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MINERAL OIL AND ANTI-OXIDANT AGENT AND PROCESS

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My invention relates to the retardation or prevention of the oxidation of mineral oils. It has long been recognized that oils of this class, whether they be saturated or unsaturated, are subject to oxidation, resulting in increase in viscosity as well as formation of asphaltic bodies and acids and that during oxidation, at elevated temperatures resinification and carbonization often takes place.

A few situations in which oxidation causes considerable difficulty are as follows:

(1.) The oxidation of lubricating oils in air compressors.

(2.) The oxidation and carbonization of lubricating oils in automobiles or other types of internal combustion engines.

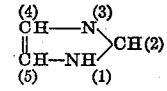
(3.) The oxidation and resinification of transformer oils.

(4.) The oxidation and carbonization of paraffin oils used in oil circulation heating systems.

By the term mineral oils it is intended to describe that large class of non-saponifiable oils of the petroleum and paraffin class, consisting mainly of hydrocarbons. It also includes mineral oils which are mixed with vegetable or animal oils, such mixtures sometimes being used as lubricants.

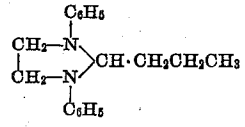
According to my invention an oil is produced having in it a small quantity of a derivative of hydroglyoxaline. The amount of the organic material added may vary greatly but quantities ranging from 0.01% to 0.5% have been found to produce good results. Of course a smaller portion may be used if the protecting action need not be so great and correspondingly the quantity may be increased above the 0.5% if it should seen desirable.

In general the compounds of this invention are easily handled, are soluble in oils and may be dissolved without danger of future separation. Their activity is not destroyed by relatively high temperatures. There are a number of such derivatives of hydroglyoxalines which function in this manner and they are all derived from the parent substance, glyoxaline, which has the following chemical constitution:



The substances described in this specification are hydroglyoxalines or substituted hydroglyoxalines and their derivatives. In general they may be prepared by heating a 1-2 diamino ethane derivative with an aliphatic, or aromatic aldehyde, although other methods of preparation may be employed.

One of the preferred members of the hydroglyoxaline group is 1-3 diphenyl 2-propyl-tetra hydroglyoxaline, which has the following chemical formula:



One method of preparing this material consists in heating 100 parts of 1-2 di (phenyl amino) ethane dissolved in alcohol with 40 parts of butyraldehyde under reflux for several hours. Upon cooling and crystallizing there is obtained a cream colored solid, which is dried and is then ready for use.

As other typical materials I may mention the following:

2-4-5 triphenyl di hydroglyoxaline
2-4-5 trifuryl di hydroglyoxaline
2-4-5 tritolyl di hydroglyoxaline
1-3 di phenyl tetra hydroglyoxaline
1-3 di ortho tolyl tetra hydroglyoxaline
1-3 di para tolyl tetra hydroglyoxaline
1-3 di xylyl tetra hydroglyoxaline
1-3 di alpha naphthyl tetra hydroglyoxaline
1-3 di beta naphthyl tetra hydroglyoxaline
1-3 phenyl ortho tolyl tetra hydroglyoxaline
1-3 phenyl alpha naphthyl tetra hydroglyoxaline
1-3 di phenyl 2-methyl tetra hydroglyoxaline
1-3 di phenyl 2-vinyl tetra hydroglyoxaline
1-3 di phenyl 2-propyl tetra hydroglyoxaline
1-3 di phenyl 2-propenyl tetra hydroglyoxaline
1-3 di phenyl 4-pseudo butyl tetra hydroglyoxaline
1-3 di phenyl 2-furyl tetra hydroglyoxaline
1-3 di phenyl 2-hexyl tetra hydroglyoxaline
1-3 di phenyl 3-beta naphthyl tetra hydroglyoxaline

