This invention relates to antioxidants for oils and compositions containing the same, and more particularly, it relates to oil compositions containing the product resulting from the condensation of an alkyl phenol and furfural or an alkyl substituted furfural; all as fully hereinafter set forth and as claimed.

Gasolines made by the thermal cracking of heavier petroleum oils, and gasolines made by the polymerization of normally gaseous hydrocarbons, contain certain undesirable constituents, for example, diolefins and cyclic olefins, which are subject to oxidational changes with resultant formation of gums and color-impairing bodies. Unless these undesirable constituents are removed or unless their oxidation is inhibited, gasolines are obtained which tend to deposit gums and to discolor in storage and in handling.

Various methods have been employed for removing the undesirable constituents from gasolines such as washing with sulfuric acid or contacting with a solid adsorbent. These methods, however, have not been entirely satisfactory in that high treating losses are encountered and in many instances, gasolines are obtained which are not sufficiently free from the undesirable gum-forming constituents.

A large number of oxidation inhibitors have been developed for obviating the effects of the undesirable constituents, but many of these inhibitors are subject to the disadvantage that they are water soluble and soluble in dilute aqueous alkali solutions so that gasolines to which they have been added tend to be deprived of the antioxidant material upon contact with water or dilute aqueous alkali solutions.

In addition to gasolines, other petroleum oils such as lubricating oils, turbine oils, transformer oils, and the like, as well as animal and vegetable oils are also subject to undesirable oxidational changes in storage and in use, which result in definite deterioration of quality and character of these oils. For example, oxidation of petroleum lubricating oils results not only in the formation of compounds which are corrosive to metals, but also in the deposition of sludge in the crankcase and the formation of varnish and gum on the pistons and cylinder walls of internal combustion engines. Oxidation of animal and vegetable oils results in the development of rancidity of the oils.

It is, therefore, an object achieved by this invention to provide an improvement agent or agents of the character indicated herein, which when incorporated in an oil will substantially retard deterioration thereof.

It is a further object achieved by this invention to provide an oil composition containing a compound which will inhibit or substantially retard deterioration of the oil. It is still further object achieved by this invention to provide an oil composition containing an antioxidant which is substantially insoluble in water and in dilute aqueous alkali solutions.

These and other objects achieved by this invention will become apparent in the following detailed description thereof.

We have discovered that animal oils, vegetable oils, and mineral oils, particularly petroleum lubricating oils, and hydrocarbon oils boiling within a gasoline boiling-point range, susceptible to deterioration, can be effectively inhibited against such deterioration without substantial modification of the other desirable properties of such oils by incorporating into the oils a small amount of a compound having the following structural formula:

\[
\begin{align*}
\text{R} & \quad \text{OH} \\
\text{OH} & \quad \text{R}
\end{align*}
\]

wherein R is selected from the class consisting of furyl and alkyl substituted furyl groups, R1 is a tertiary alkyl radical containing at least 4 carbon atoms, and R2 is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms. The R, R1, and R2 substituents are such that the compounds are insoluble in dilute aqueous alkali solutions and water, while soluble in hydrocarbon oils and serve as antioxidants when incorporated therein. The following compounds are illustrative of the compounds which fall within the scope of our invention. It should be understood, however, that these compounds are given by way of example and that our invention is not limited to these compounds except as recited in the appended claims.

- Bis(2-hydroxy-5-t-butylphenyl)-furylmethane;
- Bis(2-hydroxy-5-t-amylphenyl)-furylmethane;
- Bis(2-hydroxy-5-t-octylphenyl)-furylmethane;
- Bis(2-hydroxy-3-t-butylphenyl)-furylmethane;
- Bis(2-hydroxy-3-t-amylphenyl)-furylmethane;
- Bis(2-hydroxy-3-t-octylphenyl)-furylmethane;
- Bis(2-hydroxy-3-3,5-di-t-butylphenyl)-furylmethane;
2,515,908

