

## UNITED STATES PATENT OFFICE

2,430,864

## HYDROCARBON PEROXIDES

Adalbert Farkas and Arthur F. Stribley, Jr., Long Beach, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

No Drawing. Application January 30, 1945,  
Serial No. 575,355

22 Claims. (Cl. 260—610)

1

This invention relates to naphthene peroxides and more particularly to naphthene hydroperoxides and to methods of producing such peroxides by the liquid phase oxidation of naphthene hydrocarbons with a gas containing free oxygen. This application is a continuation-in-part of our co-pending applications, Serial No. 522,840, filed February 17, 1944, and Serial No. 548,310, filed August 5, 1944.

Peroxides have been observed in oxidates produced by liquid phase, air or oxygen-containing gas oxidation processes and more particularly those in which hydrocarbons are oxidized under conditions to produce partial oxidation products. However, in general the peroxide content of the oxidate reaches a maximum value of about 0.5% to 5.0% depending upon the conditions of oxidation and upon the particular hydrocarbon stock employed and then decreases rapidly as the oxidation proceeds. In those cases in which peroxides are the desired oxidation products the oxidation is discontinued when the peroxide content has reached a maximum and the peroxides are separated from the oxidate by various physical or chemical means to produce peroxide concentrates. The relatively low maximum content of the peroxides in liquid phase oxidates is due to the relative instability of peroxides and thus their tendency to decompose as rapidly as they are formed. Not only has difficulty been experienced in producing oxidates having relatively high content of peroxides but due to the instability of peroxides in oxidates it has also been found difficult to recover peroxides from hydrocarbon oxidates without serious decomposition and loss of the peroxides.

It is an object of our invention to provide a method for the control of liquid phase oxidation of hydrocarbons to produce a substantial proportion of hydrocarbon peroxides.

It is also an object of our invention to produce substantially pure naphthene hydroperoxides as new products.

It is a further object of our invention to provide a new and improved method for the production of peroxides of cyclic hydrocarbons from said cyclic hydrocarbons by a process involving contacting said cyclic hydrocarbons with oxygen, air or other oxygen-containing gas.

It is another object of our invention to produce hydrocarbon peroxides by treating a hydrocarbon fraction comprising naphthene hydrocarbons with a gas containing free oxygen in the presence of a basically reacting agent in such a manner that

2

hydrocarbon peroxides are produced in substantial quantities.

It is a more specific object of our invention to produce saturated cyclic hydrocarbon hydroperoxides by a process involving oxidation of saturated cyclic hydrocarbons in the liquid phase by contacting said hydrocarbons with an oxygen-containing gas in the presence of a basically reacting alkali metal compound under conditions such that peroxides are formed in substantial quantities and that other partial oxidation products are minimized.

It is a further object of our invention to provide an efficient method of separating hydrocarbon peroxides from hydrocarbons and from other partial oxidation products or hydrocarbons.

It is still a further object of our invention to provide an oil-soluble peroxide concentrate of relatively pure oil-soluble peroxide which has value as an initiator, accelerator or catalyst for oxidation or polymerization processes and the like and which has particular value as an improver for Diesel engine fuels.

Other objects, features and advantages will be apparent from the following description of our invention.

We have found that the oxidation of naphthene hydrocarbons to form peroxides of the hydroperoxide type takes place readily and can be accomplished by contacting naphthene hydrocarbons with an oxygen-containing gas, for example, air, oxygen, or air enriched with oxygen, in the liquid phase. The peroxides which are produced have the formula  $R.OOH$ , where  $R$  is a naphthene ring containing four to eight carbon atoms in the ring with or without one or more organic substituents attached to the ring or where  $R$  is a saturated condensed ring grouping with or without one or more organic substituents attached to the condensed ring nucleus. The organic substituents may be alkyl, cycloalkyl, aralkyl, or aryl radicals or combinations of these radicals.

Specific hydrocarbons which we may oxidize by our process include cyclopropane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, and the various mono-, di-, tri-, and poly substituted saturated cyclic hydrocarbons in which the substituent groups may be methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, etc., alkyl radicals, for example, methylcyclopentane, dimethylcyclopentanes, ethylcyclopentane, diethylcyclopentanes, trimethylcyclopentanes, etc., and the various isomers of these substituted cyclopentanes and similar substituted cyclohexanes, cycloheptanes, etc. The substitu-

3

ents may also be cycloalkyl, aralkyl, aryl or combinations of two or more of these radicals or one or more alkyl radicals with one or more of these radicals. Thus compounds, such as cyclopentylcyclohexane, benzylcyclopentane, phenylcyclohexane, etc., may be employed. We may also use as oxidation feed condensed ring naphthenes, such as bicyclo-(0,1,4)-heptane, bicyclo-(0,2,4)-octane, bicyclo-(1,3,3)-octane, bicyclo-(1,1,3)-heptane, bicyclo-(0,1,3)-hexane, bicyclo-(0,2,2)-hexane, indane, decahydronaphthalene, dodecahydrofluorene, tetradecahydroanthracene, tetradecahydrophenanthrene, decahydroacenaphthene and the various substituted condensed ring naphthenes in which the substituent groups may be alkyl, aralkyl, cycloalkyl, aryl or combinations of two or more of these groups.

While we may use any and all of the naphthene hydrocarbons as indicated hereinabove, we prefer to use those naphthene hydrocarbons having at least one substituent group since we have found for example that the alkyl substituted cyclobutanes, pentanes, hexanes, heptanes and octanes all oxidize more readily and yield peroxides in relatively greater proportions than do the corresponding unsubstituted naphthenes, i. e., the cyclobutane, cyclopentane, etc. The ease with which the substituted saturated cyclic hydrocarbons oxidize to produce hydroperoxides indicates that the presence of a tertiary hydrogen atom facilitates peroxide formation and it is believed that the peroxide group, i. e., the  $-OOH-$  group replaces a tertiary hydrogen more readily than it does a secondary hydrogen and that in the case of methylcyclopentane, for example, the hydroperoxide group probably enters the ring at the carbon to which the methyl group is attached. The desired reaction which we obtain by our method of oxidation does not alter the chemical structure of the hydrocarbon, i. e., ring cleavage does not occur so that the carbon skeleton of the hydroperoxide is the same as the carbon skeleton of the naphthene hydrocarbon from which the peroxide is produced.

