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## 3,5-DIALKYL-4-HYDROXY BENZYLAMINES

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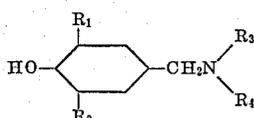
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This invention relates to novel chemical compounds having utility in the chemical arts.

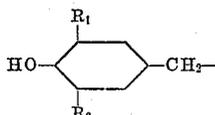
In particular, this invention relates to novel 3,5-dialkyl-4-hydroxybenzyl amines which are eminently suited for use as antioxidants.

Among the objects of this invention is that of providing new chemical compounds useful for the above and other purposes. Another object is to provide methods of preparing these new chemical compounds. Another object is to provide hydrocarbon oil normally tending to deteriorate in the presence of oxygen containing these new compounds in amount sufficient to inhibit this deterioration. Another object is to provide lubricating oil and greases normally tending to deteriorate in the presence of oxygen containing, in amount sufficient to inhibit such deterioration, a small antioxidant quantity of novel and highly effective antioxidants. Still another object is to provide turbine and other industrial oils stabilized against oxidative deterioration by the presence therein of a small antioxidant quantity of novel and highly effective antioxidants. Other objects will be apparent from the ensuing description.

The above and other objects of this invention are accomplished by providing as new compositions of matter 3,5-dialkyl-4-hydroxybenzyl amines having the general formula:



wherein  $R_1$  is an alkyl group containing from 1 to 12 carbon atoms,  $R_2$  is an alkyl group containing from 3 to 12 carbon atoms which is branched on the alpha carbon atom,  $R_3$  is selected from the group consisting of alkyl, cycloalkyl, aralkyl, aryl, alkaryl and



and  $R_4$  is selected from the group consisting of hydrogen, alkyl, cycloalkyl, aralkyl, aryl and alkaryl. In the above compounds it is preferable that the hydrocarbon radicals of the groups designated above as  $R_3$  and  $R_4$  contain the following ranges of carbon atoms: alkyl, 1 to 12; cycloalkyl, 5 to 6; aralkyl, 7 to 11; aryl, 6 to 10; and alkaryl, 7 to 15.

A preferred embodiment of this invention relates to 3,5-dialkyl-4-hydroxybenzyl amines in which at least one of  $R_3$  and  $R_4$  is an alkyl group as above-defined. The compounds of this embodiment are more effective antioxidants for oxygen-sensitive oils than are the remainder of the compounds of this invention.

A particularly preferred embodiment of this invention is 3,5-dialkyl-4-hydroxybenzyl amines in which at least

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one of  $R_3$  and  $R_4$  is an alkyl group as above-defined and  $R_1$  and  $R_2$  are both tertiary alkyl groups containing from 4 to 12 carbon atoms. These latter compounds possess outstanding effectiveness as antioxidants for a wide variety of oxygen-sensitive oils, such as lubricating oil, transformer oil, turbine oil, gear oil and the like.

The most particularly preferred embodiment of this invention is compounds described above in which  $R_1$  and  $R_2$  are tertiary butyl groups, and in which at least one of  $R_3$  and  $R_4$  is a lower alkyl group, that is an alkyl group containing from 1 to 6 carbon atoms.

Typical compounds of this invention include: N-cyclohexyl - N - (3 - methyl - 5 - isopropyl - 4 - hydroxybenzyl)amine, N - benzyl - N - (3,5 - diisopropyl - 4 - hydroxybenzyl)amine, N - benzyl - N - (3,5 - di-tert-butyl - 4 - hydroxybenzyl)amine, N - phenyl - N - (3 - methyl - 5 - (2 - octyl) - 4 - hydroxybenzyl)amine, N - (3,5 - xylyl) - N - (3,5 - di - tert - amyl - 4 - hydroxybenzyl)amine, N - cyclohexyl - N,N - bis - (3,5 - diisopropyl - 4 - hydroxybenzyl)amine, N - (p - butylbenzyl) - N,N - bis - (3,5 - di - tert - butyl - 4 - hydroxybenzyl)amine, N - benzyl - N,N - bis - (3 - methyl - 5 - (1,1,3,3 - tetramethyl - butyl) - 4 - hydroxybenzyl)amine, N - ( $\alpha$  - naphthyl) - N,N - bis - (3,5 - diisopropyl - 4 - hydroxybenzyl)amine, N - (p - tolyl) - N,N - bis - (3,5 - di - (2 - dodecyl) - 4 - hydroxybenzyl)amine, N,N - di - (phenyl) - N - (3,5 - di - (2 - hexyl) - 4 - hydroxybenzyl)amine, N - phenyl - N - (p - tolyl) - N - (3,5 - di - (2 - amyl) - 4 - hydroxybenzyl)amine, N - (p - octylphenyl) - N - (3 - ethyl - 5 - tert - butyl - 4 - hydroxybenzyl)amine, and the like.

