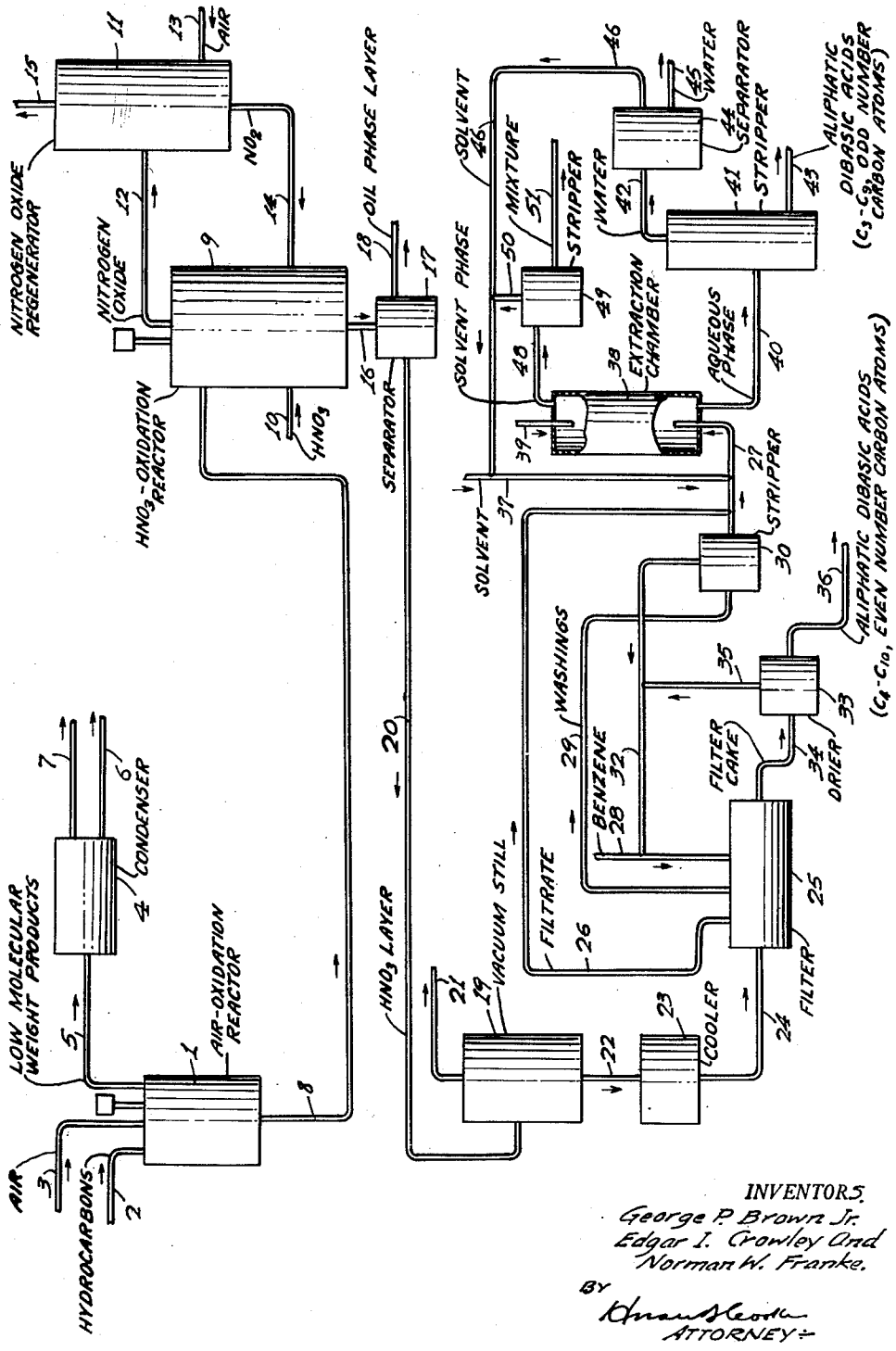
Nov. 20, 1956 G. P. BROWN, JR., ET AL 2,771,482

NITRIC ACID OXIDATION OF HYDROCARBONS

Filed Aug. 26, 1953



INVENTORS.
George P. Brown Jr.
Edgar I. Crowley and
Norman W. Franke.

BY
Howard Keck
ATTORNEY

United States Patent Office 2,771,482 Patented Nov. 20, 1956

2,771,482

NITRIC ACID OXIDATION OF HYDROCARBONS

George P. Brown, Jr., West Deer Township, Allegheny County, Edgar I. Crowley, Pittsburgh, and Norman W. Franke, Penn Township, Allegheny County, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

Application August 26, 1953, Serial No. 376,616

17 Claims. (Cl. 260—452)

This invention relates to oxidation processes for converting saturated aliphatic hydrocarbons to organic acids and more particularly to oxidation processes for converting saturated aliphatic hydrocarbons to dibasic acids.

