Sept. 12, 1950 M. R. BARUSCH ET AL **2,522,015**

METHOD FOR DI-ORGANO PEROXIDES

Filed Dec. 13, 1948 4 Sheets-Sheet 1

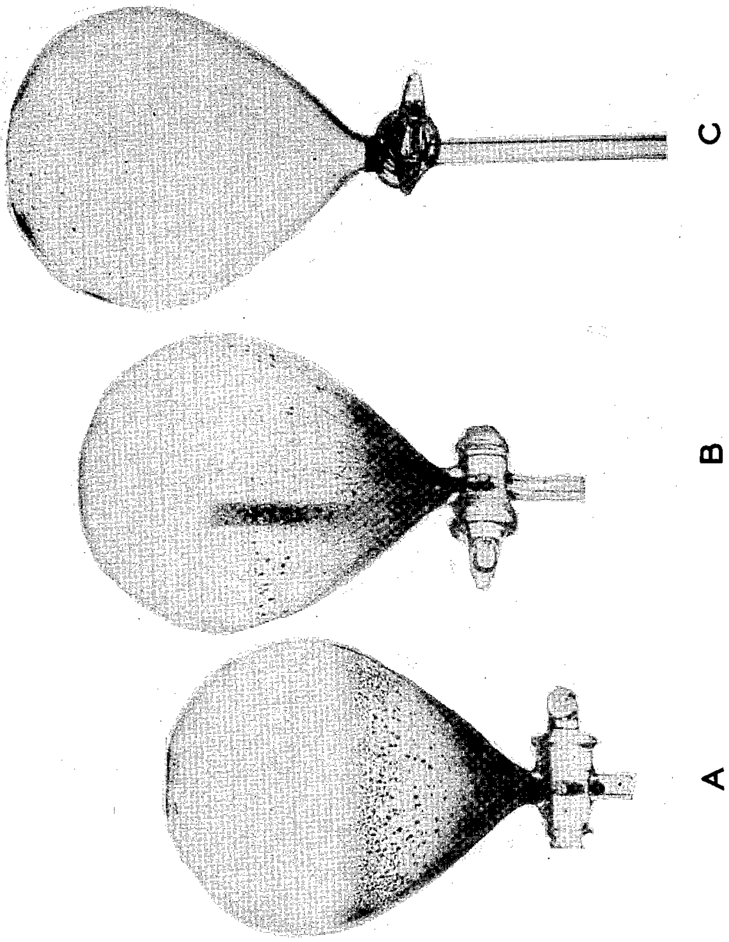

FIG. 1

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METHOD FOR DI-ORGANO PEROXIDES

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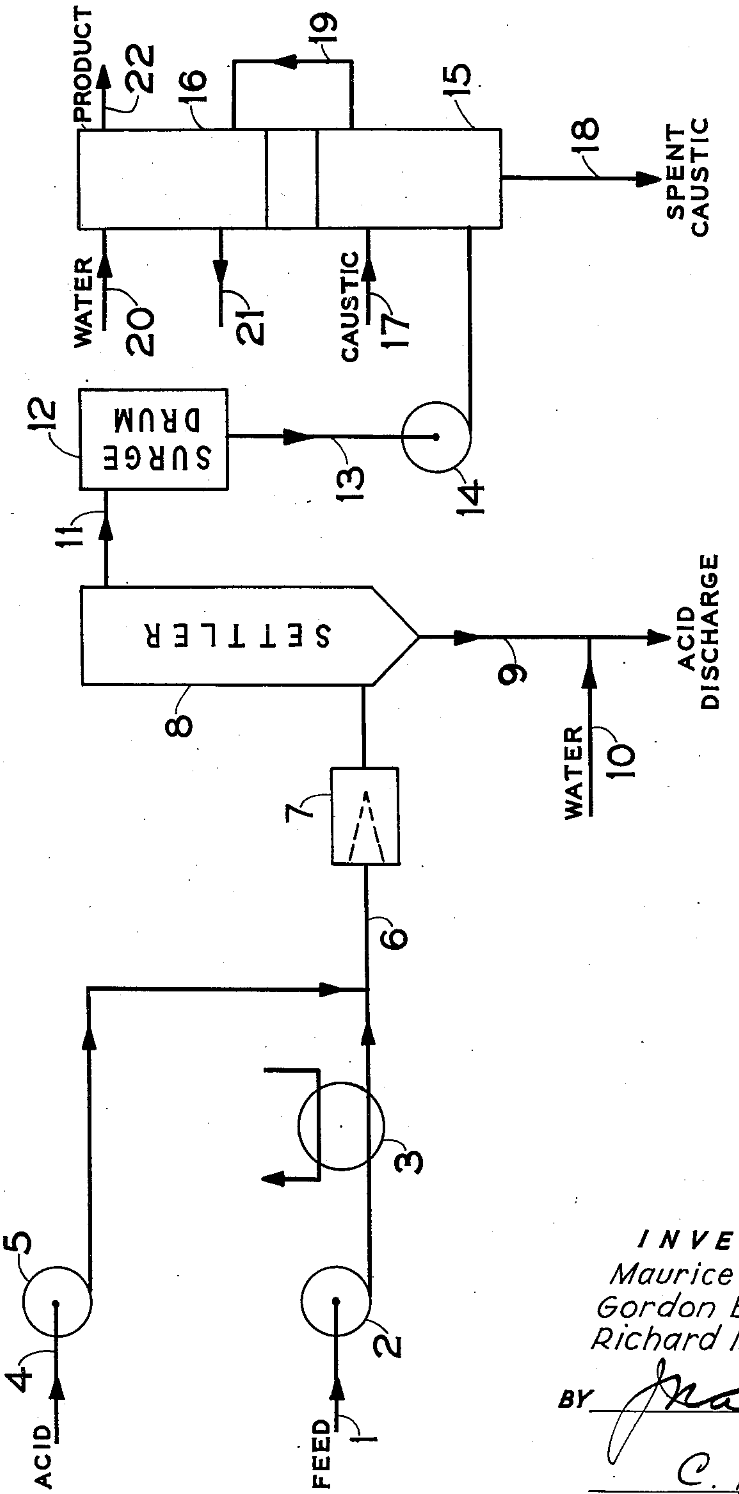

FIG. 2

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METHOD FOR DI-ORGANO PEROXIDES

