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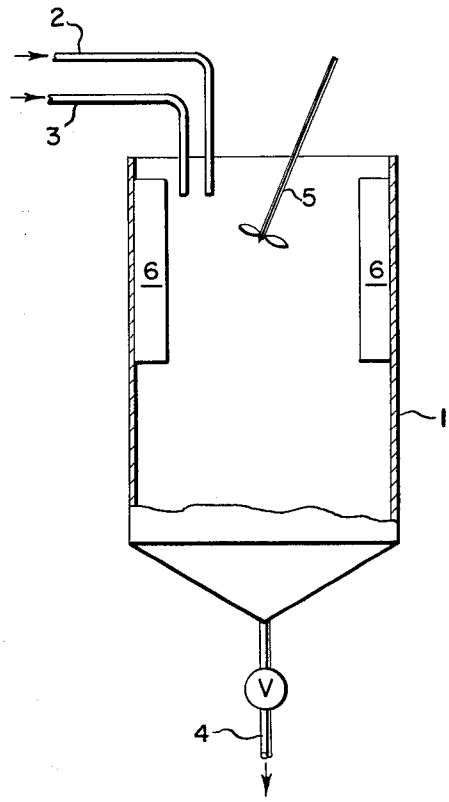

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3,255,261 PROCESS FOR PRODUCING NITROCYCLOALKANES

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This invention relates to an improved process for the nitration of saturated, cyclic hydrocarbons. More particularly, this invention is directed to an improved process for the preparation of nitrocycloalkanes by nitration of cycloalkanes with aqueous nitric acid.

It is well known that cycloalkanes react with aqueous nitric acid or with nitrogen dioxide to form a mixture of nitration products and oxidation products. For example, when cyclohexane is reacted with nitric acid, the predominant nitration product is nitrocyclohexane and the predominant oxidation product is adipic acid. Both nitrocyclohexane and adipic acid are used widely in commercial products, particularly in polymers, and nitrocyclohexane has, in recent years, become a particularly important intermediate in the production of caprolactam, a polyamide intermediate. One explanation for the observed nitration products and oxidation products in the reaction referred to above is based on the known attack of aqueous nitric acid on the saturated hydrocarbon molecule via the radical-like NO_2 intermediate to form the cycloalkyl radical. Subsequently, the hydrocarbon radical reacts with additional NO_2 by competing mechanisms to produce the corresponding nitrocycloalkane and cycloalkyl nitrite. The nitroalkane is relatively resistant to further oxidation by aqueous nitric acid but the nitrite ester is converted readily to a dibasic acid, containing the same number of carbon atoms, or to other oxidation products.

The prior art is replete with processes for the simultaneous preparation of both a nitrocycloalkane, e.g., nitrocyclohexane, and a dicarboxylic acid, e.g., adipic acid, from the corresponding cycloalkane and aqueous nitric acid. Frequently, however, it is desired to make primarily one product and to minimize or avoid the concurrent formation of other products and the resultant yield losses through undesirable consumption of nitric acid and hydrocarbon. Accordingly, in a typical commercial process for making adipic acid, the formation of nitrocyclohexane is avoided by using a two-step process in which, first, cyclohexane is partially oxidized with molecular oxygen and then the resulting product mixture comprising primarily cyclohexanol and cyclohexanone is oxidized by nitric acid to produce adipic acid.

In contrast, if the nitration product is preferred, process conditions are selected with the objective of suppressing the formation of oxidizable intermediates, such as the nitrite ester, and of minimizing the consumption of nitric acid in a sequence of oxidation reactions. Typically, continuous flow reactors are utilized to facilitate the prompt removal of organic products and spent aqueous nitric acid and to forestall sequential oxidation reactions; agitation and turbulence is maintained to promote rapid heat and mass transfer between the aqueous phase and the organic phase; the acid and hydrocarbon reactants are fed at a point remote from the point of egress to provide sufficient reaction time while minimizing premature removal of the reactants; reaction conditions of elevated temperature and pressure are selected which minimize the residence time and enhance the nitration without causing excessive thermal or oxidative degradation; and partial conversion of the hydrocarbon is accepted since, as the concentration of the nitrocycloalkane in the cycloalkane increases, more oxidizable intermediates are formed and more oxidation occurs.

