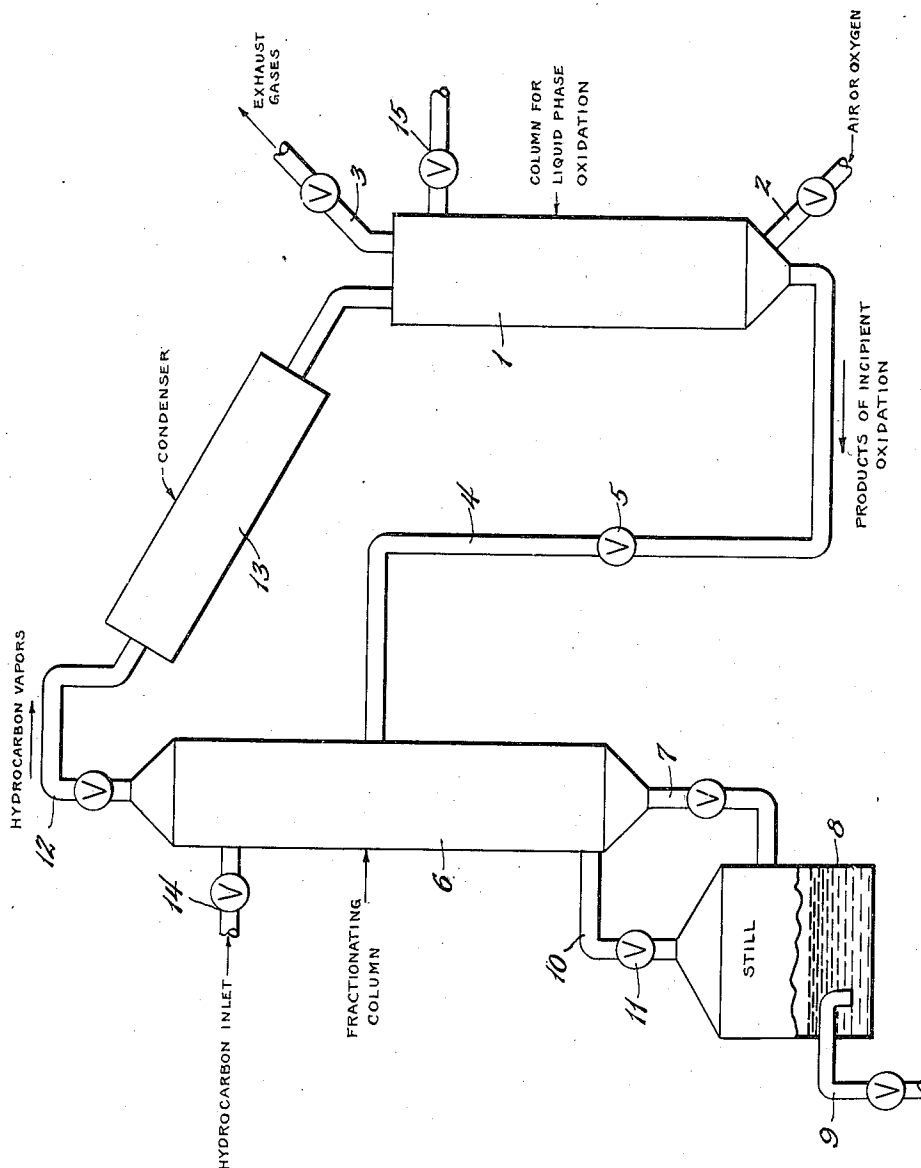


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AND PROCESS OF PRODUCING IT
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PRODUCT OF MILD OXIDATION OF LONG-CHAIN HYDROCARBONS AND PROCESS OF PRODUCING IT

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This invention relates to oxidation products, methods of producing such products, and apparatus or plants for carrying out such methods and producing such products, and more particularly relates to the oxidation of organic compounds under conditions of control enabling the production of substantial quantities of oxygen-containing bodies in a relatively low state of oxidation.

In the prior art, a great deal of work has been done in the oxidation of organic compounds, particularly the oxidation of paraffin hydrocarbons as found in petroleum, its fractions and distillates, and paraffin wax materials. In such prior art methods the conditions of oxidation have been of such character that the oxidation reactions have reached a far advanced stage, so that the bulk of products obtained have been "oxidation" acids and derivatives of same, with large losses of material due to the formation of substantial quantities of ultimate oxidation products, such as water, carbon monoxide, and carbon dioxide. While products of a lower order of oxidation than fatty acids, such as alcohols, aldehydes and ketones have been produced in such prior art oxidation processes, the presence of such products of lower stages of oxidation have been, relatively speaking, accidental, since the early products of oxidation react with oxidizing agents more readily than do the hydrocarbons, and no methods of control were known or available which did not result in very high proportions of acid-containing substances being produced. Furthermore, the acids which were produced were mostly hydroxylated or oxygenated, having little value except, perhaps, when used in conjunction with natural fatty acids in the manufacture of cheap soaps.