The preferred embodiment of this invention as above-described is illustrated by such compounds as N-methyl-N - (3,5 - diisopropyl - 4 - hydroxybenzyl)amine, N-octyl - N - (3 - methyl - 5 - tert - butyl - 4 - hydroxybenzyl)amine, N - (2 - dodecyl) - N - (3,5 - di - (2 - hexyl) - 4 - hydroxybenzyl)amine, N,N - diethyl - N - (3 - isopropyl-5-tert-butyl-4-hydroxybenzyl)amine, N,N-di-butyl-N-(3,5-diisopropyl-4-hydroxybenzyl)amine, N-methyl-N - ethyl - N - (3,5 - di - (2 - octyl) - 4 - hydroxybenzyl)amine, N - sec - butyl - N - dodecyl - N - (3,5 - diisopropyl - 4 - hydroxybenzyl)amine, N - propyl - N - N - bis - (3 - methyl - 5 - tert - butyl - 4 - hydroxybenzyl)amine, N - (sec - amyl) - N,N - bis - (3,5 - di-sec - butyl - 4 - hydroxybenzyl)amine, N - decyl - N,N - bis - (3 - ethyl - 5 - (3 - decyl) - 4 - hydroxybenzyl)amine, and the like.

The particularly preferred embodiment of this invention is illustrated by such compounds as N-heptyl-N-(3,5 - di - tert - butyl - 4 - hydroxybenzyl)amine, N-isopropyl - N - (3,5 - di - tert - amyl - 4 - hydroxybenzyl)amine, N - nonyl - N - (3 - tert - butyl - 5 - tert - amyl - 4 - hydroxybenzyl)amine; N,N - diisobutyl - N - (3,5 - di - tert - amyl - 4 - hydroxybenzyl)amine; N,N - dioctyl - N - (3,5 - di - (1,1,3,3 - tetramethylbutyl) - 4 - hydroxybenzyl)amine; N - propyl - N - amyl - N - (3,5 - di - (1,1,2,2 - tetramethylpropyl) - 4 - hydroxybenzyl)amine; N - methyl - N,N - bis - (3,5 - di-tert - amyl - 4 - hydroxybenzyl)amine; N - heptyl - N,N - bis - (3,5 - di - tert - amyl - 4 - hydroxybenzyl)amine; N - undecyl - N,N - bis - (3 - tert - butyl - 5 - tert - amyl-4-hydroxybenzyl)amine, and the like.

The most particularly preferred embodiment of this invention comprises such compounds as N-methyl-N-(3,5 - di - tert - butyl - 4 - hydroxybenzyl)amine; N - ethyl - N - (3,5 - di - tert - butyl - 4 - hydroxybenzyl)amine; N - butyl - N - (3,5 - di - tert - butyl - 4 - hydroxybenzyl)amine; N - isohexyl - N - (3,5 - di - tert - butyl-4 - hydroxybenzyl)amine; N,N - dimethyl - N - (3,5 - di - tert - butyl - 4 - hydroxybenzyl)amine; N,N - di-propyl - N - (3,5 - di - tert - butyl - 4 - hydroxybenzyl)-

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amine; N - methyl - N - ethyl - N - (3,5 - di - tert - butyl - 4 - hydroxybenzyl) amine; N - ethyl - N,N - bis - (3,5 - di - tert - butyl - 4 - hydroxybenzyl) amine; N - butyl - N,N - bis - (3,5 - di - tert - butyl - 4 - hydroxybenzyl) - amine; N - tert - amyl - N,N - bis - (3,5 - di - tert - butyl - 4 - hydroxybenzyl) amine, and the like.

