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POLYBASIC ACIDS AND METHOD FOR PRODUCING THE SAME

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This invention concerns the oxidative treatment of selected hydrocarbons in liquid phase with a free oxygen-containing gas, such as air, oxygen-enriched air, or oxygen, under controlled oxidizing conditions to produce useful organic acids in relatively high yields. A feature of the invention resides in the production of oxidation products containing important amounts of recoverable dibasic acids of useful character from suitable hydrocarbons by continuing desirable oxidation reactions to relatively high oxidation levels while suppressing undesirable competing reactions. New acidic products produced by this method also are included in the scope of the invention.

It has been known for many years that certain hydrocarbons can be oxidized in liquid phase by the action of air or oxygen under conditions preventing complete combustion to produce acidic oxidation products. The reactions occurring are quite complex and although much has been published concerning the reaction mechanism, the exact nature thereof is still not fully known at this date. The oxidation products resulting from published methods are generally mixtures of various oxygen-containing substances including acids, alcohols, ketones, keto-acids, hydroxy acids and other compounds of various degrees of oxidation. The acids obtained, particularly when oxidizing wax, waxy fractions or similar high molecular weight hydrocarbons, range from formic and other low carbon chain acids to higher numbered carbon chain, water insoluble, monobasic acids of the fatty acid type. The latter may contain from 8 or 10 carbon atoms up to 30 or more, and certain of these have been proposed for use in soap making as substitutes for naturally occurring fats and oils.

Most of the emphasis in the known methods has been placed upon obtainment of these fatty acids as the ultimate product. The early investigators employed relatively high reaction temperatures, as 160° C. or above, but it was found that such temperatures promoted formation of dark colored resinous or polymerized material, the presence of which precluded satisfactory recovery of the desired acids and otherwise devaluated the product. Since these undesirable resinous materials apparently formed at increasing rates as the oxidation treatment was prolonged, it was recommended that treatment be discontinued after only a portion of the hydrocarbons had been converted, as for example,

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20–30%. It was also discovered that by using lower oxidation temperatures, as for example, 110° C. to 140° C., and certain other expedients, there resulted better colored oxidation products, but the reaction rate was materially decreased at these lower temperatures, requiring relatively long periods of treatment. These and various other developments in the art, which include the use of special catalysts, promoter materials, special apparatus and selected operating conditions, permit obtainment of oxidation products allegedly relatively high in these long chain monobasic acids. Such acids exist in the reaction mass or product, both as free acids and as esters or other saponifiable form thereof. Conversion of all of the hydrocarbon starting material to various oxygenated compounds has been alleged in some cases, and oxidation products having acidity corresponding to saponification values almost as high as 400 have been reported.

An object of the preesnt invention is to provide an improved process for oxidizing hydrocarbons in liquid phase using oxygen, air or other free oxygen-containing gas to produce valuable acidic material in important yield. A further object is to provide such a process in which the oxidation is continued under operating conditions so controlled that there is produced an oxidized mass of relatively high saponification and acid values containing important yields of dicarboxylic acid material. A further object is to produce new and useful dicarboxylic acid compositions. Another object is to provide a process whereby valuable dicarboxylic acids may be produced in important yields from paraffinic hydrocarbons by continuous treatment with a free oxygen-containing gas.

While, as indicated hereinabove, methods are known for oxidizing wax and similar straight chain aliphatic hydrocarbons in liquid phase, using air or other free oxygen-containing gas, to produce oxidized material of almost 400 saponification value containing monobasic acid material, it is not generally recognized, as far as I am aware, that oxidation may be continued to produce a reaction mixture of substantially higher saponification value containing important amounts of useful dibasic acid material. I have discovered, in accordance with the present invention, that this may be accomplished and that the objects of the invention may be attained by conducting the oxidation under certain controlled conditions. By so controlling the reaction, the

oxidation may be continued to advanced stages, well above the levels heretofore reached in the known methods, with obtainment of new highly acidic oxidation products containing practical and recoverable yields of dibasic organic acids and other valuable difunctional compounds. Comparatively low-cost hydrocarbons, such as refined paraffin wax, slack wax or other suitable hydrocarbon fractions, can be oxidized in liquid phase by blowing with air to produce directly (i. e., without interrupting the treatment to separate components from the reaction mass) an oxidation product having relatively high acid and saponification values, which is low in, or substantially free of, unsaponifiable materials and which contains recoverable dibasic acids of the succinic acid series, ranging from 4 to about 20 carbon atoms, in important yield.