In addition to the individual naphthene hydrocarbons, indicated above, we may use as the oxidation feed mixtures of two or more naphthene hydrocarbons or we may use hydrocarbon fractions containing naphthenes. Thus fractions of straight-run gasolines containing appreciable proportions of naphthene hydrocarbons respond to our oxidation treatment to yield relatively large proportions of peroxides. Fractions of straight-run gasoline containing in the order of about 35% or more of naphthene hydrocarbons which may or may not contain aromatic hydrocarbons, the remaining constituents being paraffinic hydrocarbons, are very desirable oxidation feeds. Although the presence of aromatic hydrocarbons in the oxidation feed is not seriously objectionable, we prefer to employ fractions containing less than about 10% by volume of aromatic hydrocarbons. Again, although the oxidation feed may contain even large proportions of olefinic hydrocarbons we may prefer in certain instances to use a feed containing less than about 5% olefins and in some cases probably less than about 2% of olefins. Moreover, we prefer to oxidize a fraction having a relatively narrow boiling point range, i. e., in the order of from 50° F. or preferably 10° F. to 15° F. or even less in some instances since the products from the oxidation of such narrow boiling hydrocarbon fractions are more readily resolved into substantially pure peroxide compounds. For some uses it is not essential that

4

substantially pure peroxides be separated, i. e., when the peroxides are to be used in a Diesel fuel composition and in these instances the oxidation feed may have a wider boiling range such as in the order of 100° F. or even greater without seriously impairing the oxidation and recovery process.

Peroxides which we may produce by our process in good yields and in substantially pure form include cyclopentyl hydroperoxide, methylcyclopentyl hydroperoxide, the isomeric dimethylcyclopentyl hydroperoxides, ethylcyclopentyl hydroperoxide, the isomeric diethylcyclopentyl hydroperoxides, the isomeric methylethylcyclopentyl hydroperoxides, cyclohexyl hydroperoxide, methylcyclohexyl hydroperoxide, the dimethylcyclohexyl hydroperoxides, ethylcyclohexyl hydroperoxide, the three isomeric diethylcyclohexyl hydroperoxides, the isomeric methylethylcyclohexyl hydroperoxides, 1-4 methylisopropylcyclohexyl hydroperoxide, as well as the corresponding derivatives of cyclobutane, cycloheptane, etc., and the higher molecular weight substituted cycloparaffins.

In those instances in which mixtures of naphthene hydrocarbons are employed as oxidation feed, mixtures of peroxides are produced as would be expected. Moreover, when oxidizing hydrocarbon fractions containing both naphthene and paraffin hydrocarbons in appreciable proportions, such as the fractions of straight run gasoline referred to hereinabove, the peroxides formed, although largely naphthenic in character, may contain appreciable quantities of paraffin peroxides derived from the paraffin hydrocarbons contained in the fraction of straight run gasoline. Thus when oxidizing feeds containing both naphthene and paraffin hydrocarbons the peroxide or peroxide concentrate produced which may be referred to hereafter as a naphthene peroxide or naphthene hydroperoxide may contain open chain hydrocarbon peroxides and it is intended that the term "naphthene peroxide" when employed in such cases covers any mixtures of peroxides which are obtained by the treatment described.

The method of carrying out the oxidation to produce saturated cyclic hydrocarbon hydroperoxides comprises heating the naphthene hydrocarbon to elevated temperatures, such as about 275° F. and blowing air or other gas containing free oxygen into the heated hydrocarbon until the peroxide content of the charge reaches the desired value. When this point has been reached the charge is removed from the oxidation vessel and treated for the recovery of peroxide as described hereinbelow. While we may operate at any temperature high enough to cause the hydrocarbon molecule to combine with oxygen, such as above about 150° F. we have found that temperatures in the order of 200° F. to 325° F. or preferably between about 240° F. and 300° F., are particularly desirable. We may oxidize at ordinary atmospheric pressure or at superatmospheric pressures, such as up to about 500 pounds per square inch gage, however, we prefer to operate at pressures in the order of between about 50 and 150 pounds per square inch gage. The pressure employed in any given case will depend upon the particular hydrocarbon or hydrocarbon fraction being oxidized, upon its boiling point and upon its ease of oxidation for, as is known, other factors remaining constant, the higher the pressure the more rapid will be the oxidation. When oxidizing the lower molecular weight naph-

these hydrocarbons, such as methylcyclopentane, it is particularly desirable to operate under superatmospheric pressure in order to prevent volatilization of the hydrocarbon. The rate of air-blowing may be varied widely and will depend upon the utilization of oxygen present in the air or oxygen containing gas. Thus sufficient air or other oxidizing gas should be supplied to effect the oxidation in a reasonable period of time. It is preferable that the air be distributed or dispersed in fine bubbles in the liquid hydrocarbon since the efficiency of oxygen utilization depends to a great extent upon the degree of dispersion of the air in the liquid. In those cases in which the oxidation is carried out under superatmospheric pressure the exit gases from the oxidation vessel may be enriched with additional quantities of fresh air or oxygen and recycled to the oxidation vessel and in this manner the percentage of oxygen in the oxidizing gas may be maintained at a relatively high value without seriously reducing the efficiency of the process from the point of view of compressing large quantities of air, the oxygen content of which is not efficiently utilized in each cycle.

The proportion of peroxide in the oxidized product may be varied depending upon the conditions and the time of oxidation and we may produce hydrocarbon mixtures containing up to about 20% by weight of peroxides or even higher. Thus we may produce a material containing from about 1% to about 20% by weight of peroxide although the percentage will depend upon the particular stock being oxidized since there appears to be a variation with different hydrocarbon feeds in the relative rates of production of peroxides on the one hand and other partial oxidation products on the other.

In those cases in which the peroxides are removed from the oxidate as a peroxide concentrate or as a substantially pure peroxide the residue or the mixture of hydrocarbon and partially oxidized hydrocarbon remaining after the removal of peroxide may be further oxidized to produce more peroxide. It may be treated alone or after mixing it with additional quantities of new feed, such as enough new feed to make up the volume losses incurred during the oxidation and recovery processes. This residue is particularly good oxidation feed because it contains some peroxides which, as pointed out hereinbelow, are oxidation accelerators and/or initiators.

The type of oxidation process referred to above is a batch operation and while this method is highly satisfactory for the production of our peroxides, it is less efficient than a continuous type of operation which may be effected by oxidizing a naphthene hydrocarbon or hydrocarbon fraction containing naphthene hydrocarbons until the peroxide content has reached the desired value, at which time portions of the oxidized hydrocarbon are continuously withdrawn from the oxidation vessel, treated for the removal of peroxides, and returned to the oxidation vessel together with sufficient new or unoxidized hydrocarbon feed to maintain an approximately constant liquid level in the oxidation vessel. In this type of operation peroxides are always present in the charge being oxidized and the rate of peroxide formation is readily maintained at a high level.

