

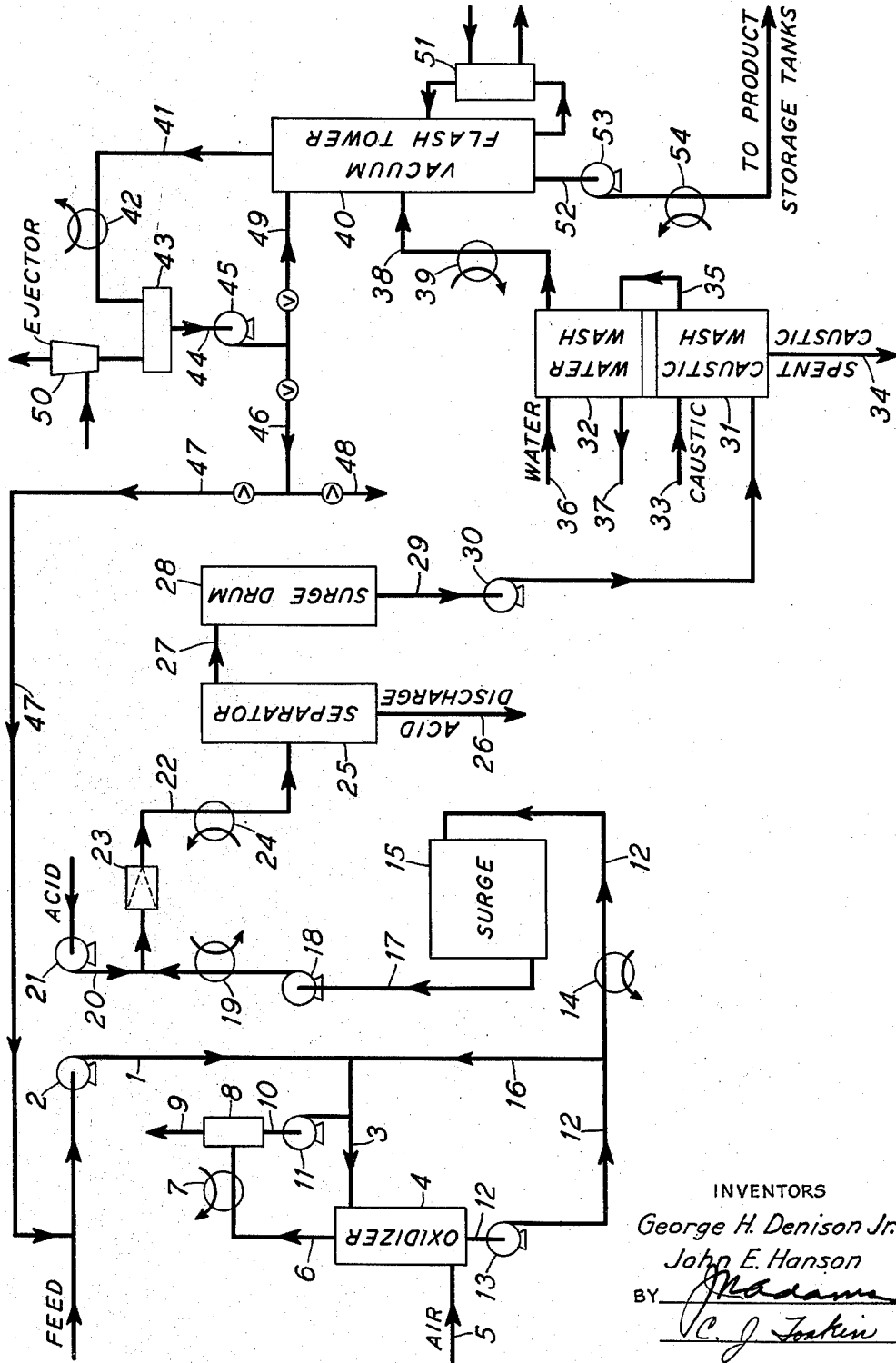
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DI-ORGANO PEROXIDE

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## DI-ORGANO PEROXIDE

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The present invention relates to a method of producing di-organo peroxides and pertains more particularly to a method of producing di-saturated hydrocarbon peroxides.

Various di-hydrocarbon peroxides are useful as germicides, fungicides, bleaching agents, polymerization catalysts, etc. In particular, the higher molecular weight peroxides, especially the di-saturated hydrocarbon peroxides, are desirable additives to Diesel fuels for improving the ignition properties as usually expressed by cetane numbers.

Heretofore, various processes have been proposed for obtaining such peroxides. However, the peroxides, especially the di-saturated hydrocarbon peroxides and the higher molecular weight peroxides, have not come into widespread use mainly because the prior methods necessarily employed expensive catalysts or expensive and/or difficultly obtainable reactants. In some processes considerable difficulties are encountered in carrying out the reaction in large or commercial scale equipment such as metallic vessels. Other disadvantages of the prior art processes are that they result in poor yields, are hazardous to carry out, or require complicated apparatus.

It is therefore an object of the present invention to provide an improved and novel process for producing di-organo peroxides without the above-mentioned disadvantages.

Another object of this invention is to provide a method of treating hydrocarbon hydroperoxide with acid under certain mild conditions to convert the hydroperoxide to di-hydrocarbon peroxide.

A further object is to provide a process of converting relatively unstable hydrocarbon hydroperoxides obtained from air-blowing saturated hydrocarbons to more stable di-hydrocarbon peroxides by acid treatment under mild conditions.

A particular object of this invention is to provide a simple and inexpensive method of producing relatively stable and peroxidic compounds from saturated hydrocarbons.

A special object of this invention is to provide a novel process of making di-(higher hydrocarbon) peroxides without the necessity of employing expensive materials.

These and other objects will be readily ap-

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parent from the following description taken together with the drawing, which illustrates a preferred mode of carrying out the present invention.

We have found that hydrocarbon hydroperoxides, particularly saturated hydrocarbon hydroperoxides, by treatment with acid under certain controlled conditions, are converted to di-hydrocarbon peroxides. In this manner, di-hydrocarbon peroxides can be obtained in an efficient and inexpensive manner without the disadvantages inherent in prior art processes. The present process also affords the advantages of high yields of the desired products, of simple operative procedures and of requiring simple apparatus.

An especially effective embodiment of the present invention involves air-blowing hydrocarbons to produce hydrocarbon hydroperoxides, which are subsequently treated with acid to obtain the di-hydrocarbon peroxides. A particular feature of the present invention is that the process does not require the use of reactants other than hydroperoxides and acid, thereby avoiding dependence upon expensive reactants such as alcohols, ketones, aldehydes, hydrogen peroxide and the like. Thus, the conversion is obtained by contacting the hydroperoxides in pure form, aside from preferred admixture with substantially inert diluents, solely with suitable acids or aqueous solutions of acids. That is, the present process is carried out under conditions wherein the hydroperoxides and acid are the only essential reactants. Restated, the acid is the sole effective agent for the conversion of a hydrocarbon hydroperoxide directly to a di-hydrocarbon peroxide, i. e., the auto-condensation of hydroperoxide to di-hydrocarbon peroxide is effected with hydroperoxide and acid as the sole reactants.

