PROCESS FOR OXIDATION

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This invention relates to partial oxidation products and methods of producing such products from hydrocarbons or hydrocarbon oils, such as petroleum and petroleum fractions. The invention also relates to alcohols and/or ketones and to methods of producing such alcohols and/or ketones from non-aromatic cyclic hydrocarbons. The invention also relates to polyvalent metal salts of phosphate esters of the partial oxidation of hydrocarbons or hydrocarbon fractions and to lubricating oil compositions containing these metal salts.

An object of the present invention is to further the progress in preparing oxygenated hydrocarbon derivatives from hydrocarbons or hydrocarbon fractions, using in this case a method which limits the extent of oxidation thereby limiting the number and complexity of oxygenated products thus allowing the more ready segregation of the oxygenated derivatives into pure compounds.

Another object of the invention is to prepare from a single hydrocarbon or from a given hydrocarbon fraction, such as a relatively narrow boiling range hydrocarbon fraction prepared from petroleum, cyclic and/or acyclic alcohols and ketones with a minimum production of the more highly oxidized products, such as aldehydes, acids, hydroxy acids, etc., and ultimate oxidation products such as water and carbon dioxide.

A further object of the invention is to provide a method for producing alcohols and/or ketones in substantial quantities from hydrocarbons.

A further object of our invention is to prepare cyclic and/or acyclic alcohols and ketones having five or more carbon atoms per molecule from non-aromatic cyclic hydrocarbons, whether used alone or mixed with acyclic or aromatic hydrocarbons boiling at or near the same temperature as the non-aromatic cyclic hydrocarbons, by a process involving oxidation with oxygen, air, or other oxygen-containing gas.

A particular object of our invention is to prepare a lubricating oil addition agent and to prepare a lubricating oil composition comprising a major proportion of a lubricating oil and a minor proportion of an addition agent, said addition agent being a polyvalent metal salt of the reaction product of phosphorus pentasulfide or phosphorus pentoxide and the cyclic and/or acyclic alcohols produced by partial oxidation of hydrocarbons.

Other objects, features and advantages of our invention will be apparent to those skilled in the art as the description thereof proceeds and from the examples submitted herein.

The invention comprises oxidizing a hydrocarbon or a relatively narrow boiling range hydrocarbon fraction in the liquid phase and under conditions such that only partial oxidation occurs, the partial oxidation products being removed continuously by processes involving fractional distillation, extractive distillation, azeotropic distillation, solvent extraction or adsorption from the slightly oxidized hydrocarbon or hydrocarbon fraction at such a rate that only minor portions of these primary oxidation products are further oxidized, thus permitting the production of relatively high yields of partial oxidation products.

The invention also comprises separating the products of partial oxidation into substantially pure compounds or into fractions comprising alcohols or ketones by relatively simple processes involving physical and/or chemical treatments, the particular method employed in a given case depending upon the character and the complexity of the oxygenated products to be separated.

The invention further comprises converting said partial oxidation products into lubricating oil addition agents and blending said addition agents with lubricating oil to produce lubricating oil compositions having improved film strength, anticorrosion and detergency characteristics.

Alcohols and ketones having five or more carbon atoms per molecule are particularly valuable products. The ketones are used in the synthesis of chemicals and perfumes, as solvents for lacquers, gums, resins, nitrocellulose, etc., and for the production of alcohols. The alcohols have use in perfumes, as antifoaming agents, as solvents for dyes, oils, waxes, gums, resins, etc., in the production of esters, acids, etc., as emulsifying agents, and in textile finishing compositions. Also alcohols produced by our oxidation process may be reacted with phosphorus pentasulfide to form the corresponding dialkyli thiophosphates and the products of this reaction may then be reacted with metals or metal oxides to form the corresponding metallic salts of the dialkyli thiophosphates and/or dialkycloalkyli thiophosphates and these compounds are excellent lubricating oil additives. When blended with mineral lubricating oils in amounts in the order of from about 0.1% to about 10% or more the metal dialkyli thiophosphates impart high film strength to the oil, they improve the stability of the oil toward oxidation, reduce bearing corrosion in an engine and, when used in conjunction with other additives having detergency characteristics, they markedly increase the detergency of the lubricating oil blends containing the latter additives. Such other additives, which may be employed in amounts in the order of from about 0.1% to about 5.0% of the finished lubricating oil composition, may be oil-soluble polyvalent metal soaps of various carboxylic acids, such as phenylated carboxylic acids, e.g., calcium phenyl stearate and magnesium phenylstearate, chlorinated and phenylated fatty acids, e.g., calcium dichlorophenylstearate.
rate and zinc dichlorophenylstearate; oil-soluble polyvalent metal salts of oil-soluble petroleum sulfonic acids, such as the calcium salts of the oil-soluble sulfonic acids prepared by treating petroleum oils, such as lubricating oil, with strong sulfuric acid. Other oil-soluble polyvalent metal salts of these acids may also be used, such as those in which the metals may be strontium, barium, magnesium, zinc, manganese, aluminum, and lead.

Lubricating oils which may be blended with our organic phosphate addition agent, or with any agent together with one of the above disclosed other additives having detergency characteristics, include all mineral lubricating oils because we find that the valuable characteristics of our addition agent are imparted to all mineral lubricating oils. We prefer to employ treated oils such as acid refined Western lubricating oils, highly solvent refined Western lubricating oils or we may use Eastern lubricating oils such as Pennsylvania oils.

The alcohols which may be prepared by the partial oxidation of hydrocarbons and which may be employed to produce desirable lubricating oil additives when treated in the above manner include the cycloaliphatic alcohols containing from five to about twelve carbon atoms and preferably seven to ten carbon atoms per molecule and the acyclic aliphatic alcohols containing from seven to about eighteen carbon atoms and preferably eight to fourteen carbon atoms per molecule.