Although we may effect the oxidation without the use of oxidation initiators, accelerators, catalysts, etc., we prefer to use a peroxide, such as a peroxide produced in the operation as an initiator or accelerator, as indicated hereinabove for sub-

sequent operations. Thus in a batch oxidation or in starting a continuous oxidation process the addition of small amounts of naphthene peroxides to the naphthene hydrocarbon to be oxidized materially increases the rate of peroxide formation in the new charge. As described hereinbelow the removal of peroxides from the oxidate by the various extraction and chemical processes is not complete. Depending upon the method employed, the treated oxidate will contain from a few tenths of one per cent to 2% or even 3% of peroxides, more complete removal being uneconomical in any given case.

In addition to the use of naphthene peroxides as initiators or accelerators we may also use for this purpose metallic catalysts, such as oil-soluble metal salts, i. e., naphthenates of iron or manganese or the like, and also metal salts of inorganic acids, such as copper chloride or copper sulfate.

As mentioned hereinabove, we prefer to operate under conditions such that the formation of peroxides takes place with the minimum production of other partial oxidation products and particularly with the minimum production of acidic oxidation products since it is known that these acidic products catalyze the decomposition of peroxides. Thus it is found that in oxidizing, for example, a gasoline fraction rich in dimethylcyclopentane, the percentage of peroxides in the partially oxidized mixture reaches a maximum of about 10% to as high as about 20% by weight and if the oxidation is continued for a longer period of time the percentage of peroxides is found to decrease. Concurrently the percentage of acids increases slowly until the peroxide content has reached a maximum and then increases far more rapidly. There is, therefore, in any given case, a limit to which the oxidation can be economically carried out when peroxides are the desired product. This limit, it should be pointed out, depends upon the particular hydrocarbon or hydrocarbon mixture being oxidized and also upon the conditions under which the oxidation is effected.

Generally we prefer to effect the oxidation in the presence of a basically reacting agent which will form salts with acids which are produced during the oxidation thus effectively removing said acids which, as indicated hereinabove, appear to be catalysts for the decomposition of peroxides. Thus by operating in the presence of such an agent we may increase the extent to which oxidation may be carried, i. e., increase the peroxide content without effecting objectionable decomposition or further oxidation of the peroxides. The basically reacting agents are preferably the basic compounds of the alkali metals, sodium, potassium and lithium. The most desirable basic compounds include the alkali metal carbonates and bicarbonates. The latter compounds may be placed within the oxidation vessel below the level of the hydrocarbon liquid in such a manner that they will be contacted by the liquid. In these instances the compounds should be in granular or lump form. They may also be used in powdered form in which case they are dispersed in the liquid being oxidized. Preferably the alkali metal carbonates or bicarbonates may be used in the form of an aqueous solution, the solution being injected into the oxidation vessel with the air stream or at any other point in the oxidation vessel where they will contact the liquid being oxidized. Thus they may be sprayed into the oxidation vessel at a point above the level of the liquid and be allowed to fall by gravity

7

through the oxidation charge. Aqueous solutions of alkali metal carbonates or bicarbonates containing from about 0.1% or less to about 10% or even as high as 15% by weight of the metal compound have been employed although in general solutions containing between about 1% and about 5% by weight are preferred.

Although the alkali metal carbonates and bicarbonates are the preferred basically reacting agents it has been found that dilute aqueous solutions of the alkali metal hydroxides may be employed. Thus aqueous solutions of sodium hydroxide containing from about 0.01% to about 2% by weight of the hydroxide may be employed as the basically reacting agent in the oxidation step of our process.

Other basically reacting agents which we may employ include metals or compounds which will react with acids formed during the period of oxidation to produce salts but which do not inhibit to an objectionable degree the oxidation reaction leading to the production of peroxides. Such other metals and compounds include the alkaline earth metals, calcium, magnesium, strontium and barium, and basically reacting compounds of these metals, such as the carbonate, oxide and hydroxide or hydrated oxide. Additional compounds which may be employed as basically reacting agents include the basically reacting oxides, hydroxides and carbonates of the metals of the iron group which metals include iron, cobalt and nickel and the basically reacting oxides, hydroxides and carbonates of the metals of the right hand column of group II of the periodic table which are not classifiable as alkaline earth metals, which metals include beryllium, zinc, cadmium and mercury.

These basically reacting agents do not appear to act as catalysts in our process for they do not increase the rates of formation of peroxides at a given temperature nor do they cause the reaction resulting in the formation of peroxides to take place at lower temperatures than those which would be required in the absence of the basically reacting agent.

Instead of effecting neutralization of acids within the oxidation chamber we may prefer in some instances to withdraw portions of the partially oxidized mixture and treat it in a separate vessel with one of the above named basic compounds, returning the deacidified oxidate to the oxidation chamber for further treatment. Thus we may continuously remove a stream of material from the oxidation chamber and pass it over a bed of one of the solid basic compounds in granular or lump form such as particles of about 10 mesh or larger, and return the acid-free oxidate continuously to the oxidation chamber. Also the acids may be removed from the oxidate by extracting it with an aqueous solution of a basic compound such as sodium bicarbonate.

It has been found that by removing acidic oxidation products in the manner described above during the period of oxidation the rate of peroxide formation is increased and that the proportion of peroxides in the finished oxidate may be carried to an appreciably higher value without objectionable decomposition occurring.

The separation of a peroxide concentrate or of substantially pure peroxides from an oxidate comprising peroxide, unoxidized hydrocarbon and other partial oxidation products of the hydrocarbon may be effected by fractional distillation, by solvent extraction, by combinations of extrac-

8

tion and distillation or by chemical means, such as by treatment with an alkali, or alkaline earth metal hydroxide or carbonate or other basic metal compound, in which case the salt of the peroxide may be formed and separated from the hydrocarbon mixture.

Fractional distillation processes may be employed to separate peroxides from other compounds present in the oxidate because the hydroperoxides boil at temperatures at least about 175° F. above the boiling point of the hydrocarbons from which they are produced. The decomposition of the peroxides during the distillation can be minimized by reducing the distillation temperature as by carrying out the distillation under reduced pressure and/or in the presence of steam, and by reducing the heating time.

Other methods for the concentration and recovery of peroxides include solvent extraction or processes involving chemical reaction which processes can be carried out at relatively low temperatures and if further purification is desired the concentrates may be distilled with steam under vacuum and under such conditions as to reduce the time of heating necessary to complete the distillation operation. In any case when distillation processes are to be employed it is desirable that the acids present in the oxidate be removed prior to distillation for, as indicated hereinabove, these acids catalyze the decomposition of hydroperoxides and their catalytic effect increases as the temperature increases.

In separating a peroxide concentrate containing in the order of about 35% or more of peroxides from the oxidized hydrocarbon we may extract the hydrocarbon with, for example, 82% aqueous methyl alcohol, separating the aqueous alcohol phase from the hydrocarbon phase and subsequently diluting the alcohol phase with water to reject an oily layer comprising a major proportion of peroxides and minor proportions of other partial oxidation products and hydrocarbon. Instead of diluting the aqueous alcoholic phase with water, this phase may be distilled preferably under reduced pressures to vaporize the alcohol and water leaving the peroxides, other oxidation products and hydrocarbon as a bottoms fraction. In this case the bottoms fraction will be a peroxide concentrate containing about 35% by weight of peroxides. This bottoms fraction may be further fractionally distilled as, for example, at a pressure of 0.1 m. m. of mercury whereby a richer concentrate comprising peroxides is obtained.