Considering the various advantages of the present process, it is an outstanding development and meritorious contribution to the art of producing di-hydrocarbon peroxides. The present process involves an unexpected and new phenomenon of conversion of hydroperoxides to peroxides by treatment with acid under mild conditions. When such acid conversion is combined with preparation of the hydroperoxides by liquid phase oxidation of hydrocarbons in

accordance with a preferred embodiment of the present invention, it is found that, contrary to the expectations of the prior art, one can efficiently and economically prepare di-hydrocarbon peroxides from hydrocarbon by simple operational steps.

To illustrate briefly the present invention, a petroleum distillate composed substantially of paraffins and naphthenes having an average chain length of ten carbon atoms was air-blown in liquid phase to obtain hydroperoxides. This intermediate product was treated with acid to produce di-hydrocarbon peroxides having the formula  $R_1-O-O-R_2$ , wherein the average chain length of each of the hydrocarbon groups  $R_1$  and  $R_2$  is about ten carbon atoms. Such di-hydrocarbon peroxides are water-insoluble liquids. No solid products were formed under varying conditions of operation in accordance with the present invention. The liquid peroxide products are particularly suited for use as a Diesel fuel ignition accelerator. Whereas both the hydroperoxide intermediate product as well as the di-hydrocarbon peroxide improve the ignition characteristic of a Diesel fuel (i. e., raise its cetane number), the di-hydrocarbon peroxide product is considerably more stable than the hydroperoxide under storage conditions, particularly as effected by contact with various agents in commercial Diesel fuels.

In accordance with the present invention, hydrocarbon hydroperoxide is converted to di-hydrocarbon peroxide by treatment under mild conditions with aqueous acid having a dissociation constant of greater than  $10^{-3}$ . With weaker acids the reaction does not proceed to an appreciable extent. The reaction does not evolve hydrogen peroxide or oxygen and evidently is not straight forward; consequently no mechanism is postulated.

The acid is usually employed in amounts ranging from 0.1-1.0, or up to about 1.5 mols of acid per mol of hydroperoxide. The larger amounts will ordinarily be employed with acids of lower concentration. A mol ratio of about 0.3 to 0.5 is preferred for acids of medium concentrations of 60% to 80% in order to obtain high conversion, such as above about 80% to 90%. In general, acid in sufficient amounts and strength to give a substantial conversion such as 50% or more, will be employed.

Suitable acids (agents capable of neutralizing a base, e. g., caustic) having dissociation constants greater than  $10^{-3}$  include the preferred mineral acids such as sulfuric, hydrochloric, phosphoric, nitric and hydrobromic acids. Other acids of sufficient strength include acetyl chloride, oxalic acid, dimethyl sulfate, etc. Sulfuric acid is usually preferred since it gives better yields and is cheaper. The acid is used in at least relatively concentrated aqueous solution; depending somewhat on the nature of the acid used, the concentration of acid preferably ranges from about 50 to 98% in aqueous solution for obtaining high yields, although less desirably lower concentrations such as to 20% may be sometimes used. With concentrations lower than about 50%, conversion is usually incomplete, while the preferred range of acid concentration gives maximum conversion.

The conditions of the process of converting hydroperoxides to di-hydrocarbon peroxide have

been generally stated as mild; the conditions may be said to be intermediate between drastic conditions of high temperature and very low temperature below 0° F. That is, the temperature is maintained relatively low, i. e., about room temperature, and the time of contact of the acid and peroxides at the reaction temperature is relatively short.

The treating temperature may be from about 0° F. or better from about 35° F. up to about 150° F. although the higher temperatures are accompanied by considerable decomposition. The reaction is exothermic and usually the temperature is maintained by cooling below about 95° F. Ordinarily an intermediate range of 50° F. to 85° F. is more suitable, and 60° F. to 80° F. is preferred.

For best results, the time of contact at reaction temperature should not be unduly prolonged and is usually less than 90 minutes, preferably below 60 minutes. The minimum time is determined by minimum mixing and separation time consistent with maintenance of the low temperatures. Short contact times of the acid phase with the organic phase of from a few seconds up to 3 minutes, which are especially preferred in order to avoid deleterious side reactions, are most conveniently obtained in continuous type operation. The longer contact times are usually necessarily employed in batchwise operation. The higher the temperature the shorter the contact time may be stated as the general rule to follow.

Hydrocarbon hydroperoxides which may be converted to di-hydrocarbon peroxides in accordance with the present invention are preferably saturated hydrocarbon hydroperoxides, including paraffin, naphthene and mixed paraffin-naphthene hydroperoxides, especially of the secondary or tertiary types. Suitable paraffins from which the hydroperoxide may be derived are normal paraffins such as, for example, butane, pentane, hexane, heptane, octane, nonane, decane, dodecane, tetradecane, hexadecane, etc. and their branched chain isomers such as isobutane, isopentanes, isohexanes, isoheptanes, isooctanes, isodecanes, isododecane, etc. or mixtures thereof. Naphthene hydroperoxides may be derived from cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, and the like. Also, the hydroperoxide derivatives of alkyl substituted naphthenes such as methyl cyclopentane, dimethylcyclopentanes, ethylcyclopentanes, diethylcyclopentanes, trimethylcyclopentanes and the similar substituted cyclohexanes, cycloheptanes, etc. may be employed. The alkyl substituents may also be propyl, isopropyl, butyl, isobutyl, tertiary butyl, etc. In case of the longer alkyl substituents, particularly of the branched chain type, the hydroperoxide group may be attached either on the naphthene ring as in the case of dimethylcyclopentane, for example, or on the alkyl chain, thus forming a naphthene substituted alkyl hydroperoxide. Preferred are the secondary and especially the tertiary hydrocarbon hydroperoxides, i. e., wherein the hydroperoxide group,  $-OOH$ , is attached to a secondary or tertiary carbon atom, respectively.

While saturated hydroperoxides are ordinarily employed in the present process when a Diesel fuel additive is desired, aliphatic hydroperoxides containing olefinic bonds or aromatic groups can be similarly converted to the di-hydrocarbon per-

oxides in accordance with the process of the present invention. Hydroperoxides derived from olefins such as octenes, decene, 2 ethyl hexene, etc., may thus be used. Hydroperoxides of isobutylene, alkyl benzenes, such as toluene, xylene, ethyl benzene, isobutyl benzene, octyl benzenes, cetyl benzenes, etc., and similar substituted naphthalenes may be employed.

In addition to purely hydrocarbon peroxides there may be used hydrocarbon peroxides which are substituted to such minor extent that the substituents do not appreciably affect the essential hydrocarbon character of the hydroperoxide. Thus, there may be employed in the present invention organo hydroperoxides, wherein the organo radical consists essentially of a hydrocarbon group as the main character of such organo radical, without excluding the presence of minor substituents such as chloro, bromo, nitro, etc. which are merely inert or which do not change the essential hydrocarbon character of the organo radical. For example, chloro-tertiary-butyl hydroperoxide, bromo-tertiary-butyl hydroperoxide, and analogous hydroperoxides derived from 1,1-dibromo-2-methyl propane, 1-chloro-1-bromo-2-methyl propane, 1,2-dichloro-2,3-dimethyl butane, 1-fluoro-2-methyl propane, 1-fluoro-3-methyl butane, 1-chloro-2-phenyl propane, 1-bromo-2-benzyl propane, 1-chloro-2-naphthyl propane, 1-chloro-2-cyclohexyl propane, 1,1-dichlorophenyl-2,2,2-trichloroethane, and the like as well as their homologues may be employed.