The compounds of this invention are white or pale yellow crystalline solids and are soluble in various organic solvents and in gasolines, diesel fuels, hydrocarbon oils and the like. These compounds are further characterized by being relatively stable, easily crystallizable materials.

The compounds of this invention are prepared by reacting a 2,6-dialkyl phenol in which one of the alkyl groups contains from 3 to 12 carbon atoms and is branched on the alpha carbon atom and the other alkyl group contains from 1 to 12 carbon atoms; formaldehyde; and a primary or secondary amine in which the hydrocarbon portion thereof is in conformity with the groups designated hereinabove as R<sub>3</sub> and R<sub>4</sub>. In conducting this process a monohydric alcohol containing from 1 to 6 carbon atoms is preferably used as the reaction solvent. The reaction temperature is in the order of about 20 to about 100° C. It is preferred to conduct the process of this invention within the range of about 50 to 90° C.

In conducting this process the relative proportions of the three reactants is varied depending upon the particular type of 3,5-dialkyl-4-hydroxybenzyl amine being prepared. Thus, when preparing the N,N-di-hydrocarbon substituted-N-(3,5-dialkyl-4-hydroxybenzyl) amines of this invention, one mole of formaldehyde and one mole of di-hydrocarbon substituted amine—i.e., secondary amine—are employed per mole of appropriate 2,6-dialkyl phenol. When preparing N-hydrocarbon-N,N-bis-(3,5-dialkyl-4-hydroxybenzyl) amines of this invention, one mole of formaldehyde and one-half of a mole of mono-hydrocarbon substituted amine—i.e., primary amine—are reacted per mole of appropriately substituted 2,6-dialkyl phenol used. When preparing the compounds of this invention which contain one hydrogen atom and one hydrocarbon group on the nitrogen atom, one mole of a formaldehyde and a large excess of primary amine are employed per mole of 2,6-dialkyl phenol used. This substantial excess of primary amine is in the order of about 8 to about 10 moles per mole of phenol used. This particular reaction is conducted in a large amount of mono-hydric alcohol solvent in order to achieve dilution of the reactants.

Thus, a facet of this invention is a process of preparing 3,5-dialkyl-4-hydroxybenzyl amines which comprises reacting a 2,6-dialkyl phenol in which one of the alkyl groups contains from 3 to 12 carbon atoms and is branched on its alpha carbon atom and the other alkyl group contains from 1 to 12 carbon atoms; formaldehyde; and an amine having the general formula



wherein R<sub>3</sub> is selected from the group consisting of alkyl containing from 1 to 12 carbon atoms, cycloalkyl containing from 5 to 6 carbon atoms, aralkyl containing from 7 to 11 carbon atoms, aryl containing from 6 to 10 carbon atoms and alkaryl containing from 7 to 15 carbon atoms and R<sub>4</sub> is selected from the group consisting of hydrogen and R<sub>3</sub> as just defined.

The compounds of this invention and the methods for their preparation are illustrated by the following specific examples wherein all parts and percentages are by weight.

#### EXAMPLE I

In a reaction vessel equipped with stirring means, reflux means, thermometer and reagent introducing means were placed 89 parts of 2,6-diisopropylphenol, 248 parts of 25 percent aqueous dimethylamine solution and 500 parts of ethanol. To this solution was added 75 parts of 37 percent formalin solution at room temperature and

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the mixture refluxed for 4 hours at 83° C. The reaction mixture was then hydrolyzed with excess cold water and the solid product filtered off to give a 98 percent yield of N,N - dimethyl - N - (3,5 - diisopropyl - 4 - hydroxybenzyl) amine, melting at 85–87° C. The analysis—calculated for C<sub>15</sub>H<sub>26</sub>NO: 76.5 percent carbon, 10.7 percent hydrogen, and 5.95 percent nitrogen. Found: 77 percent carbon, 10.6 percent hydrogen, and 5.89 percent nitrogen.

#### EXAMPLE II

In a reaction vessel equipped as described above, 103 parts of 2,6-di-tert-butylphenol, 248 parts of 25 percent aqueous dimethyl amine solution and 75 parts of 37 percent formalin solution were reacted at 75° C. in 500 parts of ethanol for 3 hours. The reaction mixture was then poured into excess cold water and the solid which formed filtered off to give a 98% yield of N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl) amine, melting point 90–92° C. The analysis calculated for C<sub>17</sub>H<sub>28</sub>NO: carbon 77.51%, hydrogen 11.1%. Found: carbon 77.60%, hydrogen 11.0%.

