unreacted ethyl benzene, acetophenone, para-tolunitrile and benzoic acid. The still bottoms were filtered hot to remove a small amount of colored bodies contained in them and then chilled. 25 g. of white crystalline para-cyanobenzoic acid were recovered. The product had a neutral equivalent of 147.5.

I claim:

1. A process which comprises intimately contacting a mixture of a polyalkyl benzene hydrocarbon containing 1 to 3 carbon atoms in each alkyl group and an alkyl

cyanobenzene containing 1 to 3 carbon atoms in the alkyl group in liquid phase with air at a temperature in the range 200° F. to 300° F. in an oxidation zone to produce a mixture of an alkyl benzoic acid and a cyanobenzoic acid.

2. A process which comprises intimately contacting a mixture of a polyalkyl benzene hydrocarbon containing 1 to 3 carbon atoms in each alkyl group and an alkyl cyanobenzene containing 1 to 3 carbon atoms in the alkyl group in liquid phase with a gas containing elemental oxygen as its sole effective oxidizing agent at a temperature in the range 200° F. to 400° F. in an oxidation zone to produce a mixture of an alkyl benzoic acid and a cyanobenzoic acid, separating the acids, intimately contacting the alkyl benzoic acid with ammonia at a temperature in the range 500° F. to 1000° F. to produce an alkyl cyanobenzene and returning the alkyl cyanobenzene to the oxidation zone with further quantities of the polyalkylbenzene hydrocarbon.

3. A process for producing aromatic nitriles which comprises intimately contacting a mixture of a polyalkyl benzene hydrocarbon containing 1 to 3 carbon atoms in each alkyl group and an alkyl cyanobenzene containing 1 to 3 carbon atoms in the alkyl group in liquid phase with elemental oxygen at a temperature in the range from 240° F. to 400° F. in an oxidation zone to produce a mixture of a benzoic acid and a cyanobenzoic acid, intimately contacting the mixture of acids with ammonia at a temperature in the range from 500° F. to 1000° F. to produce a benzene dinitrile and an alkyl cyanobenzene, separating the dinitrile as a product of the reaction and returning the alkyl cyanobenzene to the oxidation zone with further quantities of the alkyl benzene hydrocarbon.

4. A process for producing phthalonitriles which comprises intimately contacting a mixture of xylene and tolunitrile in liquid phase with air at a temperature in the range from 200° F. to 400° F. in an oxidation zone to produce a mixture of toluic acid and cyanobenzoic acid, passing the mixture of acids and ammonia over a dehydration catalyst at a temperature in the range from 550° F. to 950° F. to produce phthalonitrile and tolunitrile, separating the phthalonitrile as a product and returning the tolunitrile to the oxidation zone with further quantities of xylene.

5. A process for oxidizing methyl cyanobenzenes to cyanobenzoic acids which comprises intimately contacting a mixture of the methyl cyanobenzene with a substantial quantity of a xylene in liquid phase and air at a temperature in the range from 200° F. to 300° F.

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