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HETEROPOLYMERIC PEROXIDES FROM ALIPHATIC KETONES

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This invention relates to novel and useful heteropolymeric peroxides from aliphatic ketones. More particularly, the invention is concerned with a class of new heteropolymeric peroxides from reaction, under peroxide-forming conditions, of a ketone with a dissimilar ketone.

It is known that homopolymeric ketone peroxides may be produced by treating a ketone in an acid medium with hydrogen peroxide, or by oxidizing the ketone with a solution of persulfuric acid which has been hydrolyzed by a brief heating. The peroxides obtained in such a manner are exclusively homopolymeric peroxides which are chiefly in the dimeric and trimeric forms. Thus, when acetone is used as the initial reactant, a reaction product is obtained which consists of a mixture of dimeric and trimeric acetone peroxides. Similar homopolymeric ketone peroxides are known to result from treatment of a higher ketone.

These homopolymeric peroxides are valuable materials which may be used for various purposes. Their powerful oxidizing character makes them useful to bleach flour, textile materials, paper, and the like. They may also be applied in the manufacture of synthetic organic products such as pharmaceutical preparations. They are, however, particularly effective as ignition promoters for use with liquid fuels for Diesel and semi-Diesel engines. For the last mentioned use, the homopolymeric peroxides have several disadvantages which make them unsuitable for commercial application. For example, acetone peroxides have fairly high melting points so that they are solid at ordinary room temperature and they have poor solubility in fuels of the gas oil type. These disadvantages of the homopolymeric peroxides make it difficult or sometimes impossible to prepare concentrates of the peroxides in hydrocarbon oils which are important for economical and safe transportation of the peroxides which are considered too explosive to be shipped without diluents, and for the greater ease in apportioning these compounds in conventional types of blending equipment.

Now I have discovered that heteropolymeric peroxides of aliphatic ketones, contrary to what might be expected from knowledge of the properties of the homopolymeric peroxides, generally have very low melting points (a great many of them being liquids at ordinary temperatures) and have very good solubility in hydrocarbon oils, most of the practical members being miscible in all proportions with oils of the gas oil type. Furthermore, they are at least equal to and are gen-

erally more effective than the homopolymeric peroxides, for ignition promotion purposes. For example, the homopolymeric peroxides of acetone are solids at ordinary temperatures, the dimeric acetone peroxide having a melting point of 132°C. and the trimeric acetone peroxide possessing a melting point of 95°C. The homopolymeric peroxides of methyl ethyl ketone also have melting points above room temperature. However, the heteropolymeric peroxides which result from treatment of a mixture of acetone and methyl ethyl ketone under peroxide-forming conditions have a melting point which is below 0°C, and they are oily liquids at ordinary temperatures.

The peroxides of the invention which result from the treatment of a mixture of aliphatic ketones are true heteropolymeric peroxides. They are not merely mixtures of the homopolymeric peroxides from the individual aliphatic ketones used in mixture as the reactants. Such a mixture of ketones would be expected to obey the physical laws and have a melting point lower than that of any particular component in the mixture. While the use of a mixture of aliphatic ketones does lead to the minor formation of some homopolymeric peroxides, the reaction product may be separated into individual components and true compounds of a heteropolymeric character obtained which have such unexpected and desirable properties.

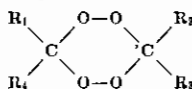
The heteropolymeric peroxides may be prepared by oxidizing a mixture of aliphatic ketones in any of the known manners which are conducive to the formation of peroxides. For example, the mixture may be oxidized in an acid medium with hydrogen peroxide, with hydrolyzed persulfuric acid, or with Caro's acid (H_2SO_5).

The known peroxides of ketones are believed to be compounds, in the case of the dimeric form, wherein two identical hydrocarbon groups of the ketones are joined through oxygen atoms. Trimeric forms contain three identical hydrocarbon groups joined through oxygen atoms. The exact nature of the oxygen linkages between the groups has not, however, been conclusively established. The heteropolymeric peroxides of the invention, while they have the same type of oxygen linkages, are compounds wherein the groups have different structural configuration of atoms, have a different number of atoms, or have both. For example, when peroxides are prepared from a mixture of acetone and methyl ethyl ketone, the dimeric product obtained, disregarding the incidental homopolymeric peroxides, is built up from

one molecule of acetone and one molecule of methyl ethyl ketone and the trimeric products are built up from one molecule of acetone and two molecules of methyl ethyl ketone and from two molecules of acetone and one molecule of methyl ethyl ketone. These three heteropolymeric peroxides exemplify compounds where the number of carbon atoms are different in the groups.