#### EXAMPLE III

In a reaction vessel equipped as in Example I were reacted 206 parts of 2,6-di-tert-butyl phenol, 38 parts of 40% aqueous methyl amine solution, 84 parts of 37% formalin solution in 500 parts of ethanol for three hours at 75° C. On cooling, the solid product precipitated out and was filtered off to give a 65% yield of N-methyl-N,N-bis-(3,5-di-tert-butyl-4-hydroxybenzyl) amine, melting point 179–181° C. The analysis—calculated for C<sub>31</sub>H<sub>48</sub>NO<sub>2</sub>: 79.63% carbon, 10.6% hydrogen. Found: 79.9% carbon and 10.3% hydrogen.

#### EXAMPLE IV

Into the reaction equipment described in Example I are introduced 178 parts of 2,6-diisopropyl phenol, 38 parts of 40% aqueous methyl amine solution, 84 parts of a 37% aqueous solution of formalin and 500 parts of ethanol. These materials are then heated to a temperature of 70° C. On completion of the reaction, the mixture is poured into an excess of cold water and the solid materials which form are filtered off to give N-methyl-N,N-bis-(3,5-diisopropyl-4-hydroxybenzyl) amine.

#### EXAMPLE V

In the reaction vessel of Example I are placed 159 parts of 2,6-di-(1,1,3,3-tetramethylbutyl)phenol, 45 parts of 37 percent aqueous formalin solution, 29 parts of 40 percent aqueous ethyl amine solution and 400 parts of methanol. This mixture is heated at 70° C. for 4 hours. On cooling and partially evaporating the solvent, N-ethyl-N,N-bis-(3,5-di-(1,1,3,3-tetramethylbutyl) - 4 - hydroxybenzyl) amine precipitates and is filtered off.

#### EXAMPLE VI

In the reaction vessel of Example I are placed 15 parts of 2-methyl-6-isopropylphenol, 8.4 parts of 37 percent aqueous formalin solution, 77 parts of 40 percent aqueous methyl amine and 400 parts of ethanol. This mixture is stirred at 30° C. for 4 hours. The solvent is removed at reduced pressure with 25 mm. of mercury and the product crystallized from the residue. The product is N - methyl - N - (3-methyl-5-isopropyl-4-hydroxybenzyl) amine.

#### EXAMPLE VII

N - octyl - N,N-bis-(3,5-di-tert-butyl-4-hydroxybenzyl) amine is prepared as follows: In the reaction vessel of Example I are placed 208 parts of 2,6-di-tert-butyl phenol, 85 parts of 37 percent aqueous formalin solution, 64 parts of octyl amine, and 500 parts of ethanol. This mixture is heated at 70° C. for 5 hours. On cooling and partially evaporating the solvent, the product is obtained as a crystalline solid.

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## EXAMPLE VIII

Using 500 parts of ethanol as a reaction solvent, N,N-dibenzyl-N-(3-isopropyl-5-tert-butyl-4-hydroxybenzyl) amine is prepared by reacting 97 parts of 2-isopropyl-6-tert-butyl phenol, 45 parts of 37 percent aqueous formalin solution and 98 parts of dibenzyl amine. The reaction is carried out at 70° C. for 4 hours. The product is recovered by partially evaporating the solvent and crystallizing the residual liquor.

## EXAMPLE IX

Using the reaction equipment described in Example I, 220 parts of 2-methyl-6-(1,1,3,3-tetramethylbutyl)phenol, 84 parts of 37 percent aqueous formalin solution and 113 parts of methyl(cyclohexyl)amine are reacted at a temperature of 73° C. for 5 hours using 800 parts of isopropanol as solvent. The reaction mixture is poured into cold water and the product crystallized from the insoluble organic portion. The product is N-methyl-N-cyclohexyl-N-(3-methyl-5-(1,1,3,3-tetramethylbutyl)-4-hydroxybenzyl)amine.