Oxidation of hydrocarbons to produce dibasic acids is known in the art. Thus, it has been shown, as in U. S. Patent No. 2,452,741 to Fleming, that cyclo-paraffins can be oxidized in air and with nitric acid in a two-stage process to produce dibasic acids. It has not been shown, however, how much process can be carried out to produce high yields of dibasic acids while maintaining the amounts of nitric acid at a minimum. It is not apparent from such process that the degree of oxidation in air in the first stage is important or critical nor that the specific manner in which the reaction with nitric acid in the second stage takes place can aid in cutting down on the amount of nitric acid needed in the second stage. Moreover, it is not apparent from such process that saturated aliphatic hydrocarbons can be similarly treated to obtain high yields of dibasic acids.

In the oxidation of saturated aliphatic hydrocarbons to produce dibasic acids, it has been known in the art to employ nitric acid as the oxidant. While the dibasic acids produced from such processes are satisfactory for commercial use, the amount of nitric acid necessary to obtain a high yield of dibasic acids is so large as to make the process commercially unattractive.

We have found that the amount of nitric acid needed to produce a high yield of dibasic acids in the nitric acid oxidation of saturated aliphatic hydrocarbons can be substantially reduced and the process made commercially attractive by subjecting a saturated aliphatic hydrocarbon to oxidation with air or other oxygen-containing gas, i. e., a gas containing free oxygen, for a time sufficient to obtain a product having a saponification number above about 100, and preferably between about 150 and about 450, and thereafter subjecting said product to further oxidation at an elevated temperature with nitric acid having a concentration above about 50, and preferably above about 60 percent, for a time sufficient to obtain substantial amounts of dibasic acids while admixing with the gaseous mixture comprising nitrogen oxides formed during said nitric acid reaction an oxygen-containing gas in amounts and for a time sufficient to regenerate said nitrogen oxides, and employing the products resulting from said regeneration in said nitric acid reaction.

Oxidation of saturated aliphatic hydrocarbons in the first stage of our process can be conducted satisfactorily either at atmospheric or elevated pressures. While oxidation of saturated aliphatic hydrocarbons in the first stage can be conducted at a temperature of about 100° C. to about 400° C., we have found that to facilitate oxidation in the first stage the oxidation is preferably conducted at a temperature of about 150° C. to about 190° C. The amount of air necessary to obtain the air-oxidized product is not critical and can vary from about

2.5 grams to about 10.0 grams per gram of air-oxidized product obtained. If oxygen is used, about 0.5 gram to about 2.0 grams per gram of air-oxidized product is sufficient.

During the oxidation of the air-oxidized products of saturated aliphatic hydrocarbons with nitric acid, the acid breaks down to form NO_2, NO, N_2O, nitrogen and some water. Additional water is present in the nitric acid reaction zone as the result of the oxidation of the air-oxidized products of saturated aliphatic hydrocarbons and, of course, since an aqueous solution of nitric acid is employed, some water is introduced into the nitric acid reaction zone with the acid. NO_2 dimerizes to form N_2O_4, which is in equilibrium with NO_2. NO_2, as well as N_2O_4, has been found to be an excellent oxidizing agent for air-oxidized products of saturated aliphatic hydrocarbons. Therefore, if the nitric acid reaction stage, or second stage, of our process is conducted in a container such that NO_2 formed during the process is prevented from escaping, NO_2 will react with the air-oxidized products of saturated aliphatic hydrocarbons in the nitric acid reactor. In addition, in the absence of substantial amounts of oxygen in the nitric acid reactor, NO formed will react with NO_2 to form N_2O_3, which is also believed to be an excellent oxidizing agent for air-oxidized products of saturated aliphatic hydrocarbons. At the same time, NO_2 and N_2O_3 will react with the water present to form nitrous as well as nitric acid, both of which are believed to be excellent oxidizing agents for the purpose of this invention. In this way, by utilizing NO_2, NO, water, other nitrogen oxides and nitrogen acids formed during the process as oxidants, the amount of nitric acid necessary in the second stage of our process for converting air-oxidized products of saturated aliphatic hydrocarbons to dibasic acids is substantially reduced.

We have additionally discovered that some of the nitrogen oxides formed during the second stage of the process can be regenerated to higher oxides of nitrogen, and these higher oxides, as well as nitrous and nitric acids formed therefrom, can be employed as oxidants in the second stage of the process. We have found that the amount of air or other oxygen-containing gas, i. e., a gas containing free oxygen, necessary to regenerate the nitrogen oxides is not critical, although we prefer to use more than the theoretical amount to insure adequate regeneration. For example, we have found that 520 grams of air or 75 grams of oxygen per 100 grams of air-oxidized products of saturated aliphatic hydrocarbons and 500 grams of 70 percent nitric acid have been sufficient for purposes of regeneration. Regeneration can be conducted in the nitric acid reactor itself or in a separate regenerator.