Filed Dec. 13, 1948 4 Sheets-Sheet 3

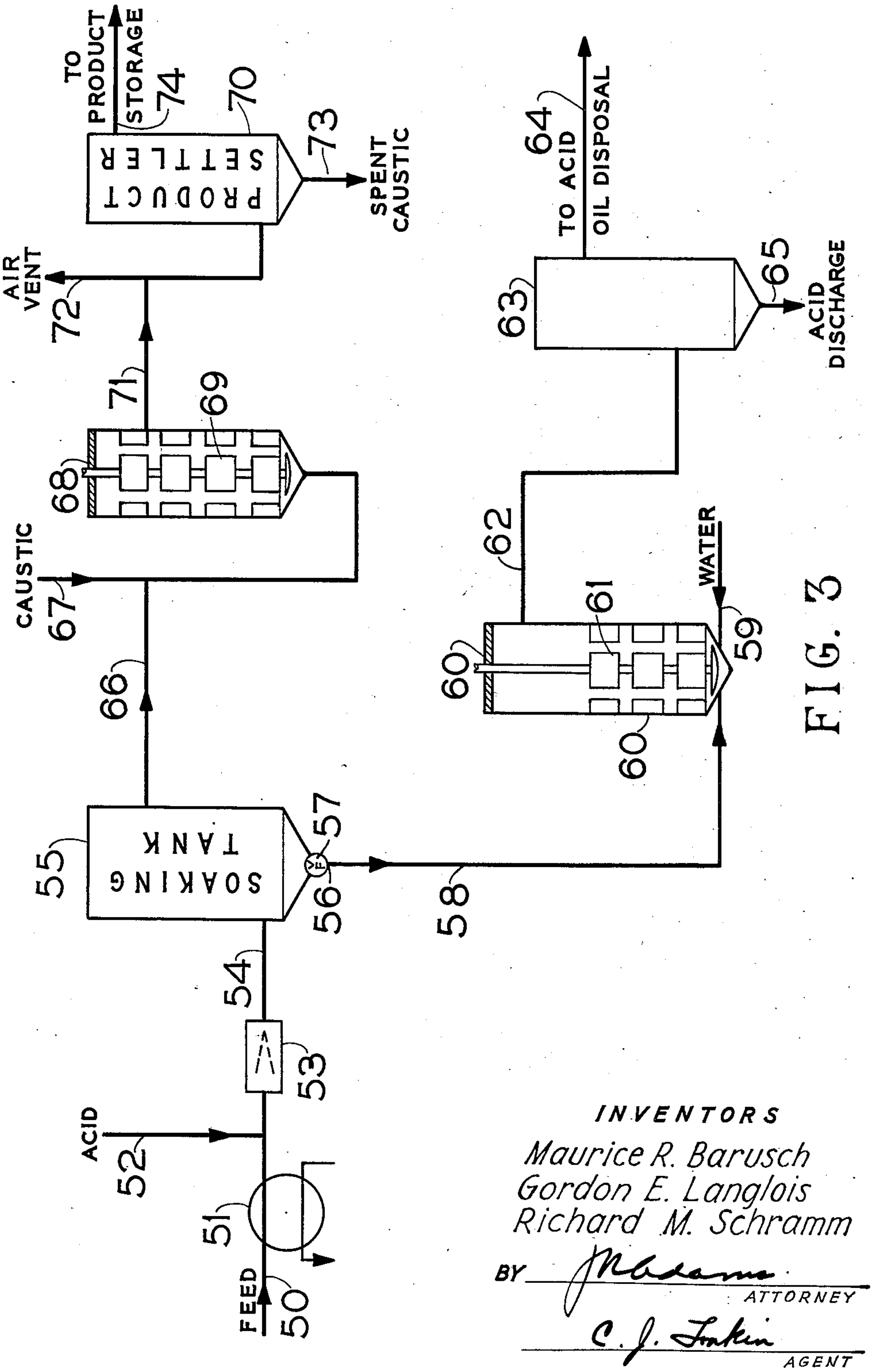

FIG. 3

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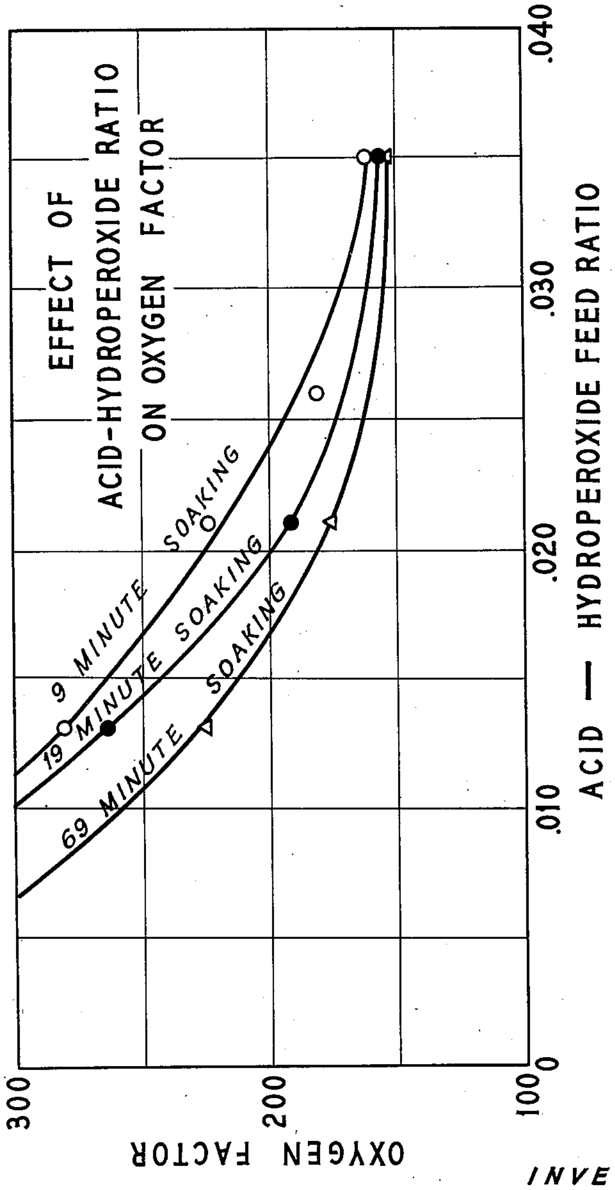

FIG. 4

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Patented Sept. 12, 1950 **2,522,015**

UNITED STATES PATENT OFFICE

2,522,015

METHOD FOR DI-ORGANO PEROXIDES

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Application December 13, 1948, Serial No. 64,982

11 Claims. (Cl. 260—610)

The present invention relates to an improved method of producing di-organo peroxides and pertains more particularly to an improved 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.