The controlled conditions employed, according to this invention, are effective selectively to promote or maintain the desired reactions producing the stated useful acidic materials. Undesirable reactions, such as those leading to the formation of resiniflable or polymerizable substances, are suppressed. This selective action holds even at relatively high oxidation temperatures at which prior investigators obtained excessive polymerization or resinification; and the present invention thus permits more rapid oxidation reaction obtainable at the higher temperatures without these detrimental results. Although reaction products containing satisfactory proportions of dibasic acid material may be produced with advantage by this process at relatively low temperatures, for example, from about 100° C. to about 120° C. or even to about 140° C., higher oxidation temperatures ranging up to 200° C. or possibly even higher can be satisfactorily employed in this invention to produce such material in a shorter time.

I have found that the oxygen utilization rate, by which is meant the rate at which oxygen of the free oxygen-containing gas supplied to the hydrocarbons is used up or combined during the oxidative treatment, is an important control factor influencing selectivity of reaction and quality of the ultimate product. Operating conditions providing relatively low oxygen utilization rates during hydrocarbon oxidation will result in resinous reaction products and cessation of the desired conversion to valuable acids at a comparatively low level of acidity, i. e., before the acidity, as measured by saponification and acid values of the product, has reached the desired degree. On the other hand, if the oxygen is caused to be utilized at relatively high rates, the desired acid-producing reactions will proceed with suppression of resin-forming reactions, and the saponification and acid values will continue to increase to comparativly high degrees at which the resulting highly acidic, relatively non-resinous products will contain good yields of useful difunctional compounds including the stated dibasic acids. Accordingly, in the process of this invention, oxygen utilization is controlled and maintained at a relatively high rate, effective to convert hydrocarbons to the stated highly acidic products.

The proper rate of oxygen utilization is obtained, and other desired results are brought about by regulation or control of certain conditions during the oxidative treatment. Important among these conditions are the rate at which the free oxygen-containing gas is supplied to the hydrocarbon reaction mixture and the intimacy of

contact provided between the liquid reaction mixture and the said gas. These two conditions are interdependent in the sense that a high rate of gas supply is not sufficient unless proper gas-liquid contact is maintained and, conversely, control of degree of contact is of no avail unless sufficient oxidizing gas is supplied to the reaction. Other control factors of importance to obtainment of the desired results include use of proper oxidizing temperature and, where a catalyst is employed, it should be present in relatively small amounts and should be of proper catalystic activity, as will be more fully described later herein.

Referring now more specifically to the control of contact between reaction liquid and oxidizing gas and its relation to oxygen utilization, the proper degree of such contact can be obtained in various ways, the actual procedure in practice depending largely upon the specific type of apparatus employed for conducting the oxidation. At this point, it will be well to describe one procedure and one form of apparatus suitable for conducting the process of the invention, and to set forth in more detail the relation between the control of operations and the results obtained.

This specific apparatus consists of a reactor in the form of a two liter glass flask, equipped with a glass, paddle-type stirrer (motor-driven) and having an oxidizing gas inlet tube of glass opening near the bottom of the flask in the vicinity of the stirrer paddle, and an outlet for effluent material. External means for heating and cooling the flask are provided. The effluent gases, which generally include oxygen, carbon dioxide, carbon monoxide and low molecular weight oxidized compounds such as formic acid, are conducted by a suitable conduit to a condenser where condensable materials are collected. Oxygen utilization for a given period of oxidation is determined by analyzing the effluent gases for amount of free oxygen and subtracting this amount from the amount of free oxygen in the gas supplied to the flask during such period. Thus, as used herein, the term "oxygen utilization" means the amount of oxygen entering into chemical combination during the rea tion. When using this particular type of apparatus, the proper oxygen utilization rate at a given temperature of oxidation is obtained primarily by combined control of the stirrer speed and rate of oxygen feed. In operation, the hydrocarbon is placed in the flask, heated to the proper oxidizing temperature and the air or other suitable free oxygen-containing gas is conducted in at a properly controlled rate with the stirrer rotating at a controlled speed to give the proper oxygen utilization, until the saponification value and acid value of the oxidation product, i. e., the liquid reaction product or material in the reactor, have reached the desired degrees.