The present process is applicable to the individual hydroperoxides or mixtures thereof. Suitable mixtures may contain, for example, several hydroperoxides of any one or more of the various types such as paraffin, naphthene, mixed paraffin-naphthene and aromatic hydroperoxides. Suitable hydroperoxides may be derived from various petroleum hydrocarbon fractions, such as straight-run gasolines which may contain both paraffins and naphthenes, other petroleum distillates, e. g., fractions having ASTM 50% boiling point within the range 200° to 450° F. or 325° to 650° F., etc.

While an individual hydroperoxide alone may be readily converted to a di-hydrocarbon peroxide in accordance with the present invention, the more active pure hydroperoxides, especially those of lower molecular weight, can be diluted with a substantially inert solvent, such as a light solvent such as pentane, hexane, etc., or light oil, such as pale oil, kerosene, etc., in order to control more readily the reaction. Ordinarily, a 5-50%, preferably 5-25%, solution of hydroperoxides in a diluent is employed in order to obtain easily controllable acid-treating conditions and/or high conversion.

The present process is especially suited for preparing stable cetane-improving Diesel fuel additives by treating higher molecular weight hydrocarbon hydroperoxides having at least 8 carbon atoms and up to about 18 carbon atoms in the hydrocarbon chain.

The hydroperoxides constituting the feed stock for the present process may generally be prepared in any suitable manner. The process of obtaining hydroperoxides by treating an alcohol with hydrogen peroxide and anhydrous sodium sulphate is described in Patent No. 2,223,807. In accord-

ance with Patent No. 2,383,919, tertiary alkyl hydroperoxides may be recovered from the reaction product of vapor phase oxidation of saturated aliphatic hydrocarbons having a tertiary carbon atom with an oxygen-containing gas and in the presence of hydrogen bromide. Patent No. 2,430,864 discloses a method of obtaining pure naphthene hydroperoxides by liquid phase oxidation of naphthenes. Schultz et al. Patents 2,317,968 and 2,365,220 disclose a more general method of liquid phase oxidation of petroleum distillates containing, for example, both paraffins and naphthenes, to produce oxygenated hydrocarbons, in which the chemically reactive oxygen content is expressed in terms of oxygen factor.

In such oxidation processes it is desirable to purify the feed material by removal of oxidation inhibitors and other materials which may have deleterious action on hydroperoxides, e. g., sulfur and nitrogen-compounds, many naturally occurring sulfur, nitrogen, oxygen-containing compounds.

A particularly advantageous feature of the present invention resides in preparing di-hydrocarbon peroxides from hydrocarbons, especially saturated hydrocarbons. Such process involves liquid phase oxidation of suitable hydrocarbons with an oxygen-containing gas under controlled conditions and thereafter subjecting the resultant hydroperoxide-containing product to acid treatment under certain mild treating conditions to produce di-hydrocarbon peroxides. This present process constitutes an improvement over the Schultz et al. process of the aforementioned Patents 2,317,968 and 2,365,220. Thereby, the cetane - improving hydroperoxide - containing product of Schultz et al. is converted to superior cetane - improving di - hydrocarbon peroxides, which are more stable in storage upon admixture with certain types of base fuels and which are substantially less corrosive. In general, the di-hydrocarbon peroxides produced from hydrocarbons in this manner are low in cost, permanent and stable in storage, and without adverse qualities from the standpoint of marketability, and where used to promote ignition, of consistently high ignition quality.

Where it is desired to produce an additive for improving the ignition qualities, i. e., cetane number, of Diesel fuels and the like, the present improvement process is particularly applicable either in conjunction with the process of Patent No. 2,365,220, wherein charging stocks corresponding to an ASTM 50% boiling point within the range 325 to 650° F. are employed, or Patent No. 2,317,968, wherein the charging stock boils within the range 200° to 450° F. For this purpose the hydrocarbon oil to be oxidized should be free from large proportions of aromatic ring structures and should contain a group of relatively volatile hydrocarbons. While straight-run petroleum distillates are often used to advantage as initial materials, fractions containing large percentages of branched chain compounds are usually preferred. Ordinarily, petroleum fractions should be acid-treated or selectively solvent refined before oxidation for optimum results. Oils containing high proportions of aromatic rings are less capable of yielding cetane-improving compounds than are oils of high paraffinicity, although the treatment of oils of high aromatic content with relatively

strong sulfuric acid or an equivalent chemical reagent for their extraction with liquid solvents such as liquid sulfur dioxide, phenol, aniline, furfural, nitrobenzene and the like in removing aromatic components for reducing their concentration, suffices to improve their amenability to treatment in accordance with the invention.

A convenient means of following the course of the oxidation process resides in the "oxygen factor" determination. The "oxygen factor" of an oil is determined as follows: A 2 to 10 ml. sample of oil at approximately 68° F. is accurately pipetted into a 250 ml. glass stoppered flask. 20 ml. of a mixture consisting of 60 volume per cent of C. P. glacial acetic acid and 40 volume per cent of chloroform are added to the oil, followed by 2.0 ml. of a saturated aqueous solution of potassium iodide. The mixture is shaken vigorously for 3 minutes and then diluted with about 50 ml. of distilled water. The liberated iodine is titrated with 0.1 normal standardized sodium thiosulfate solution, adding starch indicator just before the end point is reached. Considerable shaking is necessary near the end of the titration. Oxygen factor = (titer in ml.  $\times$  normality of thiosulfate  $\times$  1120) / (volume of sample in ml.).

The oxidation step of the process is preferably carried out within the temperature range of 250° F. to 350° F. Preferably, the oxidation is carried out with the aid of a small amount of feed stock from the previous run. An amount of feed stock between about 0.5% and 5% is usually desired. With the petroleum distillates referred to hereinabove and mentioned in the Schultz et al. patents, atmospheric pressure is normally sufficient; with other feeds, especially lower boiling hydrocarbons, superatmospheric pressures, e. g., up to 350-400 atmospheres, preferably below 100 atmospheres, may be employed. The oxidation with an oxygen-containing gas such as air is continued for a time not materially longer than is necessary to give an oil of maximum oxygen factor obtainable, and also to prevent undue formation of undesirable side reaction products. In general the oxidation step is regulated to produce an oxygen factor of at least 250 and preferably above 800 and a neutralization number of not more than 15. It is usually most desirable for best conversion of hydroperoxides to employ an excess of oxygen-containing gas. For example, sufficient air is employed so that the effluent gas is not completely deoxygenated. For increased yield it is sometimes desirable to carry out the oxidation in the presence of a basically reacting agent such as alkaline earth metals or compounds of alkaline earth metals, alkali metals, iron group metals and metals of the right-hand column of group II of the periodic table which form salts with acids produced during the oxidation; such agents, e. g., alkali metal carbonates and bicarbonates or dilute aqueous solutions of alkali metal hydroxides are used in sufficient amount to prevent accumulation of appreciable amounts of acids which tend to promote deleterious side reactions. Neutralization can likewise be effected in a separate stream withdrawn from the oxidation chamber and returned thereto after treatment. The partially oxidized oil should not be allowed to remain at or near oxidizing temperature for any considerable length of time subsequent to the attainment of the desired oxygen factor due to the secondary reactions which continue at the expense of the desired product. It is therefore of importance to quickly cool the oil as, for example, by quenching with water to a tem-

perature below that at which secondary reactions take place rapidly, namely, to a temperature below about 250° F. and preferably as low as 100° F.