## EXAMPLE X

N-hexyl-N,N-bis-(3,5-diisopropyl-4-hydroxybenzyl)amine is prepared in the reaction vessel of Example I from 178 parts of 2,6-diisopropyl phenol, 85 parts of 37 percent aqueous formalin solution, and 51 parts of hexyl amine using 600 parts of butanol as the solvent. The mixture is heated at 70° C. for 6 hours and poured into cold water. The product is filtered off as a crystalline solid.

## EXAMPLE XI

In the reaction vessel described in Example I are placed 89 parts of 2,6-di-tert-butyl phenol, 45 parts of 37 percent aqueous formalin solution, 65 parts of aniline hydrochloride and 800 parts of ethanol. This mixture is stirred at 70° C. for 12 hours and poured into dilute sodium bicarbonate solution. N-phenyl-N,N-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)amine is filtered off as a crystalline solid.

## EXAMPLE XII

At a temperature of 65° C., 208 parts of 2,6-di-tert-butyl phenol, 85 parts of 37 percent aqueous formalin solution and 130 parts of dibutyl amine are reacted in 700 parts of ethanol. After 4 hours, the reaction mixture is poured into cold water and the N,N-butyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine filtered off as a white solid.

## EXAMPLE XIII

Using 700 parts of ethanol as reaction solvent, 215 parts of 2,6-di-(2-dodecyl)phenol, 45 parts of aqueous 37 percent formalin solution, and 143 parts of N-methyl aniline hydrochloride are heated for 5 hours at 70° C. The reaction mixture is poured into cold water and the N-methyl-N-phenyl-N-(3,5-di-(2-dodecyl)-4-hydroxybenzyl)amine crystallized from the insoluble residues.

## EXAMPLE XIV

N,N-diphenyl-N-(3-isopropyl-5-tert-butyl-4-hydroxybenzyl)amine is prepared by reacting 97 parts of 2-isopropyl-6-tert-butyl phenol, 45 parts of 37 percent aqueous formalin solution, and 103 parts of diphenylamine hydrochloride in 800 milliliters of ethanol solvent. The reaction is carried out at 70° C. for 12 hours and then poured into cold water. The product is crystallized from the insoluble organic portion.

## EXAMPLE XV

Using 700 parts of ethanol as the solvent, N-methyl-N-β-naphthyl-N-(3,5-diisopropyl-4-hydroxybenzyl)amine is prepared by reacting 89 parts of 2,6-diisopropylphenol, 45 parts of 37 percent aqueous formalin solution and 110 parts of N-methyl-β-naphthyl amine hydrochloride. The reaction is carried out at 70° C. for 12 hours and

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then poured into cold dilute sodium bicarbonate solution. The product is then crystallized from the insoluble organic portion.

## EXAMPLE XVI

At 65° C., N,N-di-dodecyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine is prepared by reacting 103 parts of 2,6-di-tert-butylphenol, 45 parts of 37 percent aqueous formalin solution and 176 parts of di-dodecylamine for 6 hours. The reaction solvent used is 600 parts of ethanol. The product is obtained by pouring the reaction mixture into cold water, followed by crystallization of the insoluble residues from ligroin.

## EXAMPLE XVII

N-tert-butyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine is prepared by reacting 21 parts of 2,6-di-tert-butyl phenol, 8.4 parts of 37 percent aqueous formalin solution and 146 parts of tert-butyl amine. 1000 parts of ethanol is used as reaction solvent and the temperature is held at 30° C. for 4 hours. The solvent is evaporated at a pressure of 25 mm. of mercury and the residues poured into cold water. The product is crystallized from the insoluble organic portion.

## EXAMPLE XVIII

21 parts of 2,6-di-tert-butyl phenol, 8.4 parts of 37 percent aqueous formalin solution, and 100 parts of 2,6-diethyl aniline hydrochloride are stirred at 30° C. in 500 parts of ethanol for 12 hours. At the end of this time the solvent is evaporated at 30 mm. pressure of mercury and the residues washed with cold water. The product is crystallized from the insoluble organic portion to provide white crystals of N-(2,6-diethylphenyl)-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine.

It can be seen from the above illustrative examples that the primary or secondary amines used in the reaction can also be used in the form of their hydrohalide salts. This practice is sometimes advantageous.