2,515,908 S Bis(2-hydroxy-3,5-di-t-amylphenyl)-furyl methane; Bis(2-hydroxy-3,5-di-t-octylphenyl)-furyl methane;
Bis(2-hydroxy-3-t-buty1-5-sec-butylphenyl)-furylmethane;
Bis(2-hydroxy-5-t-buty1-3-sec-butylphenyl)-furylmethane;
Bis(2-hydroxy-3-isopropyl-5-t-butylphenyl)-furylmethane;
Bis(2-hydroxy-3-isopropyl-5-t-amylphenyl)-furylmethane;
Bis(2-hydroxy-3-isopropyl-5-t-octylphenyl)-furylmethane;
Bis(2-hydroxy-5-isopropyl-3-t-buty1phenyl)-furylmethane;
Bis(2-hydroxy-5-isopropyl-3-t-amylphenyl)-furylmethane;
Bis(2-hydroxy-5-isopropyl-3-t-octylphenyl)-furylmethane;
Bis(2-hydroxy-3-ethyl-5-t-buty1phenyl)-furylmethane;
Bis(2-hydroxy-3-ethyl-5-t-amylphenyl)-furylmethane;
Bis(2-hydroxy-3-ethyl-5-t-octylphenyl)-furylmethane;
Bis(2-hydroxy-5-ethyl-3-t-buty1phenyl)-furylmethane;
Bis(2-hydroxy-5-ethyl-3-t-amylphenyl)-furylmethane;
Bis(2-hydroxy-5-ethyl-3-t-octylphenyl)-furylmethane;
Bis(2-methyl-4-hydroxy-5-t-buty1phenyl)-furylmethane;
Bis(2-methyl-4-hydroxy-5-t-amylphenyl)-furylmethane;
Bis(2-methyl-4-hydroxy-5-t-octylphenyl)-furylmethane;
Bis(2-hydroxy-3-methyl-5-t-buty1phenyl)-furylmethane;
Bis(2-hydroxy-3-methyl-5-t-amylphenyl)-furylmethane;
Bis(2-hydroxy-3-methyl-5-t-octylphenyl)-furylmethane;
Bis(2-hydroxy-3-methyl-5-tert-butylphenyl)-5-methylfurylmethane;
Bis(2-hydroxy-3-methyl-5-tert-amylphenyl)-5-methylfurylmethane;
Bis(2-hydroxy-3-methyl-5-tert-octylphenyl)-5-methylfurylmethane;
Bis(2-hydroxy-3,5-di-t-octylphenyl)-5-methylfurylmethane;
Bis(2-hydroxy-5-t-buty1-3-sec-butylphenyl)-5-methylfurylmethane;
Bis(2-hydroxy-5-isopropyl-5-t-buty1phenyl)-5-methylfurylmethane;
Bis(2-hydroxy-5-isopropyl-3-t-amylphenyl)-5-methylfurylmethane;
Bis(2-hydroxy-3-ethyl-5-t-octylphenyl)-5-methylfurylmethane;
Bis(2-methyl-4-hydroxy-5-t-buty1phenyl)-5-methylfurylmethane;
Bis(2-hydroxy-3-methyl-5-t-amy1phenyl)-5-methylfurylmethane;
Bis(2-hydroxy-3-methyl-5-t-octylphenyl)-5-methylfurylmethane; and the like.

The molecular ratio of the alkyl phenol to the furfural may vary depending upon the number of reactive positions capable of substitution on the aromatic nucleus of the particular phenol employed and upon the final product desired, but in accordance with our invention, is advantageously maintained at about 2:1. In carrying out the reaction, it is generally desirable to maintain the reactants under an inert atmosphere. We introduce the alkyl phenol and the furfural into a reaction vessel containing a previously prepared basic catalyst. The reaction temperature is maintained at about 100°C. The reaction is allowed to proceed until no more solid appears to be formed. The solid product is then separated from the reaction mass, washed with water until neutral and then purified by recrystallization from a suitable solvent.

As examples of the alkyl phenols which may be used in accordance with our invention may be included 2-tert-buty1phenol; 2-tert-octylphenol; 4-tert-butylphenol; 4-tert-amylphenol; 4-tert-octylphenol; 2-4-di-tert-buty1phenol; 2,4-di-tert-amylphenol; 2,4-di tert-octylphenol; 2-tert-buty1-4-sec-buty1phenol;
The reaction mass thus formed was maintained under a nitrogen atmosphere and stirred continuously for five hours at a temperature of about 98° to 100° C. A viscous product was obtained. This product was dissolved in 500 ml of hexane, and washed with water until neutral. The organic phase was then treated with 75 per cent aqueous alcohol to remove any unreacted ortho-tertiary-butyl-paracresol. The hexane was then removed under vacuum in a desiccator. A solid product consisting essentially of bis(2-hydroxy-3-t-butyl-5-methyl) furymethane was thus obtained.