Solvents which may be used in place of aqueous methyl alcohol for concentrating peroxides by extraction of the partial oxidation product include oxygenated organic compounds alone or in combination with various proportions of water. It is preferred that the solvent be water soluble. Compounds of this type include the aliphatic alcohols, such as ethyl, propyl, isopropyl, butyl, isobutyl, etc., the dihydroxy alcohols, such as ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, 2,3-butanediol; polyhydroxy alcohols, such as glycerol; ethers and esters of di- and polyhydroxy alcohols, such as ethyleneglycol monophenylether, ethyleneglycol monobenzylether, diethyleneglycol monomethylether, glycol diacetate; diketones and ketoacid esters, such as acetylacetone, methylacetylacetate, etc.; amines such as diethylamine, trimethylamine, butylamine, aniline, diethylenetriamine, pyridine, morpholine; amides such as acetamide, formamide, diethylacidamide, etc.;

amino alcohols, such as ethanolamine, diethylaminoethanol, ethylethanolamine, 2-amino-2-methylpropanol, etc.

In employing the above described solvents, extraction conditions and particularly the temperatures of extraction are maintained such that the peroxides will be preferentially dissolved and the unoxidized hydrocarbons will be insoluble in the solvent or preferentially rejected by the solvent. The selection of extraction conditions will depend upon the particular solvent to be employed as will be apparent to those skilled in the art.

In a chemical method for concentrating the peroxides produced by partial oxidation of a naphthene hydrocarbon an oxidate containing about 15% by weight of peroxide is treated with aqueous sodium hydroxide containing up to about 50% by weight of NaOH at temperatures preferably in the order of atmospheric temperature or below. After thorough mixing, the treated product is allowed to settle and separate into a hydrocarbon phase and an aqueous phase which latter phase may contain a solid precipitate of the sodium salt of the peroxide, depending upon the concentration of sodium hydroxide employed. The aqueous phase is diluted with water and acidified with a mineral acid such as dilute sulfuric acid or dilute hydrochloric acid to convert the sodium salt into the hydroperoxide. The reformed hydroperoxide separates from the acidified aqueous phase as an oily layer along with other partial oxidation products and hydrocarbon. This peroxide concentrate may be fractionally distilled under vacuum to separate the peroxide in substantially pure form.

Although aqueous solutions of sodium hydroxide containing between about 5% and about 50% NaOH may be successfully employed to form the sodium salts of the hydroperoxide, we prefer to use concentrations between about 30% and about 45% by weight of NaOH for with these concentrations substantially all of the hydroperoxide which is converted into its sodium salt is insoluble in the hydrocarbon phase and only slightly soluble in the aqueous phase resulting from the extraction. The sodium peroxide salt may then be filtered or otherwise separated from the liquid materials in relatively pure form and subsequently dissolved in water and acidified with a dilute mineral acid, such as sulfuric acid, to convert the sodium salt into the hydroperoxide. The resulting hydroperoxide is relatively insoluble in the aqueous phase and forms a supernatant oily layer which may be separated from the aqueous layer by decantation. This product may be further purified if desired by fractional distillation. Peroxide concentrates produced by extraction with 30% to 45% aqueous NaOH, as just described, usually contain in the order of 75% by weight or more of hydroperoxides before distillation and may contain as high as 99+% by weight of hydroperoxide after careful fractional distillation under vacuum.

In addition to sodium hydroxide we may use other relatively strongly basic compounds of sodium, lithium, potassium, calcium, barium, strontium and magnesium to convert the hydroperoxide into its salt. Thus we may use sodium carbonate, potassium hydroxide or carbonate, lithium hydroxide or carbonate, or the hydroxides or hydrated oxides of calcium, magnesium, barium, and strontium. These compounds are preferably used in the form of an aqueous solution.

A further and particularly efficient method of

extracting peroxides, particularly the hydroperoxides from hydrocarbon oxidates, consists in extraction with alcoholic alkalies. The proportion of alcohol may be as high as about 75%. Thus a mixture comprising 75% by weight of methanol, 12.5% by weight of sodium hydroxide and 12.5% by weight of water has been found to be particularly efficient. Also a solvent comprising 25% by weight of methanol, 22% by weight of sodium hydroxide and 53% by weight of water is very effective in extracting peroxides from hydrocarbon oxidates containing peroxides. The effect of the alcohol appears to be to cause the equilibrium of the reaction of the base with peroxide to form the peroxide salt in the direction of the peroxide salt, thus increasing the efficiency of extraction over those extractions effected with aqueous alkalies. Although only methanol and sodium hydroxide were mentioned, other alcohols and other basic compounds, as above disclosed, may be employed in this extraction process.

As indicated hereinabove combinations of distillation, solvent extraction and chemical processes may be used to separate peroxides or peroxide concentrates from naphthene hydrocarbon oxidates. A particularly desirable method of recovering peroxide concentrates containing at least 75% by weight of peroxides comprises distilling an oxidate under conditions such that the distillation is effected at relatively low temperatures, i. e., using steam and/or vacuum to aid in the distillation, to remove as overhead unoxidized hydrocarbons and leave as distillation residue the peroxides together with other partial oxidation products, such as alcohols, ketones and the like. Such distillation residues will contain 50% to 65% or more of peroxides. The peroxide concentrate thus obtained is then diluted with a paraffinic hydrocarbon solvent or with a paraffinic hydrocarbon, such as propane, butane, pentane, hexane or higher paraffin hydrocarbon, isomers of these hydrocarbons or mixtures of these various paraffin hydrocarbons. The solution of the distillation residue containing large proportions of peroxides in paraffinic solvent is then treated with sodium hydroxide solution in the manner indicated hereinabove. Preferably the caustic will contain 30% to 45% by weight of sodium or other alkali metal hydroxide. This treatment results in the precipitation of the peroxides in a crystalline form which precipitate settles rapidly and is readily filtered from the solvent solution of other partial oxidation products. The precipitate, after separation of the solvent, may be dissolved in water, whereupon an oily layer and an aqueous layer are formed. The oil is separated from the aqueous phase, further diluted with solvent and again treated with sodium hydroxide. The peroxide is recovered from the aqueous layer by acidification with a mineral acid, such as sulfuric or hydrochloric acid, which causes separation into two phases, one an oily layer comprising the peroxides, and the other an aqueous layer containing inorganic salts. The latter oily layer is a peroxide concentrate containing generally 90% or more of peroxides. This concentrate may again be distilled under conditions tending to prevent decomposition to obtain a substantially pure peroxide. As a modification of this last named method of separating peroxides or peroxide concentrates, it is also feasible to employ a selective solvent extraction of the oxidate, with or without the indicated distillation process, in order to produce the first peroxide concentrate which is subsequently diluted with

paraffinic solvent and treated with concentrated caustic solution.