In the event regeneration is conducted in the nitric acid reactor, air or other oxygen-containing gas is introduced into the reactor. NO_2 formed during the process remains unaffected by the presence of oxygen but NO preferentially reacts with oxygen rather than with NO_2 to form NO_2. NO_2 in the reactor will combine with water to form nitric acid and this acid, as well as free NO_3, is present in the second stage of our process.

If the regeneration is conducted in a separate regenerator, the nitrogen oxides formed are removed from the nitric acid reactor and passed to a separate regenerator. Air or other oxygen-containing gas is also passed to the regenerator. As stated, with no substantial amounts of oxygen in the nitric acid reactor, NO, NO_2, as well as N_2O_3, are formed and these are passed to the regenerator. NO_2 remains unaffected by the presence of oxygen but NO and N_2O_3 are regenerated by the oxygen to NO_2. The NO_2 already present, as well as the NO_2 formed in the regenerator, is condensed therein

and recycled to the nitric acid reactor where the NO_2 reacts with the air-oxidized products of saturated aliphatic hydrocarbons as such or is converted by reaction with water to nitric acid. In the regenerator the NO_2 can combine with water to form nitric acid which is recycled to the nitric acid reactor.

While the amount of nitric acid employed in the nitric acid reaction zone is not critical and may be varied over a wide range, provided sufficient acid is present for the desired oxidation, we have found that charging about 2.5 to about 20 parts of aqueous nitric acid per part of air-oxidized product of saturated aliphatic hydrocarbon to the nitric acid reaction zone is sufficient to obtain the desired dibasic acids.

The pressure in the nitric acid reaction zone is similarly not critical and can be varied over a wide range, from about atmospheric to about 1,000 pounds per square inch. We prefer, however, to operate at elevated pressures to facilitate precipitation and condensation of the nitrogen oxides. For best results, we prefer to operate at a temperature of about 50° C. to about 150° C., preferably about 75° C. to about 130° C., in the nitric acid reaction zone. The residence time for the saturated aliphatic hydrocarbons in the nitric acid reaction zone necessary to obtain substantial amounts of dibasic acids varies inversely with temperature. For example, about the same amount of reaction is obtained in a period of about 30 hours at about 75° C. as is obtained in less than about two hours at about 130° C. The reaction can be carried out at a constant temperature or the temperature can be varied with time. For example, the reaction can be started out at a low temperature, say 50° C., and the temperature gradually raised to a selected maximum temperature and the reaction can be discontinued when the maximum temperature is reached or the reaction can be maintained at the selected maximum temperature for the desired length of time.

Saturated aliphatic hydrocarbons boiling above about 250° F. and having about eight or more carbon atoms or mixtures thereof can be employed as charge stock for the production of dibasic acids in accordance with our process, although, for ease of operation, we prefer to employ saturated aliphatic hydrocarbons having from about 10 to about 40 carbon atoms. Included among the saturated aliphatic hydrocarbons which can be employed in our process are petroleum waxes, paraffinic oils, foots oil, oils and waxes obtained from the Fischer-Tropsch process, n-octane, decane, cetane, etc. While we prefer to employ charge stocks consisting of saturated aliphatic hydrocarbons, we can also employ charge stocks which are predominantly saturated aliphatic hydrocarbons and which can contain cycloparaffins. Such charge stocks can be prepared from a variety of types of crude oils. When the crude oil is essentially paraffinic, the charge may be recovered by distillation but where the crude oil is of a mixed type, various combinations of treatments can be employed to obtain the charge, such as distillation and solvent extraction, distillation and crystallization, or chromatographic separation.

A method of carrying out our invention employing a first stage air oxidation and a second stage nitric acid oxidation wherein the second stage of the process is conducted in a closed container and the nitrogen oxides formed therein are regenerated in a separate regenerator and recycled to the second stage of the process, may be illustrated by referring to the single drawing which describes a flow diagram of such typical procedure. For simplicity, valves, gauges, etc., not needed for an understanding of the invention have been omitted. The drawing is hereby incorporated and made a part of the present specification.