1-3 phenyl beta napthhthyl 2-furyl tetra hydroglyoxaline
1-3 di alpha naphthyl 2-propyl tetra hydroglyoxaline
1-2-3 triphenyl tetra hydroglyoxaline
1-3 di phenyl 2-methoethyl tetra hydroglyoxaline
1-3 di ortho tolyl 2-propyl tetra hydroglyoxaline
1-3 di para tolyl 2-methyl tetra hydroglyoxaline
1-3 di xylyl 2-furyl tetra hydroglyoxaline
1-3 di alpha naphthyl 2-propenyl tetra hydroglyoxaline
1-3 di alpha naphthyl 2-phenyl tetra hydroglyoxaline
1-3 di beta naphthyl 2-methyl tetra hydroglyoxaline
1-3 phenyl ortho tolyl 2-propyl tetra hydroglyoxaline
1-3 di phenyl 2-methyl tetra hydroglyoxaline
1-3 di ortho tolyl 4-methyl tetra hydroglyoxaline
1-3 di para tolyl 4-methyl tetra hydroglyoxaline
1-3 di xylyl 4-methyl tetra hydroglyoxaline
1-3 di alpha naphthyl 4-methyl tetra hydroglyoxaline
1-3 di beta naphthyl 4-methyl tetra hydroglyoxaline
1-3 di phenyl 4-ethyl tetra hydroglyoxaline
1-3 di para tolyl 4-ethyl tetra hydroglyoxaline
1-3 di alpha naphthyl 2-methyl tetra hydroglyoxaline
1-3 di phenyl 2-propyl 4-methyl tetra hydroglyoxaline
1-3 di phenyl 2-4-dimethyl tetra hydroglyoxaline
1-3 di phenyl 2-vinyl 4-methyl tetra hydroglyoxaline
1-3 di phenyl 2-propenyl 4-methyl tetra hydroglyoxaline
1-3 di phenyl 2-furyl 4-methyl tetra hydroglyoxaline
1-3 di phenyl 2-hexyl 4-methyl tetra hydroglyoxaline
1-3 di phenyl 2-methoethyl 4-methyl tetra hydroglyoxaline
1-2-3 triphenyl 4-methyl tetra hydroglyoxaline
1-3 di ortho tolyl 2-4-dimethyl tetra hydroglyoxaline
1-3 di para tolyl 2-propyl 4-methyl tetra hydroglyoxaline
1-3 di xylyl 2-furyl 4-methyl tetra hydroglyoxaline
1-3 di alpha naphthyl 2-phenyl 4-methyl tetra hydroglyoxaline
1-3 di beta naphthyl 2-propenyl 4-methyl tetra hydroglyoxaline
1-3 di phenyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di phenyl 2-methyl 4-ethyl tetra hydroglyoxaline
1-3 di ortho tolyl 2-vinyl 4-ethyl tetra hydroglyoxaline
1-3 di xylyl 2-propyl 4-ethyl tetra hydroglyoxaline
1-3 di alpha naphthyl 2-phenyl 4-ethyl tetra hydroglyoxaline
1-3 di phenyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di ortho tolyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di para tolyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di xylyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di alpha naphthyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di beta naphthyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di phenyl 2-propyl 4-pseudo butyl tetra hydroglyoxaline
1-3 di phenyl 2-4-5-trimethyl tetra hydroglyoxaline
1-3 di phenyl 2-propenyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di phenyl 2-propyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di phenyl 2-furyl 4-5-dimethyl tetra hydroglyoxaline
1-2-3 triphenyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di phenyl 2-vinyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di ortho tolyl 2-furyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di para tolyl 2-phenyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di xylyl 2-vinyl 4-5-dimethyl tetra hydroglyoxaline
1-3 di beta naphthyl 2-4-5-trimethyl tetra hydroglyoxaline
1-3 di phenyl 2-4-4-trimethyl tetra hydroglyoxaline
1-3 di phenyl 2-vinyl 4-4-dimethyl tetra hydroglyoxaline
1-2-3-triphenyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di ortho tolyl 2-propyl 4-4-dimethyl tetra hydroglyoxaline
1-3 di phenyl 4-4-5-trimethyl tetra hydroglyoxaline
1-3 di phenyl 2-4-4-5-tetra methyl hydroglyoxaline
1-3 di phenyl 1-2-propyl 4-4-5-trimethyl hydroglyoxaline
1-2-3 triphenyl 4-4-5-trimethyl tetra hydroglyoxaline
1-3 di phenyl 2-thio tetra hydroglyoxaline
1-3 di phenyl 2-thio 4-methyl tetra hydroglyoxaline
1-3 di phenyl 2-thio 4-5-dimethyl tetra hydroglyoxaline