In selecting a paraffinic solvent for use in the above described process, it has been found that whereas, the paraffin hydrocarbons produce solutions from which the alkali metal salts of hydroperoxides may be precipitated in crystalline form, other solvents and particularly those containing appreciable proportions of naphthene or aromatic hydrocarbons do not allow the precipitation of sodium salts of the peroxides in a readily recoverable form. Thus by dissolving a peroxide concentrate containing about 60% of peroxides and 40% of other partial oxidation products in a naphtha containing approximately 50% by weight of naphthenes and 50% by weight of paraffins and having a boiling range of about 170° F. to 220° F. and subsequently treating the solution with 35% aqueous NaOH, a gelatinous product is obtained which is difficult to separate from the solvent. It appears that the sodium salts of the hydroperoxides are precipitated in an amorphous or non-crystalline form from hydrocarbon solvents other than paraffinic solvents.

A desirable oxidation procedure which has been used to produce peroxide concentrates containing as high as 65% or even 75% of peroxides comprises oxidizing a hydrocarbon fraction of petroleum, such as one boiling in the range of about 190° F. to 210° F. at a pressure of about 130 pounds gage and a temperature of about 280° F. in a continuous manner. An oxidation vessel is fitted with an inlet for oxidation feed at a point near the top of the vessel, an outlet at the top of the vessel for spent air or other oxidizing gas, an outlet at the bottom of the vessel for oxidized product and an inlet near the bottom of the vessel for oxidizing gas. By means of a spider or other form of nozzle the air is blown into the charge in such a manner that it is finely dispersed in the hydrocarbon liquid. The hydrocarbon feed is mixed with about one-half its volume or less of a 5% sodium bicarbonate solution and the mixture is pumped continuously into the oxidation vessel. At the same time air is blown into the unit in a continuous manner causing agitation of the charge as well as furnishing oxygen to effect the desired oxidation. The liquid oxidate and partially spent sodium carbonate solution is withdrawn continuously from the bottom of the unit and passed directly to a settling chamber where phase separation occurs. The aqueous phase is withdrawn from the bottom of the settler and the oxidate or upper phase is passed continuously to a fractionating column where unoxidized hydrocarbon is vaporized and the peroxides together with other oxygen-containing, non-acidic oxidation products are obtained as bottoms. The vaporized hydrocarbon material may be returned to the oxidizer as a part of the feed to that unit. The oxidate leaving the separator is substantially acidfree and by using steam to aid the distillation in the fractionator very little peroxide decomposition occurs during the distillation. The peroxide concentrate obtained as bottoms from the fractionator is relatively stable and contains about 60% of peroxides.

The peroxide concentrate from the fractionator may be treated by dilution with paraffinic solvent followed by treatment of the solvent solution with strong caustic as indicated hereinabove or it may be fractionally distilled to increase the proportion of peroxides in the concentrate. Such a distillation is preferably carried out at reduced pressures

using steam in order to effect the distillation at moderately low temperatures and thus reduce the decomposition losses. The overhead from this distillation consists primarily of ketones, alcohols and other partial oxidation products. The bottoms contain substantially all of the peroxides originally present separated from a part of the ketones, alcohols, etc.

In those instances in which it is desired to produce peroxide concentrates containing high proportions of peroxides, such as 75% and higher, by distillation of a hydrocarbon oxidate, as indicated above, it is preferable to discontinue the oxidation when the oxidate contains 7% or 8% or less of peroxide. If the peroxide content is allowed to increase above about 8%, the proportion of other partial oxidation products increases rapidly so that the ratio of peroxides to other partial oxidation products, such as ketones, alcohols, etc., decreases and since distillation of the oxidate separates substantially all the oxidation products from unoxidized hydrocarbon the proportion of peroxide in the distillation bottoms or concentrate decreases as the peroxide content of the oxidate increases above the point indicated above.

Peroxide concentrates or the substantially pure peroxides obtained by the above described processes may contain color bodies believed to be of a resinous nature and although the presence of these color bodies is not objectionable in many utilizations it is often desirable to effect their removal. A particularly satisfactory method of removing these color bodies from the hydrocarbon peroxides or from mixtures of such peroxides and other partial oxidation products such as alcohols, ketones, etc., consists in diluting the peroxide or peroxide concentrate with a relatively low boiling paraffin hydrocarbon or paraffin hydrocarbon fraction. The peroxides, alcohols, ketones, etc., are appreciably more soluble in the paraffin hydrocarbon than are the color bodies and the latter materials are rejected from solution and may be removed by settling or by filtration, or the like.

The amount of diluent employed will usually be at least equal to the volume of peroxide or peroxide concentrate being treated although smaller amounts may be effective in some cases. Preferably the volume ratio of diluent to peroxide or peroxide concentrate will be between about 1 to 1 and about 10 to 1. This treatment may be effected at ordinary atmospheric temperatures and pressures although reduced or elevated temperatures and/or pressures may be employed. After separating the color bodies the paraffinic solvent may be recovered by a topping distillation, leaving peroxides, etc., as a residue.

Paraffin hydrocarbons which are useful for separating the color bodies include the normal and isomeric paraffin hydrocarbons having from about 3 to about 7 carbon atoms in the molecule. This will include propane and the normal and isomeric butanes, pentanes, hexanes and heptanes. The higher paraffin hydrocarbons such as the normal and isomeric octanes, nonanes and possibly decanes may be used but these higher boiling paraffins are not as readily separated from the peroxides after treatment. In addition to individual hydrocarbons, mixtures of two or more of the above mentioned hydrocarbons may be employed or paraffin hydrocarbon fractions having a maximum boiling point of about 212° F. may be used.

The treatment described hereinabove for re-

moving color bodies may be employed for dehydrating the peroxides or peroxide concentrates. These latter products usually retain small quantities of dissolved water in the order of about 1% to 5% depending on their concentration and method of preparation and it has been found that dilution with light paraffin hydrocarbons causes the separation of water along with the resinous color bodies.