The lubricating oil additives may be prepared by heating and agitating a mixture of 4 gram moles of the alcohol with 1 gram mole of phosphorus pentasulfide at a temperature of 250° F. to 300° F. until the P₅S₅ is completely dissolved. Indicating that it has reacted completely with the alcohol and the product of this reaction is maintained at the same temperature and agitated with one gram mole of an oxide of one of the polyvalent metals disclosed hereinabove or with one gram atom of the polyvalent metal itself to form the metal salt of the triphosphate ester. The first reaction results in the formation of relatively large proportions of the dialkyl or dicycloalkyl thiophosphates represented by the following formula in which R represents the hydrocarbon radical of the alcohol:

\[
S = P - OR
\]

It is known that other acid thiophosphate esters are produced by the above reaction but their presence in the reaction mixture apparently does not degrade the quality of lubricating oil additives prepared from this mixture. Formulas for the other esters which are present in the reaction product of a phosphorus pentasulfide in relatively small proportions are:

\[
S = P - OH; \quad S = P - OR; \quad S = P - OR; \quad \text{and} \quad S = PO - OR
\]

Phosphorus pentoxide may be used in place of the phosphorus pentasulfide in the production of lubricating oil addition agents and in this case the oxyphosphate esters are formed. Thus 4 moles of an aliphatic or cycloaliphatic alcohol may be reacted with one mole of phosphorus pentoxide to produce the corresponding dialkyl or dicycloalkyl phosphates. These phosphate esters may then be reacted with one of the above one of these metals to form the corresponding polyvalent metal salt of the dialkyl or dicycloalkyl phosphates.

Alcohols which are useful for the above purposes are in general difficult and costly to produce and require the use of expensive chemical processes. We find that we may use any of the above alcohols, both cyclic and acyclic, which contain five or more carbon atoms per molecule, and may be converted into the corresponding alcohols as indicated hereabove.

In carrying out the production of partial oxidation products according to the principles of our invention, the hydrocarbon or narrow boiling range hydrocarbon fraction to be oxidized is contacted with oxygen, air, or other gas containing free oxygen until the proper proportion of hydrocarbon molecules oxidized is about 0.1% to about 10% or preferably about 0.5% to about 5.0% of the total molecules present and the concentration of oxygenated molecules is thereafter maintained at an approximately constant value by continuously withdrawing portions of the stream of hydrocarbon material present in the oxidation vessel, separating the oxygenated molecules from the unoxidized hydrocarbon material, as by fractional distillation, and returning the latter material to the oxidation unit together with sufficient additional feed to maintain an approximately constant level in this vessel. The volatile materials, such as any oxygenated degradation products, pass out of the unit with spent air or other gaseous oxidizing medium. This operation involving the separation of oxidation products from unoxidized hydrocarbons can be considered to be a stripping operation.

Although we may use any hydrocarbon or narrow boiling hydrocarbon fraction we prefer to employ a non-aromatic cyclic hydrocarbon, or a narrow boiling range hydrocarbon fraction, containing at least one non-aromatic cyclic hydrocarbon. Thus, hydrocarbons which may be used as feed include cyclopetanone or any of the mono, di, tri, tetra, or penta alkylcyclopentanes, such as methylcyclopentane, dimethylcyclopentane, methylcyclohexane, etc.; cyclohexane or any of the mono, di, tri, tetra, pent, or hexa alkylcyclohexanes, such as methylcyclohexane, dimethylcyclohexane, diethylcyclohexane, etc.; naphthenyl cyclopentanes or cyclohexanes containing one or more naphthenyl groups, such as bicyclopetanone, bicyclohexane and alkyl substituted bicyclopetanes and bicyclohexanes, such as methylbicyclopetanone and methylbicyclohexane; hydro aromatics, such as decahydronaphthalene and alkyl substituted hydroaromatics, such as methyldodecahydronaphthalene. Mixtures of two or more of the above mentioned hydrocarbon hydrocarbons may be employed as feed if desired when such mixtures have boiling ranges not wider than about 50° F. and preferably not wider than about 10° F. Also hydrocarbon fractions containing at least one of the above disclosed naphthenic hydrocarbons together with non-naphthenic hydrocarbons, such as paraffins or olefins or aromatics, or mixtures of these non-naph-
our invention. Such fractions should have a boiling range not wider than about 50° F. and preferably not wider than about 10° F.; hydrocarbon fractions containing one or more of the above mentioned cyclolefins or cycloolefins, paraffins, olefins and aromatics; alkenyl substituted cyclopentanes and cyclohexanes, such as ethenylcyclopentane, ethenylcyclohexane, etc.; alkyl substituted mono, di, tri, etc., alkyI cyclopentanes and cyclohexanes, such as isopropylcyclopentane, isopropylcyclohexane, etc.; mixtures of such alkenyl substituted cyclopentanes, cyclohexanes, alkyl cyclopentanes and alkyl cyclohexanes; and hydrocarbon fractions containing at least one of the alkenyl derivatives, such mixtures or fractions containing relatively low boiling ranges as specified hereinabove for mixtures or fractions suitable for treatment in our process.

Although, as is indicated hereinabove, we may treat a hydrocarbon mixture or fraction comprising at least one non-aromatic cyclic hydrocarbon together with paraffin, olefin and aromatic hydrocarbon boiling at or near the boiling point of the non-aromatic cyclic hydrocarbon, it is preferable to remove substantially all of the aromatic hydrocarbons before carrying out said treatment. Methods for separating and/or removing the aromatic hydrocarbons from such mixtures include azeotropic distillation, solvent extraction, extractive distillation and, in the case of hydrocarbon fractions which do not contain cycloolefin hydrocarbons, sulfuric acid treatment may be employed. The methods of effecting azeotropic distillation, extractive distillation and solvent extraction and the azeotrope formers or solvents which may be employed are disclosed hereinbelow.

Alcohols and ketones which may be produced by our process include the cycloaliphatic and alkycycloaliphatic alcohols and ketones, such as cyclopentanol and cyclohexanol, and cyclopentanone and cyclohexanone; the various isomeric methyl-, ethyl-, propyl-, isopropyl-, butyl-, etc., cyclopentanols, cyclohexanols, cyclopentanone and cyclohexanone; the various isomeric dimethyl-, methyl ethyl-, methyl propyl-, methyl isopropyl-, methyl butyl-, diethyl-, etc., cyclopentanols, cyclohexanols, cyclopentanones and cyclohexanones and higher molecular weight homologs of these compounds; the alkenyl cycloaliphatic alcohols and ketones, such as ethenylcyclopentanol, ethenylcyclohexanol, ethenylcyclopentanone and ethenylcyclohexanone; and the higher homologs of these compounds, such as the isomeric methylethenylcyclohexanols, methylethenylcyclohexanones, ethylpropenylcyclopentanol, etc. The aliphatic alcohols and ketones which may be produced by our process include pentanols, pentanones, the various isomeric methyl- and ethyl-pentanols and pentanones, hexanols and hexanones, the isomeric methyl-, ethyl-, propyl-, and isopropyl- hexanols and hexanones; dialkyipentanols, pentanones, hexanols, and hexanones and higher homologs of these compounds such as trimethylhexanol, dimethylethylhexanone, etc. Olefinic alcohols and ketones which may be produced include hexenol and hexenone; the various isomeric methyl-, ethyl-, etc., hexenols and hexenones; heptenol, heptanone and the various alkyl substituted heptenols and heptanones; higher 1-nenyl and 1-nenone; olefinic alcohols and ketones including octenol, octenone, nonenol, nonenone, decanol, decanone, and the alkyl substituted derivatives of these alcohols and ketones, such as the various isomeric methyl- and ethenylcyclohexanols, methylnonanones, methylynonenol, etc.