The ultimate analysis of the product as above obtained compared with the theoretical composition was as follows:

<table>
<thead>
<tr>
<th>Ultimate Analysis</th>
<th>Found for Product</th>
<th>Calculated for bis (2-hydroxy-3-t-butyl-5-methyl)furymethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>70.03</td>
<td>70.76</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10.26</td>
<td>10.03</td>
</tr>
</tbody>
</table>

The bis(2-hydroxy-3-t-butyl-5-methyl)furymethane thus obtained is insoluble in water and in dilute aqueous alkali solutions and is soluble in various organic solvents such as alcohol, acetone, ether, ligroin, gasoline, lubricating oils and other petroleum products.

When the product obtained as above described was added to a reference gasoline having an induction period of 2.6 hours under the conditions of the above mentioned A. S. T. M. test, in the proportion of 0.0002 mole per 100 ml of gasoline (0.081 gram per 100 ml), the induction period increased to 4.50 hours.

While our invention has been described above with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such illustrated examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A compound represented by the structural formula:

   ![Structural Formula 1](image1)

   wherein R is selected from the class consisting of furyl and alkyl substituted furyl groups, R<sub>4</sub> is a tertiary alkyl radical containing at least 4 carbon atoms, and R<sub>3</sub> is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

2. A compound represented by the structural formula:

   ![Structural Formula 2](image2)

   wherein R is selected from the class consisting of furyl and alkyl substituted furyl groups, R<sub>4</sub> is a tertiary butyl radical, and R<sub>3</sub> is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.
3. A compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary amyl radical, and \( R_2 \) is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

4. A compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary octyl radical, and \( R_2 \) is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

5. A compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary butyl radical, and \( R_2 \) is hydrogen.

6. A compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary butyl radical, and \( R_2 \) is a methy1 radical.

7. Bis(2-hydroxy-5-t-butylphenyl)-furylmethane.

8. Bis(2-hydroxy-3-t-butyl-5-methylphenyl)-furylmethane.

9. A new composition of matter comprising a major proportion of an oil normally tending to undergo deterioration and a small amount, sufficient to inhibit such deterioration, of a compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary alkyl radical containing at least 4 carbon atoms, and \( R_2 \) is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

10. A new composition of matter comprising a major proportion of an oil normally tending to undergo deterioration and a small amount, sufficient to inhibit such deterioration, of a compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary butyl radical, and \( R_2 \) is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

11. A new composition of matter comprising a major proportion of an oil normally tending to undergo deterioration and a small amount, sufficient to inhibit such deterioration, of a compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary butyl radical, and \( R_2 \) is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

12. A motor fuel comprising a hydrocarbon oil boiling within a gasoline boiling-point range normally tending to undergo oxidational changes and a small amount, sufficient to inhibit such oxidational changes, of a compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary alkyl radical containing at least 4 carbon atoms, and \( R_2 \) is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

13. A motor fuel comprising a hydrocarbon oil boiling within a gasoline boiling-point range normally tending to undergo oxidational changes and a small amount, sufficient to inhibit such oxidational changes, of a compound represented by the structural formula:

\[
\begin{align*}
\text{OH} & \quad \text{R} \\
\text{R}_1 & \quad \text{R}_2 \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

wherein \( R \) is selected from the class consisting of furyl and alkyl substituted furyl groups, \( R_1 \) is a tertiary butyl radical, and \( R_2 \) is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

14. A motor fuel comprising a hydrocarbon oil boiling within a gasoline boiling-point range normally tending to undergo oxidational changes and a small amount, sufficient to inhibit such oxid-
dational changes, of a compound represented by the structural formula:

wherein R is selected from the class consisting of furyl and alkyl substituted furyl groups, R₁ is a tertiary butyl radical, and R₂ is hydrogen.

10. A motor fuel comprising a hydrocarbon oil boiling within a gasoline boiling-point range normally tending to undergo oxidational changes and a small amount, sufficient to inhibit such oxidational changes, of a compound represented by the structural formula:

wherein R is selected from the class consisting of furyl and alkyl substituted furyl groups, R₁ is a tertiary alkyl radical containing at least 4 carbon atoms, and R₂ is a member of the group consisting of hydrogen and alkyl radicals containing no more than 8 carbon atoms.

19. A lubricant comprising a lubricating oil susceptible to deterioration and a small amount, sufficient to inhibit such deterioration, of bis(2-hydroxy-3-t-butyl-5-methylphenyl)-furylmethane.

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