Experience with these various nitration processes has shown that they have certain inherent disadvantages which have severely limited their utility. For example, the concurrent oxidation reactions consume both hydrocarbon and nitric acid and the yield losses represent a serious economic burden. Also, the teachings in the art require the use of a balance of interrelated process factors, some of which compete with or exclude others. Thus, mixing must be sufficient to disperse the immiscible reactants and increase phase contact but excessive agitation causes premature dilution of the feed acid through contact with spent acid. Likewise, increases in nitric acid strength or reaction temperature generally produce increased nitration of the hydrocarbon and permit shorter reaction times but, concurrently, more oxidation occurs. Also, pressures above about 70 atmospheres can be employed to permit the use of shorter reaction times thereby reducing sequential oxidation reactions, but the cost of high pressure equipment increases exponentially with pressure and adds undesirable costs to the process.

Accordingly, an object of this invention is to provide an improved process for the preparation of a nitrocycloalkane. Another object of this invention is to provide a process for producing a nitrocycloalkane in increased yields, and yet having the consumption of nitric acid per unit weight of the nitro compound produced substantially reduced. Another object of this invention is to provide a process criterion by which the competitive or exclusive factors of reaction conditions, reactor design, agitation, and reactant ratios can be combined for the preferential production of the nitrocycloalkane. Other objects and advantages will become apparent hereinafter.

In accordance with the objects of this invention it has been discovered that in the heterogenous reaction of a cycloalkane with aqueous nitric acid to produce the corresponding nitrocycloalkane, less nitric acid is consumed and improved yields of the nitrocycloalkane are obtained, provided the proportion of water in the reaction system is controlled to maintain a ratio of aqueous phase concentration by weight in the reaction to aqueous phase concentration by weight in the product effluent between about 0.05 to 0.85 and preferably about 0.05 to 0.5.

Briefly, a preferred embodiment of the invention comprises mixing cyclohexane with aqueous nitric acid to produce a reaction product mixture comprising an aqueous phase containing primarily dilute aqueous nitric acid, and an organic phase containing primarily nitrocyclohexane and unreacted cyclohexane. The reactants are vigorously agitated near the point of reactant feed thereby creating in the reactor a zone of turbulence near said reactant feed and a diminishing turbulence and dispersion gradient toward the point of egress of the product mixture in order to obtain partial phase separation of said product mixture by gravity. The aqueous and organic phase, i.e., product effluent is drawn off at and/or near the bottom of the reactor so as to maintain a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.85. The valuable nitrocyclohexane is recovered from the product effluent by any conventional method, for example, decantation, distillation, and the like.

Under conditions of complete mixing and dispersion of the phases in a continuous flow system, the nominal residence times in the reactor for both phases are the same and the concentrations of the phases in the reactor are related directly to the reactant concentrations and the feed ratio, with adjustments for materials consumed or produced in the reaction. Thus, one basis for control of the aqueous concentration in the reactor is by adjusting the amount of water introduced in the feed. However, the

relevant processes in the art teach the use of reactant proportions and aqueous nitric acid concentrations which introduce into the reactor a different proportion of water than is desired under the teachings of this invention, and the possible adjustments in the feed streams are undesirable alternatives. For example, the use of stronger nitric acid to reduce the proportion of water fed causes increased oxidation and necessitates extra equipment for nitric acid recovery; the use of a higher ratio of cycloalkane so as to decrease the proportion of water is undesirable because it results in decreased conversions to the nitrocycloalkane, and the use of an inert diluent adds the cost of cycling additional materials in larger equipment.

In most continuous operations requiring the contact of heterogenous phases, agitation and mixing are designed to maintain intimate contact between the phases and preserve an essentially homogenous dispersion throughout the contact zone. Alternatively, the mixing arrangements can be designed to establish a dispersion gradient in the system and maintain a variation from a condition of intimate dispersion at one point to a condition of partial or complete phase separation at another. Under such conditions, depending on the location along the gradient at which the effluent is removed, the system can be adjusted to a variety of steady-state conditions, and in each case the phase ratio within the overall contact zone will be different than the phase ratio in the feed and effluent streams. Concurrently, if the phase ratio in the overall contact zone is changed, the nominal residence time of each phase in the zone will change as well. Thus, by selection of appropriate equipment and conditions of mixing, the nominal residence time of the phases can be made nonequivalent and the phase ratio within a continuous reactor can be adjusted to a value different than the phase ratio in the reactor effluent.