The above disclosed alcohols may be used singly or mixtures of two or more of these alcohols may be reacted with phosphorus pentasulfide or phosphorus pentoxide and the resulting reaction product reacted with a polyvalent metal or metal oxide to produce a desirable lubricating oil addition agent. Moreover, the ketones listed above may be reduced to the corresponding alcohols and these alcohols may then be employed as above indicated in the production of lubricating oil addition agents.

Hydrocarbons or hydrocarbon fractions such as those specified hereinabove may be oxidized in the liquid phase by blowing or otherwise contacting them with oxygen, air or other oxygen-containing gaseous mixture. The liquid hydrocarbon is maintained at a temperature and a pressure high enough to cause oxidation to occur. We may oxidize at temperatures in the order of from about 100° F. to about 500° F., although we prefer to carry out the treatment at temperatures in the order of from about 200° F. to about 350° F. Pressures in the order of from about normal atmospheric pressure to about 360 pounds per square inch gauge may be employed, although we prefer to effect the oxidation at gage pressures in the order of from about 50 to about 150 pounds per square inch. The temperature and pressure selected for oxidation will vary with the compound being treated and in general the temperature used will be as low as can be successfully employed to cause the oxidation reaction to proceed at an economical rate. This general rule is followed because it is found that the use of lower temperatures reduces the amount of secondary oxidation products for a given quantity of production of primary oxidation products and also reduces the proportion of oxygenated degradation products and polymerization and/or condensation products. These latter products are defined, for the purposes of this invention, as those products which may contain oxygen or not, which have been produced during the oxidation and which contain fewer carbon atoms per molecule than the hydrocarbon stock being oxidized. Moreover, the pressures employed will vary with the particular hydrocarbon.
being treated and with the temperature. In general it is desirable that the pressure be great enough to prevent the ready volatilization of the hydrocarbon stock being oxidized, thus minimizing the required condenser and cooler capacity required to strip liquid products from the exhaust gases leaving the oxidizer.

We may carry out the oxidation without the use of oxidation catalysts since, in general, liquid phase oxidation of hydrocarbons of the types discussed hereinabove occurs readily in the absence of catalysts. However, we may employ catalysts to increase the rate of oxidation, to permit the use of lower temperatures and/or pressures which would otherwise be required, or to direct the course of the oxidation reaction. Solid catalysts which are supported in the oxidation vessel are desirable since they do not complicate the separation of partial oxidation products from unoxidized hydrocarbons and are not removed from the oxidation vessel along with portions of the partially oxidized hydrocarbon charge which are withdrawn and treated for the removal of partial oxidation products. Catalysts which are useful in our process include those oxidation catalysts comprising metals of the series having atomic numbers 20 to 31 inclusive, i.e., calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc as well as the metals magnesium, aluminum, molybdenum, silver, tin, tantalum, cerium, neodymium, platinum, thorium, and uranium. By the term oxidation catalysts comprising metals we also intend to include compounds of these metals such as oxides and salts, such as the chlorides, bromides, iodides, nitrates, sulfates, sulfites, phosphates, phosphites, vanadates, titanates, chromates, bichromates, molybdates, tungstates, uranates, etc. These metals, metal oxides or salts may be used as such or they may be dispersed on or impregnated in supports, said supports being materials such as pumice, silica gel, kaolin, kieselguhr, fuller's earth, alunina, magnesia, asbestos fiber, etc. Also, combinations of two or more of the above metals, metal oxides, or salts may be used as the catalyst. In some instances it is desirable to employ a soluble or homogeneous catalyst which would be particularly active in initiating the oxidation and in such instances an organic salt of the above dispersed metals may be employed. Thus calcium, magnesium, iron, etc., naphthenates are active oxidation catalysts. Moreover, we may prefer to use an oxidation initiator, such as a peroxide as, for example, benzoyl peroxide, nitrogen peroxide, hydrogen peroxide, etc.