Among the objects of the present invention is the production of oxidation products containing substantial quantities of oxygenated derivatives in a relatively low order of oxidation with a minimum of the more highly oxidized products, such as hydroxy acids, etc.

Further objects of the present invention include methods of control which enable such products of relatively low orders of oxidation to be produced in substantial quantities.

Still further objects and advantages will appear from the more detailed description set forth below, it being understood, however, that this more detailed description is given by way of illustration and explanation only, and not by way of limitation, since various changes herein may be made by those skilled in the art without departing from the scope and spirit of the present invention.

In illustration of this illustrative disclosure set forth below, there is shown in the accompanying drawing a diagrammatic representation of apparatus that may be utilized in carrying out the present invention.

In carrying out the present invention, liquid phase oxidation is employed, that is, the organic materials undergoing oxidative treatment in accordance with the present invention, are present in liquid or molten condition, and control of the character of oxidation products produced is determined by certain changes in the character of the liquid material during the course of the oxidation (and not from the standpoint of the materials volatilized out of the oxidation zone as has been the customary practice in the prior art methods). It has thus been found possible to interrupt the course of the oxidation process, so that products containing high quantities of low stages of oxidation may be relatively readily obtained, without the production of inordinate quantities of the products of more advanced oxidation such as hydroxylated acids. These methods of control which enable high quantities of products of low stages of oxidation to be produced have been found to be possible even though the mechanisms of the oxidation reactions are relatively complex, and secondary reactions are necessarily taking place at the same time that primary oxidation is being carried out.

In accordance with the present invention, it has been found possible to interrupt the course of the oxidation by separating the products of oxidation before more than a small percentage of the starting material has been attacked by the oxidizing agent. Thus, in spite of the hitherto uncontrolled tendency of the lower stages of oxidation to become further oxidized, these lower stages may be isolated by limiting the oxidation process and the products resulting therefrom in accordance with the amount of oxygen absorbed by the material undergoing treatment. This becomes possible in accordance with the present invention because the conditions of control are determined by the character of products present in the liquid material undergoing oxidation.

The invention is applicable to a wide variety of organic bodies, but due to its importance in connection with the oxidation of hydrocarbon materials, the latter will serve to illustrate the methods of control desirably employed in carrying out the present invention. The hydrocarbons which may be subjected to treatment in accordance with the present invention are preferably aliphatic in character, and particularly those of

high molecular weights, such as the solid hydrocarbon materials present in paraffin or paraffin wax materials or fractions thereof, as well as the high molecular weight hydrocarbon materials present in petroleum or its fractions and distillates. Furthermore, the narrower the cut of such hydrocarbon material which is subjected to oxidation, the greater is the control exercised over the character of products produced, since in accordance with the present invention the long-chain molecules are retained as far as possible intact, and the oxygen attack is directed to the production of oxygen-containing bodies, such as secondary alcohols and ketones, which for the most part retain the same number of carbon atoms as those of the hydrocarbons from which they have been produced, and which have considerably higher boiling points than the parent compound, this increase in boiling point serving as a means of separation of the product. Thus, from the higher paraffin hydrocarbon $n\text{-C}_{22}\text{H}_{46}$, secondary alcohols and ketones are produced which have a preponderance of molecules containing twenty-two carbon atoms, various isomers of the stated alcohols and ketones being present in such oxidation products. Similarly, the hydrocarbon $\text{C}_{23}\text{H}_{48}$ under the present invention yields a preponderance of secondary alcohols and ketones containing twenty-three carbon atoms to the molecule. Or if a fraction of paraffin wax corresponding to $n\text{-C}_{28}\text{H}_{58}$ is treated in accordance with the present invention, there is obtained a large quantity of a mixture of secondary alcohols, all having the empirical formula $\text{C}_{28}\text{H}_{56}\text{O}$, together with a smaller quantity of ketones, all having the empirical formula $\text{C}_{28}\text{H}_{54}\text{O}$. Fractions containing C_{30} hydrocarbons probably represent the upper limit to be utilized in connection with the present invention where distillation without extensive or serious decomposition is a factor. However, hydrocarbons as high as C_{30} which appear to be present in paraffin wax and fractions thereof, and perhaps even higher, may be treated in accordance with the present invention, particularly where distillation with more or less decomposition is permissible. Generally the lower limits of hydrocarbons utilized may be represented by hydrocarbons which remain liquid under the conditions of the process up to several atmospheres pressure. The method may be applied to compounds even at their boiling points. Hydrocarbons as low as C_8 (boiling about 150° under normal pressure) may be treated to give lower alcohols that are highly desirable, particularly in the solvent field. But generally hydrocarbons boiling under normal atmospheric pressure not lower than 200°C ., thus usually beginning with $n\text{-C}_{12}\text{H}_{26}$ and higher, will be treated in accordance with the present invention.