Using the apparatus and procedure just described, various runs were made under different conditions. Operating conditions and results of these runs appear in Tables I and II. The charge in each run was one kilogram of a 120° F. melting point paraffin wax derived from petroleum by customary sweating procedure, having dissolved therein manganese naphthenate as an oxidation catalyst, in amount equal to 1% by weight of the wax. Before each run, the flask and stirrer were thoroughly cleaned. All runs were conducted at amospheric pressure. The saponification values tabulated are those of the reaction product remaining in the reactor, and do not indicate

acidity of products volatilizing over at the reaction temperature used.

Table I

Run No.	Oxidation Temperature ° C.	Oxidizing Gas & Gas Feed Rate, Liters/hour/Kg. of Hdrocarbon Charge	Stirrer Speed, R. P. M.	Final Saponification Value, mgs./gm. KOH	Approximate Average Oxygen Utilization Rate to Reach Final Saponification Value, Liters/hour/Kg.
116A	120	Air, 13.2	900	408	1.5
123	140	Oxygen, 12	900	426	7
130	160	Oxygen, 108	450	397	23
126	180	Oxygen, 240	900	370	135

Each of the Table I runs was "dead" when the product in the reactor had reached the final saponification values shown in the table, and the reactor product in each case showed incipient resinification. By the term "dead," it is meant that after the "final saponification values" shown in the table had been reached, further passage of oxygen or air through the products resulted in further resinification, as evidenced by increase in molecular weight, but in no further production of saponifiable material, and the resinified products are of little value.

The runs tabulated in Table II show that by causing utilization of oxygen at rates higher than in the Table I runs at corresponding reaction temperatures, the saponification values of the reactor products will continue to increase well beyond 400. The products of the Table II runs were high in recoverable dibasic acids and other difunctional acidic material, and were not resinous in character.

Table II

Run No.	Oxidation Temperature, °C.	Oxidizing Gas and Gas Feed Rate, Liters/hour/Kg. of Hydrocarbon Charge	Stirrer Speed, R. P. M.	Final Saponification Value mgs./gm. KOH	Approximate Average Oxygen Utilization Rate to Reach Final Saponification Value, Liters/hour/Kg.
107	120	Oxygen, 120	900	615	10
10	140	Oxygen, 150	1,080	560	60
131	160	Oxygen, 450	1,500	550	95

The Table II operating conditions, when compared to those shown in Table I, show, as respects this particular type of apparatus, that rate of feed of oxidizing gas and stirrer speed are factors influencing oxygen utilization. Also, it is clear from these data that oxygen is utilized more rapidly at the higher oxidation temperatures. The Table II runs represent preferred embodiments, and should not be considered as limiting the scope of the invention. Use of somewhat lower oxygen utilization rates than those shown in Table II will produce suitable acidic products according to the invention.

As indicated, it is apparent from the tabulated data that the speed at which oxygen is utilized increases with increase in temperature of oxidation. Thus, the minimum degree of hydrocarbon-oxygen contact and oxygen feed rate essential to produce a product of given saponification value will increase with increase in temperature employed in the oxidation, and conditions effective to give satisfactorily high oxygen utilization at a given oxidation temperature will be ample for oxidation at lower temperatures.

In the early stages of the oxidation treatment, when the saponification value of the reactor material is relatively low, the oxygen utilization rate is higher than at the later stages. In order to obtain high conversions to dibasic acid material, operating conditions should be maintained such that relatively high oxygen utilization rates prevail until the saponification value of the reactor product has reached a value on the order of 400. In this manner, incipient resinification is avoided as the reactor product reaches higher saponification levels at which substantial proportional amounts of dibasic acids are present. The importance of maintaining high oxygen utilization rate during the early stages is exemplified in the following tabulated runs. Each of these runs was conducted at atmospheric pressure, at a temperature of 160° C., the charge being the above-described 120° F. melting point wax containing 1% manganese naphthenate catalyst.