The treatment of a hydrocarbon or hydrocarbon mixture for the production of partial oxidation products is desirably carried out in the equipment illustrated in the drawing. A column 1, consisting of any type of column or vessel suitable for the liquid phase oxidation, which if desired, may contain packing material, plates or trays, baffles, or other means of increasing the contact between the hydrocarbon material and the oxygen or oxygen-containing gas and which is arranged for heating and cooling, as by means of steam and water in internal coils, is maintained at a pressure between about normal atmospheric pressure and 300 pounds per square inch gage. Oxygen, air or other gas containing free oxygen is introduced through valved inlet 2 and exhaust gases and vapors escape through outlet 3. Partially oxidized hydrocarbon material together with unoxidized hydrocarbon material is withdrawn from the bottom of the oxidizer through line 4, the rate of flow being controlled by valve 5 and passed to fractionating column 6 containing packing material or plates or other means of aiding distillation and having a reboiler 7 to supply the heat required for fractionation. Column 6, together with its essential appurtenances constitutes the stripping section and this section and its operation may be varied as indicated hereinbelow. In those cases in which fractional distillation is employed as the means of effecting the separation of oxygenated molecules, i.e., products of partial oxidation, from unoxidized hydrocarbon molecules and oxygenated degradation products which boil at temperatures at or below the boiling point or boiling range of the hydrocarbon feed, column 6 is maintained at any desirable pressure between about 29 inches of mercury vacuum and 300 pounds per square inch gage. In these cases, the products of partial oxidation are removed from the bottom of column 6 through valved outlet 8 and the unoxidized hydrocarbon materials, together with degradation products, pass as vapors from the top of the column through line 9 and condenser 10 where the vapors are condensed and the condensate passes into reflux drum 11. A portion of this liquid is returned as reflux to the top of column 6 through line 12, the rate of liquid flow through this line being controlled by valve 13. Valved line 14 carries liquid products from reflux drum 11 to pump 15 and thence to the oxidation column 1. New feed enters the system through valved line 16 leading into line 14. Exhaust gases and vapors leaving the oxidation vessel through line 3 are passed through condenser 17 into separator 18 from which the uncondensed gases escape through line 19 and pressure control valve 20. The liquid in this separator contains an aqueous phase containing low molecular weight fatty acids, aldehydes and other preferentially water-soluble oxygenated products and a hydrocarbon phase containing in addition to unoxidized hydrocarbons, oxygenated degradation products which are preferentially soluble in the hydrocarbon phase. The aqueous phase is removed through valved outlet 21 and the hydrocarbon phase in separator 18 may be returned directly to column 1 through valved outlet 22, or it may be transferred through valved line 23 to a fractionating column 24 which is heated by means of reboiler 25 and operated under atmospheric or higher pressures, in which column the liquid product, separated from the exhaust gases and vapors from the oxidation column, is fractionated to separate as a bottoms fraction, unoxidized liquid hydrocarbons which are returned through line 26 and by means of pump 27 to the oxidation column and as overhead distillate the oxygenated degradation products, said distillate being passed from the top of column 24 through line 28, condenser 29 and into reflux drum 30. A portion of the condensed overhead is returned as reflux through line 31 and valve 32 to fractionating column 24. Oxygenated degradation products are produced through line 33 and control valve 34. A valved inlet line 35 leading to the top of fractionating column 6 may be used as an inlet line for new hydrocarbon feed or, as described hereinabove, may be used as an inlet line for solvent in cases in which extractive distillation is employed to aid in the separation of the oxygenated products and unoxidized hydrocarbon material.

Although the oxidation equipment illustrated
in the drawing and described above shows the use of fractional distillation as the means of separating or stripping the products of partial oxidation from the unoxidized hydrocarbon we may employ other means of carrying out this separation, such as those indicated hereinafter. Thus the fractionating column 6 in the drawing may be used as an extractive distillation column. In such cases, a solvent which preferentially dissolves the oxidized molecules is pumped into the top of the column through valve line 2 and flows downward through the column contacting the vapors ascending the column and extracting therefrom the partially oxidized hydrocarbon molecules. The solvent, containing the products of partial oxidation, is withdrawn as bottoms from column 6 through valve outlet 6. This mixture is then pumped to a fractionating column (not shown in the drawing) where the partial oxidation products are distilled overhead leaving the solvent as bottoms. The bottoms from this column is returned as solvent to the top of column 6.

Solvents which are useful in segregating the products of partial oxidation from the unoxidized hydrocarbons in the extractive distillation of the mixture of these two components include monohydroxy alcohols, such as ethyl, propyl, isopropyl, and higher molecular weight normal and isomeric alcohols; polyhydroxy alcohols, such as mono-, di-, tri-, etc., ethylene glycols, the ethers of these ethylene glycols, such as monomethyl, monoethyl, monobutyl, etc., ethers of mono-, di-, tri-, etc., ethylene glycols; the esters of these ethylene glycols, such as chloroform, monoalkyl esters of ethylene glycol, propylene glycol and the ethers of propylene glycol; the esters of the ethers of propylene glycols, including propylene glycol and dipropylene glycol; polyhydroxy alcohols including the trihydroxy and tetrahydroxy alcohols, such as glycerine and erythritol; hydroxy amines such as ethanolamine, diethanolamine, triethanolamine; halohydrins such as glycolchlorohydrine; amines, such as butylamine, triethylamine and diamines, such as ethylenediamine; aliphatic ketones, such as methyl ethyl ketone, diethyl ketone, methyl isopropyl ketone, etc., di-, acetyl and acetylo ketone; cyclic ketones, such as cyclopentanone, cyclohexanone, methylcycloc hexanone and methylphenyl ketone; phenolic compounds, such as phenols, naphthols, cresols, xylenols, thymol, etc.; polyhydric phenols, such as resorcinol, pyrocatechol, pyrogallol, phloroglu cinol, etc.; alkylation polyhydric phenols, such as 1-methyl-2, 3-dihydroxy benzene, etc.; saturated heterocyclic compounds having five or six membered rings in which at least one of the atoms in the ring is oxygen, nitrogen or sulfur, such as oxolane, thiole, dioxolane, dioxane, oxane, piperidine, morpholine, dithiane, etc.; derivatives of such five and six membered heterocyclic ring compounds, such as N-ethylpyridoline, tetrahydrofururyl alcohol, dibutanol, N-ethylypyr idine, N-methylmorpholine, N-phenylmorpholine, etc.; nitro paraffins, such as nitromethane, nitroethane, nitropropane, nitrobutanes, nitropentanes, etc.; nitro alcohols, such as 2-nitro-1-ethanol, 2- and 3-nitro-1-propanol, etc., the nitro derivatives of unsaturated aliphatic hydrocarbons, such as nitroethylene and nitropropylene; the halogenated derivatives of the aforementioned nitro paraffins and nitroalcohols, such as chloronitromethane, 1-chloro-1-nitroethane, etc., nitro aromatic compounds, such as nitrobenzene, nitroiluenes, nitroxylene, etc.; and alky nitrites including the normal and isomeric nitrites from butyl to octynitrate.

The choice of solvent to be employed will generally depend upon the characteristics of the hydrocarbon stock being oxidized and upon the characteristics of the partial oxidation products being separated since it is preferable that the solvent does not form an azeotrope with the unoxidized hydrocarbon stock under the conditions of operation and it is preferable that the solvent have a boiling point at least 50° F. and preferably more than 70° F. above the boiling point of the hydrocarbon stock being treated. It is desirable also that the boiling point of the solvent be sufficiently different from the boiling point or boiling point range of the partial oxidation product that it may be separated therefrom by fractional distillation.