In the co-pending application of Denison and Hanson, Serial No. 64,984, filed Dec. 13, 1948, there is described a process of converting organo hydroperoxides by means of acid to di-organo peroxides.

It is an object of the present invention to provide an improvement over the process of acid-induced conversion of hydroperoxides to peroxides of said Denison and Hanson application.

It is a particular object of this invention to provide an improved process of converting organo hydroperoxide to di-organo peroxide, wherein sludge formation is prevented.

It is another object to provide a method of converting organo hydroperoxide to di-organo peroxide with high yields.

A further object is to provide an improved continuous process of converting organo hydroperoxides to di-organo peroxides.

These and other objects will be readily apparent from the following description taken together with the drawing, wherein:

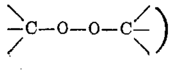
Fig. 1 illustrates the effect of contact time on sludge formation in accordance with the improved process of the present invention.

Fig. 2 is a schematic flow sheet of one embodiment for carrying out the present invention.

Fig. 3 is a schematic view of another embodiment for continuous operation in accordance with the present invention.

Fig. 4 is a graph illustrating the relation of acid-hydroperoxide feed ratio to extent of conversion.

Briefly, the process of said Denison and Hanson application involves treatment of an organo hydroperoxide, in which the organo group consists essentially of a hydrocarbon group, under mild conditions, with an acid having a dissociation constant of at least 10^{-3} in an amount and of sufficient concentration to convert a substantial proportion of said organo hydroperoxide to di-organo peroxide (i. e., containing the group

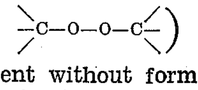


$$>C-O-O-C<)$$

The mild treatment comprises contacting an organo hydroperoxide, such as a saturated hydrocarbon hydroperoxide, with acid, e. g., sulfuric acid, for less than about 90 minutes at a temperature below about 150° F.

The process does not require the use of reactants other than hydroperoxides and acid, thereby avoiding dependence upon expensive reagents 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 process is carried out under conditions wherein the hydroperoxide and acid are the only essential reactants. Restated, the process is an autocondensation of organo hydroperoxides to di-organo peroxides with hydroperoxide and acid as the sole reactants. The process involves an unexpected and new phenomenon of conversion of hydroperoxides by treatment with acid under mild conditions. When such acid conversion is combined with preparation of the hydroperoxides by liquid phase oxidation of hydrocarbons, it was found that, contrary to expectation of the prior art, one can efficiently and economically prepare di-hydrocarbon peroxides from hydrocarbons by simple operational steps.

It has now been found that in order to obtain high yields and practical conversions of organo hydroperoxide to di-organo peroxide (i. e., containing the group



$$>C-O-O-C<)$$

by acid treatment without formation of heavy plastic sludge and without other deleterious side effects, the hydroperoxide and acid must be vigorously agitated (i. e., intimately contacted) in the minimum time and the admixture immediately settled into two layers, followed by a "soaking" period for the peroxy layer. That is, the acid must be momentarily dispersed throughout the hydroperoxide phase, followed immediately by rapid disengaging into distinct layers of acid and peroxy material, after which the peroxy layer is allowed to stand until the conversion is substantially complete or until a substantial amount of additional conversion is obtained.

In contrast to the improved process of the present invention, if the acid is vigorously agitated with high molecular weight hydroperoxide, particularly hydroperoxides derived from oxidation of higher hydrocarbons, for the full time necessary for the desired relatively high completeness of reaction, there is formed a heavy plastic sludge which cannot be easily handled and tends to cause serious mechanical difficulties in commercial operation, particularly in continuous treating. This sludge is to be distinguished from the fluid acid oils usually encountered in acid treatments generally. Because of its nature, including its stickiness, the sludge avoided by the present invention tends to plug valves, pumps, etc., and sticks to walls of vessels and conduits, which necessitates periodic cleaning of equipment. Such sludge deposits are exceedingly difficult to remove with solvents and have required plant shut downs for removal by mechanical means, such as scrapers.

Lower molecular weight hydroperoxides due to their lower stability also require short extensive contact time in order to obtain high conversions and to avoid deleterious side effects.

Thus, the present invention of obtaining substantially complete conversion of organo hydroperoxide to di-organo peroxide may be generally stated as involving the steps of vigorously and intimately contacting hydroperoxide with acid for a time substantially less than necessary to obtain the desired relatively high conversion, preferably for as short a time as possible, immediately thereafter settling the admixture into an acid and a peroxy layer, and allowing the peroxy layers to stand for sufficient time to allow the conversion to proceed to at least 60%, preferably 75% or more completion with most hydroperoxide feeds and acid-hydroperoxide ratios. In general, sufficient time is allowed in this "soaking period" to effect a substantial amount of additional conversion, such as for example, at least an additional 5–10%; with low initial conversions, greater additional conversions result from the soaking period than when the initial conversion is relatively high. As stated above, such process obtains high conversion without deleterious sludge formation or other disadvantageous side effects.

It has been found in every test that the disadvantageous sludge formation is encountered when high molecular weight hydroperoxide is extensively and intimately contacted with acid until the desired relatively high conversion is obtained. However, there are variations between different acids as to the maximum vigorous contact time permissible before sludge formation becomes troublesome. Sludge formation is particularly prone to occur with higher molecular weight hydroperoxides (i. e., having at least six carbon atoms), especially hydroperoxides derived from hydrocarbons by air oxidation; consequently, the present improved process is highly advantageous with and preferably applied to such hydroperoxides. Also, sludge formation is particularly prone to occur with sulfuric acid, possibly due to its oxidizing properties in common with nitric acid. Thus, sulfuric acid and high molecular weight hydroperoxides derived from oxidation of hydrocarbons are used for preliminary illustrative purposes in connection with the extensive contact time in the acid conversion.

In such treatments particularly, the thorough dispersion of acid in the hydroperoxide phase should be kept below about 3 minutes and preferably below about 20 seconds down to as short a time as possible, such as, for example, a fraction of a second. Usually the finer and more thorough dispersion obtained, the shorter is the contact time necessary for the same conversion.

When longer contact times than about 3 minutes for the thorough sulfuric acid-peroxy material dispersion are employed, sludge formation presents considerable practical and operational difficulties. Thus, for example, when the acid is allowed to remain dispersed in the peroxy material for such longer times, e. g., 10 to 30 minutes, a large amount of sludge is formed which is difficult to handle and tends to clog valves, pumps, etc. If longer times, such as up to 3 hours, are employed, there is formed a much greater amount of sludge, and also the sludge is harder and more difficult to handle.