It is sometimes desirable to wash this partially oxidized oil with dilute caustic solution (such as up to 5% caustic) to remove acidic substances and salts or soaps of organic acids before proceeding with the subsequent treatment. A 5% aqueous caustic solution in an amount equivalent to about that theoretically required to effect neutralization is preferably used. A materially stronger caustic solution tends to destroy or remove the desired hydroperoxides, as does a substantial excess of the caustic. In most cases it is advantageous to dispense with the caustic wash and proceed with the subsequent treatment.

Further complete discussions of the steps of partial oxidation, quenching and caustic washing a chosen feed stock as well as analytical methods for the determination of oxygen factor and neutralization number are given in U. S. Patents Nos. 2,365,220 and 2,317,968 to Schultz et al.

It is ordinarily not advantageous to concentrate the hydroperoxides, such as obtained from the aforementioned oxidation process, before the subsequent acid treatment. Such concentration is sometimes desirable and may be effected by fractional distillation, preferably under reduced pressure, by solvent extraction, such as with 90% aqueous methanol or by chemical means or combinations of such methods. As chemical means the hydroperoxides may be extracted or precipitated as salts by treatment with an alkali or basic metal compounds, such as alkaline earth metal hydroxides or carbonates; after separation from the mixture the salt may be dissolved in water and acidified with dilute acid to reform the hydroperoxide.

Referring now to the acid treating step: The preferred feed therefor is obtained by the above-described liquid phase oxidation of substantially saturated hydrocarbons. Such unconcentrated feed mixture usually has a hydroperoxide content of about 8 to 15%, although hydrocarbon solutions resulting from oxidation or from dissolution of hydroperoxides in hydrocarbons may contain greater or smaller amounts of hydroperoxides such as from 5 to 25% and be effectively treated by acid. As noted above, the hydroperoxides are preferably in dilute solutions for the acid treating step. The illustrative feed stock containing 8 to 15% hydroperoxides (having an average of ten carbon atoms) will have an oxygen factor ranging from 800 to 1500. To cause conversion of the hydroperoxides to dihydrocarbon peroxides in such a feed stock, it has been found in general that treatment with between 0.1 and 0.75 pound of 50% to 98% acid, e. g., sulfuric acid, per gallon of the partially oxidized unconcentrated feed stock is most satisfactory. It has further been found that under the mild operating conditions, such as at a temperature of 60° to 80° F., etc., as hereinabove set forth, a treatment with about  $\frac{1}{8}$  to  $\frac{1}{4}$  pound of 75% sulfuric acid per gallon of the above feed gives optimum results. While for the purpose of obtaining optimum short reaction time the more concentrated acid and/or higher acid to hydroperoxide are used, lower ratios or acid of the lower concentrations may be employed. Thus, for conversions of above about 50%, the mol ratio of acid to hydroperoxide may range from 0.1 to 1.0, or up to 1.5 mols of acid per mol of hydroperoxide. For example, the following table presents

data showing the results of treating a feed stock, such as referred to above, having an oxygen factor of 1070 and hydroperoxide content of about 10% or about 2.2 mols per gallon, the hydroperoxides having an average of about ten carbon atoms. The reaction temperature was maintained at about 70° F. and sulfuric acid of 75% concentration was used at the indicated ratios.

TABLE I

Amount of Acid (Lbs./gal. of feed stock)	Mol Acid/Mol hydroperoxide	Oxygen Factor of Product
0.25	0.478	162
0.165	0.317	177
0.10	0.191	303
0.05	0.096	452

It will be seen that the optimum minimum amount of acid corresponds to a ratio of about 0.3 mols of acid per mol of hydroperoxide.

Preferably the treating time is kept to a minimum well below the 90 minutes noted above in order to avoid deleterious side reactions; for example, in acid treating the oxygenated product produced from a mixed paraffin-naphthene petroleum distillate boiling in the range 308° to 366° F. the sludge which is an oil-insoluble material formed when using a contact time of over 20 minutes and which may be separated and disposed of, is practically eliminated by limiting the contact time to less than about 3 minutes.

For control purposes it has been ascertained that when the temperature is controlled as above indicated the reduction in the value of the oxygen factor serves as a criterion for the maintenance and attainment of optimum conditions for the acid treatment. In general it has been observed that in treating feed stocks obtained from liquid phase oxidation it is not advisable to attempt to acid treat to extinction of oxygen factor, since the additional treatment necessary to chemically effect the last portions of oxygen factor responsive compounds tends to cause decomposition of the peroxides. Hence, conditions of acid treatment are preferably adjusted to give a reduction to about 10 to 20% of the original oxygen factor value. For example, in treating a feed stock containing 8% hydroperoxides having an average of ten carbon atoms in the molecule, such conversion yields a reaction product containing about 5½ to 6½% di-hydrocarbon peroxide.

Batchwise acid treatment can be applied to hydroperoxide-containing mixtures such as the above-mentioned partially oxygenated oil. It has been found that the temperature may be readily controlled to the desired value, for example, by adding the total sulfuric acid employed in several dumps with a cold water wash between each dump to counteract the heat evolved in the reaction. When treating the above-mentioned oxygenated oil feed stock the ¼ pound per gallon of sulfuric acid was conveniently added in four dumps together with the intermediate cold water washes for cooling. Instead of using cold water washes for cooling, external cooling and/or refrigerating coils inserted into the mixing chamber may be employed to control the temperature. The acid treated oil is preferably washed with water after the last acid treatment to remove excess acid, is then washed with dilute caustic until neutral, and finally with water until salt and caustic-free. It is preferable to use a 10%

excess of 5% aqueous caustic over that required for neutralization.

Mixing of the acid and hydroperoxide containing feed followed by immediate separation in a continuous manner has been found preferable in order to obtain minimum contact time. Various continuous mixers, such as turbomixers, mixing nozzles, etc., may be employed. An efficient separator or series of separators of various designs may be used, followed by continuous water wash of the non-aqueous peroxide phase. External refrigeration may be applied to the mixer itself and/or to the feed streams to the mixer as well as the mixed effluent stream in order to maintain the desired temperature preferably at 60° to 80° F. The water-washed product is then caustic treated, either continuously or batchwise, as noted hereinabove. A particularly effective procedure for obtaining optimum short contact time and high yields without appreciable deleterious side reactions involves the steps of mixing the hydroperoxide and acid by means of a spray nozzle, then immediately passing the resultant mixture to a settler, from which the acid layer is continually drawn off. With immediate dilution of the withdrawn acid layer with water, sludge formation is substantially completely prevented. With long intervals before dilution, sludge tends to be formed in the acid. The treated upper layer as immediately separated from the acid is appreciably reduced in oxygen factor. Upon standing out of contact with the acid layer for a short time, such as 5-20 minutes, preferably about 10 minutes, the oxygen factor of the separated upper layer drops further to the desired low value, showing completion of the reaction. Then the product is water- and caustic-washed.

