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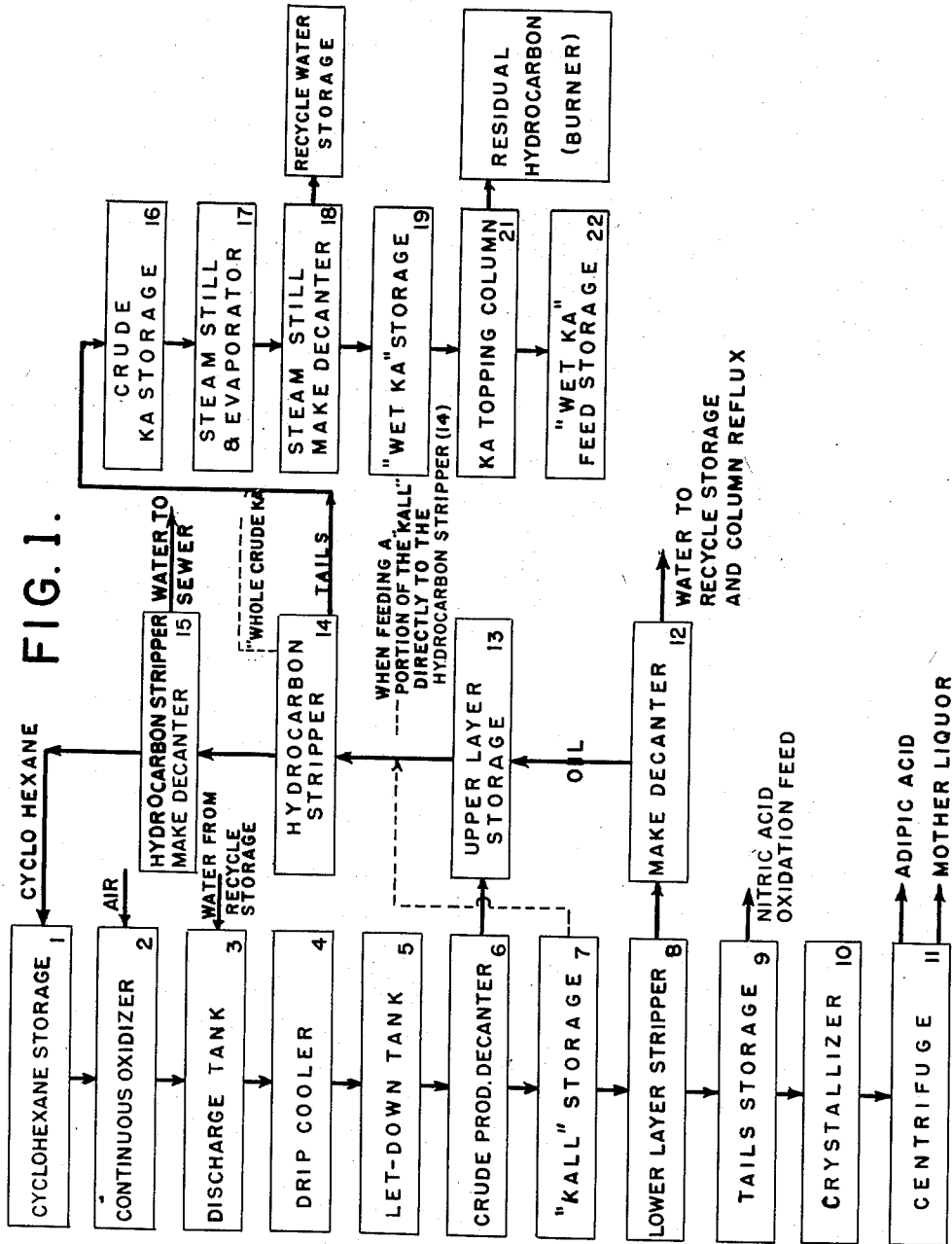
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2,703,331