While other acids, such as hydrochloric acid, can be vigorously agitated with the peroxy material for longer periods without sludge formation, as will hereinafter appear, all acids require thorough contacting with the peroxy material for substantially less than the time necessary for substantially complete conversion in order to avoid sludge formation. However, the short contact times noted above for sulfuric acid may be employed with other acids and are in fact usually preferred, particularly in continuous treating.

After the step of vigorous contacting of acid and peroxy material, irrespective of the nature of the acid, the phases are immediately allowed to disengage into separate layers, as in a suitable separator or settler. Thereafter, the layers are preferably separated continually, for example, by continuous withdrawal of the lower acid layer; however, after said phases are disengaged into the layers, no sludge is formed by the peroxy hydrocarbon layer standing on the acid layer for up to 15 or 30 or more minutes, so that immediate separation of the quiescent layers is not necessary.

After the extremely short thorough contact period, it is preferable that the peroxide-containing upper layer stand for at least 1 minute, preferably at least 5 minutes, and ordinarily less than 60 minutes, either while standing on the acid layer or including the time after removal of the peroxy layer to another vessel. Even longer times are not ordinarily disadvantageous. As stated above, the conversion reaction continues to a substantial additional extent during this soaking period. Thereafter, the peroxy layer is preferably caustic treated and then water washed, or water washed and then caustic washed, or otherwise suitably treated with an alkaline material.

As the acid layer is removed from the settler, is is preferably diluted with water in order to avoid any tendency toward sludge formation in the separated acid.

The present improvement of momentary extensive contact between acid and the peroxy material followed by the preferred standing of the peroxy layer when incorporated in the acid conversion method of Denison and Hanson gives an improved process of obtaining di-organo peroxides. By the present invention, higher yields without formation of troublesome sludge are obtained than are possible with other methods, and, further, such high yields are obtained in an efficient and economical manner.

The improved process of converting organo hydroperoxides to di-organo peroxides is described hereinbelow in more detail.

In accordance with the present invention, hydrocarbon hydroperoxide is converted to dihydrocarbon peroxide by extremely short extensive contact 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 amount 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, in reasonable soaking times, 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 oxtaining high yields, although less desirably lower concentrations such as to 20% may be sometimes used. Other things being equal, conversion is usually unsatisfactory in reasonable soaking times with concentrations lower than about 50%, while the preferred range of acid concentration gives maximum conversion in practical soaking times.

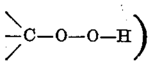
The conditions of the process of converting hydroperoxides to di-hydrocarbon peroxide have been generally stated as mild; the conditions may be said to be intermediate between drastic conditions of high temperature and very low temperature below 0° F. That is, the temperature is maintained relatively 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.

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, 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.

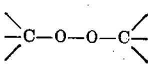
While saturated hydroperoxides are ordinarily employed in the present process when a Diesel fuel additive is desired, aliphatic hydroperoxides containing olefinic bonds or aromatic groups can be similarly converted to the di-hydrocarbon peroxides in accordance with the process of the present invention. 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 hydroperoxides 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 (i. e., containing the group



$$\left(\geq C-O-O-H\right)$$

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-dichloro-phenyl-2,2,2-trichloroethane, and the like as well as their homologues may be employed. The di-organo peroxides resulting from the treatment of organo hydroperoxide, as exemplified above, contain the group



$$\geq C-O-O-C\leq$$

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 accordance 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.

It is particularly advantageous to prepare 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. By such improvement over the Schultz et al. process of Patents 2,317,968 and 2,365,220, 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.×normality of thiosulfate×1120)/(volume of sample in ml.).

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 di-hydrocarbon 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 ⅛ to ½ 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 ratios are used, lower ratios or acid of the lower concentrations may be employed. Thus, for conversions of above about 50% in reasonable soaking times, 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.

As noted below, there is a relation between the ratio of acid to hydroperoxide and the length of the "soaking" period, in which the acid-treated peroxy layer is allowed to stand until the desired relatively high conversion is obtained. In general, the less acid employed, the longer the soaking period must be to obtain the desired conversion.

In accordance with the present inventive improvement as applied particularly to the conversion of high molecular weight hydroperoxides with sulfuric acid, the time of extensive contact between the acid and hydroperoxide is most desirably kept below about 3 minutes and is preferably as short as possible, such as of the order of a fraction of a second up to about 20 seconds, whereby the formation of heavy plastic sludge and other deleterious side effects are avoided.

Experiments illustrating the effect of time on the sludge formation were carried out as follows: Into each of three glass separatory funnels (500 c. c. capacity) were placed acid and hydroperoxide precooled to about 34° F. The hydroperoxide was a solution of about 10% hydroperoxides having an average of about ten carbon atoms as obtained by liquid phase oxidation of a petroleum distillate containing predominantly paraffins and naphthenes and boiling in the range of 308° to 366° F.; said hydroperoxide solution was used in an amount of 300 c. c. for each experiment. Aqueous sulfuric acid of 75% concentration was used in an amount equivalent to one-quarter pound of 100% acid per gallon of hydroperoxide solution.

The funnels containing acid and hydroperoxide were shaken vigorously and continuously for different periods of time, with the temperature of the two-phase admixture at about 80° F. Thereafter, the phases separated rapidly, within a few seconds, into two phases, at which time a small amount of acid was drawn from each of the funnels and an inspection made. The funnels were then drained and photographed; Fig. 1 of the drawings is a photograph of the separatory funnels of the three experiments, which funnels are labeled A, B, and C, corresponding to the experiment numbers.

In experiment A, the acid-peroxy admixture was thoroughly shaken for one minute. No third phase or droplets of sludge or extraneous material was formed, nor was the peroxy product layer contaminated. As shown in Fig. 1, the sides of funnel A were absolutely clean.

In experiment B, the extensive contact between phases was continued for 3 minutes. A very slight amount of black or tarry particles was found and remained as a coating on the sides of the funnel in the area occupied by the peroxy layer. The fine deposit of black particles of incipient sludge formation in funnel B will be seen in Fig. 1.

Experiment C employed a 5-minute extensive contact time, which resulted in an appreciable amount of black droplets or particles deposited on the sides of separatory funnel C.

These experiments show that extensive contact for one minute does not cause sludge to form; further, they show that sludge formation begins at about a 3-minute contact time, which is the borderline, and that when the contact is extended for a longer period, such as up to 5 minutes, then sludge formation gets well under way.