Where the hydroperoxides have been concentrated, such as by fractional distillation of the liquid phase oxidation product to yield a mixture having an increased oxygen factor of at least 1000, preferably about 3000 to 7000, or up to 15,000, the concentrate may be acid-treated as described above, except a correspondingly greater amount of acid per gallon of feed stock is used to obtain the hereinbefore-indicated proper acid-hydroperoxide ratio and to give a final product having an oxygen factor not greater than about 20% of the oxygen factor of the concentrate.

Where the hydroperoxides are separated from the unreacted hydrocarbons by chemical means, i. e., by precipitation as salts, the reformation of the hydroperoxide and conversion to di-hydrocarbon peroxides can be carried out in one operation by employing sufficient acid to form the hydroperoxide from the salt plus enough acid for the desired conversion of hydroperoxide to di-hydrocarbon peroxide.

For some purposes, the di-hydrocarbon peroxide containing product thus obtained in the above-described batchwise or continuous acid-treating methods is ready for use; for example, when the oil feed stock chosen for oxidation is suitable for use as a Diesel fuel, the product is now an improved Diesel fuel. If, however, the oil feed stock selected is not a suitable Diesel fuel as, for instance, by reason of its low boiling range or if the object is to produce a blending agent which may be added to a Diesel fuel stock to increase the cetane number, the acid-treated oxygenated oil may be added to a base stock in an amount to produce a fuel having the desired cetane number.



It is frequently desirable, however, to obtain the di-hydrocarbon peroxides in substantially pure or more concentrated form, and in such cases the di-hydrocarbon peroxides may be concentrated by distillation or other suitable means, for example, by solvent extraction or adsorption fractionation or by combinations of such methods. The hydrocarbonaceous material separated from the di-hydrocarbon peroxides and concentrates thereof may be recirculated to the air-blowing step, preferably after subjecting it to acid treatment as is the original feed stock, in order to render it more suitable for conversion to hydroperoxides. In many cases it will be found preferable to concentrate by distillation and this method is illustrated and more fully described below.

Ordinarily, it is preferable to concentrate the di-hydrocarbon peroxides by removing the relatively lower-boiling material from the mixture. The portion removed may contain substantially only inert hydrocarbons which may be recycled after suitable treatment to the oxidation step of the process or may be otherwise utilized or discarded. The distillation residue may vary between about 5% and 40% of the original charge depending on conditions of previous treatment and expected uses; for example, where the undistilled product contains about 5-10% peroxides, distillation may be carried out until only about 20% of the original volume remains in the still. The bottoms remaining in the still may contain the di-hydrocarbon peroxides in amounts from about 20-70% or more, usually of the order of 40% or in some cases to substantially pure peroxides. For example, when the acid treatment described above and the concentration step of the process is applied to a hydroperoxide feed derived from liquid-phase oxidation of a hydrocarbon fraction having an average of ten carbon atoms per molecule, the resultant concentrated peroxide-containing oil will have an oxygen factor of not greater than 600 and preferably less than 300. It has been found that concentration by fractional distillation may best be carried out at a subatmospheric pressure, such as 10-30 mm. of mercury or lower. Satisfactory pressures are determined by the properties of the charging stock being concentrated. In general, a higher pressure is usable with a lighter charging stock. The temperature desirably is maintained below 350° F., preferably below 250° F., and especially of the order of 200° F.

Solvent extraction may be used in place of fractional distillation or following distillation, in order to further concentrate the peroxides. Although a variety of extraction solvents may be used, including relatively concentrated aqueous aliphatic alcohols such as isopropyl alcohol etc., polyhydroxy alcohols such as ethylene glycol, glycerol, etc., ethers and esters of the latter class such as diethylene glycol, monomethyl ether, glycol diacetate, etc., pyridine and its homologues, water-soluble ketones, such as acetone, it is preferable to use aqueous methanol as the extraction agent. The peroxides may be extracted from the mixture with 75 to 95%, preferably about 90%, aqueous methanol by continuous or batchwise extraction. Thereafter, the extract phase may be diluted with water to free the peroxides as an oily layer. The separation of the peroxides from the aqueous alcoholic extract phase may also be carried out by distillation, preferably under reduced pressures, to vaporize the alcohol and water. If desired, the extract so obtained may be subjected to distillation in

order to further concentrate the di-hydrocarbon peroxides.

As a final step, the product may be washed with a small amount of caustic, such as 5-40% caustic, for example 1 to 2% of 15% caustic, and then water washed. In case the peroxide concentrate is relatively high in acid content, it is most desirable, in addition, to water wash before the caustic wash.

Referring to the drawing, one preferred embodiment of the present invention is carried out as follows: A suitable feed, such as a petroleum fraction containing predominantly paraffins and naphthenes and boiling in the range of 308° to 366° F. is introduced via line 1 through pump 2 and line 3 into an oxidizing chamber, such as oxidizer 4, for converting the hydrocarbons to hydroperoxides; air or other oxidizing agent is introduced into oxidizer 4 through line 5. Ordinarily, batchwise oxidation is employed, although continuous operation with or without recycle of the effluent oxygenated hydrocarbon may be used. Distributing means (not shown) may be provided within oxidizer 4 to provide efficient contact between the air and hydrocarbons. At the start of the oxidation, the oxidizer and the feed materials are heated to oxidizing temperature. After heating, say, for the first hour of the operation, cooling is employed to control the exothermic reaction. The rate of introduction of air or other suitable means, such as internal or external coolers, may be used to control the temperature within the oxidizer at the desired temperature of about 300° F. Partially deoxygenated gas, together with entrained liquid or gaseous hydrocarbon and reaction products leave the oxidizer 4 via line 6 through a cooling and condensing unit 7 and enter separator 8 where the mixture is separated, the water layer formed therein being disposed of separately. Gas and uncondensed vapors are removed via line 9. The hydrocarbonaceous liquid is withdrawn from condensing unit 8 through line 10 and pump 11 and recirculated to oxidizer 4 via line 3.

When, in batchwise operation, the hydrocarbon has been treated to the degree desired, as measured by the oxygen factor and neutralization number of samples withdrawn at suitable intervals or other control means, the oxygenated hydrocarbons are withdrawn from oxidizer 4 by means of line 12 and pump 13. Preferably the oxidation product withdrawn from oxidizer 4 is rapidly cooled in cooling means 14 to about 100° F. and then may be passed to an intermediate surge or storage tank 15.

In continuous type operation, part of the oxygenated hydrocarbons may be recirculated through lines 16 and 3 to oxidizer 4 and it is sometimes advantageous to recirculate the main body of hydrocarbons in oxidizer 4 by passing hydrocarbons via a closed circuit including lines 12, 16 and 3 and pump 13. In some instances, two or more oxidizers in series may be substituted for oxidizer 4, in which case the hydrocarbons are circulated from the first oxidizer to subsequent oxidizers and are withdrawn from the last oxidizer in the series.

The hydroperoxide intermediate is then taken from surge or storage tank 15 and passed via line 17 and pump 18 through cooler 19. With addition of metered amounts of acid introduced through line 20 and pump 21 the hydroperoxide-containing mixture passes through line 22 and a mixing nozzle 23 or other suitable mixing device

wherein efficient contact between the acid and hydroperoxide is obtained, causing the conversion of the hydroperoxide to di-hydrocarbon peroxide. The reaction mixture passes through cooling means 24 which, with cooler 19, may form part of a relatively high capacity refrigeration system to maintain the desired temperature, such as 80° F.