Although the peroxides produced by our process have many valuable utilizations, as described hereinbelow, they are of particular value in the preparation of high quality Diesel engine fuels. Diesel engines or other engines of the auto ignition type require fuels having high cetane numbers. Cetane number is related to the interval between the instant of fuel injection and the instant of ignition of the fuel in the combustion chamber of an engine and is described and defined on page 172 of the 1943 issue of the A. S. T. M. Standards on Petroleum Products and Lubricants, prepared by the A. S. T. M. Committee D-2 on Petroleum Products and Lubricants. Thus ordinary high quality Diesel fuel has a cetane number of in the order of 40-47 and it is desirable in many instances to increase this value to a value between about 50 and about 55. Although by means of special refining processes, such as extraction of ordinary distilled fuel with liquid sulfur dioxide, heavy acid treatment, and the like, it is possible to obtain an increase in the cetane number of the fuel, such methods are costly and wasteful of the fuel to the relatively high losses during such refining treatments. We have found that by adding our naphthene peroxides, naphthene peroxide concentrates or the oxidants themselves to Diesel fuels we are able to increase appreciably the cetane number of these fuels. It has been found, for example, that by the addition of an amount of peroxide concentrate equivalent to 0.3% of peroxide in the finished fuel to a Diesel fuel having a cetane number of 47.3 the cetane number is increased to 51.5 and similarly 1.07% peroxide added to the same fuel increases the cetane number to 56.6. It will be seen that additions of relatively small proportions of our peroxides cause rather large increases in the cetane number of Diesel fuels. We may use between about 0.1% and about 5.0% of the peroxides or amounts of the oxides or the concentrates which would contain the stated amounts of peroxides. The peroxides are effective in increasing the cetane number of ordinary Diesel engine fuels and have been found to be particularly efficient in improving the cetane number of treated fuels wherein the treatment consists of sulfuric acid treatment, selective solvent extraction, clay treatment and the like, which treatment in itself also tends to improve cetane number. Such treatments not only remove ignition delaying constituents of the fuels but also render the fuel more susceptible to cetane number improvement on the addition of peroxides. Moreover, peroxides are found to be more stable in the pretreated fuels.

Other uses of our peroxides are as catalytic agents in one phase or two phase polymerization processes, such as in the polymerization of butadiene and styrene in the production of synthetic rubbers, as a drying accelerator in oils, paints, varnishes, etc., as an accelerator in curing synthetic resins, as an accelerator in the vulcanization of certain synthetic rubbers, as a bleaching agent, et. These peroxides may be used as oxidation agents and also as oxidation initiators,

accelerators, or catalysts since they are found to aid in the oxidation of hydrocarbons, particularly those which do not oxidize readily in the absence of catalytic agents.

Another valuable use of our peroxides is in anti-vesicant preparations. Mustard gas and other vesicant compounds are rendered harmless by the application of anti-vesicant pastes or liquids containing hydrocarbon peroxides. Thus peroxides or peroxide concentrates produced as indicated herein may be added in small quantities to petrolatum, lanolin, soap-base or other ointments to produce particularly effective antivescant preparations. Also solutions of peroxides in mineral or fatty oils or in organic solvents are valuable anti-vesicants. The peroxide is believed to oxidize the vesicant to an inactive form. Thus mustard gas is probably oxidized to the corresponding and harmless sulfone.

In using our peroxides as Diesel fuel additives, as oxidation agents, as catalytic agents or as initiators or accelerators, as indicated hereinabove, we may use the substantially pure peroxide separated by any of the methods described herein, we may use peroxide concentrates or we may use the oxidates directly without concentrating the peroxides therein. In some instances we may desire to prepare the substantially pure peroxides and subsequently dilute the peroxides by dissolving them in a solvent such as a hydrocarbon fraction different from the hydrocarbon or hydrocarbon fraction from which the peroxides were originally produced, in a chlorinated hydrocarbon solvent, in an oxidized or other oxygen-containing hydrocarbon solvent, in an aromatic solvent such as benzene, toluene etc., or other solvent, depending upon the use to which the peroxides are to be put. Thus when the peroxides are to be used as Diesel fuel additives they may be first dissolved in a portion of the Diesel fuel to give a peroxide concentrate which may later be dissolved in additional quantities of the same or like Diesel fuel to produce a finished high grade fuel. Or where the peroxides are to be used as oxidation accelerators the substantially pure peroxide may be dissolved in a portion of the hydrocarbon or other compound which is to be oxidized to form a peroxide concentrate and this concentrate may then be dissolved in further quantities of said compound to produce the oxidation stock.

The following examples will serve to illustrate further our invention but are not to be taken as in any way limiting the broader aspects of our invention.

#### Example I

A 2,000 ml. portion of a dimethylcyclopentane-paraffin mixture, boiling between about 194° F. and 198° F., containing about 65% by volume of dimethylcyclopentane and having a gravity of 61.7° A. P. I. was placed in a pressure vessel, heated to 265° F. and blown with air at a rate of 5 cubic feet per hour for a period of three hours. A pressure of 100 pounds per square inch gauge was maintained in the oxidation vessel during the period of air blowing. Analysis of the oxidate indicated the presence of 6.6% by weight of peroxides and an acid number of 10.7 mg. of KOH/ml. The oxidized dimethylcyclopentane fraction was cooled to atmospheric temperature and removed from the oxidation unit.

A portion of the oxidate was treated for the recovery of peroxides in the following manner: A 100 ml. portion was extracted twice with 15 ml. portions of 18% aqueous sodium hydroxide at a temperature of 41° F. The extracts were com-

15

bined, diluted with 100 ml. of water and neutralized with 75 ml. of 10% sulfuric acid. An oily layer separated from the diluted and acidified aqueous layer and this oily layer was found to have a peroxide content, calculated as dimethylcyclopentyl hydroperoxide, of 62% by weight.

#### Example II

A 19 gallon portion of a dimethylcyclopentane-rich gasoline fraction containing 65% by volume of dimethylcyclopentanes and having a boiling range of 194° F. to 198° F. to which was added a small amount of a peroxide concentrate so that the resulting blend had a peroxide content of 0.19% by weight was oxidized at a pressure of 85 to 90 pounds per square inch gage and a temperature of 270° F. to 275° F. using an air rate of 500 cubic feet per hour for a period of 1.67 hours. The oxidation was discontinued at this time and the product was cooled and withdrawn from the oxidation vessel. This oxidate had a peroxide content, calculated, as dimethylcyclopentyl peroxide, of 4.2% by weight and an acid number of 2.5 mg. KOH/ml.

To 17.5 gallons of oxidate containing 4.2% by weight or 2,000 grams of peroxide was added one gallon of 40% by weight NaOH and the mixture thoroughly agitated at about 70° F. After standing approximately one hour to allow phase separation, 10 gallons of hydrocarbon layer was decanted. This layer contained 0.6% by weight or 170 grams of peroxides. The aqueous phase consisting of a mixture of solid precipitate and an emulsion of hydrocarbon oil and water was diluted with 2 gallons of water and thoroughly agitated. On standing an additional 5 gallons of hydrocarbon oil was separated which contained 2% by weight or 281 grams of peroxides. The aqueous layer comprising a solution of the sodium salt of the hydroperoxide in water was acidified with 3 gallons of 10% sulfuric acid. After thorough mixing the acidified product was allowed to stand and 800 grams of an oily layer containing 81% by weight or 648 grams of peroxides was obtained.