While, therefore, the invention is applicable to hydrocarbon mixtures of various characters, particularly those of high molecular weights, such as fractions from paraffin wax, or fractions from petroleum oils, etc., due to the fact that the degradation of the molecule is very restricted under the disclosed methods of oxidation herein, by using a narrow range boiling point fraction, or a close cut of hydrocarbon material, the nature of the products can be largely directed to a molecule containing a carbon content corresponding with that of the cut or fraction employed for oxidation. Where a mixture, within a narrow range of boiling points of hydrocarbon materials of high molecular weights are em-

ployed, the resulting product will contain mixtures of secondary alcohols and ketones having a carbon chain corresponding with each of the carbon contents of the hydrocarbons present in the mixture or cut subjected to oxidation treatment.

It has been found that the products of such liquid phase oxidation may be segregated from the oxidation zone at the time that there is such preponderance of secondary alcohols and ketones in the oxidation products. This can be accomplished easily by removing the residual products (that is, the products less volatile than the parent compound) from the oxidation zone when the desired content of secondary alcohols and ketones have been produced—a feature which becomes possible because it has been found that the oxidation product may be separated from the parent compound at that point. This is further possible because the absorption of oxygen at such point can be limited, and the extent of limitation of absorption of oxygen in the liquid products undergoing treatment can thus be utilized for interrupting the oxidation process, and recovery of the relatively low stages of oxidation products. Thus if the oxidation is interrupted, or the liquid products removed from the oxidation zone at a time where the liquid material has reacted with one atom of oxygen per ten molecules of hydrocarbon undergoing treatment, a product preponderatingly high in secondary alcohols and ketones is obtainable. While the ratio of oxygen to hydrocarbon material may be somewhat greater than that indicated above, that ratio represents a desirable one at which to interrupt the oxidation reaction, and generally the amount of oxygen absorption should not exceed that indicated, but may be considerably less, depending on the operating conditions, such as the temperatures at which the oxidation is carried out, the presence or absence of catalysts, the use of superatmospheric pressures, etc., under which it becomes possible to segregate the product when the ratio of reaction of oxygen is considerably less, such as one atom of oxygen per twenty molecules of hydrocarbon, or one atom of oxygen per fifty molecules of hydrocarbon, or one atom of oxygen per hundred molecules of hydrocarbon, and running up as high as one atom of oxygen to one thousand molecules of hydrocarbon undergoing treatment. While higher ratios may be used as, for example, one to five or even one to two, in such cases higher proportions of acids or esters are produced, and where secondary alcohols and ketones are most desired, the indicated preferred ratios are better. By restriction of the extent of reaction of oxygen as thus set forth, it becomes possible to materially increase the percentage of the oxidation products of the lower order of oxidation, and particularly to produce large quantities of such lower oxidation products as secondary alcohols and ketones with relatively minor quantities of carboxylic acids. While, of course, it must be understood that in all these oxidation reactions there is a complex production of oxygenated and other derivatives, including volatile products and products which are non-volatile under the conditions of treatment, products, including solids, containing a preponderance of secondary alcohols and ketones, less volatile than the original hydrocarbon, are readily obtainable. Thus, although in the products from the oxidation zone, primary alcohols and fatty acids, mostly having a carbon chain less than that of the hydrocarbon material un-

dergoing treatment, are produced, and the condensates from the gases and vapors from the reaction zone include complex mixtures of lower aldehydes, ketones, alcohols, acid, lactones, etc., together with water, and which, therefore, segregate into two layers, one aqueous, and the other substantially non-aqueous; the bulk of products produced under the controlled conditions of oxidation of the present invention are the secondary alcohols and ketones, the other oxidation products being only minor in amount. The true gaseous materials produced are substantially carbon dioxide, carbon monoxide and hydrogen.

The temperatures under which the oxidation is carried out may vary within relatively substantial limits. The actual temperature employed depends on a number of considerations, including the other conditions of operation. Generally, the temperature will be above 100° C., since below that temperature the rate of oxidation is too slow for most purposes. Further, as a general rule, the temperature will not usually exceed 300 or 350° C., and the preferred range of temperatures will lie within that sphere, usually from 150 to 250° C. Temperatures of from 175° C. to 225° C. are particularly desirable at which to carry out the processes of the present invention when pure synthetic hydrocarbons are being oxidized. With petroleum fractions or substances which already contain oxygen, the optimum temperature is usually lower than with pure synthetic hydrocarbons, but may sometimes be higher. The proportion of secondary alcohols is greater the lower the temperature. Thus at 175° C., the process is desirably carried out to produce large quantities of secondary alcohols and ketones, as compared with other oxidation products; while the higher temperatures cause more rapid oxidation and a decrease in the proportion of secondary alcohols in the product, with a decided increase in the proportion of degradation products. This is true, for example, in a comparison of processes carried out at 175° C. and 225° C., respectively, where the absorption of oxygen is in the ratio of one atom of oxygen to ten molecules of hydrocarbon. However, if at a higher temperature, such as 225° C., the oxidation is interrupted when only half as much oxygen has been absorbed, that is one atom of oxygen to twenty molecules of hydrocarbon, the proportions of secondary alcohols: ketones: other products are not vastly different from the ratio of those products produced at temperatures of 175° C., where the absorption of oxygen is one atom of oxygen to ten molecules of hydrocarbon. So that the temperature employed depends in part on the other conditions of operation, the extent of absorption of oxygen, the nature and source of the material undergoing oxidation, etc.