Thus the products of the invention are the heteropolymeric peroxides resulting from treatment under peroxide-forming conditions of at least two aliphatic ketones possessing a different number of atoms and/or a different structural configuration of atoms.

The heteropolymeric peroxides of the invention in the dimeric form may have a structural formula represented by the formula



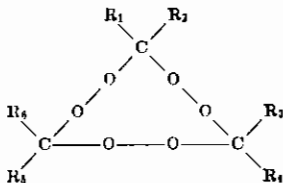
wherein R_1 , R_2 , R_3 and R_4 are aliphatic hydrocarbon radicals, with the linkage to the radical being on a carbon atom thereof and the group



is dissimilar from the group



by structural configuration of atoms and/or number of atoms therein. In the case of the trimeric form of the heteropolymeric peroxides, the structural formula may be as follows:



wherein R_1 , R_2 , R_3 , R_4 , R_5 , and R_6 are aliphatic hydrocarbon radicals, with the radical linkage being on a carbon atom thereof and the group



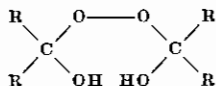
is dissimilar from the groups



and



by structural configuration of atoms and/or number of atoms therein. However, the exact structural configuration of peroxides of ketones has not been conclusively established in the art. For example, the formula



has also been proposed for the dimeric peroxides. Therefore, while the above-mentioned formulae

may further clarify the invention, I do not wish to be limited to compounds with these formulae owing to the uncertainty which is at present prevalent in the art.

The heteropolymeric peroxides may be prepared from a mixture of any suitable ketones. Examples of ketones are acetone, methyl ethyl ketone, methyl isopropyl ketone, mesityl oxide, diacetyl, acetyl acetone.

The reaction products containing heteropolymeric peroxides from a mixture of aliphatic ketones may be used as such in numerous applications or they may be separated and purified by any suitable method such as steam distillation, fractional crystallization, solvent extraction, and the like. A very useful class of heteropolymeric peroxides are those resulting from the use of acetone as one reactant and a dissimilar ketone as the other. It is preferable to use a ketone containing not more than 12 carbon atoms per molecule for the second reactant.

The heteropolymeric peroxides are in general very useful materials which, besides being particularly suitable for use in fuels which application is claimed in my copending application Serial No. 291,361, filed August 22, 1939, may also be used for bleaching flour, textiles, paper pulp, and the like; for preparation of pharmaceuticals and other synthetic products; for oxidizing agents for promoting the drying of paints and varnishes; for bactericides and germicides; and the like.

The invention may be more clearly indicated by the following example which is given for illustrative purposes only.

About 163 cm³ of highly concentrated sulfuric acid were added to 130 cm³ of water and after the mixture had cooled down to room temperature, 113 gms of hydrogen peroxide of 30 per cent. concentration were added. The mixture was then cooled to approximately -18° C., and a mixture of 36 gms of methyl ethyl ketone and 29 gms of acetone added in portions while stirring, care being taken that the temperature did not rise above 0° C. After addition of the ketones the mixture was allowed to stand for about 15 minutes and then water was added until the total volume was one liter, whereupon a colorless viscid upperlayer separated. This layer was freed of acid and any traces of unconverted ketones by washing with water, and then dried over sodium sulfate and filtered. The product was purified by steam distillation. The distillation yielded a small quantity of first runnings containing dimeric and trimeric acetone peroxide while the main mass consisted of the desired heteropolymeric peroxides with some methyl ethyl ketone peroxides in the least volatile fraction.

The ignition promotion qualities of the heteropolymeric peroxides were tested by adding them to a Diesel fuel and noting the increase in cetane number of the fuel. The cetane number of the Diesel fuel containing no added peroxides was about 41. The addition of about one per cent, heteropolymeric acetone-methyl ethyl ketone peroxides increased the cetane number to about 56. Addition to the fuel of one per cent, trimeric acetone peroxide or of one per cent, methyl ethyl ketone peroxide increased the cetane number of the same fuels only to about 53.

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