A saturated aliphatic hydrocarbon is charged into oxidation reactor **1** by line **2** and an oxygen-containing gas such as air by line **3**. The saturated aliphatic hydrocarbon is vigorously agitated at an elevated temperature in reactor **1** for a time sufficient to obtain an oxidized product having a saponification number above about 100 and preferably between about 150 and about 450. A catalyst such as vanadium pentoxide can be employed to facilitate oxidation in reactor **1**. Volatilized lower molecular weight products produced during the air-oxidation step are removed overhead from reactor **1** and passed to condenser **4** by line **5**. The condenser is preferably maintained at a temperature of about 35° F. to about 90° F. by any suitable means. Any temperature sufficient to condense a large part of the volatilized lower molecular weight products can be employed. The condensed lower molecular weight products in condenser **4** resolve themselves into two phases, an upper organic phase comprising oxidized hydrocarbons, including lower organic acids, esters and aldehydes, and a lower aqueous phase comprising formic, acetic and propionic acids, and are removed from condenser **4** by line **6**. Uncondensed lower molecular weight products comprising excess air, nitrogen, carbon monoxide and carbon dioxide are removed from condenser **4** by line **7**.

The air-oxidized product is removed from reactor **1** by line **8** and passed to nitric acid reactor **9**, and nitric acid is led to reactor **9** by line **10**. The pressure in reactor **9** is maintained at an elevated pressure. The nitric acid reactor can be a stainless steel pressure vessel equipped with a stirrer and, in the instant embodiment, is provided with a nitrogen oxide regenerator **11**. The air-oxidized product and nitric acid are heated in reactor **9**, by means not shown, and stirred. If desired, reactor **9** can be operated continuously, in which case a coil-type reactor or a number of vessels in series can be employed. Nitrogen oxides formed during the process are removed overhead from reactor **9** by line **12** and passed to nitrogen oxide regenerator **11**. A controlled amount of air or other oxygen-containing gas is introduced by line **13** into regenerator **11** and, as noted, N_2O_3 and NO, are regenerated therein to NO_2 which, along with the NO_2 already present, is condensed therein and recycled by line **14** to reactor **9**. The pressure in regenerator **11** is of the same order as that existing in reactor **9** and the temperature is sufficiently low, from about 80° F. to about 0° F., preferably from about 40° F. to about 20° F., so as to enable the NO_2 in the gases to condense and be returned to reactor **9**. N_2, N_2O and CO_2, as well as excess oxygen-containing regenerating gas, are removed overhead from regenerator **11** by line **15**.

At the end of the reaction period in reactor **9**, the oxidized product, which may comprise an upper oil-phase layer and a lower nitric acid layer, is removed from the reactor by line **16** and passed to separator **17** which is maintained at a temperature of about 100° F. to about 40° F. and preferably about 80° F. to about 60° F. The upper oil-phase layer, if present, may amount to about 10 percent (based on air-oxidized charge), and generally comprises a mixture of C_4 to C_{12} dibasic and C_6 to C_{20} monobasic acids. The oil-phase layer, if present, is decanted and removed from separator **17** by line **18** and the nitric acid layer is sent to vacuum still **19** by line **20**. Nitric acid is removed overhead from vacuum still **19** by line **21** and can be sent to an absorption tower, where the nitric acid can be reconcentrated with fresh NO_2 and air, or can be sent to a distillation zone where it can be reconcentrated by distillation. If desired, nitric acid so obtained and so reconcentrated can be recycled to line **10** for use in reactor **9**.

The residue from vacuum still **19**, discharged through line **22** to cooler **23**, comprises a slurry of solid and liquid acids. The slurry is cooled, preferably to a temperature of about 75° F. to about 65° F., and allowed to stand in cooler **23** for several hours to permit crystallization of some of the dibasic acids present in the slurry. The slurry in cooler **23** is then removed by line **24** and is passed to filter **25**, which can be a plate and frame press. The filtrate from this filtration step is removed

by line 26 and passed to line 27 and, after sufficient filter cake has formed in filter 25, filtration is stopped and the cake is washed with benzene from line 28. The benzene washings are removed from filter 25 by line 29 and passed to stripper 30. Benzene is removed overhead from stripper 30 and recycled by line 32 to line 28, and that remaining from the benzene washings not going overhead in line 32 is passed to line 27. The filter cake, after the benzene washings, is transferred to dryer 33 by conveyor line 34. In dryer 33, any benzene present in the filter cake is removed overhead by line 35 and recycled to line 28 by means of line 32. The residue from dryer 33 is removed therefrom by conveyor line 36 and comprises a mixture of aliphatic dibasic acids.

To the filtrate and the residue remaining from the benzene washings in line 27 is added any solvent or diluent which would have a preferential attraction for monobasic acids, such as diethyl ether, ethylpropyl ether, dipropyl ether, dimethyl ether, benzene, carbon tetrachloride, ethyl carbonate, chloroform, trichloroethylene, etc., through line 37, and the resulting solution is passed upwardly into the base of extraction chamber 38. We have found diethyl ether to be especially effective in our process, and our discussion will be with reference to it. Water or a dilute aqueous solution of a mineral acid such as hydrochloric acid, nitric acid, etc., is introduced into the top of chamber 38 by line 39 and is mixed therein with the solution entering from line 27, resulting in a lower aqueous phase and an upper ether phase.