PROCESS FOR SEPARATING ADIPIC ACID PRECURSORS

Filed Nov. 6, 1953

3 Sheets-Sheet 1



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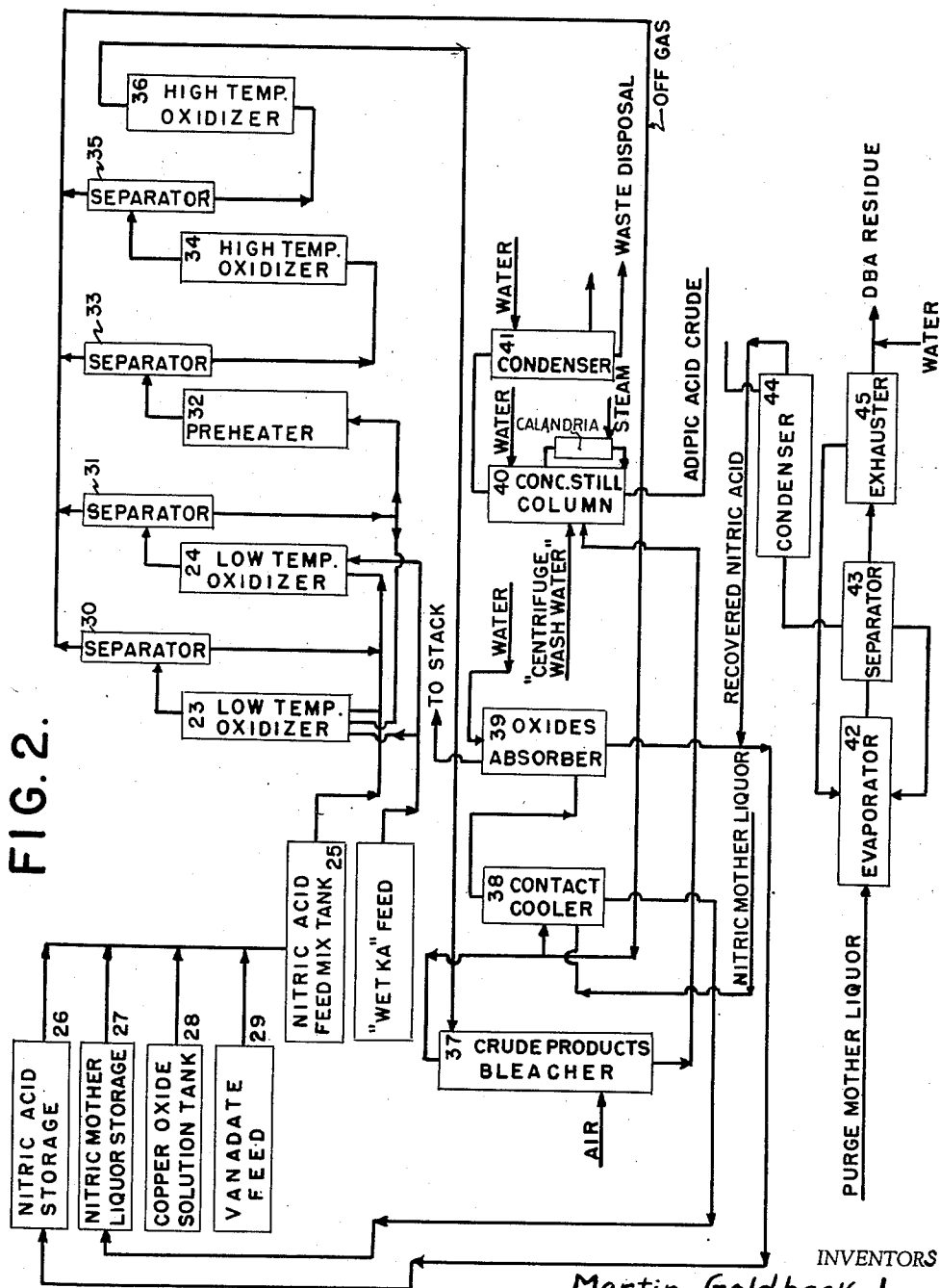
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3 Sheets-Sheet 2



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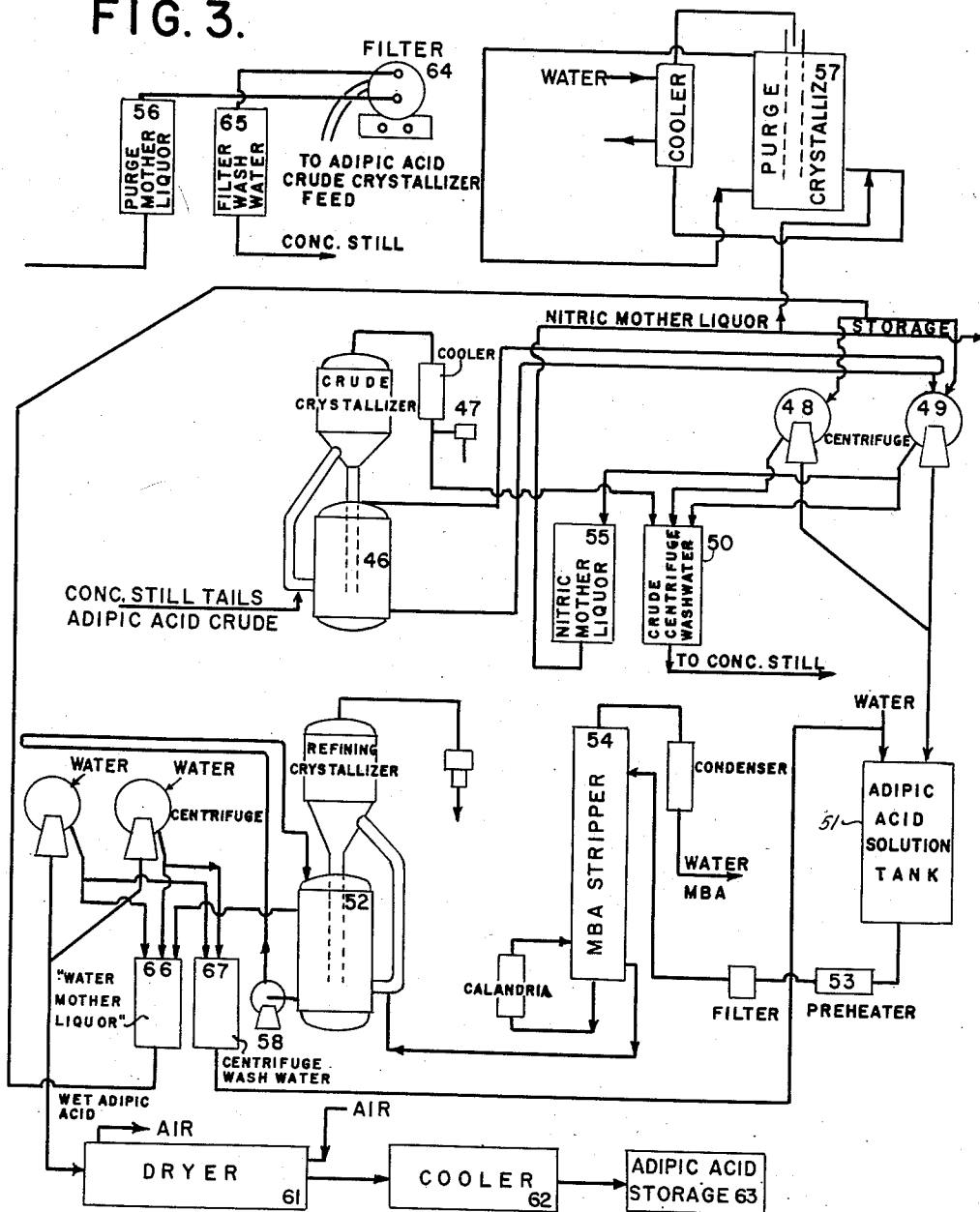
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3 Sheets-Sheet 3