Accordingly, a preferred means for controlling the proportion of the aqueous phase relative to the weight of the reactor contents in the nitration is by operating the continuous process so that the nominal residence time of the aqueous phase in the reactor is different than the nominal residence time of the organic phase and the proportion of the aqueous phase in the reactor is maintained within the required weight ratio. One way to accomplish this control in the reactor is to permit phase separation so that each phase can be regulated and removed as desired but this alternative is inappropriate because of the necessity to agitate and disperse the phases for effective reaction and for transfer of mass and heat. Therefore, one preferred means is to carry out the process with agitation, preferably in a reactor having baffles mounted on the inner wall of the reactor, thus creating a turbulence gradient with a variation from a condition of intimate mixing near the feed inlet to a condition of partial phase separation toward and at the egress points so that the aqueous phase and organic phase or mixtures of the phases can be removed as required to maintain the desired phase ratio and the desired retention time for each phase in the reaction zone.

It will be apparent to those skilled in the art that the necessary turbulence gradient and variable residence time for the immiscible phases can be created by known techniques of design and operation in cylindrical, tubular, or spherical reactors using the alternatives of vertical or horizontal flow, various means of agitation and phase dispersion, and appropriate positions and sizes for feed lines and take-off lines. Thus a number of alternative techniques of phase dispersion and mixing in heterogenous systems may be employed to attain the ratios of aqueous phase concentration in the reactor to aqueous phase concentration in the product effluent as required in the preferred embodiment. That is, a desired degree of mixing and dispersion can be achieved by various empirical combinations or design choices, as in the selection of the shape, size, and speed of the agitator; in the selection of the contour, shape, and size of the reactor; and in the selection of the form, size, and number of internal baffles.

For a further understanding of the invention reference is made to the attached schematic drawing which illustrates one convenient method of reactor arrangement and process operation.

Referring to the drawing, vertical reactor **1**, which is capable of withstanding the operating pressures used, is provided with reactant feed lines. The cycloalkane is introduced into the reactor through line **2** and aqueous nitric acid is introduced through line **3** at or near the top of reactor **1**. The product effluent is removed through one or more lines **4** at or near the bottom of the reactor using either direct withdrawal or suitable dip-tubes. In general one or more agitator devices **5** and baffles **6** are selected and positioned within reactor **1** so as to maintain turbulence and phase dispersion of the reaction mixture near the top of the reactor and to provide a diminishing vertical turbulence gradient and a partial phase separation toward the point of egress of the reaction mixture near the bottom of the reactor by utilizing the tendency for the heavier aqueous phase to separate and settle to the bottom of the reactor. Then the required amounts of water and organic product are removed through appropriate outlets—at or near the bottom of the reactor to maintain the proper ratio while the preferred steady-state conditions of mass flow and reactor hold-up are maintained.

While the quantity and the nominal residence time of the aqueous phase are controlled conveniently in a continuous flow system, it is understood that similar advantages can be obtained in a batch or semicontinuous system. Thus, in a modification of this invention in a batch process the hydrocarbon is charged to the reactor and aqueous nitric acid is fed into the reactor. The aqueous phase is drawn off intermittently or continuously to maintain the aqueous phase concentration in the reactor at a minimum, between about 1 to 20% by weight and preferably between about 1 to 10% by weight.

Using nitration processes known in the art, at operating pressures below 60 atm., the nitric acid consumption is from 1 to 4 parts per part of nitrocyclohexane produced and the consumption of cyclohexane exceeds 1 part per part of nitrocyclohexane produced. Under the improved process of this invention, the consumption of nitric acid is reduced to less than 0.9 part per part of nitrocyclohexane and the consumption of cyclohexane is reduced to 0.75–0.85 part per part of nitrocyclohexane produced, depending upon the feed ratio used. Furthermore, in the improved process conversion of the nitric acid is substantially complete and the minimum residual nitric acid in the aqueous phase of the product can be discarded without a serious economic penalty.