The acid-peroxide mixture is then introduced into a suitable separator system, such as a gravity separator 25, wherefrom the acid and peroxide-containing mixture are separately discharged through lines 26 and 27, respectively. Preferably the acid is separated from the peroxide-containing mixture as soon as possible after contact. Thence the peroxide-containing mixture passes through a surge drum 28, line 29 and pump 30 to a treating unit comprising, for example, a lower section 31 for caustic wash and an upper section 32 for subsequent water wash. Caustic such as 20° Bé. aqueous caustic is introduced into lower section 31 through line 33 and discharged as spent caustic through line 34. The caustic-washed peroxides and hydrocarbons pass from section 31 through line 35 to water-wash section 32 having water inlet line 36 and water outlet line 37.

The caustic and water-washed peroxide-containing mixture flows through effluent line 38 through heating means 39 which may be a heat exchanger or the like, to a fractional distillation column, such as vacuum flash tower 40. Therein the relatively volatile inert components consisting primarily of unoxidized hydrocarbons are taken overhead via line 41 through condenser 42 into separator drum 43 and thence through line 44, pump 45 and valve-controlled lines 46 and 47 to feed line 1 for recirculation through the system and further oxidation, or are removed from the system via valve-controlled line 48. If desired, the recirculated overhead hydrocarbonaceous material may be acid treated as is the original feed stock. Part of the overhead condensate is returned as reflux to tower 40 via valve-controlled line 49. Suitable vacuum generating means, such as a steam ejector 50 attached to drum 43 is provided to maintain the desired vacuum in the distillation or flash tower 40. The tower 40 is also provided with suitable heating means such as steam reboiler 51 or the like. Concentrated peroxide withdrawn from tower 40 through line 52, pump 53 and cooling means 54 passes to product storage.

The drawing of the above-described embodiment omits for sake of simplicity such auxiliaries as valves, flow, level and pressure controllers, metering devices, temperature regulators and the like, as will be readily supplied by one skilled in the art.

Where hydroperoxides are not prepared from liquid phase oxidation of hydrocarbons such as in oxidizer 4, the illustrated equipment in the line of flow prior to the surge or storage tank 15 may be omitted, and hydroperoxides preferably in solution in an inert solvent, such as liquid hydrocarbons, are introduced into the system starting with line 17 and pump 18.

As illustrative of the present invention the following examples are given:

*Example 1.*—16.5 c. c. of technical dimethyl cyclopentyl hydroperoxide (about 85% purity and having an oxygen factor of 11,700) was diluted to 165 c. c. with n-pentane, and the resultant solution (an oxygen factor of 1084) treated with

0.25 lb./gal. of 75% sulfuric acid at 40–50° F. over an hour period. After separating from the aqueous acid phase, the upper oily layer was water washed and neutralized with sodium bicarbonate. Upon evaporating off the n-pentane, 13.6 c. c. of product was recovered, which had an oxygen factor of 4370. At 0.5% concentration in an untreated Diesel fuel having a cetane number of about 41, the product caused an increase of an average of 12.2 cetane numbers. At the same concentration in the same fuel, technical dimethyl cyclopentyl hydroperoxide of about 60% purity gave only a cetane number increase of 6.5.

*Example 2.*—To 100 c. c. of 88.7% tertiary butyl hydroperoxide, there was slowly added over a two-hour period 50 c. c. of 65% sulfuric acid while maintaining the temperature below about 7° C. After allowing the mixture to stand overnight, an additional 50 c. c. of 75% sulfuric acid was added in 30 minutes time at a temperature below 0° C. Thereafter with the reaction vessel placed in a cold water bath to start, the temperature was permitted to warm to room temperature. After separation of phases, the upper layer was washed free of hydroperoxide with several 10 c. c. portions of 40% caustic. After a final water wash, 55 c. c. of di-(tertiary butyl) peroxide was obtained. This product was determined to be fairly pure by its lack of oxygen factor and measurement of density, boiling point and refractive index.

*Example 3.*—A number of individual hydrocarbons of approximately 98% or better purity were first oxygenated by placing a sample of each hydrocarbon in a vessel fitted with an air inlet, a sampling device, a water trap, and a reflux condenser. This apparatus was immersed in a constant temperature oil bath maintained at peroxidation temperature. After sufficient time for the contents to reach the bath temperature, air was passed through the hydrocarbon via a distributing plate in the bottom of the oxidizing vessel. Samples were withdrawn from the main body of the hydrocarbon at periodic intervals. The oxygen factor (indicating the hydroperoxide content) of the sample and acid content were determined. When the oxygen factor reached a maximum or shortly thereafter, the stock was removed from the apparatus, cooled and neutralized with 50% by volume of 5% sodium bicarbonate to remove acids. The peroxidized material was then added in 2.5% and 10% concentrations to a Diesel fuel base (derived from waxy California crude) and the cetane number of the blend determined. The results obtained in this manner are given in the Table II below, wherein the "peak oxygen factor" is that obtained by determination on withdrawn samples whereas the "blending oxygen factor" is the final oxygen factor of the product prior to blending. (The latter value is usually lower since the neutralization reduces the peroxide content approximately 10% and air blowing was generally not stopped until the peak had been passed, resulting in a lower peroxide content.) The cetane number increase for the unperoxidized material was obtained in order to show the true effect of the peroxide since only 5 to 20% of the unconcentrated blown material was peroxides; hence cetane number increase was corrected in accordance with such blanks. The relative effectiveness of the different hydroperoxides is given as the increase in cetane number per 1000 oxygen factor, in order to bring the effectiveness of the peroxides to a common basis.



**TABLE II**  
*Results of peroxidation of pure hydrocarbons*

Compound	Peroxidation Temp., °F.	Peak, O. F.	Blend- ing, O. F.	Cetane Number Increase						Relative Ef- fectiveness, ΔCN/1000 O. F.	
				Peroxidized		Unperoxi- dized		Corrected		2.5%	10%
				2.5%	10%	2.5%	10%	2.5%	10%		
n-Decane.....	275	719	580	8.6	15.7	+0.5	+3.1	8.1	12.6	13.8	21.3
n-Dodecane.....	300	529	302	3.2	10.6					(10.6)	(33.1)
Octene-1.....	240	1,142	902	7.5	14.6	+0.1	+0.4	7.4	14.2	8.2	15.7
Decene-1.....	250	849	614	5.1	10.1	+0.1	+0.6	5.0	9.5	8.2	15.4
Ethylcyclohexane.....	235	2,148	1,250	7.0	13.3	-0.6	-1.3	7.6	14.6	6.1	11.7
Iso-Propylcyclohexane.....	300	1,422	956	5.6	12.0	-0.7	-1.5	6.3	13.5	6.6	14.1
Ethylbenzene.....	265	2,050	1,868	5.5	8.3	-1.4	-3.5	6.9	11.8	3.7	6.3
o-Xylene.....	275	2,624	564	1.5	1.7	-0.6	-2.6	2.1	4.3	3.7	7.6
p-Xylene.....	275	86	66	-0.9	-3.2	-1.2	-2.9	0.3	-0.3	4.8	
Iso-Propylbenzene.....	300	215	211		0.2	-0.6	-2.9		3.1		14.7
p-Methyl-4-isopropylbenzene.....	275	3,685	3,170	6.7	11.3	-1.4	-3.3	8.1	14.6	2.6	4.6
Tech. Trimethylbenzenes.....	300	2,340	1,915	5.3	8.3	-0.9	-4.5	6.2	12.8	3.2	6.7
Tech. Diethylbenzenes.....	300	384	311	-0.2	0.0	-0.9	-3.2	0.7	3.2	2.3	
Tech. Monoamylbenzenes.....	300	492	370	2.7	3.4	-0.8	-3.3	3.5	6.7	9.5	18.1
Petroleum distillate <sup>1</sup> .....	300	1,320	754	6.7	11.6	-0.8	-1.7	7.5	13.3	9.6	16.9
Do. <sup>2</sup> .....	300		800	5.2	10.2	-0.8	-1.7	6.0	11.9	7.5	14.9