FIG. 3.



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**PROCESS FOR SEPARATING ADIPIC ACID PRECURSORS**

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7 Claims. (Cl. 260—533)

This invention relates to improvements in the oxidation of cyclohexane to adipic acid. These improvements are directed particularly to the process which involves oxidation of cyclohexane with molecular oxygen (e. g. air) to primary oxidation products (cyclohexanol, cyclohexanone, peroxides, and various other oxidized products) followed by oxidation of these primary products to adipic acid by means of nitric acid. In the aforesaid process, according to the prior art (U. S. 2,439,513 and 2,557,282), the unoxidized cyclohexane is recovered after the initial oxidation, and the cyclohexane-free product is fed to the nitric acid oxidizer. In this manner the cyclohexanol and cyclohexanone do not have to be isolated and the ultimate yield of adipic acid is extraordinarily high because of the fact that miscellaneous adipic acid precursors are ultimately converted to adipic acid in the nitric acid oxidation step.

In the process just described the nitric acid oxidation step is not as efficient as it could theoretically be, because various primary oxidation products which are present in the nitric acid oxidation feed give rise to succinic and glutaric acids, and these acids must be removed in an adipic acid recrystallizer. The overall cost of the process, and particularly the cost of adipic acid recrystallization, could be greatly lowered if the nitric acid oxidizer feed contained a lower percentage of succinic and glutaric acids precursors.

A number of methods for producing nitric acid oxidizer feeds which selectively contain adipic acid precursors, i. e., which have been at least partially purged of succinic and glutaric acids or their precursors, have been devised, but in general these methods are not justifiable on economic grounds, since all of the previously known techniques for selection of adipic precursors are more expensive than the removal of the by-products by adipic acid recrystallization; this is true, for example, of methods which involve esterification of non-volatile ingredients of the crude primary oxidation product after removal of cyclohexanol, cyclohexanone, etc., followed by separation of succinic and glutaric esters by distillation. Other methods which have been tried include selective extraction of glutaric acid from the non-volatile residue (after removal of cyclohexanol and cyclohexanone) by means of boiling benzene (solubility of glutaric acid exceeds 10%, while the solubility of adipic acid is only 0.06%), coupled with extraction of adipic acid in boiling xylene (solubility exceeds 17%), succinic acid being only very slightly soluble in each of these boiling solvents (0.01% in boiling benzene and 0.142% in boiling xylene). Fractional crystallization, and partition chromatography (using water-silicic acid as a stationary phase and n-butanol-chloroform as a mobile phase) have been investigated with fairly good success. However, these methods are not as simple and inexpensive as would be desired in a case such as this, where the cost of improving the feed to the nitric acid oxidizer plus the cost of nitric acid oxidation of the improved feed, and separation of pure adipic acid, must be compared economically with the nitric acid oxidation of unimproved feed followed by removal of the undesirable constituents in the adipic acid recrystallization step. These methods have not heretofore proved to be sufficiently attractive from the comparative economic standpoint to justify their adoption.

An object of this invention is to provide an improved method for producing a nitric acid oxidizer feed in the cyclohexane oxidation process hereinabove described, said improved method being one which is comparatively

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economical, and which preferably produces a nitric acid oxidizer feed embodying an optimum combination of (1) low losses of the adipic acid precursors, (2) low consumption of nitric acid, and (3) low proportionate amount of succinic acid and glutaric acid or precursors thereof in the nitric acid oxidizer feed.