Run No.	O_2 Feed Rate Liters/hour/Kg. of Hydrocarbon Charge	Stirrer Speed R. P. M.	Final Acid Value (When Oxidation Ceased)	Final Saponification Value (When Oxidation Ceased)	Approximate Average Utilization Rate, Liters/hour/Kg. Up to 400 Sap. Value	Approximate Average Utilization Rate, Liters/hour/Kg. Up to Final Sap. Value	$CO+CO_2$ Sap. Value
130	108	450	157	397	23	----	----
142	70	900	179	426	35	----	2.9
143	120	900	263	572	52	31	2.0
131	450	1,500	263	550	134	95	1.0

A further important and unexpected result flowing from use of high rates of oxygen utilization is that high yields of reactor product are obtained. This is due to the finding that the proportional amount of carbon dioxide and monoxide gases produced during the reaction is less when oxygen utilization is higher. As shown in the right-hand column of the above table, in run 131 the ratio of equivalents of carbon oxide gases to equivalents of saponifiable material produced was only one-third as high as in run 142. Oxygen utilization was much lower in run 142 than in run 131. This means that at higher oxygen utilization rates, as well as conserving hydrocarbon charge, less of the oxygen of the feed gas is wasted in forming carbon oxides.

The following tabulated runs, conducted at 140° C., and using as charge the above described 120° F. melting point wax containing 1% manganese naphthenate catalyst, illustrate in a manner similar to the above tabulated 160° C. runs, comparative oxygen utilization rates employed to reach certain saponification values when oxidizing at temperature of 140° C.

Run Number	Approximate Average Oxygen Utilization Rate, L/hour/Kg.		Final Saponification Value
	Up to 400 Sap. Value	Up to final Sap. Value	
123	7	7	426
144	11	8	509

Similarly satisfactory results are obtainable using other types of apparatus than that described above. For example, the reaction may be conducted using a pressure converter. Such converter may take the form of a steel tower, and may be equipped with means for subdividing the entering oxidizing gas, as a perforated or foramimous gas distributor so situated that the gas passes through a column of the hydrocarbon liquid in small bubbles. The reaction should be conducted under a suitably elevated pressure, using adequate amounts of oxidizing gas, so that the desired oxygen utilization rate will result. The pressure vessel preferably should be equipped with internal cooling coils situated in order efficiently to control the temperature of the reaction which is highly exothermic.

Using an unpacked steel tower equipped with a porous inlet air distributor and cooling coils, hydrocarbons were oxidized in liquid phase by blowing air therethrough under the conditions and with the results shown in Table III. The hydrocarbon charge was a 120° F. melting point wax similar to that employed in the runs of Tables I and II. All gas volumes shown are corrected to atmospheric conditions. Manganese naphthenate in amount equivalent to 0.5% by weight of the hydrocarbon charge was used as catalyst.

Table III

Run No.	AR48	AR61
Average temperature, ° C.	121	111
Average pressure #/sq. in.	28	42
Air feed rate L./hr./Kg. (Average)	185	296
Final acid value	286	325
Final saponification value	500	548
Acid/saponification ratio	0.57	0.59
Average oxygen utilization L./hr./Kg.	17	23

Certain catalysts may be used in the method

of this invention with advantage. At the lower temperatures of operation of the oxidation process, as at 100° C. to say 140° C., it is particularly desirable to employ an added catalyst in order to aid in the start of the reaction. Oxidations at higher temperatures of say above 160° C. in some instances may be conducted without addition of catalyst. The catalyst selected must be of relatively high activity. Certain salts of manganese, whose anion is sufficiently soluble in hydrocarbons, are the preferred catalysts. Others giving satisfactory results are manganese acetate, formate, stearate and naphthenate. Manganese dioxide likewise is suitable. Certain other salts of acids are suitable, and these include lead naphthenate and cerium stearate, ammonium vanadate and titanium stearate. These catalysts are effective in relatively small proportional amounts; and, in fact, the presence of relatively large amounts of such catalysts often tends to retard or stop the desired oxidation reaction before the desired amount of dibasic acid material is formed. In general, the presence of catalysts of the above character, in amounts equivalent to not more than 1 atom of the catalyst metal to about 100 to 150 molecules of the hydrocarbon charge, gives the best results; and variation in catalyst amount in this range produces no material difference in results. In the case of manganese naphthenate, this corresponds to not more than about 1% of this catalyst. Amounts as low as 0.01% or as high as about 2% of manganese naphthenate have been satisfactorily employed. As the amount of catalyst added at the start of the reaction is increased above about 2%, the tendency is to kill the reaction before the desired saponification value is reached, and this tendency is more evident with increasing amounts added. Oxidation promoters, such as previously oxidized hydrocarbons, may be added if desired, and are particularly desirable in aiding the start of the oxidation at low oxidation temperatures.