The above disclosed solvents may be used to separate the products of partial oxidation from the unoxidized hydrocarbon by the well known process of solvent extraction in the liquid phase. Such solvent extraction may be carried out batchwise or preferably by batch countercurrent or continuous countercurrent extraction. In such processes the oxidized products are dissolved by the solvent and separated as an extract phase which is subsequently fractionally distilled to separate the oxidation products and the solvent, and the unoxidized hydrocarbons or raffinate phase may be returned to the oxidizer directly or after fractionally distilling or otherwise treating it to remove small quantities of solvent. In addition to the solvents disclosed above we may employ aqueous solutions of mineral acids such as sulfuric acid, sulfurous acid, nitric acid, hydrochloric acid, phosphoric acid, etc., as the solvents to effect the separation of oxidized products from the unoxidized hydrocarbons. The addition of about 2 to 4 volumes of water to the aqueous mineral acid solution of the alcohols and/or ketones causes the separation of the alcohols and/or ketones as an upper phase which is substantially insoluble in the diluted mineral acid phase and which may be decanted from the latter phase. For example, 65% sulfuric acid is an excellent selective solvent for the primary oxidation products obtained in our partial oxidation process.

We may employ azeotropic distillation to separate the unoxidized hydrocarbons from the products of oxidation using fractionating column 6 in the drawing as the azeotroping column. This method is desirably employed in those cases in which the products of oxidation boil at or near the boiling point of the hydrocarbon being oxidized. The compound selected for the azeotrope former forms a minimum boiling point azeotrope with the unoxidized hydrocarbons and thus facilitates the separation of said hydrocarbons from the oxidation products. Azeotrope formers which may be employed may be selected from the list of solvents disclosed hereinafter for use in extractive distillation processes. In selecting the particular azeotrope former to use in a specific case it is important that the boiling point of the solvent used as azeotrope former is not more than 50° F. and preferably not more than about 20° F. above the boiling point of the hydrocarbon being oxidized.

In carrying out the azeotropic distillation the azeotrope former is mixed with the feed to the fractionating column 6 in line 4 in a sufficient
quantity to distill overhead all of the unoxidized hydrocarbon together with said azeotrope former leaving the oxidized products as bottoms, substantially free of unoxidized hydrocarbon and said azeotrope. Overhead distillate of the azeotrope is withdrawn from reflex drum 11, through line 14 and valve 38 to an azeotrope former recovery unit where the azeotrope former is separated, as by solvent extraction, from the unoxidized hydrocarbon. The separated unoxidized hydrocarbon is returned to the oxidizer through valve inlet 16 to line 14, and pump 15. We may also use an adsorption process for the removal of partial oxidation products from the mixture of unoxidized and oxidized hydrocarbons withdrawn from the oxidation vessel. In this case the product withdrawn from the oxidizer through line 4 is contacted with a solid adsorbent, such as activated charcoal, or a mineral adsorbent, such as silica gel, alumina, fuller's earth, bentonite, etc., in a percolator. In such a system the oxidized molecules are adsorbed and the unoxidized hydrocarbon after removal of the oxidized products is discharged from the percolator and returned to the oxidizer for further treatment. Two percolators containing an adsorbent are connected in parallel so that one may be used for adsorbing oxidation products, while the spent adsorbent in the other percolator is being treated for the recovery of adsorbed products and otherwise regenerated. Regeneration of the spent adsorbent may be accomplished by a steam stripping operation in which steam or superheated steam is blown through the percolator, after first draining all of the unoxidized hydrocarbon from the unit, and the steam containing the oxidation products is condensed and cooled and passed through a separator vessel where the aqueous phase is separated from the oxidation products.

The crude partial oxidation product, which may be stripped from its mixture with unoxidized hydrocarbon leaving the bottom of the oxidizer by any of the above mentioned processes, consists primarily of molecules having the same number of carbon atoms as the parent hydrocarbon and containing one atom of oxygen. This product comprises alcohols, ketones, or mixtures of alcohols and ketones, which may be produced by a primary oxidation reaction involving only the addition of one atom of oxygen per molecule. Thus, for example, the partial oxidation of methycyclohexane proceeds in the manner illustrated by the following equations:

\[
\begin{align*}
\text{Methycyclohexane} & + 1/2 \text{O}_2 \rightarrow \text{1-methycyclohexanol} \\
\text{CH}_3\text{C}_8\text{H}_{15} & + \text{O}_2 \rightarrow \text{CH}_3\text{C}_8\text{H}_{15}\text{OH} \\
\text{CH}_3\text{C}_8\text{H}_{16} & + \text{O}_2 \rightarrow \text{2-heptanone} \\
\end{align*}
\]

In the first reaction the oxygen atom enters the tertiary carbon atom and the tertiary hydrogen atom attaches itself to the oxygen forming a cycloaliphatic alcohol. In the second reaction the oxygen atom replaces the tertiary hydrogen and in this case the ring breaks at position 1, the tertiary hydrogen atom shifting to the end carbon atom of the carbon chain and the reaction results in the formation of an acyclic aliphatic ketone.

Other types of ketones which may be produced by partial oxidation and which may be present in the oxidized product together with the alcohols or ketones of the types noted above are the cycloaliphatic ketones. These compounds are produced by the reaction between one molecule of oxygen and one molecule of the hydrocarbon and this type of reaction may be represented by the following equation:

\[
\begin{align*}
\text{Cyclohexane} + \text{O}_2 & \rightarrow \text{Cyclohexanone} \\
\text{CH}_3\text{C}_8\text{H}_{15} & + \text{O}_2 \rightarrow \text{CH}_3\text{C}_8\text{H}_{15}\text{COH} \\
\end{align*}
\]

In this case one atom of oxygen replaces the two hydrogen atoms attached to one of the carbon atoms forming a cyclic ketone and the thus freed hydrogen atoms combine with the second oxygen atom to form water.

The proportion of alcohol to ketone in a given partial oxidation product will depend upon the particular hydrocarbon being oxidized, the catalyst employed, and upon the temperature and pressure maintained in the oxidizer and may therefore be varied within certain limits by changing the hydrocarbon feed and/or the conditions of treatment. Thus the controlled partial oxidation of methycyclohexane at relatively low pressures and temperatures results in the production of approximately equal quantities of methycyclohexanol and 2-heptanone, whereas the oxidation of 1,3-dimethycyclopentane under similar conditions of temperature and pressure results in the formation of large proportions of 5-methylhexanone-2 and relatively small proportions of 1,3-dimethycyclopentanone.