These objects are accomplished by a process, to be described hereinafter, which will be more readily understood by reference to the accompanying flow diagram showing the oxidation of cyclohexane and separation of various crude products which can be oxidized further to adipic acid by means of nitric acid. As has been previously disclosed, the maximum yields of adipic acid from cyclohexane are obtained by subjecting all of the cyclohexane-free oxidation product to nitric acid oxidation. However, it has also been discovered, according to the present invention, that the adipic acid yield penalty which results from the use of a mixture of volatile primary oxidation products (mostly cyclohexanone, cyclohexanol, cyclohexyl formate, cyclohexyl higher esters including valerate, monobasic acids, and some cyclohexanediol), called "Wet KA," as hereinafter defined, while excluding at least a part of the non-steam-volatile ingredients of a water extract of the total oxidation mixture, hereinafter called "KALL," is small enough to justify using "Wet KA" or combinations of "Wet KA" and "KALL" ingredients (the latter embodiment being called "Wet KA+KALL," in the nitric acid oxidizer, instead of the total crude oxidation product, hereinafter called "Whole Crude KA." As is apparent from the flow diagram, either of these crudes can be withdrawn from the "KA" plant, i. e., the plant for converting cyclohexane to its primary oxidation products. The yield penalty just mentioned varies with the cyclohexane conversion, and is about 5.6% (based on weight of adipic acid formed) when the cyclohexanone conversion to all products is 6.5%, and about 9.75% when the cyclohexanone conversion is 11%. Furthermore, according to the present invention, it has been discovered that the use of "Wet KA" or "Wet KA+KALL" greatly improves the quality of product obtained in the nitric acid oxidation step and eliminates a major part of the succinic and glutaric acid which would otherwise have to be removed in the final adipic acid recrystallizers. The nature of the improvement can better be understood by reference to the prior art process disclosed in U. S. P. 2,557,282 (cf. also U. S. P. 2,557,281) wherein all of the cyclohexane oxidation products, after removal of unreacted cyclohexane, were sent to the nitric acid oxidizer. In contrast with this, the present process employs that part of the oxidation product (after cyclohexane stripping) which is steam-volatile, and moreover, the present invention provides an efficient series of operations whereby this oxidizer material (called "Wet KA") is recovered. In particular embodiments, this "Wet KA" is used in combination with at least a part of the "KALL" and as a result of using "Wet KA" or "Wet KA+KALL," all or part of the non-volatile oxidation product is excluded from the nitric acid oxidizer.

The present invention is further explained by means of the accompanying drawing, and the examples which follow.

Fig. 1 illustrates the liquid phase air oxidation of cyclohexane by a process in which the cyclohexane is pumped from the cyclohexane storage supply 1 through three stirred autoclave-oxidizers in series, equipped with reflux condensers for water take-off 2, and into the discharge tank 3, a sufficient amount of water being injected to prevent plugging of the lines with water soluble solid, thence through coolers 4 to a let-down tank 5 and a decanter 6 wherein the oil layer is permitted to separate from the aqueous layer. The latter is sent to a storage tank 7, from which it is withdrawn to a stripper 8 which quickly distills all steam-volatile ingredients. The stripper residue is conducted to storage tank 9 from which it can be withdrawn for feeding to the nitric acid oxidation step, or fed to the crystallizer 10 where it is cooled to produce adipic acid crystals. The crystals are removed by means of the centrifuge 11 which also produces a mother liquor. The steam volatile ingredients from the continuously operated stripper 8 (aqueous phase being returned to the

stripper) are conducted through another decanter 12 to a storage vessel 13 where it is admixed with the oil layer from decanter 6. The oil layer from the storage vessel 13 is fed to a hydrocarbon stripper 14 which removes wet cyclohexane and none of the higher boiling organics, the latter remaining behind with condensed steam as single phase distillation residue. The wet cyclohexane is decanted in the decanter 15, and the recovered cyclohexane is returned to the hydrocarbon storage 1. When "KALL" as a whole, instead of the volatile organic matter therein, is sent to the hydrocarbon stripper 14 directly, the distillation residue after stripping cyclohexane is "Whole Crude KA." In the prior art method of operation this material was sent to the nitric acid oxidizer. In the method of the present invention, which requires "KALL" stripping 3 tails from the stripper 14 are converted to a more refined precursor, i. e. "Wet KA." To do this, the distillation residue from the stripper 14 is withdrawn and sent to storage 16. This oil is subjected to steam distillation with the water phase continuously returned to the still 17. The oil phase (i. e. "Wet KA") in the distillate is decanted 18 and conducted to the "Wet KA" storage vessel 19, the water layer being recycled to the still through a storage vessel 20. The "Wet KA" prior to use in nitric acid oxidation is passed through a topping column for production of a very small amount of hydrocarbon-water distillate 21. This is merely a safety precautionary measure to remove any traces of hydrocarbon which may be present as contamination, the purpose of the topping being to eliminate any hazard from a contact of gaseous hydrocarbon with nitric fumes. This hydrocarbon is sent to the waste burner. The topped "Wet KA" is conducted to the storage vessel 22.