Regarding hydrocarbon charge stocks, highly paraffinic hydrocarbons are preferred. Materials containing substantial portions of aromatics are, in general, to be avoided since the presence of certain aromatics tends to retard the reaction, particularly as it approaches advanced oxidation stages. Various saturated straight chain paraffinic hydrocarbons of relatively high molecular weight are eminently suitable. These include paraffinic gas oil fractions, paraffinic scale waxes of, for example, 105–108° F. melting point and 120° F. melting point, and various slack waxes derived from paraffinic crudes. Desirably deoiled waxes of high melting points, such as refined scale waxes, are employed. Many other hydrocarbons of this character may be used.

Table IV illustrates typical composition and quality of the reactor or oxidation product resulting from the controlled hydrocarbon oxidation method of this invention, and also sets forth compositions at lower oxidation levels for comparative purposes to indicate the progressive composition changes as the oxidation proceeds from low to high levels. The said product is a complex mixture of oxidized compounds and the exact structure of all compounds present therein is unknown. However, determination of various groups present, such as free hydroxyl, ester, carboxyl and "lactone" groups, and the ratio of certain of these groups to others affords an insight as to the composition of the mixtures. In the table, the columns headed "Free OH groups," "Ester groups" and "Lactone groups" indicate,

respectively, proportions of compounds containing these groups in the entire saponifiable portions of the oxidation products at various oxidation levels.

In the method for determination of ester values (E) and "lactone" values (L), a portion of the oxidized product from the reactor was dissolved in alcohol and titrated in the usual way at room temperature with 1N.KOH to find the acid value; then refluxed while adding KOH dropwise until the length of time the indicator color (thymolphthalein) persisted began to increase rapidly. The amount of KOH thus added dropwise represents the easily saponified material, which may be termed "lactone value" since it has been found that "lactone" groups present hydrolyze rapidly under these conditions, whereas esters will remain unchanged for a longer period which may be at least 15–30 minutes. An excess of KOH then was added and the mixture was refluxed for 1 hour, after which it was titrated back with 1N. hydrochloric acid to disappearance of color. The amount of alkali used up during the 1 hour reflux represents the ester value. Total saponification value equals the sum of the acid, "lactone" and ester values.

The OH values, representing free hydroxyl groups present, were determined by the method described by Smith, Bryant and Mitchell in volume 61 of Journal American Chemical Society of 1939 at page 2407 which, in brief, consists in esterification of the oxidation product to acetates in acetic acid-dioxane solution at about 60° C. with boron trifluoride, followed by titration with Fischer reagent to determine water produced.

The tabulated crystalline yields represent dibasic acid crystals obtained by subjecting the oxidation reactor products of the various runs to a continuous pyrolytic distillation in which a stream of the material was rapidly vaporized in a flash chamber maintained at 275–300° C., followed by fractionation of the distillate from said distillation, and filtration of crystals from the fractions.

Table IV

Saponification value (S) of reactor product (mgs. KOH per gram)	(Unsubstituted) Free OH Groups $\frac{OH}{S}\times 100$	Ester Groups $\frac{E}{S}\times 100$	"Lactone" Groups $\frac{L}{S}\times 100$	Yield of crystalline dibasic acids based on reactor product, per cent by weight	Unsaponifiable material, per cent by weight in reactor product
224	15	25	----	0	49
280	13	22	22	1	35
336	13	21	21	2	25
392	7	----	----	3	18
471	----	17	22	6	11
504	5 to 6	14	27	10	5
560	3	13	26	20	1
616	3	7 to 10	28	34	trace