The following examples are intended to illustrate but not to limit the invention, and to show the unexpected improvements achieved by the process of this invention over the teachings of the prior art.

Example 1

Cyclohexane was fed at a rate of 150 lb. per hr. and 60% nitric acid was fed at a rate of 50 lb. per hr. into a cylindrical autoclave having a diameter of 12 in. and a nominal capacity of 8.4 gal. The reactant mixture was agitated with a flat paddle, 5.5 in. in diameter, rotating at 500 r.p.m. and the reaction conditions were maintained at 200° C. and 500 p.s.i.g. A liquid level control was set to provide a nominal retention time of 12 min. for the organic phase, and the product mixture, containing an organic phase to aqueous phase weight ratio of approximately 4 to 1, was removed through a bottom outlet 2 in. in diameter. Under these conditions the ratio of the steady-state aqueous phase concentration by weight in the reactor to the aqueous phase concentration in the product stream or effluent was in the range of 0.15 to 0.25. The organic phase in the product effluent contained 21 to 22% nitrocyclohexane. The nitric acid consumption was

0.85 lb. HNO_3 per lb. of nitrocyclohexane, and the cyclohexane consumption was 0.8 lb. per lb. of nitrocyclohexane.

Under substantially equivalent reaction conditions, but with the ratio of the aqueous phase concentration in the reactor to the aqueous phase concentration in the product stream maintained at approximately 1 by removal of the product through a 0.5 in. diameter dip tube from a point 5 in. above the bottom of the reactor, the organic phase in the effluent contained 15–16% nitrocyclohexane and the nitric acid consumption was 1.3 lb. HNO_3 per lb. of nitrocyclohexane, and the cyclohexane consumption was 0.9 lb. per lb. of nitrocyclohexane.

Example 2

The cylindrical reactor described in Example 1 was modified by mounting 2 in. wide vertical baffles to the cylinder wall in a radial position at three equidistant locations with the baffles extending from the top of the reactor to points 6 in. above the bottom outlet. Using the conditions of temperature, pressure and agitation of Example 1, with the agitator impeller at a point 8 in. above the bottom and with a liquid operating level of 13 to 15 in. in the reactor, the ratio of the aqueous phase concentration in the reactor to the aqueous phase concentration in the product was 0.23, when the feed ratio was 0.2 lb. HNO_3 per lb. of cyclohexane. Results of runs made using different feed ratios are shown in the following table.

Feed Acid Ratio (lb. HNO_3 per lb. cyclohexane)	Wt. percent of Nitrocyclohexane in Product Oil	Acid Consumption (lb. HNO_3 per lb. nitrocyclohexane)
0.06	8.3	0.68
0.15	18.0	0.77
0.20	22.9	0.81
0.27	28.2	0.88
0.34	33.0	0.92

Example 3

The cylindrical reactor described in Example 1 was modified by mounting 2 in. wide vertical baffles to the cylinder wall in a radial position at four equidistant locations with the baffles extending from the top of the reactor and following the curvature of the bottom to points adjacent to the 2 in. diameter bottom outlet. Using the conditions of temperature, pressure and agitation of Example 1, with the agitator impellor at a point 3 in. above the bottom and with a liquid operating level of 13 to 15 in., the ratio of aqueous phase concentration in the reactor to the aqueous phase concentration in the product effluent was 0.35 when the feed ratio was 0.2 lb. HNO_3 per lb. of cyclohexane, the organic phase in the effluent contained 21.6% nitrocyclohexane, and the nitric acid consumption was about 0.86 lb. HNO_3 per lb. of nitrocyclohexane.

When the bottom outlet for product removal was changed to 0.5 in. in diameter, the ratio of aqueous phase concentration in the reactor to the aqueous phase concentration in the product effluent was 0.43 when the feed ratio was 0.2. Results of runs made using different feed ratios are shown in the following table.