In the process just described the cyclohexane oxidation can be carried out at temperatures between 50° and 175° C., under a pressure between 50 and 250 pounds per square inch. The percentage conversion of cyclohexane for practical results is kept within the range of about 5% to 30%. Various innovations and improvements, such as intermediate water scrubbing of the reaction mixture before it is sent from one stirred autoclave to another, addition of mineral acid during hydrocarbon stripping and KA recovery, or the introduction of a peroxide decomposition step after the oxidized product is withdrawn from the last oxidizer (by introducing iron salt, increasing the cobalt concentration, or injecting a molybdenum compound, etc., or by passing the liquid through a fixed bed of such peroxide-decomposing materials) have beneficial effects, and may be used in the process of this invention, although they are not essentially a part thereof. The oxidation catalyst is preferably a cobalt salt such as cobalt naphthenate, and the quantity of catalyst may be from 0.1 to 1000 parts per million parts of cyclohexane; however, it is not absolutely essential that any catalyst of any kind be introduced. While the preferred temperature is about 145° to 150° C., this depends in part upon the quantity of catalyst present, as shown in the following table. There is a threshold temperature which is determined by cobalt concentration, and below the threshold temperature the reaction is very slow. At 5 p. p. m. of cobalt the threshold temperature for cyclohexane derived from petroleum is 155° C.; at 20 p. p. m. it is 145° C., and at 50 p. p. m. it is 138° C. These threshold temperatures vary inversely as the logarithm of the catalyst concentration. The yields of adipic acid and its precursors vary with the threshold temperature, as shown by the data contained in the following table:

Table I.—The effect of cobalt catalyst concentration (and air oxidation temperature) on adipic acid yield via nitric acid oxidation of "Whole Crude KA," when the oxidation temperature is the threshold temperature

Catalyst Conc. (p. p. m. Co).....	5	20	50
Air Ox. Temp. (° C.).....	155	145	138
Cyclohexane Conv. (Percent).....	12	12	12
Adipic Acid Yield.....	69.9	72.4	75.7

The corresponding yields for oxidation of "Wet KA" are about 6% lower in each instance, i. e., the incremental percentage difference is about 6%.

The nitric acid oxidation of "Wet KA" is preferably carried out as illustrated in Figure 2. The "Wet KA" feed is pumped into each of two low temperature nitric acid oxidizers 23 and 24, wherein the temperature is held

at 80° C. Into the first of these is also pumped a nitric acid catalyst feed 25, made up by mixing aqueous nitric acid 26 and nitric acid mother liquor 27, with copper oxide 28, and ammonium vanadate 29 sufficient to bring (in the illustrated embodiment) the concentration of copper to 0.15%, and of vanadium to 0.05%, the concentration of the nitric acid feed being controlled at 50% HNO<sub>3</sub>. The pressure in the oxidizers 23 and 24 is maintained at 35–50 pounds per square inch, and this same pressure prevails in the separators 30 and 31 which operate at a temperature of 80° C., and into which the liquid and off-gas from the oxidizers flow. The off-gas is withdrawn at the top of each separator and combined. The liquid from the first separator 30 supplements the nitric acid-catalyst feed, which is pumped into the second oxidizer. A fixed portion of the liquid from the second separator 31 is recycled to the 1st converter 23 while the excess is pumped to a preheater 32, a separator 33 for removal of vapor, a high temperature reactor 34 operating at 100–110° C., another gas-liquid separator 35 and still another high temperature reactor 36 operating at 100–110° C. Air is introduced into the liquid from the last oxidizer in sufficient quantity to bleach the liquid, at a temperature of 100–110° C. The off-gas produced in this bleacher 37 is combined with the off-gas stream from the separators 30, 31, 33 and 35 contacted with "nitric mother liquor," to be described hereinafter, and cooled in a contact cooler 38. Gases vented from the cooler are sent through an absorber column 39 where they come in contact with water. The unabsorbed gases are sent to the stack. The absorbed oxides are sent to recovered nitric acid storage and used as needed for recycling to the nitric acid feed supply. The reaction product is withdrawn from the bleacher 37 and sent to a vacuum concentrating still 40, into which steam is injected, heat being introduced through a calandria, there being a condenser 41 between the still column and the vacuum jet. Simultaneously, in this same concentrating still, a stream called "centrifuge wash water," also to be described hereinafter, is concentrated, in admixture with the stream from the bleacher. The concentrated adipic acid solution is withdrawn from the base of this concentrator.

A stream designated "purge mother liquor," to be defined hereinbelow, is purged of volatile condensable products by cycling it through a vacuum evaporator 42, and a separator 43, from which the condensable products are condensed 44 and forwarded to the nitric acid storage. The molten liquid from the separator 43 is exhaustively freed of volatiles 45, which are returned to the evaporator 42. The exhausted non-volatiles ("DBA") are withdrawn from the exhaustor.

The purification of the crude adipic acid (withdrawn from the concentrating still 40) is accomplished by means of the following series of operations (cf. Figure 3). The crude adipic acid concentrate is sent to a "crude crystallizer" 46 containing an upper member and a lower member as shown. Crystals pass to the base of the lower member. The feed enters this "crude crystallizer," from the top of which liquid can be withdrawn and sent through a cooler, equipped with a liquid seal 47. From the bottom of the lower member of the "crude crystallizer" a slurry is withdrawn recirculated to the said lower member, a purge from this recirculation line being sent to centrifuges 48 and 49 in parallel.