It is apparent from the data of Table IV that continuance of the oxidation reaction to the higher oxidation levels is accompanied by increase in crystalline dibasic acid yields and decrease in the proportion of free hydroxy- and ester-containing compounds. The Table IV data show a five-fold decrease in ratio of free OH value to saponification value from the lowest to the highest oxidation levels. It is thought that the relatively low proportional amounts of certain hydroxyl and ester compounds of readily resinifiable nature, characterizing the more highly oxidized products of this invention, constitute an important factor responsible for the relatively high yields of dibasic acids and low resinifying or polymerizing tendencies. No aldehydes, detectable by recognized tests, are present in the highly oxidized products. As shown in Table IV, accelerated yields of crystalline dibasic acids were obtained as the oxidation was continued after reactor products had reached about 400 saponification value. For obtainment of optimum crystalline dibasic acid yields and other advantageous results, it is preferred to continue the treatment to products of higher saponification value, as for example, to saponification values of 500 or above, where the reactor product is substantially all saponifiable.

The following Table V further illustrates quality of products obtained by liquid phase oxidation of a 120° F. melting point wax with air under various conditions. The analysis and other values shown apply to the reactor product; i. e., to the oxidation product not volatile at the designated reaction temperatures.

Table V

Run No.	Temperature, °C.	Saponification Value, mgms./gm. KOH	Molecular Weight	Specific Gravity @ 25° C.	Chemical Analysis, Per Cent by Weight		
					Carbon	Hydrogen	Oxygen
131	120	280	335	----	68.1	10.0	21.8
131 (Cont.)	120	414	355	----	64.3	8.4	27.3
SS 22	120	560	352	1.18	56.2	7.7	36.0
107	120	618	350	1.14	56.4	8.1	35.6
126	180	370 (dead)	1,025	1.06	65.7	8.9	25.4

All of the tabulated runs, except No. 126, were conducted under conditions resulting in adequate oxygen utilization according to this invention, and the products resulting therefrom were not resinous in nature. Run No. 126 was conducted under such conditions of lowered oxygen utilization that no further gain in saponification value of the product over 370 occurred on continued air treatment. This run No. 126 is thus designated "dead" at this saponification value level. The product from run No. 126 was of a dark resinous character, the presence of resins or polymers being evidenced by the considerably

higher molecular weight characterizing this product, as compared to those from the other tabulated runs. No substantial gain in molecular weights occurs as the saponification value increases above about 400, as shown in runs Nos. 131, SS 22 and 107, although there is a gain in oxygen combined.

The crude reactor product, or oxidation product as it is sometimes termed herein, contains saturated dibasic acids, including succinic, glutaric, adipic, suberic and higher carbon atom dibasic acids of this series up to 18 or 20 carbon atoms in chain length. Some of these are present in the reactor product as free acids which may be obtained directly therefrom in crystalline form, while others are combined with other radicals in non-crystalline compounds which may be decomposed to form additional free acids. Indications are that this non-crystalline portion contains, besides free dibasic acids, also water-soluble lactonic and ester compounds, the latter of which are probably esters of monobasic and dibasic hydroxy acids in which the hydrogen of the hydroxyl group has been replaced by an acyl group. Water-insoluble monobasic acids, having about 5 carbon atoms and up, and monobasic acid esters also may be present. The monobasic acids may be separately recovered and further purified, if desired, or may be recycled to oxidation.

In some cases, the crude oxidation product containing these dibasic acids and other difunctional compounds, or fractions thereof, may be used, without further processing, as a plasticizer, polymer intermediate and in various other applications; or, if greater purity or particular acids are desired, it may be separated into constituents by various methods. A fraction containing a mixture of crystalline dibasic acids may be obtained by hot water extraction of the crude reactor product. For example, a reactor product resulting from oxidation of wax as above-described and having saponification and acid values of 622 and 375, respectively, was heated with an equal volume of water, with agitation. The resulting water extract contained about 30% by weight of dibasic acids, based on the reactor product, and had an acid value of 717 and a saponification value of 829. Distillation of the extract under 3 mm. pressure gave a fraction boiling between 130° C. and 185° C. which yielded on filtration 44% of crystalline dibasic acids, mainly of 4 and 5 carbon chain length, and a fraction boiling between 185° C. and 255° C. which on filtration yielded 17% of crystalline dibasic acids containing 6 and higher numbers of carbon atoms in the chains. The latter fraction also yielded about 12% of non-crystalline dibasic acids having an acid value of 509 and a saponification value of 695, as filtrate. This material should find important use as a plasticizer.