The difference in boiling points enables separation of products to be carried out, as indicated by the following considerations. Primary alcohols with which the present invention is not greatly or directly concerned, in the range of $C_{15}H_{34}O$ boil about 55° higher than the hydrocarbon with the same number of carbon atoms. As the molecular weight increases, there is a progressive decrease in this difference. Thus, primary $n-C_{26}H_{54}O$ would have a boiling point about 35° C. higher than $n-C_{26}H_{54}$. In general, secondary alcohols boil considerably lower than primary alcohols of the same empirical formula, and the further the hydroxyl group from the

end of the chain, the lower is the boiling point. Thus, in a mixture of isomers of the character produced in accordance with the present invention, those with the hydroxyl group toward the center of the carbon chain would boil, in the C_{18} range, some 15 or 20° C. lower than those with the hydroxyl group on the carbon atom next to the end—and some 20 or 25° C. higher than the parent hydrocarbon; in the C_{28} derivatives there would be a proportionate decrease in all differences. Since the hydrocarbon, $n-C_{23}H_{48}$, boils at around 230° C. under 15 mm. pressure, and since the boiling points of its derivative alcohols range between about 245 and 255 or 260° C., these factors must be taken into consideration in determining how high in the series it is possible to distill the alcohols without serious decomposition, in effecting separations. It may be said generally that they are fairly stable up to about 300° C. Alcohols derived from $n-C_{28}H_{58}$ probably represent the approximate upper limit for distillation without too great decomposition.

It should also be kept in mind in this connection that mixtures of hydrocarbons, such as those obtained by fractional distillation of paraffin wax, yield more rapid oxidation than synthetic hydrocarbons. (Note that a closely cut fraction of paraffin wax will absorb oxygen just as fast as a more inclusive fraction, even from the very first.) But the rapidity of oxidation with such mixtures is more particularly pronounced in the early stages, so that the desired products obtained, namely high quantities of secondary alcohols and ketones with respect to acids or other products, is still obtained. Furthermore, when such mixtures are employed, there is usually a higher proportion of volatile liquid products.

Pressures may also vary materially, and pressures both above atmospheric and below atmospheric, as well as atmospheric pressures may be employed. Desirably the oxidation is carried out at atmospheric or higher pressures, while the fractionation of the products from the oxidation zone may desirably be carried out under vacuum. Catalysts may be included and may vary in character, such as, for example, metals, metallic salts or oxides, silica gel, pumice, charcoal, etc. And the process may be operated either as a batch process or in a continuous manner.

While other types of oxidizing agents may be employed, oxygen is the preferred oxygenating agent, and may be utilized either as pure oxygen, or in the form of air. The presence of moisture, such as in the form of steam, also affects the character of products produced. A dry oxygen-containing gas gives less oxidation, particularly at lower temperatures, while moist oxygen-containing gases favor aldehydic constituents. Gaseous catalysts, such as oxides of nitrogen, particularly nitrogen peroxide, may be introduced in minor quantities, such as 0.5% with the oxygen-containing gases, the products from oxidations carried out in the presence of oxides of nitrogen generally being highly colored, or at least more highly colored than those produced in the absence of such catalysts.

The process is desirably carried out by passing the current of oxygen-containing gases through the liquid hydrocarbon material heated to the desired temperature. The entering oxygen-containing gas may be utilized for mixing or stirring or agitating purposes, or mechanical means

for causing contact between the entering gas and the liquid material may be employed. The liquid hydrocarbon material is desirably preheated to the desired temperature before introducing the oxygen-containing gas, although the pre-heating of the liquid material may be carried only to lower temperatures at which some oxidation will take place before introducing the oxygen-containing gas. The oxidation reactions are exothermic, so that the heat generated in the reaction will serve to maintain the desired temperature. If the conditions of the process are such that the heat developed during reaction is dissipated materially by radiation or conduction, heating by external means may be necessary to maintain the desired temperature. Insulation may also be applied to the walls of the reaction chamber to maintain the heat. Or where the conditions of operation are such that the heat tends to build up, means for dissipating such heat may be employed, including cooling of the reaction zone, as by means of fins thereon, or the application of cooling material to the reaction zone; or the introduction of steam or inert gases with the oxygen-containing gases may be employed to control the reaction temperature.

Various methods of carrying out the processes and producing the described products may be employed, as exemplified in the specific examples given below.