The aqueous phase is removed from the base of chamber 38 by line 40 and passed to stripper 41. Water is stripped from the aqueous phase in stripper 41 and removed overhead by line 42, while a mixture comprising aliphatic dibasic acids is removed by line 43. Water in line 42 is passed to separator 44, wherein water is removed by line 45 and any ether which may have been carried by the water is removed by line 46 and recycled to line 37.

The ether phase is removed overhead from chamber 38 by line 48 and passed to stripper 49, wherein ether is removed by line 50 and recycled to line 37 by line 46, and a complex mixture comprising higher dibasic acids, monobasic acids and nitrogen-containing acids is removed by line 51. If desired, the acids removed in line 51, as well as any upper oil-phase layer removed from separator 17 by line 18, can be recycled to either air-oxidation reactor 1, nitric acid reactor 9 or both.

The product obtained in line 36 comprises a mixture of aliphatic dibasic acids containing from about 4 to about 10 carbon atoms, predominantly acids having an even number of carbon atoms, and the product obtained in line 43 comprises a mixture of aliphatic dibasic acids containing about 3 to about 9 carbon atoms per molecule, predominantly acids having an odd number of carbon atoms.

The following example shows the large amount of nitric acid needed in a typical nitric acid oxidation process for converting paraffin hydrocarbons to dibasic acids.

EXAMPLE 1

100 parts of a 132° F. melting point refined paraffin wax and 400 parts of 90 percent nitric acid were placed in a glass flask equipped with a reflux condenser and a stirrer. The mixture was heated to 75° C. and maintained at that temperature for 30 hours. The stirrer was operated during the entire period to insure thorough mixing of the reactants. During the course of the experiment 3,150 parts of 97 percent nitric acid was added to maintain the acid concentration at 90 percent. At the end of 30 hours the reaction was complete as shown by the disappearance of the wax phase. After removal of the nitric acid by distillation under vacuum, the product was a viscous liquid containing suspended solids. 65.8 parts of a mixture of dibasic acids was recovered from the crude product by the combination of filtration and ether water extraction. 2,323 parts of 90 percent nitric acid was recovered from the experiment indicating a consumption of 19.9 parts of nitric acid (as 100 percent HNO_3) per part of dibasic acid produced.

In order to show the substantial decrease in the consumption of nitric acid in contrast to a conventional process as disclosed above in Example 1, we have run the following typical experiment in accordance with our invention.

EXAMPLE 2

110.2 parts of a 132° F. melting point refined paraffin wax was placed in a flask equipped with a stirrer and a condenser. The wax was heated to 160° C. and maintained at that temperature while air was blown through the molten wax. The wax was stirred vigorously throughout the reaction period of 19.5 hours. 100 parts of the air-oxidized wax having a saponification number of 232 was obtained. In addition to the air-oxidized wax, 5.7 parts of a mixture, consisting principally of formic, acetic and propionic acids, and 14.4 parts of a mixture of volatile aldehydes, esters and other oxygenated compounds, were also recovered as condensate from the exhaust air stream.

The 100 parts of air-oxidized wax was placed in a stainless steel stirred autoclave along with 500 parts of 70 percent nitric acid. A second pressure vessel was connected to the top of the autoclave in such fashion that the lower oxides of nitrogen given off during the reaction passed into the second vessel, where they were regenerated with air to higher oxides which were then condensed on a cooling coil in the vessel and returned by gravity through a line to the reaction vessel. The contents of the reaction vessel were maintained at 90° C. for 30 hours. The stirrer was operated during the reaction period to insure mixing of the reactants, and air was passed through the auxiliary vessel throughout the reaction period to reoxidize the nitrogen oxides. The products from the run were treated as in Example 1, and 53.1 parts of dibasic acids and 460 parts of 55 percent nitric acid were recovered from this experiment. The consumption of nitric acid is, therefore, 1.82 parts (as 100 percent HNO_3) per part of dibasic acid recovered.

A comparison of the results obtained in Example 2, run in accordance with one method of operating our invention, with those obtained in Example 1, which is typical of a conventional nitric acid oxidation process for converting paraffin hydrocarbons to dibasic acids, shows that we are able to obtain more than a tenfold reduction in the consumption of nitric acid. Thus, by preoxidizing the saturated aliphatic hydrocarbons in air prior to treatment with nitric acid, the amount of oxidation necessary in the nitric acid reactor to produce dibasic acids is substantially reduced, resulting in a substantial reduction of nitric acid consumed per part of dibasic acids produced. By regenerating a portion of the nitrogen oxides to higher oxides of nitrogen, and in turn converting a portion of the latter oxides of nitrogen to nitric acid, we are able to utilize the nitric acid more efficiently than if the reaction were conducted in such a way that the nitrogen oxides formed in the process were removed and permitted to escape from the reaction area.