For increased crystalline dibasic acid production, the non-crystalline portion remaining after separation of crystalline acids should be recycled to the oxidation reactor for further oxidation. In this manner, the non-crystalline filtrates and water-insoluble portions from the above extraction procedure, or any other desired portions containing non-crystalline material, may be reoxidized with improvement in over-all yield. If desired, however, the monobasic acids may be separated from the non-crystalline portion prior to its recycle to oxidation.

Controlled heating of the reactor product under certain conditions improves the crystallinity, apparently due in part to decomposition of the potentially dibasic acid compounds mentioned above

to form free dibasic acids. The continuous rapid pyrolytic distillation referred to hereinabove affords an effective procedure for this purpose, and may be applied to the entire reactor product resulting from the controlled oxidation or to extracts or other suitable portions thereof.

The mixture of dibasic acids, derived from the oxidation reactor product by any of these methods, may be further purified as by distillation and recrystallization from water or benzene, and, if desired, individual dibasic acids may be separated therefrom by suitable methods. One such method comprises autoclaving the dibasic acids with methanol, distilling the resulting esters into fractions, separately hydrolyzing the esters with hydrochloric acid, and subsequently recrystallizing. The following proportions of individual, substantially pure crystalline acids were obtained by such procedure:

	Per cent
Succinic acid	20
Glutaric acid	19
Adipic acid	19
Suberic acid	3
Non-crystalline dibasic acids	39

Higher carbon atom acids, likewise, may be recovered from the oxidation product in substantially pure form. Thus, a filtrate, resulting from separation of other dibasic acid crystals, was fractionally distilled under vacuum and a fraction boiling between 214° C. and 230° C. at 5 mm. pressure was filtered to yield dibasic acid in the carbon atom range of brassylic acid in the form of white powdery crystals having an acid value of 463 and being slightly soluble in benzene and ether.

The invention thus permits the obtainment from low-cost raw materials of valuable difunctional materials useful in the various arts.

I claim:

1. In the partial oxidation of predominantly paraffinic hydrocarbons in liquid phase by contacting the same under oxidizing conditions with a stream of gas containing free oxygen, the method of forming acidic material and suppressing resinification reactions comprising contacting said hydrocarbons at an oxidizing temperature from about 120° C. to about 180° C. with said gas, controlling the rate of feed of said gas to said hydrocarbons and the gas distribution therein to maintain dispersed in said hydrocarbons an amount of gas sufficient to cause combination of said oxygen at an average rate related to the oxidizing temperature as follows: substantially above 1.5 liters of oxygen per hour per kilogram of hydrocarbons at an oxidizing temperature of 120° C., substantially above 23 liters of oxygen per hour per kilogram of hydrocarbons at an oxidizing temperature of 160° C., and substantially above 135 liters of oxygen per hour per kilogram of hydrocarbons at an oxidation temperature of 180° C.

2. The method as described in claim 1 in which the oxidation reaction is conducted in the presence of an oxidation catalyst.

3. The method as described in claim 2 in which the oxidation catalyst is a metal salt of an organic acid present in an amount equivalent to not more than 1 atom of metal to about 100 to 150 molecules of the hydrocarbon charge.

4. The method as described in claim 3 in which the oxidation catalyst is a manganese salt of an organic acid.

5. The method as described in claim 1 in which

the oxidation reaction is continued until the saponification value of the reaction mass exceeds 400 and the reaction mass contains a substantial proportional amount of dibasic acid material.

6. The method as described in claim 5 in which the rate of combining oxygen in the reaction mass is greater at the earlier stages of the reaction when the reaction mass is of less than 400 saponification value than it is during subsequent stages thereof.

7. The method as described in claim 6 in which the oxidation reaction is conducted in the presence of a manganese naphthenate oxidation catalyst in an amount equivalent to from about 0.01% to about 2% of the hydrocarbon charge.