For example, a current of oxygen was passed through the high molecular weight saturated paraffin hydrocarbon corresponding with the formula $n-C_{22}H_{46}$ at a temperature maintained at approximately 175° C. until one atom of oxygen had been absorbed per ten molecules of hydrocarbon. After removal of degradation products and unchanged hydrocarbon by fractional distillation, the residual product in the still consisted almost entirely of secondary alcohols and ketones, the former in large preponderance, having the same carbon chain as was present in the original hydrocarbon. Small quantities of primary alcohols and fatty acids were found, but most substances of the latter classes appeared to have a shorter carbon chain than the hydrocarbon treated, since they escaped during the fractional distillation. Some of the lower acids combined with the alcohols to form esters which were essentially non-volatile. Aldehydes of high molecular weight and complex oxidation products, such as hydroxy acids, were not found in substantial quantities. At least ninety percent of this residual product consisted of secondary alcohols and ketones having twenty-two carbon atoms in the molecule, and the secondary alcohols themselves constituted at least 65% of the product. Some of the acids present also contained twenty-two carbon atoms in the molecule. Of the true gases formed during the oxidation treatment, only carbon dioxide, carbon monoxide, and hydrogen were present in any substantial amount. In the volatile products given off from the oxidation zone, the acids were found to include formic, about 50%, and acetic, propionic and butyric, each about 12 to 15%, with higher acids in decreasing amounts. The total weight of volatile acids was only about 5% of the weight of hydrocarbon oxidized. The volatile liquid products also included mixtures of aldehydes, ketones, lactones, and alcohols, the latter being mostly secondary, but such volatile products were relatively small as compared with the secondary alcohols and ketones present in

the residual material in the still. While such still products, constituting the residues from the oxidation, include various fatty acids, and very small amounts of dibasic, hydroxylated, and oxygenated acids, the ketones and secondary alcohols preponderate in the product. Thus the residual product from such oxidation of this hydrocarbon resulted in a direct oxidation product preponderating in secondary alcohols and ketones having twenty-two carbon atoms in the molecule and containing various isomers of such alcohols and ketones. The hydrocarbon which was recovered in the fractional distillation was reused in a subsequent batch.

Instead of carrying out the process by the batch method referred to, an integral method of oxidation may be used. For example, a portion of the high molecular weight hydrocarbon $n-C_{22}H_{46}$ was oxidized with air until one atom of oxygen was absorbed per fifty molecules of hydrocarbon at temperatures of 175° C. and 225° C., respectively. The oxidation mixtures thus obtained were subjected to fractional distillation under reduced pressure (15 mm.) until 90% had distilled. The distillates were again oxidized to the same slight extent, and then combined with the previous residue, and again distilled fractionally, leaving slightly greater residues this time. These incipient oxidations and subsequent fractionations were repeated a number of times, care being taken in the latter step that none of the higher boiling oxidation product was removed—which was effected by leaving some hydrocarbon in the residue. The final residues obtained weighed approximately 85% as much as the original hydrocarbon subjected to treatment, and such residues consisted chiefly of oxidation products, there being about 10% of unchanged hydrocarbon. The products were refluxed in butyl alcohol with an excess of sodium hydroxide, after which calcium chloride was added in order to form the crystalline calcium soaps. The butyl alcohol was removed, and the calcium soaps and non-acidic constituents were separated in the usual way. The residual oxidation product obtained by integral incipient oxidation at 175° C. was found to consist of about 80% secondary alcohols, about 15% ketones, and about 5% acidic constituents, most of the latter having carbon chains considerably shorter than the original, but the alcohols and ketones showing a carbon content the same as that of the hydrocarbon subjected to treatment. At 225° C., the corresponding product consisted of about 60% secondary alcohols, about 15% ketones, and about 25% acids, most of the latter again showing unmistakable evidence of degradation. In both cases at 175° C. and 225° C., the stream of waste gases carried off quantities of condensable (in ice) products of lower molecular weights, which in the former case weighed about 10% of the weight of the original hydrocarbon, and in the latter about 18%. These condensates were complex mixtures of lower aldehydes, ketones, alcohols, acids, lactones, etc., together with water. The gaseous products consisted of carbon dioxide, carbon monoxide and hydrogen. Lower hydrocarbons were not found to any substantial extent in either the gaseous or volatile liquid products.

A closely cut fraction of paraffin wax boiling at from 240° to 242° C. at 15 mm. was subjected to integral incipient oxidation in the manner described immediately above. Oxidation, particularly in the early stages, was observed to be

more rapid than with individual high molecular weight specific hydrocarbons, but the ultimate results obtained under the process were not substantially different. The ratio of higher secondary alcohols to ketones to acids was about 75:10:15 at 175° C., and about 55:15:30 at 225° C. A somewhat higher proportion of volatile liquid products was obtained at each temperature; that is, about 15 and 25%, respectively.

Here again, the products obtained include the preponderating proportions of secondary alcohols and ketones, and particularly those having a carbon content corresponding with that of the hydrocarbon from which produced. Thus in the treatment of a fraction of paraffin wax corresponding with n -C₂₈H₅₈, there was obtained a large quantity of a mixture of secondary alcohols all having the empirical formula C₂₈H₅₆O, and a smaller quantity of ketones all having the empirical formula C₂₈H₅₆O.