The short contact times of the present process are most conveniently obtained in continuous type operation. Suitable contacting means include turbo mixers, orifice mixers (especially of the low-volume, high-velocity type), and like devices, which are applicable in continuous treating. Batchwise operation, although usually less desirable, can be carried out by employing mixers capable of vigorous agitation and by introducing the acid and hydroperoxide, both pre-cooled to low temperatures, such as below 20–40° F.

During the extensive acid contact stage, the temperature can be maintained at the desired temperature, preferably at 60° to 80° F., by applying external refrigeration to the mixer itself and/or to the feed streams to the mixer as well as the mixed effluent stream. When using orifice mixers, most effective temperature control is usually obtained by pre-cooling the feed streams.

After the momentary extensive contact, the two-phase admixture is caused to separate into layers immediately or as quickly as possible, so that the total extensive contact time is kept below that time necessary for the desired high conversions, for example, in the case of sulfuric acid, below about 3 minutes and preferably below about 20 seconds, as stated above. This rapid separation into an acid layer and a peroxy layer may be accomplished by passing the two-phase admixture into a gravity settler or other suitable separator capable of causing said rapid disengaging of the phases.

As stated above, it is then usually desirable to separate the layers within a short time, such as by continually withdrawing the acid layer to maintain a minimum amount of acid in the settler. On removal of the acid layer, the acid by itself is preferably diluted with water, since the strong acid solution tends to form sludge on standing for long times such as more than about a few hours or the acid phase becomes very viscous, either of which effects cause handling difficulties. The acid oil formed upon dilution is separated and disposed of in any suitable manner.

After the momentary extensive acid contact, the peroxy layer, as immediately formed in a settler, is allowed to stand until a substantial additional amount of conversion is obtained. While the conversion is usually allowed to proceed until at least 60% complete and preferably at least 75% complete, in some instances the momentary extensive contact will give fairly low initial conversions and the additional conversion obtained in the soaking period will be employed in bringing the conversion up to about 50% of theoretical completeness, particularly with hydroperoxides containing aryl groups or with low acid-hydroperoxide ratios. As stated above, the length of this soaking period depends upon the ratio of acid to hydroperoxide, and with less acid a longer soaking time is required for the desired conversion. The upper limit for the time of soaking is not critical and is only governed by practical considerations of equipment size and convenience. For example, there is not objection to allowing the peroxy layer to stand for 1 to 2 hours; for example, where a large tank is available for use in a continuous process, the longer soaking periods and lower acid-hydroperoxides may be employed. In general, the soaking period is only limited to that necessary for the desired conversion within a reasonable time, as consistent with available equipment facilities. Subject to the overriding criterion of allowing sufficient time for the desired completeness of conversion, the peroxy layer is usually allowed to stand for at least 1 minute, up to about 60 minutes, ordinarily 5 to 30 minutes, after the momentary extensive contact with acid. Although the major portion of the conversion takes place in the first stage of momentary contact with acid, as shown by an appreciable reduction in oxygen factor, the conversion continues during this additional period, i. e., "soaking" period, as shown by the further drop of the oxygen factor to the desired low value.

Thereafter, the peroxy layer is preferably separately treated to remove the last traces of acid, soaps, organic contaminants, e. g., organic acids, filterable material, etc. This may be accomplished either by an alkaline wash (e. g., caustic wash) followed by a water wash or by a water wash and then caustic wash. In some instances, there is a tendency for a first water wash to form emulsions and a small amount of hard tar which collects at the interface; consequently, in such cases, it is preferable to wash first with fairly strong caustic (e. g., 5–25%) and then with water. When treating first with concentrated caustic instead of water, separation was rapid and clean and ony two homogeneous phases were formed, with no tars or solids present. Preferably, the upper limit for caustic strength is set by the formation of insoluble precipitates, which occurs above about 25% caustic strength. An excess of caustic, usually amounting to 120% to 170% of the amount necessary to neutralize to phenolthalein end point, is ordinarily employed, the lesser amounts being used in continuous counter-current contacting and the higher amounts in batchwise operation.

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.

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 greaer than about 20% of the oxygen factor of the concentrate.

For some purposes, the di-hydrocarbon peroxide-containing product thus obtained in the above described 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 unreacted material and the di-hydrocarbon peroxides may be separated or concentrated by distillation or other suitable means, for example, by solvent extraction or adsorption fractionation or by combinations of such methods. 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 and having an oxygen factor of about 1100, 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.

Although usually unnecessary as a final step, the product may, if desired, 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 sometimes desirable to water wash before the caustic wash.

The drawings of the hereinbelow-described embodiments omit 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.

Referring to Fig. 2 of the drawings, a preferred embodiment of the present invention is carried out as follows: A suitable feed, such as 10% hydroperoxide solution in unreacted hydrocarbons, as derived from liquid phase partial oxidation of a petroleum fraction containing predominantly paraffins and naphthenes and boiling in the range 308° to 366° F. is passed by means of line **1** and pump **2** through cooling means **3**. With addition of metered amounts of acid introduced through line **4** and pump **5**, the hydroperoxide-containing mixture passes through line **6** and a mixing nozzle **7** or other suitable mixing device wherein efficient contact between the acid and hydroperoxide is obtained, causing conversion of the hydroperoxide to di-hydrocarbon peroxide. The resultant admixture consisting of a fine dispersion of acid throughout the hydroperoxide solution is then immediately passed into separator, such as gravity settler **8**, wherein separate layers of acid and peroxy material are rapidly formed. The extensive contact within the mixing nozzle **7** is of the order of a fraction of a second and the time from the extensive intermixing within nozzle **7** to separation into layers in settler **8** is a matter of a few seconds, preferably as short as possible and usually less than 20 seconds. It is usually most desirable to draw off the acid layer continually via line **9** in a manner to maintain as small as possible an acid layer in settler **8**; suitable means, such as a float valve (not shown), may be provided for this purpose.

The withdrawn acid layer is preferably immediately diluted with water by means of line **10**, and after separation of the acid oil formed on dilution, the acid may be passed to a regenerator.

The treated upper layer of peroxy material as immediately separated from the acid phase is appreciably reduced in oxygen factor. This peroxy layer is allowed to stand for a short time, such as about 10 minutes, within which time the oxygen factor drops further to the desired low value. The period of "final conversion," i. e., "soaking period" is obtained in settler **8** and during the passage of the peroxy material therefrom via line **11** through surge drum **12**, line **13**, and pump **14**. In continuous operation, a settler of sufficient size is employed to give the desired "soaking" time.