Feed Acid Ratio (lb. HNO_3 per lb. cyclohexane)	Wt. percent of Nitrocyclohexane in Product Oil	Acid Consumption (lb. HNO_3 per lb. nitrocyclohexane)
0.06	8.2	0.69
0.15	16.2	
0.20	19.8	0.88
0.34	26.1	1.17

Example 4

Cyclohexane was fed at a rate of 15 ml. per min. and 60% nitric acid was fed at a rate of 3 ml. per min. into a cylindrical autoclave having a diameter of 2 in. and a nominal capacity of 300 ml. The reactant mixture was agitated vigorously with a rotating impellor located about 2 in. from the bottom, the reaction conditions were maintained at 200° C. and 520 p.s.i.g., and the nominal liquid retention time was 10 min. When the products were removed through a 0.187 in. diameter side port at a point just above the impeller, the ratio of the steady-state aqueous phase concentration in the reactor to the aqueous phase concentration in the product effluent was 0.83, the organic phase contained 20% nitrocyclohexane and the nitric acid consumption was 1 g. HNO_3 per g. of nitrocyclohexane. When the ratio of the aqueous phase concentrations was maintained in the range of 0.11 to 0.17 by removal of the products through a 0.187 in. diameter outlet at the bottom, the product oil contained 23.5% nitrocyclohexane and the acid consumption was 0.85 g. NHO_3 per g. of nitrocyclohexane.

When 30% nitric acid was used in place of the more concentrated acid, the ratio of aqueous concentrations with the side take-off arrangement was 0.77, the product oil contained 13.8% nitrocyclohexane and the nitric acid consumption was 1.5. In contrast, with the bottom take-off arrangement, the ratio of the aqueous concentrations was approximately 0.06, the product oil contained 23% nitrocyclohexane and the acid consumption was 0.85.

Example 5

In a 300 ml. glass autoclave, 97.5 g. of cyclohexane was preheated and 36.7 g. of 60% nitric acid was fed into the reactor during a period of 15 min. while the reactor was maintained at approximately 200° C. and 500 p.s.i.g. When the spent aqueous acid was allowed to accumulate in the reactor, the organic product oil contained 14.4% nitrocyclohexane, the consumption of nitric acid was 1.6 g. HNO_3 per g. of nitrocyclohexane, and the off-gas at the end of the run contained 44 mol percent CO_2. In contrast, when the spent aqueous acid was removed periodically during the run, the product oil contained 16.9% nitrocyclohexane, the consumption of acid was 1.4, and the off-gas contained 22 mol percent CO_2.

Example 6

In a continuous nitration of cyclohexane using 60% nitric acid, a temperature of 195–200° C., a pressure of 500–520 p.s.i.g., and a feed ratio of 0.2 part of nitric acid per part of cyclohexane, the ratio of the steady-state aqueous phase concentration in the reactor to the aqueous phase concentration in the product effluent was 0.47. Under these conditions the nitric acid consumption was 1.2 parts per part of nitrocyclohexane produced, the cyclohexane consumption was 1.05 parts per part of nitrocyclohexane, and the hydrocarbon loss to water-soluble products analyzed as loss to carbon was 0.12 part of carbon per part of nitrocyclohexane. In contrast, when the reactor was modified to change the phase distribution and decrease the aqueous concentration in the reactor, the reactor to product aqueous phase ratio was 0.20 to 0.25, the nitric acid consumption was reduced to 0.87 part per part of nitrocyclohexane, the cyclohexane consumption was reduced to 0.92 part per part of nitrocyclohexane, and the loss to water-soluble products was reduced to 0.07 part of carbon per part of nitrocyclohexane.

Any cycloalkane may be used in the process, particularly a cycloalkane having from 3 to 20 carbon atoms and, preferably, from 5 to 12 carbon atoms. Representative of these cycloalkanes are, for example, cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclodecane and cyclododecane, and the like. Because of the importance of the product nitrocyclohexane, a preferred cycloalkane starting material is cyclohexane.

Aqueous nitric acid is used in the process as the nitrating agent and the nitric acid may have a concentration in the range of from 10 percent to 95 percent by weight and preferably from about 30% to 68% by weight. The temperature at which the nitration reaction is conducted may be from 140° C. to 220° C. and preferably from 170° C. to 210° C. The nitration reaction is conducted at pressures that are sufficient to keep the cycloalkane in the liquid state. Higher pressures can be used; however, it is not necessary and the process is usually conducted below about 60 atmospheres.