These processes of producing higher secondary alcohols and ketones by the "integral" (that is, continuously incipient) oxidation of higher fractions of petroleum hydrocarbons, fractions of paraffin wax, high molecular weight paraffin and other hydrocarbons, etc., may be carried out in a continuous manner by effecting the continuous removal of products from the field of oxidation as soon as expedient after formation, in order to prevent their destruction by progressive oxidation. This result may, for example, be effected by use of a fractionating column into which the slightly oxidized hydrocarbon fraction passes continuously, the higher boiling alcohols and ketones, etc., being swept by reflux into the still below, where they accumulate. The unoxidized portion and the lower boiling products of oxidation (such as lower alcohols, ketones, acids, unsaturated hydrocarbons, etc.) go to the top of the column where a low boiling cut consisting of degradation products may be taken off if desired. At a lower plate hydrocarbon having almost the original composition may be taken off, and such hydrocarbon recirculated to the oxidizer, and thence back to the fractionating column. Fresh hydrocarbon fraction of the same boiling point as the original is fed to the oxidation zone continuously to replace that removed by oxidation. It is to be noted that the oxidation proceeds at a higher rate (which is particularly desirable at temperatures of 150° C. and lower) if the substance being oxidized contains a small quantity of oxidation product. This is best achieved under such continuous method by allowing a portion, or perhaps all, of the degradation product to go to the oxidizer, together with the recirculated hydrocarbon.

The drawing illustrates a diagrammatic apparatus that can be utilized in carrying out such continuous process. A column 1 consisting of any type of column suitable for liquid phase oxidation, such as a trickle column, and which may contain baffles, contact elements, etc., if desired, is maintained desirably at atmospheric or higher pressure, the principal portion of the hydrocarbon materials to undergo treatment being obtained from the condenser described below. Air or oxygen is introduced through the valved pipe 2, while exhaust gases may be taken off from the valved outlet 3, which may be fitted with a condenser, if desired. From the bottom of column 1, the products of incipient oxidation are carried together with large quantities of unchanged hydrocarbon through pipe line 4, provided with valve 5, to the fractionating column

6, the latter desirably operating under vacuum. In column 6 the partially oxidized hydrocarbon is subjected to fractionation. The liquid products from column 6 pass through valved outlet 7 into the still 8, maintained at the desired temperature for removal of any unoxidized hydrocarbons, oxygenated degradation products, etc., so that the residues in the still contain the desired secondary alcohol and ketone, or related products, which may be drawn off from the still as desired through the valved outlet 9. The pipe 10 having valve 11 returns the products distilled out of still 8 to the bottom of the column 6. Hydrocarbon vapors together with some degradation oxygenated products pass out of column 6 through the valved outlet 12 to a condenser 13, the condensate from which passes into column 1. The fresh hydrocarbon material desired for treatment may be introduced, either into the fractionating column 6, as through the valved inlet 14, or into the trickle column through the valved inlet 15. Such apparatus may be operated in the manner described immediately above, particularly in the oxidation of the higher molecular weight paraffin hydrocarbons in the production of large quantities of secondary alcohols and ketones.

These methods enable the production of large quantities of secondary alcohols and ketones, as well as other products, and derivatives of secondary alcohols and ketones by commercially feasible methods at relatively low cost. New types of products are thus obtainable, which have never heretofore been produced in the art. The secondary alcohols and ketones may be readily separated from the acids present in the liquid phase oxidation residual products by treatment with alkali and distillation, the acids remaining fixed, and the secondary alcohols and ketones being distilled over. The secondary alcohols and ketones may also be readily segregated as groups from each other by methods which are generally known, such as chemical combination of the alcohols with phthalic anhydride or sulphuric acid.

As noted, the secondary alcohols predominate in the product, and if desired the ketones may be reduced by catalytic or chemical means and converted into further quantities of secondary alcohols. Or if desired the secondary alcohols can be readily oxidized to ketones, either chemically or by controlled air oxidation in presence or absence of a catalyst. The secondary alcohols are a mixture including most if not all of the possible isomers from the given hydrocarbon, some of the isomers being present to much greater extent than others, however. Segregation of individual isomers is not essential, since the complex mixture of isomeric products may be utilized as an entity, and, indeed, is often to be preferred to an individual species as, for example, in the preparation of synthetic waxes. Thus the alcohols may be converted into esters of either organic or inorganic acids, and desirably may be esterified with the higher fatty acids, such as lauric, stearic, or oleic, or other acids, such as dibasic acids, for example, to form waxes. Highly valuable synthetic waxes may be produced in this way, and products substantially water white in color obtained if both the alcohol and acid are distilled shortly before being combined to form the esters. Esterification of such secondary alcohols may take place with acids from an extraneous source, or from acids produced by the oxidation.