The importance of regenerating the nitrogen oxides formed during the nitric acid reaction stage of the process can be shown by comparing the results obtained in the following example with those in the previous examples.

EXAMPLE 3

100 parts of a 132° F. melting point refined paraffin wax and 500 parts of 70 percent nitric acid were charged to a rocking autoclave which was then sealed. The autoclave and contents were heated to 90° C. and maintained at that temperature for 30 hours during which

time gaseous oxygen was added. The yield of dibasic acid recovered from this experiment was 37.7 percent, and the nitric acid consumption was 2.23 parts (as 100 percent HNO_3) per part of dibasic acid recovered.

The economy in nitric acid consumption brought about merely by regenerating and using the nitrogen oxides formed during the nitric acid reaction stage of the process is evident from comparison of the nitric acid consumptions in Examples 1 and 3. However, the yield of dibasic acids in Example 3 is relatively low and the consumption of nitric acid is still higher than desired in commercial operations. As shown in Example 2, improvement in yield of dibasic acids and consumption of nitric acid is obtained in the two-stage process with regeneration and use of the nitrogen oxides formed during the second stage of the process.

While Example 2 illustrates the saving in nitric acid consumption in a two-stage oxidation process in which nitrogen oxides are regenerated in an outside regenerator and recycled to the nitric acid reactor, the following example illustrates the reduction obtained in nitric acid consumption by introducing the oxygen-containing gas in the nitric acid reactor and regenerating the nitrogen oxides therein.

EXAMPLE 4

110.2 parts of a 132° F. melting point refined paraffin wax was placed in a glass flask equipped with a stirrer and a reflux condenser. The wax was heated to 160° C. and maintained at that temperature for 12.8 hours, during which period the wax was stirred and air blown therethrough. 100 parts of air-oxidized wax having a saponification number of 238 was recovered. To the 100 parts of air-oxidized wax was added 500 parts of 70 percent nitric acid and the mixture charged to a stainless steel rocking autoclave. The reactor and contents were heated to 90° C. over a period of 4 hours and maintained at that temperature for 26 hours more, during which time gaseous oxygen was added. The yield of dibasic acid from this experiment was 53.9 percent and the nitric acid consumption was 1.04 parts of nitric acid (as 100 percent HNO_3) per part of dibasic acid recovered.

While in Example 4 we have shown the reduction obtained in nitric acid consumption by introducing the oxygen-containing gas in the nitric acid reactor and regenerating the nitrogen oxides therein, where the charge consists of a refined paraffin wax, the following example illustrates a similar type of operation where the charge consists of recrystallized foots oil.

EXAMPLE 5

211 parts of foots oil obtained from sweating of paraffin wax was dissolved in a solution comprising 90 percent by volume of acetone and 10 percent by volume of trichloroethylene, in the proportion of one kilogram of foots oil to three liters of the solvents, by heating at a temperature of about 50° C. The resulting solution was chilled to a temperature of about 0° C. over a period of about 5 hours, after which it was filtered. The resulting wet cake was again dissolved in three liters of the same solvent by heating to about 50° C. The latter solution was chilled to a temperature of about 0° C. over a period of about 5 hours, after which it was filtered, resulting in a wet cake comprising recrystallized foots oil and some solvent. After drying of the wet cake a yield of 56.5 percent of recrystallized foots oil was obtained.

119 parts of the recrystallized foots oil so obtained was air oxidized at a temperature of about 180° C. for about 8.5 hours to obtain 100 grams of a product having a saponification number of about 185. The product was placed in a stainless steel rocking autoclave with 500 parts of 70 percent nitric acid. Gaseous oxygen was introduced intermittently into the autoclave which was held at a temperature of about 90° C. for a period of about 30 hours. The yield of dibasic acids from this run was 51.6 percent and the nitric acid consumption was 1.10 parts of nitric acid (as 100 percent nitric acid) per part of dibasic acid recovered.

As shown in Examples 4 and 5, our two-stage oxidation process, including regeneration of nitrogen oxides in the nitric acid reactor, shows a marked reduction in nitric acid consumption over the conventional single stage nitric acid oxidation process and, in fact, shows a reduction in the amount of nitric acid consumed over the process set forth in Example 2 wherein regeneration of nitrogen oxides is conducted in a separate regenerator.

While the reduction of nitric acid in our process depends to a large extent on the manner in which the second stage thereof is conducted, such reduction is likewise dependent upon the extent to which the saturated aliphatic hydrocarbons are oxidized in the first stage. This is shown in the data in the following table. The experiments reported in the table were made as in Example 4 and experiment 3 in the table is, in fact, Example 4.