From these centrifuges 48 and 49 the liquid effluent ("nitric mother liquor") is withdrawn, and the wet adipic acid cake in the centrifuges is thereafter washed with "water mother liquor," which is obtained as described below. From the latter operation the liquid is the "centrifuge wash water," referred to in Figure 2, which is sent to a wash water hold-up tank 50 and subsequently fed to the concentrating still 40. The washed cake from centrifuges 48 and 49 is dissolved in water in solution tank 51. The solution is preheated (53) and sent to a stripping column 54 and condenser for withdrawal of a monobasic acid-containing purge called "MBA Stripper Make." The tails from the stripping column 54 are cooled and conducted to the refining crystallizer 52.

From the refining crystallizer 52, having a lower member and an upper member, the slurry withdrawn at the lower portion is continuously circulated through the pump 58 to the centrifuges 59 and 60, a return line to the crystallizer being also provided as shown. These

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centrifuges produce refined adipic acid which is thereafter removed, dried (61), cooled (62) and stored. The mother liquor ("water mother liquor") which is withdrawn from the centrifuges 59 and 60 is collected in a tank 66 and withdrawn as needed for wash water to centrifuges 48 and 49. Water used to wash the wet adipic acid cake on centrifuges 59 and 60 is sent to tank 67 where it is admixed with make-up water and sent to the solution tank 51. From the refined crystallizer 52 a portion of the mother liquor is decanted and conducted to a storage tank 66. A portion of this is withdrawn as rinse water for the crude centrifuges 48 and 49 and the remainder is added to the solution tank 51.

A part of the "nitric mother liquor," referred to in Figure 3, from centrifuges 48 and 49 is withdrawn from storage tank 55 as needed for feed to purge crystallizer 57 wherein it is cooled further. The crystals thus produced being removed by a rotary vacuum filter 64. The mother liquor ("purge mother liquor," referred to in Figure 2), is sent to the "purge mother liquor" storage tank 56 from which it is withdrawn as needed for feed to the evaporator as shown in Fig. 2. The wet adipic acid cake is out from the rotating drum into a line leading to the crude crystallizer 45. The wet cake is conveyed through the line by slushing with water.

In the process hereinabove described the relative rates of flow in the various purge lines can be adjusted at the discretion of the operator to prevent buildup of any undesirable constituents in the reaction system.

The reaction conditions specified above for the nitric acid oxidation step can be varied somewhat. Thus the oxidation temperature in the low temperature oxidizers is generally between 40° and 90° C., preferably 60° to 80° C., while in the high temperature oxidizers it is generally between 90° and 120°, preferably about 105° C. The ratio of nitric acid to organic feed in the recirculated mixture is generally within the range of 5:1 to 40:1, preferably 15:1 to 25:1. The pressure in the oxidizers is generally from 2 to 10 atmospheres. The weight ratio of HNO<sub>3</sub>: organic feed in the oxidizers should preferably be 2.5:1 to 6.0:1. The bleacher is operated at 70° to 110° C., preferably about 90° to 110° C.

The use of "Wet KA" or "Wet KA-KALL" (the non-volatile part of the "KALL" may be treated with a selective solvent as disclosed in Example 3 for recovering an additional amount of adipic acid, if desired) instead of "Whole Crude KA" as hereinabove described increases quite surprisingly the overall rate of production of adipic acid from a plant of given size, and when rates of production, rather than cyclohexane consumption, are of paramount importance, the present invention is of outstanding utility.

#### EXAMPLE 1.—EFFECT OF USING OIL DISTILLATE FROM STEAM DISTILLATION OF "WHOLE CRUDE KA" IN THE NITRIC ACID OXIDATION OF PRIMARY OXIDATION PRODUCTS OF CYCLOHEXANE

In a plant for manufacturing adipic acid from cyclohexane by liquid phase air oxidation followed by nitric acid oxidation of primary oxidation products (cf. U. S. Patents 2,439,513 and 2,557,282), the initial air oxidation step was carried out continuously in batteries of three autoclaves connected in series, each autoclave being equipped with a condenser for removal of water as formed (pressure, 130 pounds per sq. in. gauge; catalyst cobalt naphthenate, 1 p. p. m. cobalt; temperature 153° C.; total conversion, 11%; air rate, 11 volumes (S. T. P.) per unit volume of reactor space per hour). The separation of crude products was carried out as shown in Fig. 1, as above described. The nitric acid oxidation step in these experiments was performed under the conditions described above, in connection with Figures 2 and 3. Comparisons were made to show the effect of using this oil instead of "Whole Crude KA" in the nitric acid oxidation step.

The oil contained 65.5% of the organic matter in "Whole Crude KA" and contained 10.7% water. The remainder of the organic matter present in "Whole Crude KA" was essentially non-volatile with steam and amounted to 34.5% of the organics charged. This oil was produced, as stated hereinabove, at a cyclohexane conversion (i. e. percentage of fed cyclohexane oxidized to all products) of 11%. An analysis of the oil (basis, anhydrous components in "Whole Crude KA"=100%) at this conversion was as follows: Cyclohexanol 29.2%, cyclohexanone,

26.5%; cyclohexyl formate, 3.49% high boiling esters calculated as cyclohexyl valerate, 1.93%; 1,2-cyclohexanediol, 0.53%; and monobasic acids calculated as valeric, 3.29%. The effect of using this oil distillate upon quantity of succinic and glutaric acids produced in the nitric acid oxidation step is shown in Table II.