The reactant ratios used in the process range from about 0.01 to 0.5 part by weight of net nitric acid per part of cyclohexane, and preferably, from about 0.05 to 0.3 part of net nitric acid per part of cyclohexane.

The specific aqueous phase concentration in the product effluent is dependent not only on the aqueous content of the feed, as determined by the reactant ratio and acid strength, but also on the reactant conditions and on the quantity of water and other products formed in the reaction. In addition, the aqueous phase concentration in the reactor is controlled by a variety of methods of operation and mixing as described herein. Thus, the aqueous phase concentration in the reactor and in the product effluent will vary according to the selection of the reactant ratio, acid strength, and reaction conditions. In a typical example, utilizing 60% nitric acid and 0.2 part by weight of net nitric acid per part of cyclohexane, the aqueous phase concentration is approximately 20% by weight, and the aqueous phase concentration in the reactor, as described in a preferred embodiment of the invention, is from about 1% to 17% by weight and, preferably, from about 1% to 10% by weight.

The process of the present invention may be a batch operation or a continuous system; of course, the latter is more desirable. The nominal residence time of the organic phase in the reactor is from about 1 to 30 minutes and preferably from about 5 to 15 minutes.

We claim:

1. In a process for the production of nitrocycloalkane by the nitration of a cycloalkane in the liquid state with aqueous nitric acid, the improvement which comprises maintaining a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.85.

2. In a continuous process for the production of nitrocycloalkane by the nitration of a cycloalkane in the liquid state with aqueous nitric acid, the improvement which comprises maintaining a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.85.

3. In a continuous process for the production of nitrocyclohexane by the nitration of cyclohexane in the liquid state with aqueous nitric acid, the improvement which comprises maintaining a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.85.

4. In a continuous process for the production of nitrocyclohexane by the nitration of cyclohexane in the liquid state with aqueous nitric acid, the improvement which comprises maintaining a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.5.

5. In a continuous process for the production of nitrocyclohexane by the nitration of cyclohexane in the liquid state with aqueous nitric acid having a concentration of nitric acid in a range of from 10% to 95% by weight at a temperature of from 140° C. to 220° C. and at reactant ratios within a range of from 0.01 to 0.5 part by weight of nitric acid per part of cyclohexane, the improvement which comprises maintaining a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.85.

6. In a continuous process for the production of nitrocyclohexane by the nitration of cyclohexane in the liquid state with aqueous nitric acid having a concentration of nitric acid in a range of from 30% to 68% by weight at a temperature of from 170° C. to 210° C. and at reactant ratios within a range of from 0.05 to 0.3 part by weight of nitric acid per part of cyclohexane, the improvement which comprises maintaining a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.5.

7. In a batch process for the production of nitrocycloalkane by the nitration of a cycloalkane in the liquid state with aqueous nitric acid, the improvement which comprises maintaining an aqueous phase concentration of water in the reactor from about 1 to 20 percent by weight.

8. The process according to claim 7 wherein the cycloalkane is cyclohexane.

9. The process according to claim 8 wherein the ratio of the aqueous phase concentration in the reactor is from about 1 to 10 percent by weight.

10. A process for the production of nitrocyclohexane which comprises mixing in a reactor cyclohexane and aqueous nitric acid near the point of reactant feed in such a manner as to create a zone of turbulence near said reactant feed and a diminishing turbulence and dispersion gradient toward the point of egress of the reaction product mixture and thereby allowing a partial phase separation of said product mixture by gravity and permitting a selection of the point of removal of said product mixture to maintain a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.85 and recovering nitrocyclohexane.

11. A process for the production of nitrocyclohexane which comprises mixing in a reactor cyclohexane and aqueous nitric acid near the point of reactant feed in such a manner as to create a zone of turbulence near said reactant feed and a diminishing turbulence and dispersion gradient toward the point of egress of the reaction product mixture and thereby allowing a partial phase separation of said product mixture by gravity and permitting a selection of the point of removal of said product mixture to maintain a ratio of aqueous phase concentration by weight in the reactor to aqueous phase concentration by weight in the product effluent of from about 0.05 to 0.5 and recovering nitrocyclohexane.

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