Table I.—Effect of saponification number of air-oxidized wax on yield

Experiment No.	1	2	3	4
Saponification No. of Charge to Nitric Acid Stage	0	148	238	382
Yield of Dibasic Acids, percent of Charge to Nitric Acid Stage	37.7	46.9	53.9	57.8
Yield of Dibasic Acids, percent of Total Product	34.3	50.6	57.1	73.4
Nitric Acid Consumption Parts/Part of Dibasic Acid	2.23	1.36	1.04	1.22
Gaseous Oxygen Consumption Parts/Part of Dibasic Acid	1.63	1.20	1.01	0.76

From these data it is evident that controlled air oxidation prior to nitric acid oxidation results in improved yields of dibasic acids and reduced oxidant consumption. While it is true that the air used in the first stage of the process is part of the total oxygen employed, the cost or difficulty of air blowing at atmospheric pressure is trivial compared to the cost or difficulty of oxidation with nitric acid and compressed oxygen in a pressurized reactor.

Another unexpected observation in our process is illustrated in the data in Table II. These data are the results of runs which were made under the same conditions except that the concentration of the nitric acid in the second stage was varied as shown. Run No. 2 in this table is Example 4 shown above.

Table II.—Effect of nitric acid concentration upon yield of dibasic acids

Experiment No.	1	2	3
Nitric Acid Concentration, percent	90	70	50
Yield, percent of Air-oxidized Wax	60.5	53.9	27.4
Nitric Acid Consumption Parts/Part of Dibasic Acid	1.19	1.04	1.69

These data show increased yields of dibasic acids obtained with the higher concentrations of nitric acid. While the yield of dibasic acids with about 90 percent nitric acid is greater than that obtained with about 70 percent nitric acid, it is apparent that the nitric acid consumption per part of dibasic acid produced is at a minimum with about 70 percent nitric acid. Moreover, since the cost or difficulty of reconcentrating nitric acid above about 70 percent is out of proportion to a corresponding reconcentration below about 70 percent, minimum cost is obtained with about 70 percent nitric acid and this is especially preferred.

As previously noted, we have also found that the amount of time necessary to oxidize the preoxidized material in the second stage of the process can be substantially reduced by conducting the second stage at increased temperatures. This is shown in Example 6 where the

temperature in the nitric acid reaction stage is raised to about 110° C.

EXAMPLE 6

110.2 parts of 132° F. melting point refined paraffin wax was placed in a flask equipped with a stirrer and a condenser. The wax was heated to 160° C. and maintained at that temperature while air was blown through the molten wax. The wax was stirred vigorously throughout the reaction period of 19.5 hours. 100 parts of air-oxidized wax having a saponification number of 232 was obtained. To 100 parts of the air-oxidized wax in a stainless steel rocking autoclave was added 500 parts of 70 percent nitric acid. The contents of the vessel were maintained at a temperature above about 50° C. for a total of about 6 hours, of which about 2 hours were at about 110° C. Products from this run comprised 58.3 parts of dibasic acids. The consumption of nitric acid (as 100 percent HNO_3) amounted to 1.65 parts per part of dibasic acid recovered.

Thus, it will be apparent by comparing Example 6 with the preceding examples that the amount of time necessary to obtain a high yield of dibasic acids can be substantially reduced by conducting at least a portion of the second stage of the process at the higher temperatures.

Obviously, many modifications and variations of the invention, as hereinabove set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the production of dibasic acids from a charge stock consisting essentially of saturated aliphatic hydrocarbons boiling above about 250° F. and having at least eight carbon atoms, comprising subjecting the charge stock to oxidation with an oxygen-containing gas for a time sufficient to obtain a product having a saponification number above about 100 and thereafter subjecting said product to further oxidation at an elevated temperature of about 50° C. to about 150° C. with nitric acid having a concentration above about 50 percent for a time sufficient to obtain substantial amounts of dibasic acids while admixing with the gaseous mixture comprising nitrogen oxides formed during said nitric acid reaction an oxygen-containing gas in amounts and for a time sufficient to regenerate said nitrogen oxides, and employing the products resulting from said regeneration in said nitric acid reaction.

2. A process for the production of dibasic acids as in claim 1 wherein the charge stock is a petroleum wax.

3. A process for the production of dibasic acids as in claim 1 wherein the charge stock comprises recrystallized foots oil.

4. A process for the production of dibasic acids as in claim 1 wherein the concentration of the nitric acid is about 70 percent.

5. A process for the production of dibasic acids as in claim 1 wherein the concentration of the nitric acid is about 70 percent and the charge stock is a petroleum wax.