In those instances in which alcohols are the desired products and mixtures of alcohols and ketones are obtained as products of partial oxidation the ketones may be reduced to the corresponding alcohols. This reduction may be carried out on the mixture of alcohols and ketones and in this instance the resulting alcohols would be a mixture of cyclic and acyclic alcohols, or the crude product may first be separated into a ketone fraction and an alcohol fraction by fractional distillation or by a chemical treatment as indicated hereinbelow and the ketone fraction, subsequently reduced to the corresponding alcohol.

The reduction may be carried out by any of the well known processes for reducing or hydrogenating organic compounds, such as hydrogenation with gaseous hydrogen over a nickel, copper, or platinum catalyst.

This segregation of the partial oxidation products into a fraction consisting primarily of alcohols and a second fraction consisting primarily of ketones may be effected in any convenient manner. In some instances it is possible to accomplish this separation by fractional distillation. Thus, for example, when oxidizing methycyclohexane the products of partial oxidation comprise 1-methycyclohexanol which boils at about 315° F. and 2-heptanone which boils...
at 302°F. These compounds can be separated by careful fractional distillation. Improved separation by fractional distillation may often be realized by carrying out the distillation at reduced pressures, or at pressures greater than atmospheric pressure because the vapor pressures of the alcohol and ketone components do not change to the same extent with changes in distillation pressure and thus the spread between the boiling points of the component that becomes greater with changes in pressure, often allowing separation of components which boil at the same temperature under ordinary atmospheric pressures.

Chemical methods of separation, wherein a chemical reagent is caused to react, or form an addition compound with one of the components of the mixture, may also be employed. For example, the product of partial oxidation may be washed with a concentrated aqueous solution of sodium bisulfite which forms an addition product with the ketone. The alcohol which is unaffected by this treatment may then be decanted from the aqueous solution of the ketone addition compound and then decomposed as by warming with alkalis, such as dilute sodium hydroxide or with an acid, such as dilute sulfuric acid, releasing the ketone which may be decanted from the remaining aqueous phase. The alcohol and the ketone may be further purified by fractional distillation.

In those cases in which more than one alcohol and/or more than one ketone is formed by the oxidation reaction, as for example, when the hydrocarbon feed to the oxidizer contains more than one naphthene hydrocarbon, the ketones may be separated from the alcohols, as indicated above, and the separated components may then be fractionally distilled to separate individual alcohols and/or ketones in those cases in which the boiling points of the individual alcohols and ketones are sufficiently far apart to allow such separation to be made. However, in many instances it is not essential that the alcohol component be separated into individual compounds since mixtures of alcohols produced in such a process are entirely satisfactory for most of the uses indicated heretofore. Moreover, mixtures of ketones of similar type may be reduced to the corresponding alcohols and the thus produced mixture of alcohols may be employed without further separation.

The following specific examples further illustrate the invention.

Example I

Methylcyclohexane was pumped into the oxidation column, heated to a temperature of 250°F. and maintained at a pressure of about 50 pounds per square inch gage. Air was introduced at the bottom of the vessel at the rate of 65 cubic feet per barrel of methylcyclohexane per minute for a period of about 20 minutes until analysis of the oxidation charge showed the presence of one atom of combined oxygen per 200 molecules of methylcyclohexane. At this time fresh feed was started into the oxidizer at a rate such that the liquid level in the oxidizer remained constant throughout the operations described below. Partially oxidized methylcyclohexane was removed from the bottom of the column and transferred to a fractionating column maintained at normal atmospheric pressure and a temperature such that the temperature in the vapor line leading from the top of the column was 212.5°F. Unoxidized methylcyclohexane distilled overhead from this fractionating column and was condensed and returned to the oxidizer for further oxidation and oxidized products were removed as bottoms from the fractionating column, said oxidized products being further treated as described hereinbelow. Exhaust gases and vapors leaving the top of the oxidation column were passed through a condenser and into a separator. The condensed liquid being returned directly to the oxidizer and the uncondensed gases, consisting primarily of spent air, were vented to the atmosphere.

The oxygenated product obtained as bottoms from the fractionating column consisted primarily of a mixture of equal parts by weight of 1-methylcyclohexanol and 2-heptanone. A portion of this mixture was extracted with a saturated aqueous sodium bisulfite solution to separate the 2-heptanone, as an addition product with the sodium bisulfite, from the 1-methylcyclohexanol. The extracted cyclohexanol was subsequently fractionally distilled at reduced pressure to produce a substantially pure 1-methylcyclohexanol as a heart cut boiling between 150°F. and 160°F. at 22 mm. of mercury pressure. The bleachable addition product with the ketone was decomposed by treatment with dilute sulfuric acid, the freed ketone was separated by decantation from the aqueous layer, washed with additional quantities of water and finally fractionally distilled to produce a heart cut boiling between 300°F. and 304°F. at normal atmospheric pressure and consisting substantially of pure 2-heptanone. This latter fraction was reduced to the corresponding alcohol, 2-heptanol, by hydrogenation over a nickel catalyst at 300°F. and 400 pounds per square inch pressure for a period of 4 hours.

A second portion of the oxygenated product obtained as bottoms from the fractionating column and comprising a mixture of 1-methylcyclohexanol and 2-heptanone was hydrogenated in the manner indicated above for producing the separated 2-heptanone. The product comprised a mixture of 1-methylcyclohexanol and 2-heptanol.

To illustrate one use of the alcohols prepared as above, to 467 grams of 1-methylcyclohexanol, the 2-heptanol, or the mixture of these alcohols, is added 222 grams of powdered phosphorus pentasulfide and the mixture is agitated and heated to 278°F. for a period of three hours at which time the phosphorus pentasulfide has completely dissolved. To the resulting solution is added 82 grams of zinc oxide and the agitating and heating is continued for an additional four hours at which time the product is filtered hot (378°F.) to remove small amounts of unreacted zinc oxide. This product may be added to an SAE 30 highly solvent refined Western lubricating oil having Saybolt Universal viscosities of 540 seconds at 100°F. and 64 seconds at 210°F. and a viscosity index (Dean and Davis System) of 90, in the ratio of about 1 part by weight of the zinc salt to 99 parts of the lubricating oil and the resulting mixture heated to about 250°F. and agitated until the zinc salt is dissolved and thoroughly mixed in the oil to produce a lubricating oil composition which is a particularly desirable lubricant for internal combustion engines. This lubricating oil composition possesses improved film strength, anti-corrosion and detergency characteristics. Also, 1 part of the above described zinc salt may be blended in a similar manner with 1 part of the calcium salt of oil-soluble petroleum sulfonic acids produced by treating petroleum with strong sulfuric acid and 98 parts
of the above mentioned highly solvent refined Western lubricating oil to produce a lubricating oil composition having high film strength and anti-corrosion characteristics and particularly high detergent characteristics.