#### Example III

A 2,000 ml. portion of dimethylcyclopentane-paraffin mixture boiling between about 194° F. and 198° F. and having a gravity of 61.7° A. P. I. to which had been added 3% by weight of dimethylcyclopentyl hydroperoxide was oxidized for a period of 4.5 hours at 240° F. and 100 pounds per square inch pressure using an air rate of 5 cubic feet per hour. The oxidate contained 10% by weight of peroxide and had an acid number of 10.0 mg. KOH/ml. A portion of the oxidate was treated with 38% NaOH solution and the resulting precipitate of the sodium salt of dimethylcyclopentyl hydroperoxide was separated by filtration. This salt was dissolved in water and acidified with 10% sulfuric acid. The dimethylcyclopentyl hydroperoxide, which separated as an oily layer, was distilled at a pressure of 0.1 m. m. of mercury to produce a substantially pure compound having the formula  $(CH_3)_2C_5H_7.OOH$ .

#### Example IV

A 1,500 ml. portion of substantially pure methylcyclohexane having a gravity of 51.8° A. P. I. was oxidized for a period of six hours at a temperature of 275° F. and a pressure of 100 pounds per square inch gage using an air rate of 5 cubic feet per hour. The product contained 8.7% by weight of peroxides calculated as methylcyclohexyl hydroperoxide and had an acid number of 4.2 mg. KOH/ml.

16

The oxidate was treated with 38% NaOH. The sodium salt of the hydroperoxide filtered from the liquid mixture, dissolved in water and acidified with dilute sulfuric acid. The oily layer which separated from the acidified aqueous solution was distilled under a pressure of 0.1 m. m. of mercury to produce a substantially pure methylcyclohexyl hydroperoxide having the formula



#### Example V

A 1293 ml. portion of technical methylcyclopentane (approximately 95% purity) having a gravity of 57.1° A. P. I. was oxidized for a period of four hours at a temperature of 260° F. and a pressure of 100 pounds per square inch gage using an air rate of 5 cubic feet per hour. The oxidate contained 6.7% by weight of methylcyclopentyl hydroperoxide and had an acid number of 6.7 mg. KOH/ml.

A substantially pure hydroperoxide having the formula  $CH_3.C_5H_9.OOH$  was separated from this oxidate in a manner similar to that employed in Examples III and IV.

#### Example VI

A fraction of petroleum boiling between about 200° F. and about 260° F. and consisting of about 62% naphthenes, 28% paraffins and 10% aromatics was oxidized in a continuous manner in the presence of a 5% sodium bicarbonate solution, the bicarbonate solution being mixed with the feed to the oxidizer, by blowing with air at a temperature of about 275° F. and a pressure of about 130 pounds gage. When the peroxide content of the oxidate reached a value of 8% by weight oxidate was withdrawn from the bottom of the oxidation vessel together with partially spent bicarbonate solution at such a rate as to maintain a constant liquid level in the oxidizer. The withdrawn material was passed to a separator where the partially spent bicarbonate solution was allowed to settle and the clear, water-free oxidate was pumped from the separator into a fractionating column maintained at such a temperature that the overhead or top column temperature was between about 190° F. and about 200° F. and steam was introduced into the bottom of the column at such a rate that substantially all of the unoxidized hydrocarbons present in the oxidate were vaporized at the above-named temperature and passed as overhead from the fractionator. This overhead was condensed, separated from water and returned as part of the feed to the oxidizer. The bottoms from the fractionator contained 65% by weight of peroxides and were substantially free from acids.

#### Example VII

A 2,000 ml. portion of substantially pure methylcyclohexane having a gravity of 51.8° A. P. I. was oxidized for a period of six hours at 285° F. and a pressure of about 90 pounds per square inch gage using an air rate of 6 cubic feet per hour. The product contained 7.3% peroxides and 5% of other partial oxidation products. The oxidate was treated with 35% NaOH solution and filtered. The precipitated sodium salts were dissolved in water and two phases resulted, one an aqueous phase containing sodium peroxide, the other an oil phase containing hydrocarbons, partial oxidation products and about 10.5% by weight of hydrocarbon peroxides. A 322 gram portion of the oil phase was diluted with two liters of "Skellysolve A," Skellysolve A being a commer-

cial paraffinic solvent comprising substantially pure pentanes. To the diluted oil layer was added 50 ml. of 35% NaOH and the product was filtered. The precipitate comprising sodium salts of the peroxides was dissolved in water and acidified. The resulting oily layer, consisting essentially of peroxides, was vacuum distilled to produce a distillate containing 92.2% methylcyclohexyl hydroperoxide.

#### Example VIII

The peroxide concentrate produced in Example VI as a distillation bottoms in the topping distillation of the oxidate which contained 65% by weight of peroxides was diluted with 20 volumes of Skellysolve A. The diluted concentrate was extracted with sufficient 35% aqueous NaOH to precipitate substantially all of the peroxides as sodium salts and the precipitated salts were then removed from the solvent solution by filtration. The precipitate was dissolved in water and acidified with sulfuric acid to reconvert the sodium salts to hydroperoxides. The peroxide content of the oily layer separating from the aqueous salt solution was approximately 90%. Vacuum distillation of the 90% concentrate resulted in the production of a peroxide concentrate containing 95+% of peroxides.

#### Example IX

A substantially pure methyl cyclohexane having a gravity of 51.8° A. P. I. was oxidized in a continuous manner in the liquid phase in the presence of a 5% sodium bicarbonate solution by blowing with air at a temperature of about 285° F. and a pressure of 100 pounds per square inch gage. The bicarbonate solution was injected into the oxidation vessel together with the feed. When the peroxide content of the oxidate reached a value of 10% by weight oxidate was withdrawn from the bottom of the oxidizer together with partially spent bicarbonate solution at such a rate as to maintain a constant liquid level in the oxidizer. The withdrawn material was passed to a separator from which a water-free oxidate was pumped to a fractionating column in which the oxidate was separated into an overhead fraction comprising unoxidized hydrocarbons which overhead fraction was condensed and returned as feed to the oxidation vessel and a bottoms fraction comprising methylcyclohexyl hydroperoxide.