The secondary alcohols may be converted into

so-called sulfonated alcohols (which are really sulfated alcohols) and sold commercially in the form of their sodium salts. These products it will be noted will be derived from the secondary alcohols, and offer new derivatives of great moment in the art, since the secondary alcohols and their derivatives are very much more soluble in organic solvents than are the products derived from primary alcohols, and emulsify even more readily in aqueous solutions. Thus in the form of detergents, detergents prepared from the secondary alcohols are better than those prepared from primary alcohols, and, further, detergents and wetting agents prepared from the very high molecular weight secondary alcohols are, in general, more efficient than those prepared from secondary alcohols in the molecular weight range of the primary alcohols ordinarily used in the prior art for preparing detergents. Thus the alkali or alkaline earth salts of half esters with phthalic anhydride or sulfuric acid may be employed as very stable emulsifying agents or detergents of great value, superior to even the derivatives of primary alcohols now on the market under such names as "Dreft" and "Gardinol." The new types of detergents derived from the combination of these secondary alcohols with phthalic anhydride, for example, possess certain valuable advantages over known prior art products, as, for example, in the processing of textiles.

These alcohols may be employed in preparing oil-soluble metallic salts of half phthalates, half sulfates, etc., partial phosphates, and so on, to be used as driers. Thus derivatives of lead, cobalt, manganese, etc., of this character may be produced.

It is thus apparent that aside from the use of the derivatives themselves, the secondary alcohols may be converted into a variety of compounds, such as the alkali or alkaline earth salts of the half phthalates, and other partial esters, as detergents, or into a wide variety of metallic salts of the half phthalates and other partial esters as driers, etc., for valuable exploitation in the art. The waxes produced from these synthetic secondary alcohols and a variety of monobasic and polybasic acids enable the production of snow-white waxes with a wide variety of melting points and other properties to be produced for use in lacquers or other surface finishes, synthetic resins, etc.

In the production of driers, the various metal salts may be employed as indicated above, and in general various alkali or alkaline earth salts, and other metallic salts of partial esters with organic or mineral acids, such as phthalic, sulfuric, phosphoric, etc., may be produced. The half phthalates, as well as other partial ester salts are soluble in petroleum hydrocarbons and in a wide variety of organic solvents, in which characteristic they far exceed similar derivatives of primary alcohols.

Instead of conversion into other derivatives, the secondary alcohols may be employed as such, as, for example, for addition to mineral oils within the lubricating range to enhance the desired properties of such lubricating oils.

Similarly the ketones may be converted to secondary alcohols by reduction, and utilized in that form in any of the manners set forth above, or the ketones may be employed as such without any necessary segregation of individual components therefrom, the product or entity being used as such. They may be added to lubricating oils for desirable improvement in properties.

Also, the ketones may be combined with hydrocyanic acid to form hydroxy nitriles which may be hydrolyzed to form alpha-hydroxydialkylacetic acids. These latter are readily dehydrated and/or reduced to alpha, beta dialkyl acrylic acids and/or dialkyl acetic acids. The hydroxy nitriles are readily converted into amino nitriles, thence to alpha amino-dialkyl acetic acids. The substituted acrylic acids and addition products and other derivatives of same, as well as the other branched chain acids, offer attractive possibilities in a number of fields. The salts of the higher dialkyl acetic acids are soluble in oils, in contradistinction to those of the higher straight-chain acids.

The fatty acids produced under the conditions set forth hereinabove are not generally extensively oxygenated or hydroxylated, and hence are highly valuable in the making of soap, or in the preparation of waxes, as by combination with the secondary alcohols formed in the oxidation itself.

The volatile condensible products, as indicated above, represent a very highly complex mixture including acids, aldehydes, ketones, and lactones particularly as the more important components therefrom, from which desired components or groups of components may be segregated as desired.

While the invention has been particularly emphasized by illustration in connection with the oxidation of high molecular weight paraffin hydrocarbons of saturated character, it may be employed in the oxidation of other types of derivatives, both hydrocarbon and hydrocarbon derivatives, including saturated and unsaturated hydrocarbons, particularly of the paraffin type, and more particularly of high molecular weight, and both liquid and solid paraffin hydrocarbons may thus be treated to produce valuable products. Unsaturated paraffin hydrocarbons or aliphatics may be treated, as well as fractions of various types, both liquid and solid, obtained from petroleum, aromatic hydrocarbons, etc. Thus branched chain compounds may be oxidized in accordance with the present invention. Such compounds ordinarily absorb oxygen at the tertiary C atom. The tertiary alcohol so formed is generally unstable, and would be dehydrated to form asymmetric dialkyl or trialkyl ethylenes, which may be further oxidized to form ketones and lower aldehydes. Other types of products may also desirably be treated in accordance with the present invention, including fatty acids or their esters, and other long chain compounds. The process may thus be applied to oxidation of any constant boiling organic compound, mixture, or azeotrope to produce derivatives that can be separated by fractional distillation, and the carbon content of which corresponds closely with that of the compound subjected to oxidation. Thus fatty esters may be oxidized to mono-hydroxylated fatty acid esters, and chlorinated hydrocarbons to chlorhydrins. The latter class may later be converted to aminohydrins, thence to amino or anilino-waxes or resins, etc.