8. In the partial oxidation of predominantly paraffinic hydrocarbons in liquid phase by contacting the same under oxidizing conditions with a gas containing free oxygen, the method of forming acidic material and suppressing resinification reactions comprising contacting said hydrocarbons at an oxidizing temperature of at least about 150° C. with said gas, controlling the rate of feed of said gas to said hydrocarbons and the gas distribution therein to maintain dispersed in said hydrocarbons an amount of gas sufficient to cause combination of said oxygen at an average rate related to the oxidation temperature as follows: substantially about 7 liters of oxygen per hour per kilogram of hydrocarbons at a 140° C. temperature, substantially above 23 liters of oxygen per hour per kilogram of hydrocarbons at a 160° C. temperature and substantially above 135 liters of oxygen per hour per kilogram of hydrocarbons at a 180° C. temperature.

9. In the partial oxidation of predominantly paraffinic hydrocarbons in liquid phase by contacting the same under oxidizing conditions with a stream of gas containing free oxygen, the method of forming acidic material and suppressing resinification reactions comprising contacting said hydrocarbons at an oxidizing temperature with said gas, controlling the rate of feed of said gas to said hydrocarbons and the gas distribution therein to maintain dispersed in said hydrocarbons an amount of gas sufficient to cause combination of said oxygen at an average rate related to the oxidizing temperature as follows: at least about 10 liters of oxygen per hour per kilogram of hydrocarbons at 120° C., at least about 60 liters of oxygen per hour per kilogram of hydrocarbons at 140° C. and at least about 95 liters of oxygen per hour per kilogram of hydrocarbons at 160° C., and continuing the oxidation reaction until the reaction mass contains a substantial proportion of polycarboxylic acid material and reaches a saponification value of at least about 500.

10. The method as described in claim 9 in which a crystalline dibasic acid portion is separated from the oxidation reactor product.

11. In the partial oxidation of predominantly paraffinic hydrocarbons in liquid phase by contacting the same under oxidizing conditions with a stream of gas containing free oxygen, the method of forming acidic material and suppressing resinification reactions comprising contacting said hydrocarbons at an oxidizing temperature of at least about 120° C. with said gas, controlling the rate of feed of said gas to said hydrocarbons and the gas distribution therein to maintain dispersed in said hydrocarbons an amount of gas sufficient to cause combination of said oxygen at an average rate related to the oxidizing temperature as follows: substantially above 1.5 liters of oxygen per hour per kilogram of hydrocarbons at an oxidation temperature of 120° C. substantially above 23 liters of oxygen per hour per kilogram of hydrocarbons at an oxidation temperature of 160° C. and substantially above 135 liters of oxygen per hour per kilogram of hydrocarbons at an oxidation temperature of 180° C.

12. The method as described in claim 11 in which the oxidation reaction is continued until the reaction mass contains a substantial proportional amount of dibasic acid material.

13. The method as described in claim 12 in which a noncrystalline portion is separated from the oxidation reactor product and subjected to further oxidation.

14. The method as described in claim 13 in which a monobasic acid portion is removed prior to subjecting the noncrystalline portion to further oxidation.

15. In the partial oxidation of predominantly paraffinic hydrocarbons in liquid phase by contacting the same under oxidizing conditions with a gas containing free oxygen, the method of forming acidic material and suppressing resinification reactions comprising contacting said hydrocarbons at an oxidizing temperature with said gas, controlling the rate of feed of said gas to said hydrocarbons and the gas distribution therein to maintain dispersed in said hydrocarbons an amount of gas sufficient to cause combination of said oxygen at an average rate related to the oxidizing temperature as follows: substantially above 1.5 liters of oxygen per hour per kilogram of hydrocarbons at an oxidizing temperature of 120° C., substantially above 23 liters of oxygen per hour per kilogram of hydrocarbons at an oxidizing temperature of 160° C., and substantially above 135 liters of oxygen per hour per kilogram of hydrocarbons at an oxidation temperature of 180° C., and continuing the oxidation reaction until the reaction mass reaches a saponification value of at least about 400.

16. An acidic hydrocarbon oxidation reactor product resulting from the oxidation of predominantly paraffinic hydrocarbons in liquid phase with free oxygen comprising a complex mixture of straight chain dibasic acids of at least four carbon atoms and oxidized organic substances containing ester and lactone groups, said composition being further characterized by a saponification value above 400, not more than about 17% of which represents ester groups and at least about 22% of which represents lactone groups, with the remainder representing acid value.

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