#### Example X

A fraction of petroleum boiling between about 200° F. and about 260° F. and consisting of about 62% naphthenes, 28% paraffins and 10% aromatics was oxidized in a continuous manner in the presence of a 3% sodium carbonate solution, the carbonate solution being mixed with the feed to the oxidizer, by blowing with air at a temperature of about 275° F. and a pressure of about 130 pounds gage. When the peroxide content of the oxidate reached a value of 8% by weight oxidate was withdrawn from the bottom of the oxidation vessel together with partially spent carbonate solution at such a rate as to maintain a constant liquid level in the oxidizer. The withdrawn material was passed to a separator where the partially spent carbonate solution was allowed to settle and the clear, water-free oxidate was pumped from the separator into a fractionating column maintained at such a temperature that the overhead or top column temperature was between about 190° F. and about 200° F. and steam was introduced into the bottom of the column at such a rate that substantially all of

the unoxidized hydrocarbons present in the oxidate were vaporized at the above-named temperature and passed as overhead from the fractionator. This overhead was condensed, separated from water and returned as part of the feed to the oxidizer. The bottoms from the fractionator contained 65% by weight of peroxides and were substantially free from acids.

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

We claim:

1. A method for the production of hydrocarbon peroxides comprising oxidizing a saturated cyclic hydrocarbon containing from 4 to 8 carbon atoms in the ring in the liquid phase with a gas containing free oxygen at temperatures of from 150° F. to 325° F. and at a pressure of from normal atmospheric pressure to 500 pounds per square inch gage pressure to maintain said liquid phase, to an acid number not exceeding about 10.7 mg. KOH per ml., to produce an oxidate containing hydroperoxide of said cyclic hydrocarbon in substantial amount and separating hydroperoxide from the oxidate.
2. The method of claim 1, in which the oxidation is carried out in the presence of a relatively small amount of a saturated cyclic hydrocarbon peroxide.
3. The method of claim 1, in which the hydrocarbon is a petroleum fraction comprising at least 35% of saturated cyclic hydrocarbons containing from 4 to 8 carbon atoms in the ring, and not more than 10% of aromatics.
4. The method of claim 1, in which the oxidation is carried out in the presence of a relatively small amount of a saturated cyclic hydrocarbon peroxide and the hydrocarbon oxidized is a petroleum fraction comprising at least 35% of saturated cyclic hydrocarbons containing from 4 to 8 carbon atoms in the ring, and not more than 10% of aromatics.
5. The method of claim 1, in which the hydrocarbon is methyl cyclohexane.
6. A method for the production of hydrocarbon peroxides comprising oxidizing a saturated cyclic hydrocarbon containing from 4 to 8 carbon atoms in the ring in the liquid phase with a gas containing free oxygen at temperatures of from 150° F. to 325° F. and at a pressure of from normal atmospheric pressure to 500 pounds per square inch gage pressure to maintain said liquid phase, in the presence of an amount of a basically reacting agent selected from the group consisting of the alkaline earth metals, and the basically reacting compounds of the alkali metals, the alkaline earth metals, the metals of the iron group, and the metals of the right hand column of group II of the periodic table which forms salts with acids formed during the oxidation to maintain the presence of the basically reacting agent, to produce an oxidate containing hydroperoxide of said cyclic hydrocarbon in substantial amount and separating hydroperoxide from the oxidate.
7. The method of claim 6, in which the oxidation is carried out in the presence of a relatively small amount of a saturated cyclic hydrocarbon peroxide.
8. The method of claim 6, in which the hydrocarbon is a petroleum fraction comprising at least 35% of saturated cyclic hydrocarbons containing from 4 to 8 carbon atoms in the ring, and not more than 10% of aromatics.

9. The method of claim 6, in which the hydrocarbon is methyl cyclohexane.

10. The method of claim 6, in which the basically reacting agent is an alkali metal bicarbonate.

11. The method of claim 6, in which the basically reacting agent is an alkali metal carbonate.

12. The method of claim 6, in which the basically reacting agent is an alkali metal hydroxide.

13. The method of claim 6, in which the basically reacting agent is sodium bicarbonate.

14. The method of claim 6, in which the basically reacting agent is sodium carbonate.

15. The method of claim 6, in which the hydrocarbon is methyl cyclohexane and the basically reacting agent is an alkali metal bicarbonate.

16. The method of claim 6, in which the hydrocarbon is methyl cyclohexane and the basically reacting agent is an alkali metal carbonate.

17. The method of claim 6, in which the hydrocarbon is methyl cyclohexane and the basically reacting agent is an alkali metal hydroxide.

18. The method of claim 1, in which the hydroperoxides are separated from the oxidate by treating said oxidate with an aqueous solution of a basic compound of a metal selected from the class of metals consisting of potassium, sodium, lithium, calcium, barium, strontium and magnesium to form the corresponding metal salt of the peroxides, separating the hydrocarbon phase from the resulting reaction product, acidifying the reaction product to reform the peroxide thereby causing the peroxide to separate as an oily layer containing a substantially higher peroxide content than said oxidate.

19. The method of claim 6, in which the hydroperoxides are separated from the oxidate by treating said oxidate with an aqueous solution of a basic compound of a metal selected from the class of metals consisting of potassium, sodium, lithium, calcium, barium, strontium and magnesium to form the corresponding metal salt of the peroxide, separating the hydrocarbon phase from the resulting reaction product, acidifying the re-

action product to reform the peroxide thereby causing the peroxide to separate as an oily layer containing a substantially higher peroxide content than said oxidate.

20. A substantially stable water insoluble saturated cyclic hydrocarbon hydroperoxide concentrate produced by oxidizing a saturated cyclic hydrocarbon containing from 4 to 8 carbon atoms in the ring in the liquid phase with a gas containing free oxygen at temperatures of from 150° F. to 325° F. and at a pressure of from normal atmospheric pressure to 500 pounds per square inch gage pressure to maintain said liquid phase to an acid number not exceeding about 10.7 mg. KOH per ml., and separating hydroperoxide concentrate from the oxidate.

21. The hydroperoxide concentrate of claim 20, in which the oxidation is of a petroleum fraction comprising at least 35% of saturated cyclic hydrocarbon containing from 4 to 8 carbon atoms in the ring, and not more than 10% of aromatics.

22. The hydroperoxide concentrate of claim 20, in which the hydrocarbon oxidized is methyl cyclohexane.

ADALBERT FARKAS,  
ARTHUR F. STRIBLEY, JR.

#### REFERENCES CITED

The following references are of record in the file of this patent:

#### UNITED STATES PATENTS

| Number    | Name         | Date          |
|-----------|--------------|---------------|
| 1,981,384 | Friedolshein | Nov. 20, 1934 |
| 1,436,136 | Zerner       | Nov. 21, 1922 |
| 1,995,324 | Penniman     | Mar. 26, 1935 |
| 1,689,599 | Ramage       | Oct. 30, 1928 |
| 1,924,786 | Hartmann     | Aug. 24, 1933 |

#### FOREIGN PATENTS

| Number  | Country       | Date          |
|---------|---------------|---------------|
| 156,141 | Great Britain | Mar. 31, 1922 |