As indicated in the foregoing examples, the C atom in the 2 position of substituted 2-3-dihydroglyoxaline (or of substituted 2-3-4-5 tetra hydroglyoxaline) may have attached thereto any of the following: H, S, CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $CH_3CH_2CH_2CH_2$, $(CH_3)_2CH.CH_2$, $CH_3CH_2CH_2CH_2CH_2$, $(CH_3)_2CH.CH_2CH_2$, C_6H_5, $C_6H_4CH_3$, $C_6H_3(CH_3)_2$, $C_6H_5CH_2$, $CH_2CH=CH$, $CH_2=CH$, $CH_3CH_2CH_2CH=C(C_2H_5)$, C_4H_3O, $CH_3CH_2CH_2CH_2CH_2CH_2$, or in general any aliphatic or aromatic groups, whether saturated or unsaturated. These radicals I consider members of the class which may be designated, and in some of the appended claims are identified, by the term "2 modifying group."

Independent of the special member which may be used in "2 modifying group," one or more of the hydrogen atoms which are attached to the nitrogen atoms in the 1-3 positions may be replaced by any of the following: CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $CH_3CH_2CH_2CH_2$, $(CH_3)_2CH.CH_2$, $CH_3CH_2CH_2CH_2CH_2$, $(CH_3)_2CH.CH_2CH_2$, C_6H_5, $C_6H_4CH_3$, $C_6H_3(CH_3)_2$, $C_6H_5CH_2$, $CH_2CH=CH$, $CH_2=CH$, $CH_3CH_2CH_2CH=C(C_2H_5)$, C_4H_3O, $CH_3CH_2CH_2CH_2CH_2CH_2$, or in general any aliphatic or aromatic group, whether saturated or unsaturated. These radicals I consider members of a class which may be designated, and in some of the appended claims are identified, by the term "1-3 replacement group."

One or both of the C atoms may also in the 4-5 positions have attached thereto one or more of the following: H, CH_3, CH_3CH_2, $CH_3CH_2CH_2$, $(CH_3)_2CH$, $CH_3CH_2CH_2CH_2$, $(CH_3)_2CH.CH_2$, $CH_3CH_2CH_2CH_2CH_2$, $(CH_3)_2CH.CH_2CH_2$, C_6H_5, $C_6H_4CH_3$, $C_6H_3(CH_3)_2$, $C_6H_5CH_2$, $CH_2CH=CH$, $CH_2=CH$, $CH_3CH_2CH_2CH=C(C_2H_5)$, C_4H_3O, $CH_3CH_2CH_2CH_2CH_2CH_2$, or in general any aliphatic or aromatic group, whether saturated or unsaturated. These I consider members of a class which may be designated, and in the appended claims I have identified, by the term "4-5 modifying group."

It is to be understood, however, that strongly negative groups such as C_6H_5CO, CH_3CO, or groups containing halogens, or nitro groups, may not be used in any positions of the compounds.

The above examples and their derivatives are of value in practicing this invention and serve to indicate the wide range of materials of this type which are within the purview thereof. However, they are given only as examples and many modifications may be made without departing from the spirit of the invention.

For example it is not only possible to use the free bases of the above series but it is also possible to use salts or soaps formed from these materials without materially affecting the anti-oxidant value.

The new product may be produced by simply stirring into the mineral oil to be rendered anti-oxidant an appropriate quantity of the aforesaid anti-oxidant agent.

The tetra hydroglyoxaline derivatives referred to in this specification are prepared in general by the action of aldehydes on the corresponding 1-2 diamino ethane derivatives and are considered to have the glyoxaline constitution as given. However, I do not wish to be bound by any of the theories or constitutions given in this specification but desire to protect the class of materials formed in this manner.