Thence the peroxide-containing mixture passes to a treating unit comprising, for example, a lower section **15** for wash and an upper section **16** for subsequent wash. Caustic, such as 24% aqueous caustic, is introduced into lower section **15** through line **17**, and spent caustic is discharged through line **18**. The treated peroxides and hydrocarbons pass from section **15** through line **19** to water-wash section **16** having inlet line **20** for water and water discharge line **21**. The caustic- and water-washed peroxy material flows through effluent line **22** as product which may be suitably treated as desired. For example, the product may be worked up by fractional distillation, solvent extraction, etc., in order to remove the diluent, such as the unoxidized hydrocarbons of the exemplary feed stock.

Referring to schematic Fig. 3 of the drawings, another arrangement of apparatus which has been effectively used to convert hydroperoxide to peroxide in a continuous manner comprises briefly an orifice mixer, a soaking tank and turbomixers for separately caustic treating the peroxy material and quenching the separated acid with water.

In more detail, hydroperoxide feed stock is introduced into the system through line **50**, passing through precooler **51**, and thereafter the chilled hydroperoxide together with acid introduced through line **52** is passed through orifice mixer **53**, wherein extensive momentary contacting is obtained.

The effluent from mixer **53** passes via line **54** into the bottom portion of soaking tank **55**, wherein the phases immediately separate into respective layers of peroxy material and acid.

A bottom outlet **56** in soaking tank **55** is a float valve **57**, which operates to continually withdraw the separated acid layer into line **58**. The withdrawn acid passes together with quenching water introduced via line **59** into the bottom of turbomixer **60** operating as an acid quencher and having impeller **61** for thoroughly mixing said acid and water. The resultant mixture discharges via line **62** into settler **63**, which allows acid oil formed as an upper layer to be withdrawn through line **64** for suitable disposal. The diluted acid is discharged from settler **63** through line **65**.

The size of soaking tank **55** in conjunction with the feed rate employed are arranged to control the residence time of the peroxy material in soaking tank **55** to the desired soaking period to obtain the desired substantially complete conversion. Thence the upper peroxy layer passes via line **66** together with suitable caustic introduced via side line **67** into the bottom of turbomixer **68** operating as a caustic treater and provided with impeller **69** for thorough mixing of caustic and peroxy material. The effluent mixture passes from turbomixer **68** to product settler **70** via line **71**, which is preferably provided with air vent **72**.

Spent caustic is withdrawn via line **73** from the bottom of product settler **70** and the upper layer of product is discharged via line **74** to product storage.

The above-described apparatus was operated a large number of times and over periods as long as six hours without any indication that serious operating difficulties would be encountered in such a system. On a number of occasions the apparatus was started up twenty hours or more after having been shut down at the end of a previous run without any intervening cleanup. Thus it appears that even after this period, the acid phase which was held up in the soaking tank was sufficiently fluid so as not to interfere with the operation of the float valve. Furthermore, when the system was drained after such an experiment, no substantial amount of tar or heavy plastic sludge was observed to be clinging to any parts of the apparatus. Also, the yields obtained in these runs were usually over 90% by weight.

In one series of experiments, the water-acid ratio employed in quenching the acid withdrawn from the soaking tank was maintained at a 10 to 1 level. Under these conditions a very fluid acid oil was obtained as a result of quenching the withdrawn acid layer. In another series of experiments using a water-acid ratio of 0.5 to 1 the quenched acid was quite fluid and showed no tendency to form heavy or sticky tars.

During one series of experiments in said apparatus, turbomixer **68** instead of being used as a caustic treater was used to water wash the product withdrawn from the top of the soaking tank; thereafter the water-washed product was caustic treated. The water feed rate was 25% of the flow rate for the peroxy material. Under these conditions there was a tendency to form emulsions which required considerably more settling area for complete separation. With primary water washing there was also a tendency to form a small amount of hard tar which collected at the interface. On the other hand, when the peroxy product withdrawn from the soaking tank was first treated with concentrated caustic instead of water, the subsequent separation was rapid and clean, and only two homogeneous phases were formed with no tars or solids present.

In the series of experiments carried out in the above-described apparatus of Fig. 3, the hydroperoxide feed stock was obtained by air oxidation, substantially in accordance with U. S. Patents 2,365,220 and 2,317,968, of an acid-washed petroleum distillate relatively free from asphaltic and resinous materials and composed of about 41% paraffins, 47% naphthenes and 12% aromatic ring compounds, and having a gravity of 46.4° A. P. I., a boiling range of 310–364° F.; the oxygen factor of the air-blown stock was about 900. The hydroperoxide feed stock was introduced at a feed rate such that the residence time in the soaking tank was slightly over 9 minutes. The temperature at the outlet from the soaking tank was maintained at or slightly below 80° F. by suitable precooling of the hydroperoxide feed stock. Under these conditions the peroxy material near the bottom of the soaking tank usually had a temperature of about 70° F. The acid layer in the bottom of the soaking tank, however, continued to generate heat at a relatively rapid rate and reached a temperature of about 120° F. before it ran out of the tank. The turbomixer **60** operating as an acid quencher reached a temperature slightly above 125° F. The temperature in the caustic treating turbomixer **68** usually was about 100° F. At the usual hydroperoxide feed rate of 170 c. c. per minute, the pressure drop across the orifice mixer **53** was about 12 p. s. i.

Example 1.—A number of runs were made in the above-described apparatus of Fig. 3 and under the general conditions outlined above to determine the effect of varying acid rates on the oxygen factor of the product. The results of these experiments are shown in Table I and in the graph in Fig. 4. The ratios of acid to hydrocarbon feed stock are given on a volumetric basis. The temperatures given in the table were taken for the hydroperoxide feed immediately after precooler **51** and also within the soaking tank at points adjacent the inlet and outlet. Oxygen factors were determined for the product as it left the soaking tank via line **66** and also for the product after additional soaking periods of 10 and 60 minutes; thus data were obtained for soaking periods of 9, 19 and 69 minutes.

Table I

Run No.	I—*a*	I—*b*	I—*c*	I—*d*
Acid-Hydroperoxide Feed Ratio	0.013	0.021	0.026	0.035
Temperatures, °F.:				
Precooled Feed	48	39	30	27
Tank inlet	72	72	67	70
Tank Outlet	77	77	77	78
Oxygen Factors, at soaking times of:				
9 minutes	280	225	180	160
19 minutes	265	190	-------	155
69	225	175	-------	155

It will be seen from the data in Table I that both high acid to hydroperoxide ratios and long soaking times favor the production of low oxygen factor products, i. e., substantially complete conversion of the hydroperoxide to peroxide. For the conditions imposed by the limitations of the apparatus employed, an acid to hydroperoxide feed ratio of 0.026 appeared to be optimum in obtaining a satisfactory product without deleterious side effects such as formation of heavy plastic sludge. For other feed stocks, different acids and/or different apparati, other combinations of acid rate and soaking time may be more desirable for optimum results than indicated by the experiments reported in Table I above.