<sup>1</sup> NOTE: Uncorrected for the effectiveness of the unoxidized hydrocarbon.  
<sup>2</sup> NOTE: These compounds did not reach a peak at the end of 40 hours.  
<sup>3</sup> NOTE: This distillate had a hydrocarbon analysis of 50% paraffins, 48% naphthenes and 2% aromatics; an API gravity of 50.6; an aniline point of 146; acid wash aniline point of 151; an average molecular weight of 139; a boiling range of 308-366° F. with a 50% ASTM distillation point of 328° F. and a 90% point of 341° F.

**Example 4.**—The hydrocarbon hydroperoxide mixtures obtained in accordance with Example 3 above were treated with acid at temperatures of about 60-80° F. as indicated in the following Table III:

**TABLE III**

*Results of acid catalyzed condensation of peroxidized hydrocarbons*

Hydroperoxide From	Oxygen Factor		Corrected CN	
	Before	After	2.5%	10%
n-Decane, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	561	107	7.0	11.5
n-Decane, 36% HCl, 25%.....	561	16	3.0	4.4
n-Decane, 48% HBr, 25%.....	561	29	2.3	4.6
Octene-1, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	902	372	4.0	9.8
Decene-1, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	614			9.7
Decene-1, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	504	123	3.0	7.8
Decene-1, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	375	67	1.1	6.2
Ethylcyclohexane, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	1,250	278	5.8	12.3
Ethylbenzene, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	1,868	905	4.2	9.7
o-Xylene, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	564	45	1.0	2.9
Tech. Monoamylbenzene, 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	363	85	1.3	3.1
Petroleum distillate, <sup>1</sup> 75% H <sub>2</sub> SO <sub>4</sub> , 0.25 lb./gal.	800	100	4.9	9.8

<sup>1</sup> Same distillate as in Table II.

**Example 5.**—700 c. c. of a petroleum distillate, which after washing with one-half pound of 96% sulfuric acid per gallon, was relatively free from asphaltic and resinous materials and was composed of about 41% paraffins, 47% naphthenes and 12% aromatic ring compounds, had a gravity of 46.4° A. P. I. boiled within the range of 310° F. and 364° F. and had a cetane number of about 35, was oxidized in a treater similar to oxidizer 4 shown in the drawing.

In this oxidation, the oil plus 18 c. c. of feed stock from a previous run was air-blown for three hours at a temperature of about 300° F. and at a rate of two volumes of air per volume of oil per minute. The hydroperoxide-containing oil from this operation had an oxygen factor of 801

and cetane number of 77. This product was washed with a ten per cent excess of 10% aqueous caustic to give a product having a neutralization number of 1. This neutralized hydroperoxide-containing oil was then treated with one-quarter pound of 75% sulfuric acid per gallon of oil added in five dumps over a period of fifteen minutes at a temperature of about 75° F. to convert the hydroperoxides to di-hydrocarbon peroxides. The product had an oxygen factor of 98, a neutralization number of 0.04, and a cetane number of 65.5, and constituted a highly desirable Diesel motor fuel for use as such or in a blend with other lower quality components. For example, when 5% of this partially oxidized acid treated product was added to an untreated Diesel fuel base from waxy California crudes and having a cetane number of 42, the cetane number of the blended fuel was raised to 47.7.

The foregoing example covering oxidation and acid treating steps illustrates the practice of the invention by a procedure wherein a concentrating step is not employed.

**Example 6.**—The di-hydrocarbon peroxide-containing product resulting from acid treatment in Example 5 is distilled at 5 mm. of mercury pressure and 130° F. until 80% of its volume has been removed. The vaporized portion had an oxygen factor of 13 and a neutralization number of less than 0.005, while the concentrate remaining in the still had an oxygen factor of 670 and a neutralization number of 0.033. Three per cent of this concentrated product was added to an untreated Diesel base fuel derived from waxy California crude and boiling within the range of 340° F. to 576° F. and having a cetane number of 41.1. The cetane number of this blended fuel after sixteen days of storage was 52.4.

**Example 7.**—700 c. c. of the same acid washed petroleum distillate feed as used in Example 5 was fed to the oxidizing reactor. 18 c. c. of feed stock was added and the mixture air-blown for three hours at 300° F. using an air rate of two volumes per volume of oil per minute. The resulting product had an oxygen factor of 1175 and neutralization number of 11. This hydroperoxide-containing product was treated with one-quarter pound of 75% sulfuric acid per gallon

for fifteen minutes at 70° F. The acid treated product was washed with 5% caustic and water and had an oxygen factor of 164 and a neutralization number of 0.01. The resultant di-hydrocarbon peroxide-containing product was distilled at 5 mm. of mercury pressure and 122° F. until twenty per cent of the original volume remained as a residue or concentrate. This remaining concentrate of di-hydrocarbon peroxides had an oxygen factor of 740 and a neutralization number of 0.1. Three per cent of this concentrated product was blended with an untreated Diesel base derived from waxy California crude and having a cetane number of 41.1. After sixteen days' storage this blend showed a cetane number of 50.9 or an increase in cetane number of 9.8.

*Example 8.*—A petroleum distillate feed similar to that used in Example 5 was oxidized and caustic washed as outlined in Example 5. 17% of this hydroperoxide-containing product was blended with an automotive Diesel fuel boiling within the range of 308° F. to 578° F. and having a chart cetane number of 42. This blended stock having an oxygen factor of 153 was then treated with one-quarter pound of 93% acid per gallon of stock at about 70° F. to convert in situ the hydroperoxides to di-hydrocarbon peroxides. The finished stock had an oxygen factor of 2.2 and a cetane number of 50.5.

*Example 9.*—A petroleum distillate similar to that used in Example 5 was air-blown and caustic washed as in Example 5 and thereafter exhibited an oxygen factor of 839 and a neutralization number of .12. This product was distilled at 30 mm. pressure and a temperature under 200° F. to separate the higher boiling fraction as a concentrate of hydroperoxides constituting about 12.5% of the original liquid volume.

Two per cent of this concentrated product having an oxygen factor of 6240 was then blended in a refined distillate derived from California crude and boiling within the range of 388° F. to 656° F. and having a cetane number of 41. After forty-eight hours' storage, this blend had a cetane number of 48.2.