The thio tetra hydroglyoxaline derivatives are prepared in general by the action of carbon disulfide on the corresponding 1-2

diamino ethane derivative and are considered to have the hydroglyoxaline constitution. However, I do not wish to be bound by this theory but desire to claim that class of materials formed by the reaction of this carbonyl chloride and 1-2 diamino ethane derivatives.

As illustrative of the manner in which the foregoing materials may be used and the effect which they produce the following examples are given.

A sample of a high grade commercial oil used in internal combustion engines was heated to 130° C. in a constant temperature bath and a rapid stream of oxygen introduced. At the end of regular intervals, the oil was examined and found to have increased in viscosity and considerable sludge was formed. Another sample of this oil, containing 0.01% of 1-3 diphenyl 2-propyl tetra hydroglyoxaline, was treated under identical conditions and it was found that the rate of oxidation was materially decreased, resulting in less increase in viscosity and much less sludge formation.

A highly refined mineral oil such as is used for medical purposes was treated with oxygen at 130° C. and the viscosity and sludge was found to increase materially. Acid formation also took place during oxidation.

Another sample of this same oil, containing 0.01% of 1-3 diphenyl 2-4 dimethyl tetra hydroglyoxaline was treated under the same conditions and it was found that the acidity of the oil increased to a much lesser extent. The increase in viscosity and sludge formation did not occur to nearly the extent of that exhibited by the same oil in the absence of this inhibitor.

It is apparent that all compounds of this class will not have anti-oxidant properties to the same degree; some of them being more active than others. One skilled in the art can readily choose the particular compound for the particular purpose for which it is to be used.

Having described my invention, what I claim is:

1. The method of retarding the oxidation of mineral oils consisting in adding to the oil a derivative of hydrogenated glyoxaline containing no strongly negative groups.

2. A mineral oil having incorporated therein as an oxidation retarding agent, a derivative of hydrogenated glyoxaline containing no strongly negative groups.

3. A mineral oil to which has been added a derivative of di hydroglyoxaline containing no strongly negative groups.

4. A mineral oil to which has been added a tetra hydroglyoxaline derivative containing no strongly negative groups.

5. A mineral oil to which has been added a di-aryl tetra hydroglyoxaline containing no strongly negative groups.

6. A mineral oil to which has been added a tetra hydroglyoxaline derivative, wherein, aromatic radicals are substituted in the 1-3 positions, and aliphatic radicals in one of the 2-4-5 positions.

7. A mineral oil to which has been added a tetra hydroglyoxaline derivative, wherein, aromatic radicals are substituted in the 1-3 positions and an aliphatic radical in the 2 position.

8. A mineral oil to which has been added a tetra hydroglyoxaline derivative, wherein, aromatic radicals are substituted in the 1-3 positions and in one or more of the 2-4-5 positions.

9. A mineral oil to which has been added a derivative of tetra hydroglyoxaline, wherein, the carbon atom in the 2 position has attached thereto a radical which is a member of the "2 modifying group," substantially as described.

10. A mineral oil to which has been added a tetra hydroglyoxaline derivative, wherein, the carbon atom in the 2 position has attached thereto an aliphatic radical.

11. A mineral oil to which has been added a tetra hydroglyoxaline derivative, wherein the carbon atoms in the 2 position have attached thereto a propyl radical.

12. A mineral oil to which has been added a tetra hydroglyoxaline derivative, wherein, one of the hydrogen atoms attached to the nitrogen atoms in the 1 or 3 positions is replaced by a radical which is a member of the "1-3 replacement group."

13. A mineral oil to which has been added a tetra hydroglyoxaline derivative, wherein, one of the hydrogen atoms attached to the nitrogen atoms in the 1-3 positions is replaced by an aliphatic radical.

14. A mineral oil to which has been added a derivative of tetra hydroglyoxaline wherein, one of the hydrogen atoms attached to the nitrogen atoms in the 1 or 3 positions is replaced by an aromatic radical.

15. A mineral oil to which has been added a derivative of tetra hydroglyoxaline wherein, one of the hydrogen atoms attached to the nitrogen atoms in the 1 or 3 positions is replaced by a phenyl radical.