Table II.—Oxidation of adipic acid precursors, "Whole Crude KA," and distilled "KA"

Description of Organic material	"Whole Crude KA"	"KA" of Example 1
Yield in terms of lbs. of product per lb. of anhydrous organic feed:		
Adipic acid.....	0.921	1.205
Glutaric acid.....	0.119	0.049
Succinic acid.....	0.071	0.019
lbs. of Nitric acid consumed per lb. of adipic acid synthesized.....	1.28	1.02

#### EXAMPLE 2.—EFFECT OF USING "WET KA" INSTEAD OF "WHOLE CRUDE KA" IN THE NITRIC ACID OXIDATION

The oxidation process illustrated in Example 1 was modified by using, as the nitric acid oxidizer feed, "Wet KA" obtained as shown in Fig. 1. The results were as shown in Table III. These results show that the quality of the feed for nitric acid oxidation was substantially better than when "Whole Crude KA" was used. By this method of operation the crude cyclohexane oxidation product is treated with water and two layers were formed as shown in Fig. 1. The upper hydrocarbon layer and the steam volatile portion of the aqueous lower layer ("KALL") were admixed and processed in the hydrocarbon stripping column. After removal of hydrocarbon by stripping in the above described operation, the residue was subjected to exhaustive steam distillation with water layer reflux and subsequent dehydration of the non-volatile residue. Nitric acid oxidation of the oil distillate by the method above-described gave results shown in the following table.

Table III.—Oxidation of adipic acid precursors, "Wet KA" process

Description of Organic Feed	"Wet KA"
Yield in terms of lbs. of product per lb. of anhydrous whole crude "KA":	
Adipic acid.....	0.901
Glutaric acid.....	0.076
Succinic acid.....	0.032
lbs. of nitric acid consumed per lb. of adipic acid synthesized.....	1.08

#### EXAMPLE 3.—EFFECT OF USING "WET KA" SUPPLEMENTED WITH SELECTED "KALL" NON-STEAM-VOLATILE PRODUCTS IN THE NITRIC ACID OXIDATION

To determine the effect of using a selective solvent to effect a favorable partition between adipic, glutaric, and succinic acids and their respective precursors, contained in "KALL," a specimen of "KALL" from which volatiles had been stripped was agitated with one-half of its weight of chloroform. The chloroform extract was separated and the residue, freed of chloroform, was subjected to nitric acid oxidation under the plant conditions described above. For comparison, an untreated "KALL" sample, freed of steam volatile ingredients, also was oxidized in a similar manner. The results of nitric acid oxidizing the untreated and chloroform-treated "KALL" residues are shown in Table IV.

Table IV.—Selective extraction of glutaric and succinic acids, or precursors thereof, from "KALL" residue

Description of Organic Feed	Untreated "KALL" Residue	Chloroform-Treated "KALL" Residue
Yield in terms of lbs. of product per lb. of anhydrous KALL Organics:		
Adipic acid.....	0.553	0.508
Glutaric acid.....	0.220	0.044
Succinic acid.....	0.138	0.036
lbs. of nitric acid consumed per lb. of adipic acid synthesized.....	1.30	0.59

While the foregoing examples serve to illustrate the best methods of practicing the invention, it should be recognized that the illustrated procedures are not the only ones which can be used. For instance, in Example 2, the process can be modified by supplementing the nitric acid oxidizer feed with at least a part of the tails from the lower layer stripper 8, as shown in Fig. 1. Other modifications which concern the oxidation conditions are also possible. For example, a wide variety of catalysts may be used in place of copper and vanadium compounds in the nitric acid oxidation step, and the selection of particular catalysts in that step is not a part of the present invention. Moreover, the quantities of catalysts may be varied quite widely. For example, the nitric acid may contain as much as 0.3% of copper, or even more, without any serious disadvantage.

The invention is highly useful in improving the large scale manufacture of high quality adipic acid, employed in the production of nylon. The value and utility of the invention can be more fully understood by considering the fact that "Wet KA" contains only about 63 to 66% of the organic matter in the "Whole Crude KA," yet yields about 90% as much as adipic acid as does the latter mixture. This means that the productivity of the nitric acid oxidation plant is increased, in terms of adipic acid produced per unit weight of organic materials charged, by as much as 40%, by using the "Wet KA" process of this invention, while the amount of nitric acid consumed, per pound of adipic acid produced, as well as the quantity of nitrogen oxides requiring recycle, is also considerably lowered. These improvements are achieved without loss of any of the adipic acid derived through cyclohexanol or cyclohexanone, and without loss of a major part of the other adipic acid precursors present in the total crude product obtained in the liquid phase air oxidation of cyclohexane.