Controlled oxidation of mono- or di-, etc., chlorinated hydrocarbons yields a large percentage of mono-, di, etc., chlorhydrins. These are highly valuable compounds. For example, they may be caused to react with ammonia, aniline, alkyl cyanides, etc. to form aminohydrins, anilino-hydrins, cyanohydrins, etc., which are of value in several manufacturing processes, for example, in the formulation of synthetic resins, of hydroxy

secondary alkyl amides, or of amino or anilino alkyl derivatives, or of monohydroxy acids.

Having thus set forth my invention, I claim:

1. The process of producing oxidation products which comprises subjecting a heated high molecular weight paraffin hydrocarbon in liquid condition to the action of an oxygen-containing gas until not more than one atom of oxygen per two moles of hydrocarbon has been absorbed to produce a product containing a preponderance of secondary alcohols and ketones, and removing the oxidation product when it contains a preponderance of secondary alcohols and ketones.

2. The process of producing oxidation products which comprises subjecting a heated mixture of high molecular weight paraffin hydrocarbons in liquid condition to the action of an oxygen-containing gas until not more than one atom of oxygen per ten moles of hydrocarbon has been absorbed, and removing the liquid oxidation product from the oxidation zone.

3. The process of producing oxidation products which comprises subjecting a constant boiling organic composition while in liquid condition and at a temperature above 100° C. to the action of an oxygen-containing gas until not more than one atom of oxygen per two moles of hydrocarbon has been absorbed to produce a product containing a preponderance of hydroxylated bodies is obtained, and removing such product while containing a preponderance of hydroxylated bodies.

4. The process of producing oxidation products which comprises subjecting a heated composition containing a high molecular weight paraffin hydrocarbon in liquid condition to the action of oxygen until the oxygen absorbed amounts to from one atom of oxygen per ten moles of hydrocarbon to one atom of oxygen to one thousand moles of hydrocarbon, and removing the liquid oxidation product from the oxidation zone.

5. The continuous method of producing oxidation products which comprises subjecting a heated high molecular weight paraffin hydrocarbon in liquid condition to incipient oxidation until not more than one atom of oxygen per two moles of hydrocarbon has been absorbed to produce a product containing a preponderance of secondary alcohols and ketones, removing the liquid oxidation product from the oxidation zone, segregating the secondary alcohols and ketones in substantial amount from the liquid oxidation product, and returning the unoxidized portion to the oxidation zone for further oxidation treatment.

6. The process of producing oxidation products which comprises subjecting a heated composition containing a paraffin hydrocarbon in liquid condition and having a carbon content of from C_6H_{12} to $C_{30}H_{62}$ at temperatures between 100° C. and 350° C. to the action of an oxygen-containing gas until not more than one atom of oxygen per ten moles of hydrocarbon has been absorbed, and

removing the liquid oxidation product when it contains a preponderance of secondary alcohols and ketones.

7. The process of producing oxidation products which comprises subjecting a heated composition containing a paraffin hydrocarbon in liquid condition and having a carbon content of from $C_{12}H_{26}$ to $C_{28}H_{58}$ at temperatures between 100° C. and 350° C. to the action of an oxygen-containing gas until not more than one atom of oxygen per ten moles of hydrocarbon has been absorbed, and removing the liquid oxidation product from the oxidation zone when it contains a preponderance of second alcohols and ketones.

8. The method of producing oxidation products which comprises subjecting a heated high molecular weight paraffin hydrocarbon in liquid condition to incipient oxidation until not more than one atom of oxygen per two mols of hydrocarbon has been absorbed to produce a product containing a preponderance of secondary alcohols and ketones, removing the liquid oxidation product from the oxidation zone and segregating the secondary alcohols and ketones in substantial amount from the liquid oxidation product.

9. The method of producing oxidation products which comprises subjecting a heated high molecular weight paraffin hydrocarbon in liquid condition to incipient oxidation until not more than one atom of oxygen per ten mols of hydrocarbon has been absorbed to produce a product containing a preponderance of secondary alcohols and ketones, removing the liquid oxidation product from the oxidation zone and segregating the secondary alcohols and ketones in substantial amount from the liquid oxidation product.

10. A liquid phase direct oxidation product of a high molecular weight paraffin hydrocarbon, said product containing a complex mixture of isomeric secondary alcohols and isomeric ketones, the isomers having any single carbon value selected from the group consisting of from nine to thirty carbon atoms.

11. A liquid phase direct oxidation product of a high molecular weight paraffin hydrocarbon, said product containing a complex mixture of isomeric secondary alcohols, the isomers having any single carbon value selected from the group consisting of from twelve to twenty-eight carbon atoms.

12. A liquid phase direct oxidation product of a high molecular weight paraffin hydrocarbon, said product containing a complex mixture of isomeric ketones, the isomers having any single carbon value selected from the group consisting of from twelve to twenty-eight carbon atoms.

13. The liquid phase direct oxidation product of a high molecular weight paraffin hydrocarbon, said product containing a complex mixture of isomeric secondary alcohols and isomeric ketones resulting from the process of claim 1.

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