As further illustrations of the various aspects of the present invention, the following series of experiments are also given:

Example 2.—A hydroperoxide feed stock was obtained by air oxidation substantially in accordance with U. S. Patents Nos. 2,365,220 and 2,317,968, of an acid-washed petroleum distillate, relatively free from asphaltic and resinous materials and composed of about 41% paraffins, 47% naphthenes, and 12% aromatic ring compounds, and having a gravity of 46.40 A. P. I., of boiling range of 310°–364° F., and a cetane number of about 35. This hydroperoxide feed stock had an oxygen factor of about 900. Into a glass turbomixer was introduced 500 c. c. of said hydroperoxide feed stock, chilled to 48° F., and 12.5 c. c. of 75% sulfuric acid. During the reaction the temperature rose to 77° F. After a given period of vigorous agitation, the acid was allowed to settle to form separate phases of acid and peroxy material. Thereafter, samples of the peroxy layer were withdrawn at intervals for oxygen factor determination. The results are given in Table II below, wherein the times indicated refer to total time elapsed from the beginning of the acid treatment.

Table II

Run No.	II—*a*	II—*b*
Time of agitation, seconds	60	20

Time, Minutes	Oxygen Factor	Time, Minutes	Oxygen Factor
2.5	170	2.0	225
6	165	5	190
10	160	10	175
60	155	60	160

From the above experiments it is clear that a reaction which decreased the oxygen factor continued after the initial vigorous contacting of acid and hydroperoxide. Where this initial contacting was more prolonged, the decrease in oxygen factor was greater at a given interval after the contacting was begun. No sludge was formed in the above experiments.

Example 3.—In another series of experiments, the same feed stock and 75% sulfuric acid as in Example 1 were thoroughly contacted for a fraction of a second by passing them through an orifice mixer, instead of using a turbomixer as in Example 2. The temperature of the reaction mixture immediately leaving the orifice mixer was about 65° F., and the reaction mixture was cooled to keep the temperature below about 80° F. most of the time thereafter, although in each experiment there was a brief rise to about 90° F. before cooling was started. The reaction mixture leaving the orifice mixer was allowed to separate immediately in a settling vessel. Samples were taken from the peroxy layer at intervals for determination of the oxygen factor. The results are given in Table III below.

Table III

Run No.	III—*a*	III—*b*
Feed rates, c. c./min.:		
Hydroperoxide feed	230	175
Acid	5.75	4.6
Pressure across orifice ......p. s. i.	20	12

Time, Minutes	Oxygen Factor	Time, Minutes	Oxygen Factor
3	195	1	255
6	185	3	195
10	165	5	175
60	165	10	160
		60	155

The above experiments with the orifice mixer show clearly the decline of oxygen factor which continues after vigorous contacting is halted. No sludge was formed in these experiments.

Example 4.—In another series of experiments with the same hydroperoxide feed stock and 75% sulfuric acid employed in Example 2, the reactants were contacted in a first turbomixer and then the whole reaction mixture quenched with water in a second turbomixer after given treating times. Subsequent to the water quench, the peroxy material was separated and analyzed for oxygen factor. The hydroperoxide feed was precooled to the temperatures indicated below, and the temperatures in the first turbomixer, i. e., the acid treater, were as indicated below. The results are given in Table IV below, wherein the relative feed ratio of hydroperoxide feed, acid and water are also indicated.

Table IV

Run No.	IV-*a*	IV-*b*	IV-*c*	IV-*d*
Average treating time, minutes	1.04	1.97	5.7	0.97
Temperatures °F.:				
Feed inlet	40	30	14	
Acid treator	81	82	80	80
Relative feed rates:				
Hydroperoxide feed	40	40	40	20
Acid	1	1	1	1
Water	10	10	10	10
Oxygen factor of product	280	260	195	200

With the feed rates used in runs IV—*a*, IV—*b* and IV—*c*, a contact time of at least five minutes was necessary in this system to obtain an acceptable oxygen factor, which, however, results in the formation of a very heavy and sticky sludge. With the higher acid to hydroperoxide ratio of run No. IV—*d*, the sludge formed, which amounted to about 0.3% by volume of the feed, appeared to be more fluid and possibly capable of being handled. This last run compared with the others shows that sludge handling difficulties can be somewhat minimized by using higher acid to hydroperoxide ratios.

Example 5.—A hydroperoxide feed stock similar to that described in Example 2, except that it had an oxygen factor of 785, was treated with hydrochloric acid in a separatory funnel, using 400 c. c. of hydroperoxide feed stock chilled to about 36° F. and 36 c. c. of concentrated hydrochloric acid (12 molar). The acid and hydroperoxide were vigorously agitated for 15 seconds and 5 minutes, respectively, in two experiments, the temperature rising to about 75° F. Directly after the vigorous agitation, the reaction mixture was allowed to separate into two layers and thereafter samples were withdrawn from the peroxy layer for oxygen factor determination. The results are given in the following Table V, wherein the times indicated include the period of vigorous agitation:

Table V

Run No.	V—*a*	V—*b*
Time of agitation	*Seconds* 15	*Minutes* 5

Time, Minutes	Oxygen Factor	Time, Minutes	Oxygen Factor
1.5	530	7.0	310
7.0	410	41	240
32	340	150	200
320	250	310	180

It will be noted from the above tests that there is a decrease in oxygen factor, i. e., further conversion of hydroperoxide to peroxide, in the soaking period after the initial vigorous agitation with hydrochloric acid. After about 45 minutes, sludge began to form in the separated acid, indicating that 10 to 15 minutes of vigorous agitation would cause sludge formation.