*Example 10.*—A petroleum distillate similar to that employed in Example 5 was oxidized, neutralized, and concentrated as in Example 9. One portion of the hydroperoxide concentrate was treated with one-quarter pound of 75% sulfuric acid per gallon at 77° F. for fifteen minutes and a second portion was treated with one and one-half pounds of 75% sulfuric acid per gallon at 77° F. for twenty minutes. The two products had oxygen factors of 3920 and 840, respectively. Two per cent of each of these products was added to an automotive base fuel having a cetane number of 40.9. After ninety-six hours of storage the blended fuels had cetane numbers of 49.1 and 50.8, respectively.

*Example 11.*—The storage stability in Diesel fuel of a hydroperoxide-containing mixture derived from the petroleum distillate of Example 6 and concentrated as in Example 6 was compared with di-hydrocarbon peroxide-containing mixture obtained by treatment of this hydroperoxide mixture with 1½ lb. of 75% sulfuric acid per gallon in a manner similar to that described in Example 7. Each of these products was added in amounts of 2% to an automotive Diesel base fuel derived from southern California crude and having a cetane number of 36. The cetane numbers

of each of the resultant blends at various times are indicated in the following Table IV:

TABLE IV

Blending Agent	Oxygen Factor of Blending Agent	Cetane Improvement		
		15 min.	48 hrs.	96 hrs.
Hydroperoxide stock	6,240	12	7	6
Di-hydrocarbon peroxide stock	840	11	11	10

The data of the above table illustrates the greater storage stability of the di-hydrocarbon peroxides. Likewise, the di-hydrocarbon peroxides having higher molecular weight hydrocarbon radicals of above 8 carbon atoms have been found to be superior in storage in the presence of moisture or water to lower dialkyl peroxides or hydroperoxides.

*Example 12.*—To compare corrosivity of the hydroperoxide stock and peroxide stock mentioned in Example 11 above, lead corrosion tests were carried out by immersing a lead strip ½" x 1½" x ⅛" in a beaker of the sample maintained for 24 hours at about 225° F., and the loss in weight noted. The results showing that the hydroperoxide stock is considerably more corrosive than the di-hydrocarbon peroxide stock, are given in the following Table V:

TABLE V

Blending Agent	Oxygen Factor	Per Cent Added to Automotive Diesel Fuel Base	Lead Corrosion
Hydroperoxide stock	839	Per cent	Mg.
Di-hydrocarbon peroxide stock	141	10	158
		10	7

As indicated hereinabove, the products of the present invention, particularly the peroxides derived from higher molecular weight saturated hydrocarbons, such as paraffins and naphthenes having above 6 carbon atoms and especially 8 to 12 carbon atoms, may be used in concentrated form (i. e., 40 to 60% concentration) as excellent Diesel fuel additives for increasing the cetane number thereof. Such concentrated di-hydrocarbon peroxides may be incorporated in Diesel fuel in amounts between about 0.2% and 25% of the base fuel, desirably between about 0.75% and 15%, and especially about 1% to 8% of the base fuel. While ordinarily the base fuel is preferably substantially free from large proportions of aromatic ring compounds (i. e., the base fuel should contain less than 20% and especially below 10% of aromatics), it is sometimes satisfactory to use a base fuel having higher aromatic contents, such as 20% to 40% and to impart the desired ignition qualities thereto by addition of the di-hydrocarbon peroxides, especially those derived from saturated hydrocarbons having about 8 to 12 carbon atoms. Higher aromatic contents may be used in some cases up to 100% aromatics, since the products of the present invention give the same effect in various fuel of the same cetane number. Where the original hydrocarbon used to form the hydroperoxide or the hydrocarbon diluent for the hydroperoxide is a suitable Diesel fuel, the product resulting from acid treatment may be used without concentration as the whole or major portion of the Diesel fuel.

The present products may also be used in improving the ignition qualities of other fuels such as jet or turbine fuels, etc.

While the process of the present invention is particularly applicable to the production of dihydrocarbon peroxides for use as ignition accelerators, the products, in unconcentrated, concentrated, or substantially pure form, may be beneficially used in other applications. For example, the products may be employed as vulcanization accelerators, polymerization catalysts and initiators, such as in the polymerization of polymerizable unsaturated compounds, including both the conjugated and unconjugated unsaturated polymerizable compounds, etc. For the latter purpose, the di-hydrocarbon peroxides derived from aromatic ring compounds are sometimes most suitable; for example, aromatic hydroperoxides obtained such as from air-blowing aromatic compounds, such as toluene, xylene, etc., may be converted to peroxide by the acid treatment of the present process.

The products may, in general, be used as catalysts for various chemical reactions or as intermediates in organic synthesis. Likewise, these products may be used as basic chemicals for forming desired derivatives thereof. Also, the products as such or derivatives thereof may be employed as insecticides, gum solvents, etc.

The present application is a continuation-in-part of our co-pending application, Serial No. 666,701, filed May 2, 1946.

We claim:

1. The process of autocondensing organo hydroperoxide to di-organo peroxide, wherein said organo group consists essentially of a hydrocarbon group, which comprises contacting said organo hydroperoxide with strong acid as the sole reactants, under the following mild conditions: the contact time being less than 90 minutes, the temperature being below about 95° F., the acid having a dissociation constant of at least  $10^{-3}$ , and said acid being present in an amount and of sufficient concentration to autocondense a substantial proportion of said organo hydroperoxide to di-organo peroxide.

2. The process of claim 1 wherein said hydroperoxide reactant is dissolved in a substantially inert diluent.

3. An improved method of producing a dihydrocarbon peroxide comprising bringing into

contact for less than 90 minutes and at a temperature below 95° F., a hydrocarbon hydroperoxide and an acid as the sole reactants, said acid having a dissociation constant of at least  $10^{-3}$  and being present in sufficient amount and concentration to autocondense a substantial proportion of said hydroperoxide to a di-hydrocarbon peroxide.

4. The process of claim 3, wherein said hydroperoxide is a saturated hydrocarbon peroxide.

5. The process of claim 3, wherein said hydroperoxide contains at least 6 carbon atoms.

6. The process of claim 3, wherein said hydroperoxide is a tertiary hydrocarbon peroxide.

7. The process of claim 3, wherein said hydroperoxide is a secondary hydrocarbon peroxide.

8. The process of claim 3, wherein ratio of acid to hydroperoxide is about 0.1 to about 1.0 mol of acid per mol of hydroperoxide.

9. The process of claim 3, wherein ratio of acid to hydroperoxide is about 0.3 to 0.5 mol of acid per mol of hydroperoxide.

10. The process of claim 3, wherein said acid is a mineral acid.

11. The process of claim 3, wherein said acid is sulfuric acid.

12. The process of claim 3, wherein said acid is 50 to 98% aqueous acid.

13. The process of autocondensing a hydrocarbon hydroperoxide to a di-hydrocarbon peroxide which comprises contacting said hydrocarbon hydroperoxide for less than 90 minutes with a 50 to 98% aqueous solution of a mineral acid having a dissociation constant of at least  $10^{-3}$  at a temperature of 50 to 85° F. with an acid to hydroperoxide ratio of about 0.1 to 1.5 mols of acid per mol of hydroperoxide, wherein said hydroperoxide and acid are the sole reactants.

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