6. A process for the production of dibasic acids from a charge stock consisting essentially of saturated aliphatic hydrocarbons boiling above about 250° F. and having at least eight carbon atoms, comprising subjecting the charge stock to oxidation with an oxygen-containing gas for a time sufficient to obtain a product having a saponification number above about 100, and thereafter subjecting said product to further oxidation at an elevated temperature of about 50° C. to about 150° C. with nitric acid having a concentration above about 50 percent for a time sufficient to obtain substantial amounts of dibasic acids while introducing an oxygen-containing gas into the nitric acid reaction stage of the process in amounts and for a time sufficient to regenerate nitrogen oxides formed during the nitric acid reaction, and employing the products resulting from said regeneration in said nitric acid reaction.

7. A process for the production of dibasic acids as in claim 6 wherein the charge stock is a petroleum wax.

8. A process for the production of dibasic acids as in claim 6 wherein the charge stock comprises recrystallized foots oil.

9. A process for the production of dibasic acids as in claim 6 wherein the concentration of the nitric acid is about 70 percent.

10. A process for the production of dibasic acids as in claim 6 wherein the concentration of the nitric acid is about 70 percent and the charge stock is a petroleum wax.

11. A process for the production of dibasic acids from a charge stock consisting essentially of saturated aliphatic hydrocarbons boiling above about 250° F. and having at least eight carbon atoms, comprising subjecting the charge stock to oxidation with an oxygen-containing gas for a time sufficient to obtain a product having a saponification number above about 100, and thereafter subjecting said product to further oxidation at an elevated temperature of about 50° C. to about 150° C. with nitric acid having a concentration above about 50 percent for a time sufficient to obtain substantial amounts of dibasic acids while removing from the nitric acid reaction stage of the process a gaseous mixture comprising nitrogen oxides formed during the nitric acid reaction, passing said gaseous mixture to a regeneration zone, introducing an oxygen-containing gas into said regeneration zone to regenerate nitrogen oxides in the gaseous mixture, and recycling the products resulting from said regeneration to said nitric acid reaction.

12. A process for the production of dibasic acids as in claim 11 wherein the charge stock is a petroleum wax.

13. A process for the production of dibasic acids as in claim 11 wherein the charge stock comprises recrystallized foots oil.

14. A process for the production of dibasic acids as in claim 11 wherein the concentration of the nitric acid is about 70 percent.

15. A process for the production of dibasic acids as in claim 11 wherein the concentration of the nitric acid is about 70 percent and the charge stock is a petroleum wax.

16. A process for the production of dibasic acids from a charge stock consisting essentially of saturated aliphatic hydrocarbons boiling above about 250° F. and having at least eight carbon atoms, comprising subjecting the charge stock to oxidation with an oxygen-containing gas for a time sufficient to obtain a product having a saponification number above about 100 and thereafter subjecting said product to further oxidation at elevated temperatures of about 50° C. to about 110° C. for about 6 hours, of which about 2 hours are at about 110° C., with nitric acid having a concentration above about 50 percent for a time sufficient to obtain substantial amounts of dibasic acids while admixing with the gaseous mixture comprising nitrogen oxides formed during said nitric acid reaction an oxygen-containing gas in amounts and for a time sufficient to regenerate said nitrogen oxides, and employing the products resulting from said regeneration in said nitric acid reaction.

17. A process for the production of dibasic acids from a charge stock consisting essentially of saturated aliphatic hydrocarbons boiling above about 250° F. and having at least eight carbon atoms, comprising subjecting the charge stock to oxidation with an oxygen-containing gas for a time sufficient to obtain a product having a saponification number above about 100 and thereafter subjecting said product to further oxidation at an elevated temperature of about 50° C. to about 150° C. with nitric acid having a concentration above about 50 percent for a time sufficient to obtain substantial amounts of dibasic acids while admixing with the gaseous mix-

ture comprising nitrogen oxides formed during said nitric acid reaction an oxygen-containing gas in amounts and for a time sufficient to regenerate said nitrogen oxides, and employing the products resulting from said regeneration in said nitric acid reaction; removing unreacted nitric acid from the dibasic acid product, filtering said latter product to remove a fraction of dibasic acids and obtain a filtrate comprising a second fraction of dibasic acids, dissolving the filtrate in a low molecular weight aliphatic ether, extracting the ether solution with a solution comprising water to obtain an ether layer and an

aqueous layer and stripping water from the aqueous layer to recover said second fraction of dibasic acids.

References Cited in the file of this patent

UNITED STATES PATENTS

1,895,799	James	Jan. 31, 1933
2,009,664	James	July 31, 1935
2,298,387	Kenyon et al.	Oct. 13, 1942
2,365,290	Price et al.	Dec. 19, 1944
2,636,047	Riethof et al.	Apr. 21, 1953