Example II

A naphthenic fraction of petroleum boiling between 192°F. and 198°F. prepared by careful fractionation of a straight run gasoline derived from a highly naphthenic crude oil and containing about 50% by volume of a mixture of dimethyleclopentanes was charged to the oxidation column, heated to 250°F. and maintained at a pressure of 60 pounds per square inch gage. Air was introduced into the oxidation column at a point near the bottom of the column at the rate of 65 cubic feet per barrel of charge per minute and exhaust gases and vapors were led from the top of the column through a condenser and into a separator from which condensed liquid flowed by gravity back to the oxidizer and uncondensed gases were allowed to escape to the atmosphere. The air blowing was continued for a period of approximately 20 minutes at which time analysis of the liquid in the oxidizer indicated the presence of approximately 0.5% of molecules containing oxygen. At this time fresh feed was pumped into the oxidizer at such a rate that the liquid level in the column remained constant throughout the following operations. The slightly oxidized hydrocarbon fraction was withdrawn from the bottom of the oxidizer and transferred to a fractionating column maintained at normal atmospheric pressure and at a temperature such that the vapor leaving the top of the column had a temperature of 198°F. This overhead vapor consisting of unoxidized hydrocarbon material was condensed, part of the condensate being returned to the fractionating column as reflux and part of it being pumped back into the oxidizer along with the new hydrocarbon feed referred to above.

Products of partial oxidation were withdrawn as bottoms from the fractionating column, and transferred to a second fractionating column from which a fraction boiling between about 284°F. and 302°F. was produced as a side cut. This fraction, which amounted to about 50% by volume of the oxidized fraction obtained as bottoms from the first fractionating column comprised a mixture of aliphatic ketones having seven carbon atoms per molecule. The overhead fraction from the second fractionating column contained lower boiling alcohols and ketones, i.e., having fewer than seven carbon atoms per molecule, and the bottoms from this column contained a mixture of dimethyleclopentanes and higher molecular weight alcohols and ketones together with oxygenated polymerization products. The mixture of aliphatic ketones boiling between about 284°F. and 302°F. was reduced to a mixture of the corresponding aldehydes by liquid phase hydrogenation with gaseous hydrogen over a nickel catalyst at 300°F. and 400 pounds per square inch gage for a period of four hours. The hydrogenated product was fractionally distilled and the mixture of alcohols obtained as a heart cut boiling between about 283°F. and 291°F. of alcohol amounted to about 90% by volume of the mixture of ketones.

To illustrate one of the uses of the mixture of alcohols prepared as indicated above, to 465 grams of the alcohol is added 222 grams of phosphorus pentasulfide and the mixture is agitated and heated to 275°F. for three hours. To this product is then added 82 grams of zinc oxide and the heating and agitating continued for an additional four hours at which time the hot product is filtered to remove any unreacted zinc oxide. The resulting zinc salt may be blended with the lubricating oil described in Example I in the ratio of about 1 part of the zinc salt to 99 parts of the lubricating oil, or 1 part of the zinc salt may be blended with 1 part of a calcium salt of oil-soluble petroleum sulfonic acids and 98 parts of the same lubricating oil to produce lubricating oil compositions having high film strengths, anti-corrosion and detergent characteristics which are desirable features of lubricants for internal combustion engines and particularly Diesel engines. In each of the above instances the blending may be accomplished by heating to about 250°F. and agitating the ingredients until the added salts are completely dissolved and mixed in the lubricating oil.

The foregoing description and examples are not to be taken as in any way limiting but merely illustrative of our invention for many variations may be made by those skilled in the art without departing from the spirit or scope of the following claims.

We claim:

1. A process for the treatment of a saturated cyclic hydrocarbon to produce substantially only those partial oxidation products containing the same number of carbon atoms per molecule as said saturated cyclic hydrocarbon and containing one atom of oxygen per molecule, comprising contacting said saturated cyclic hydrocarbon in the liquid phase in an oxidation vessel with a gas containing free oxygen at temperatures between about 400°F. and about 450°F. and at pressures between about 50 pounds and about 300 pounds per square inch gage until between about 0.1% and about 10% of the molecules are oxidized, thereafter maintaining said proportion of oxidized molecules by withdrawing partially oxidized liquid from said oxidation vessel, passing said partially oxidized liquid to a fractionating column wherein said mixture is vaporized and distilled, withdrawing vaporized partial oxidation products containing one atom of oxygen per molecule from the bottom of said fractionating column, condensing said vaporized unoxidized hydrocarbon and returning the condensed vaporized unoxidized hydrocarbon together with additional quantities of saturated cyclic hydrocarbon to said oxidation vessel, passing exhaust gases and vapors from said oxidation vessel through a condenser and into a separator from which uncondensed gases are exhausted and returning condensed hydrocarbon from said separator to said oxidation vessel.

2. A process for the treatment of a saturated cyclic hydrocarbon to produce substantially only those partial oxidation products containing the same number of carbon atoms per molecule as said saturated cyclic hydrocarbon and containing one atom of oxygen per molecule, comprising contacting said saturated cyclic hydrocarbon in the liquid phase in an oxidation vessel with a gas containing free oxygen at temperatures between about 50°F. and about 100°F. and 500°F. and at pressures between about 50 pounds and about 300 pounds per square inch gage between about 0.1% and about 10% of the molecules are oxidized, thereafter maintaining said proportion of oxidized molecules by withdrawing partially oxidized liquid from said oxidation vessel, passing
said partially oxidized liquid to a fractionating column wherein unoxidized hydrocarbon is vaporized and distilled, withdrawing unoxidized partial oxidation products containing one atom of oxygen per molecule from the bottom of said fractionating column and returning the condensed vaporized unoxidized hydrocarbon and returning the condensed vaporized unoxidized hydrocarbon together with additional quantities of saturated cyclic hydrocarbons to said oxidation vessel, passing exhaust gases and vapors from said oxidation vessel through a condenser and into a separator from which uncondensed gases are exhausted, passing a condensed hydrocarbon phase from said separator to a fractionating column wherein oxygenated degradation products are vaporized and distilled leaving unoxidized hydrocarbon as distillation bottoms and returning said bottoms to said oxidation vessel.