Example 6.—In carrying out experiments in the same manner and conditions as in run No. III—*b* of Example 3 with a hydroperoxide feed stock obtained by air-blowing n-decane at 300°

F. to an oxygen factor of 561, the following results are obtained, without sludge formation:

Table VI

Time, minutes	Oxygen factor
1	200
5	115
60	105

Example 7.—When the product of air-blowing ethyl cyclohexane at 265° F. to an oxygen factor of 1250 is substituted for the hydroperoxide feed stock in Example 6, the following results are obtained, without sludge formation:

Table VII

Time, minutes	Oxygen factor
1	420
5	315
60	280

Example 8.—When the product of air oxidation of octene-1 at 240° F., which product has an oxygen factor of 902, is substituted for the hydroperoxide feed stock of Example 3, the following results are obtained, without sludge formation:

Table VIII

Time, minutes	Oxygen factor
1	460
5	395
60	370

Example 9.—Ethylbenzene on air oxidation at 265° F. yields a product having an oxygen factor of 1868. When this product is substituted for the hydroperoxide feed stock in Example 6, the following results are obtained, without sludge formation:

Table IX

Time, minutes	Oxygen factor
1	1020
5	920
60	905

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 approximately the same effect in various fuels 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., for example, as combustion accelerators in gas turbine fuels.

While the process of the present invention is particularly applicable to the production of di-hydrocarbon 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.

We claim:

1. In the method of producing di-organo peroxide by contacting organo hydroperoxide with an acid having a dissociation constant of at least 10^{-3} in an amount and of sufficient concentration to autocondense a substantial proportion of said organo hydroperoxide to di-organo peroxide while maintaining the temperature below about 95° F., wherein said hydroperoxide and acid are the sole reactants, the improvement which comprises extensively contacting said hydroperoxide with acid for a relatively short period less than sufficient to effect the desired completeness of auto-condensation and thereafter separating the phases of acid and resultant peroxy material into layers and allowing the layer of peroxy material to stand for sufficient time without further treatment to effect a substantial amount of additional autocondensation whereby the desired relatively high conversion is obtained.

2. In the method of producing di-organo peroxide by contacting organo hydroperoxide with an acid having a dissociation constant of at least 10^{-3} in an amount and of sufficient concentration to autocondense a substantial proportion of said organo hydroperoxide to di-organo peroxide while maintaining the temperature below about 95° F., wherein said hydroperoxide and acid are the sole reactants, the improvement which comprises extensively contacting said hydroperoxide

with acid for a relatively short period less than sufficient to effect an autocondensation of at least 60% completeness and thereafter separating the phases of acid and resultant peroxy material into layers and allowing the layer of peroxy material to stand for sufficient time without further treatment to effect said autocondensation to at least 60% completeness.

3. In the process of autocondensing organo hydroperoxide to di-organo peroxide, wherein said organo group consists essentially of a hydrocarbon group, by contacting said organo hydroperoxide at a temperature below about 95° F. with an acid having a dissociation constant of at least 10^{-3} in an amount ranging from 0.1 to 1.5 mols of acid per mol of hydroperoxide, said amount and the acid concentration being sufficient to autocondense a substantial proportion of said organo hydroperoxide to di-organo peroxide, wherein said hydroperoxide and acid are the sole reactants, the improvement which comprises bringing said hydroperoxide and acid into extensive contact to form a fine dispersion of acid in said hydroperoxide for a relatively short time less than sufficient to effect a 75% complete conversion, then rapidly settling said phases into separate layers of acid and resultant peroxy material, and thereafter causing said layer of peroxy material to stand for at least 1 minute without further treatment, but for sufficient time to effect at least 75% complete conversion.

4. The process of claim 3 wherein said hydroperoxide is a high molecular weight hydroperoxide containing at least six carbon atoms.

5. A continuous process of autocondensing organo hydroperoxide to di-organo peroxide, wherein said organo group consists essentially of a hydrocarbon group, comprising bringing a stream of said hydroperoxide into extensive contact at a temperature below 95° F. with acid having a dissociation constant of at least 10^{-3}, wherein said hydroperoxide and acid are the sole reactants, and discharging the resultant admixture of acid and resulting peroxy material into a settling zone wherein said admixture separates into layers of peroxy material and acid, said contacting and settling into layers being effected continuously to restrict the extensive contact time to a relatively short period insufficient to convert at least 75% of organo hydroperoxide to di-organo peroxide, and thereafter maintaining said layer of peroxy material without further treatment for a sufficient time to obtain an overall conversion of at least 75% of the original hydroperoxide to peroxide.

6. The process of claim 5 wherein the time of extensive contact is not more than 1 minute.

7. The process of claim 5 wherein said hydroperoxide is a high molecular weight hydroperoxide containing at least six carbon atoms.

8. A continuous process of autocondensing organo hydro-peroxide to di-organo peroxide, wherein said organo group consists essentially of a hydrocarbon group, comprising extensively contacting a stream of said hydroperoxide with acid having a dissociation constant of at least 10^{-3}, wherein said hydroperoxide and acid are the sole reactants, at a temperature below 95° F., continuously separating the resulting admixture within 3 minutes after said extensive contact into respective layers of resultant peroxy material and acid, maintaining said layer of peroxy material without further treatment for 1 to 30 minutes in a soaking zone whereby autocondensation of at least 75% completeness is obtained, continuously withdrawing said peroxy material from the soaking zone and treating the same with alkaline material in excess over that necessary to neutralize said peroxy material to phenolthalein end point, continuously withdrawing said separated acid layer, and continuously quenching said withdrawn acid with water within a relatively short time after withdrawal.

9. The process of claim 8, wherein said acid is sulfuric acid.

10. In the method of autocondensing hydrocarbon hydroperoxide to di-hydrocarbon peroxide by contacting said hydroperoxide with an acid as the sole reactants at a temperature below about 95° F., said acid having a dissociation 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, the improvement which comprises bringing said hydroperoxide into extensive contact with said acid, followed by separation of said acid and resultant peroxy material into layers, such that the time of extensive contact between acid and peroxy material is less than about one minute, removing said separated acid layer and diluting the same with water, causing said layer of peroxy material to stand for 1 to 30 minutes after said period of extensive contact with acid, and thereafter washing said peroxy material with water.

11. In the method of autocondensing hydrocarbon hydroperoxide to di-hydrocarbon peroxide by contacting said hydroperoxide with about 0.1 to 1.0 mols of about 60–80% aqueous sulfuric acid per mol of hydroperoxide at a temperature of 60° to 80° F., wherein said hydroperoxide and acid are the sole reactants, the improvement which comprises extensively contacting said hydroperoxide with said acid, followed by separation of said acid and the resultant peroxy material into layers, such that the time of extensive contact between acid and peroxy material is less than one minute, removing said separated acid layer as it is formed and then diluting said acid with water, causing said layer of peroxy material to stand for 1–30 minutes after said period of extensive contact with acid, and thereafter treating said peroxy material with an alkaline material in excess over that necessary to neutralize the peroxy material to phenothalein end point.

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