While the embodiments of the invention hereinabove described in detail are the ones which are best employed in completely new installations for the manufacture of adipic acid, it will be appreciated that certain modifications thereof are desirable where the objective is to convert an already existing plant, originally designed for production of "Whole Crude KA," and oxidation thereof of adipic acid by air or nitric acid oxidation. For converting such a plant to one applying the present invention, it is advisable in certain instances to separate the lower layer from the oxidizer effluent (water having been injected therein), strip steam-distillable oil therefrom, and combine the said oil with oil distillate obtained by steam distilling the hydrocarbon layer after recovery of hydrocarbon. In this method of operation, as in the other embodiments hereinabove described, it is significant that the water which is injected into the oxidizer effluent has the effect of extracting into the lower layer some of the oxidized organic matter present in the hydrocarbon phase. In fact, it is desirable to inject water in sufficient quantity (ca. 0.1 to 0.5 part by weight per unit weight of the resulting aqueous layer) to dissolve solid matter, and to reduce losses of non-volatile ingredients by extraction of an appreciable quantity of such ingredients from the hydrocarbon phase into the aqueous phase. Such extraction facilitates the direct recovery of adipic acid (cf. steps 10 and 11, Fig. 1). The water which is injected is preferably condensate water which has been withdrawn to a storage tank from one or more of the steam distillate decanters (cf. 18, Fig. 1). The effluent, prior to injection of this water is relatively water-free, because, as is known in the art, the cyclohexane oxidizers are preferably equipped with condensers which continuously remove water as condensate substantially as fast as it is formed by the oxidation reaction.

We claim:

1. In the process for manufacturing adipic acid by oxidizing cyclohexane in the liquid phase to primary oxidation products comprising chiefly cyclohexanol and cyclohexanone, with molecular oxygen, followed by oxidation of primary products to adipic acid by means of nitric acid, the improvement which consists in employing as the oxidizable feed to the nitric acid oxidizer the oil distillate obtained by injecting water into the effluent from a liquid

phase cyclohexane oxidation reaction vessel, separating the hydrocarbon and aqueous phases in the resulting mixture, removing steam distillable oil from said aqueous phase, adding said oil to the said hydrocarbon phase, stripping substantially all of the hydrocarbon from the resulting mixture, and exhaustively steam distilling the resulting residue whereby an oil which is suitable for use as the oxidizable feed to the nitric acid oxidizer is obtained.

2. Process of claim 1 wherein the liquid phase oxidation of cyclohexane with molecular oxygen is carried out at a temperature between 50° and 175° C. under a pressure of 50 lbs. and 150 lbs. per sq. in. and the oxidation is continued until the conversion of cyclohexane is within the range of from 5% to 30%, the nitric acid oxidation step being carried out in two temperature stages the temperature in the first stage being between 40° and 90° C. while the temperature in the second stage is between 90° and 120° C., the weight ratio of nitric acid: organic feed in the nitric acid oxidizers being 2.5:1 to 6.5:1, the pressure in the nitric acid oxidation step being maintained within the range of from 2 to 10 atmospheres.

3. In the process for manufacturing adipic acid by oxidizing cyclohexane in the liquid phase with molecular oxygen to primary oxidation products comprising chiefly cyclohexanol and cyclohexanone, followed by oxidation of primary products to adipic acid by means of nitric acid, the improvement which comprises employing as the feed to the nitric acid oxidizer the mixture of cyclohexane oxidation products, comprising chiefly cyclohexanol and cyclohexanone, obtained by injecting water into the effluent from a liquid phase cyclohexane oxidation reaction vessel, separating the hydrocarbon and aqueous phases in the resulting mixture, said aqueous phase containing material extracted from said hydrocarbon phase by the said injected water, and steam distilling the said aqueous phase, whereby a residue containing non-steam-distillable organic matter is obtained, excluding at least a part of the said organic matter from the nitric acid oxidizer feed and including substantially all of the steam-distillable oil in the remainder of the cyclohexane oxidation product, other than recovered hydrocarbon.

4. Process of claim 3 wherein 5 to 30% of the said cyclohexane is oxidized by the said molecular oxygen.

5. Process of claim 4 wherein the quantity of injected water is from 0.1 to 0.5 times the weight of aqueous layer.

6. Process of claim 5 wherein the only oxidizable organic material included in the nitric acid oxidizer feed is the said steam-distillable oil.

7. In the process for manufacturing adipic acid by oxidizing cyclohexane in the liquid phase with molecular oxygen to primary oxidation products comprising chiefly cyclohexanol and cyclohexanone, followed by oxidation of primary products to adipic acid by means of nitric acid, the improvement which comprises employing as the feed to the nitric acid oxidizer the mixture of cyclohexane oxidation products, comprising chiefly cyclohexanol and cyclohexanone, obtained by continuing the liquid phase oxidation with molecular oxygen until from 5 to 12% of the cyclohexane is oxidized, while removing as condensate substantially all of the water produced by the oxidation reaction, injecting water into the effluent from the oxidation vessel wherein the said conversion is reached, the quantity of the said injected water being from 0.1 to 0.5 times the total weight of the resulting aqueous layer, separating the hydrocarbon and aqueous phases in the resulting mixture, said aqueous phase containing material extracted from hydrocarbon phase by said injected water, exhaustively steam distilling said aqueous phase, whereby a residue containing non-steam-distillable organic matter and a steam-distilled oil is obtained, excluding at least a part of the said non-steam-distillable organic matter from the nitric acid oxidizer feed, and including in the feed to the nitric acid oxidizer substantially all of the steam distillable ingredients of the cyclohexane oxidation product other than recovered hydrocarbon.

No references cited.