3. A process for the treatment of a naphthene hydrocarbon to produce partial oxidation products containing the same number of carbon atoms per molecule as said naphthene hydrocarbon and containing one atom of oxygen per molecule, comprising contacting said naphthene hydrocarbon in the liquid phase in an oxidation vessel with a gas containing free oxygen at temperatures between about 200° F. and about 350° F. and at pressures between about 50 pounds and about 150 pounds per square inch gage until between about 0.1% and 10.0% of the molecules are oxidized, thereafter maintaining said proportion of oxidized molecules by withdrawing partially oxidized liquid from said oxidation vessel, passing said liquid to a fractionating column in which unoxidized hydrocarbon is vaporized and distilled and from which partial oxidation products comprising 1-methylcyclohexanol and 2-heptanone are obtained as distillation bottoms, condensing said vaporized methylcyclohexane and returning the condensed 1-methylcyclohexane together with a sufficient quantity of additional methylcyclohexane feed to maintain an approximately constant liquid level in said oxidation vessel, hydrogenating said partial oxidation products comprising 1-methylcyclohexanol and 2-heptanone to produce a mixture comprising 1-methylcyclohexanol and 2-heptanone.

4. A process as in claim 3 wherein said partial oxidation product obtained as distillation bottoms comprising 1-methylcyclohexanol and 2-heptanone is separated into a fraction comprising 1-methylcyclohexanol and another fraction comprising 2-hexanone and said fraction comprising 2-hexanone is hydrogenated to produce 2-hexanol.

5. A process for the treatment of dimethylcyclopentane to produce partial oxidation products having at least five carbon atoms per molecule and containing one atom of oxygen per molecule comprising contacting said dimethylcyclopentane in the liquid phase in an oxidation vessel with a gas containing free oxygen at temperatures between about 200° F. and about 350° F. and at pressures between about 50 pounds and about 150 pounds per square inch gage until between about 0.1% and about 10.0% of the molecules are oxidized, thereafter maintaining said proportion of oxidized molecules by withdrawing partially oxidized liquid from the said oxidation vessel, passing said liquid to a fractionating column wherein unoxidized dimethylcyclopentane is vaporized and distilled and from which partial oxidation products comprising 1-methylcyclohexanol and 2-
cyclopentane feed to maintain an approximately constant liquid level in said oxidation vessel, constantly passing exhaust gases and vapors from said oxidation vessel through a condenser and into a separator from which uncondensed gases are exhausted and from which condensed hydrocarbon liquid comprising dimethylcyclopentane is returned to said oxidation vessel.

9. A method for the treatment of a dimethylethylcyclopentane fraction of petroleum boiling between about 192°F. and 198°F. to produce ketones and alcohols having seven carbon atoms per molecule comprising contacting said dimethylcyclopentane fraction in the liquid phase in an oxidation vessel and in the absence of added oxidation catalyst with a gas containing free oxygen at temperatures between about 200°F. and about 350°F. and at pressures between about 50 pounds and 150 pounds per square inch gage until between about 0.1% and 10.0% of the molecules are oxidized, thereafter maintaining said proportion of oxidized molecules by withdrawing partially oxidized liquid from said oxidation vessel, passing said liquid to a fractionating column in which unoxidized dimethylcyclopentane fraction is vaporized and distilled and from which, partial oxidation products comprising ketones and alcohols having seven carbon atoms per molecule are obtained as distillation bottoms, condensing said partially oxidized dimethylcyclopentane fraction and returning the condensate to said oxidation vessel together with a sufficient quantity of additional dimethylcyclopentane fraction to maintain an approximately constant liquid level in said oxidation vessel, constantly passing exhaust gases and vapors from said oxidation vessel through a condenser and into a separator from which uncondensed gases are exhausted and the condensed unoxidized dimethylcyclopentane fraction is returned to said oxidation vessel.

10. A process as in claim 9 wherein said ketones are aliphatic ketones.

11. A process as in claim 9 wherein said alcohols are saturated cyclic alcohols.

12. A method for producing aliphatic ketones having seven carbon atoms per molecule comprising airblowing a naphthenic fraction of petroleum boiling between about 192°F. and 198°F. and containing dimethylcyclopentane in the absence of oxidation catalyst at a temperature of about 250°F. and at a pressure of about 60 pounds per square inch gage until about 0.1% and 10.0% of the molecules are oxidized, there-

after maintaining said proportion of oxidized molecules by withdrawing partially oxidized liquid from said oxidation vessel, passing said liquid to a fractionating column in which unoxidized hydrocarbons are vaporized and distilled and from which partial oxidation products are obtained as distillation bottoms, condensing said partially oxidized hydrocarbons and returning the condensed hydrocarbons to said oxidation vessel together with a sufficient quantity of said naphthenic fraction of petroleum to maintain an approximately constant liquid level in said oxidation vessel, fractionally distilling said partial oxidation products obtained as distillation bottoms to separate therefrom a fraction boiling between about 284°F. and about 302°F. comprising said aliphatic ketones having seven carbon atoms per molecule.

13. A method of producing aliphatic alcohols having seven carbon atoms per molecule comprising airblowing a naphthenic fraction of petroleum boiling between about 192°F. and 198°F. and containing dimethylcyclopentane in the absence of oxidation catalyst in an oxidation vessel at a temperature of about 250°F. and a pressure of about 60 pounds per square inch gage until between about 0.1% and 10.0% of the molecules are oxidized, thereafter maintaining said proportion of oxidized molecules by withdrawing partially oxidized liquid from said oxidation vessel, passing said liquid to a fractionating column in which unoxidized hydrocarbons are vaporized and distilled and from which partial oxidation products are obtained as distillation bottoms, condensing said partially oxidized hydrocarbons and returning the condensed hydrocarbons to said oxidation vessel together with a sufficient quantity of said naphthenic fraction of petroleum to maintain an approximately constant liquid level in said oxidation vessel, separately fractionally distilling said partial oxidation products obtained as distillation bottoms to separate a fraction boiling between about 284°F. and 302°F. comprising a mixture of aliphatic ketones having seven carbon atoms per molecule hydrogenating said mixture of aliphatic ketones with gaseous hydrogen at about 300°F. and at a pressure of about 400 pounds per square inch gage in the presence of a nickel catalyst to produce a mixture of alcohols containing seven carbon atoms per molecule.

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