16. A mineral oil to which has been added a derivative of tetra hydroglyoxaline, wherein, both hydrogen atoms attached to the nitrogen atoms in the 1-3 positions are replaced by a radical which is a member of the "1-3 replacement group."

17. A mineral oil to which has been added a derivative of tetra hydroglyoxaline, wherein, both hydrogen atoms attached to the nitrogen atoms in the 1-3 positions are replaced by a phenyl radical.

18. A mineral oil to which has been added a derivative of tetra hydroglyoxaline, wherein, each of the carbon atoms in the 4-5 posi-

tions has a radical attached thereto which is a member of the "4-5 modifying group."

19. A mineral oil to which has been added a derivative of tetra hydroglyoxaline, wherein each of the carbon atoms in the 4-5 positions has two radicals attached thereto both of which are members of the "4-5 modifying group."

20. A mineral oil to which has been added a derivative of tetra hydroglyoxaline, wherein, each of the carbon atoms in the 4-5 positions has a hydrogen atom attached thereto and substituted in one or more of the 1-2-3 positions by a hydrocarbon residue.

21. A mineral oil to which has been added a derivative of tetra hydroglyoxaline, wherein, each of the carbon atoms in the 4-5 positions has two hydrogen atoms attached thereto and substituted in one or more of the 1-2-3 positions by a hydrocarbon residue.

22. A mineral oil to which has been added 1-3 diphenyl 2-propyl tetra hydroglyoxaline.

23. A mineral oil having incorporated therein hydroglyoxaline in which the constituents in the 1-3-4-5 positions are taken from the group comprising hydrogen, hydrocarbon and furyl residues, and in the 2 position from the group comprising hydrogen, hydrocarbon and furyl residues, and sulphur, and containing at least one substituent other than hydrogen.

24. A mineral oil having incorporated therein hydroglyoxalines in which the substituents in the 1-3 positions are taken from the group comprising hydrogen, hydrocarbon and furyl residues, and in the 2 position from the group comprising hydrogen, hydrocarbon and furyl residues, and sulphur, and containing at least one substituent other than hydrogen.

25. A mineral oil having incorporated therein hydroglyoxalines in which the substituents in the 1-3 positions are taken from the group comprising hydrogen, hydrocarbon and furyl residues, and containing at least one substituent other than hydrogen.

26. A mineral oil having incorporated therein hydroglyoxalines in which the constituents in the 2 position are taken from the group comprising hydrogen, hydrocarbon and furyl residues, and sulphur, and containing at least one substituent other than hydrogen.

27. A mineral oil having incorporated therein hydroglyoxalines in which the substituents in the 1-3-4-5 positions are taken from the group comprising hydrogen and hydrocarbon residues, and in the 2 position from the group comprising hydrogen, sulphur and hydrocarbon residues, and having at least one substituent other than hydrogen.

28. A mineral oil having incorporated therein hydroglyoxalines having hydrogen atoms as the 4-5 substituents, and as the 1-3 substituents a member of the group comprising hydrogen, hydrocarbon and furyl residues, and as the 2 substituents a member of the group comprising hydrogen, sulphur, and hydrocarbon and furyl residues, and having at least one substituent other than hydrogen.

29. A mineral oil having incorporated therewith hydroglyoxalines having hydrogen atoms as the 4-5 substituents, and as the 1-3 substituents members of the group comprising hydrogen, hydrocarbon and furyl residues, and having at least one substituent other than hydrogen.

30. A mineral oil having incorporated therewith hydroglyoxalines having hydrogen atoms as the 4-5 substituents, and as substituents in the 2 position members of the group comprising hydrogen, sulphur and hydrocarbon and furyl residues.

31. The product described in claim 28 in which there are two hydrogen atoms attached to each 4-5 C atom.

32. The product described in claim 29 in which there are two hydrogen atoms attached to each 4-5 C atom.

33. The product described in claim 30 in which there are two hydrogen atoms attached to each 4-5 C atom.

In testimony whereof, I affix my signature.

HAROLD A. MORTON.