To illustrate the useful properties of the novel compounds of this invention, recourse is had to the Polyveriform oxidation stability test as described in the paper entitled "Factors Causing Lubricating Oil Deterioration in Engines" (Ind. & Eng. Chem., Anal. Ed. 17, 302 (1945)). See also "A Bearing Corrosion Test for Lubricating Oils and Its Correlation with Engine Performance" (Anal. Chem., 21 737 (1949)). This test effectively evaluates the performance of lubricating oil anti-oxidants. The test equipment procedure employed and correlations of the results with engine performance are discussed in the first paper above cited. By employing various compounds of this invention in oxygen-sensitive lubricating oil, effective inhibition of oxidative deterioration is achieved.

Comparative tests were conducted using the method and apparatus essentially as described in the publication first above mentioned. One minor modification was that the steel sleeve and copper test piece described in this publication were omitted from the apparatus. In these tests an initially additive-free, 95 V.I. solvent-refined SAE-10 crankcase oil was used. The principal test conditions consisted of passing 70 liters of air per hour through the test oil for a total period of 20 hours while maintaining the oil at a temperature of 280° F. Oxidative deterioration of the oil was further promoted by employing as oxidation catalysts 0.05 percent by weight of ferric oxide (as ferric 2-ethyl hexoate) and 0.10 percent by weight of lead bromide, both of these amounts being based upon the weight of oil employed. Various lubricating oils of this invention were prepared by blending small amounts of typical compounds of this invention with other individual portions of the above lubricating oil. These compositions were then subjected to the above stringent oxidation test. The results of these tests are shown in Table I.

Table I.—Effect of antioxidants on oxidation of lubricating oil

Test No.	Additive	Additive Conc., percent by wt.	Acid No.	Viscosity Increase at 100° F., percent
1	None		5.6	189
2	N,N - dimethyl - N - (3,5 - diisopropyl - 4 - hydroxybenzyl) amine	1.0	2.9	63
3	N,N - dimethyl - N - (3,5 - diisopropyl - 4 - hydroxybenzyl) amine	2.0	2.0	51
4	N,N - dimethyl - N - (3,5 - di-tert - butyl - 4 - hydroxybenzyl) amine	1.0	0.27	8
5	N,N - dimethyl - N - (3,5 - di-tert - butyl - 4 - hydroxybenzyl) amine	2.0	0.18	8
6	N - methyl - N, N - bis - (3,5 - di-tert - butyl - 4 - hydroxybenzyl) amine	1.0	0.17	9
7	N - methyl - N, N - bis - (3,5 - di-tert - butyl - 4 - hydroxybenzyl) amine	2.0	0.20	12

By referring to the data presented in Table I, it is immediately apparent that the compounds of this invention effectively inhibit oxidative deterioration of lubricating oil. Furthermore, comparison of the results of Tests 4-7 inclusive with those of Tests 2 and 3 shows that while the preferred compounds of this invention (in this case N,N-dimethyl-N-(3,5-diisopropyl-4-hydroxybenzyl)amine) are very effective antioxidants, the most particularly preferred compounds of this invention (e.g. those used in Tests 4-7) are outstanding. For example, by comparing the results of Test 4 with Test 2 and Test 5 with Test 3, it is obvious that the most particularly preferred compounds of this invention are about ten times as effective as the preferred compounds of this invention. Generally speaking, this difference in effectiveness between the most particularly preferred compounds and the preferred compounds of this invention is in the order of a ten-fold difference.

To still further demonstrate the preeminence of the most particularly preferred compounds of this invention as antioxidants for use in lubricating oil, another series of comparative tests was conducted. In this instance the test procedure used was essentially as described above with the exception that still more stringent test conditions were employed. These conditions were brought about by conducting the Polyveriform oxidation stability test at a temperature of 300° F. In these tests comparisons were made between a sample of the above-described, additive-free crankcase lubricating oil and a separate portion of this oil with which had been blended 3 percent by weight of N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine. In Table II are shown the results of these tests.

Table II.—Effect of antioxidants on oxidation of lubricating oil

Test No.	Additive	Neutralization No.	Viscosity Increase at 100° F., percent
1	None	8.8	115
2	N,N - dimethyl - N - (3,5 - di-tert - butyl - 4 - hydroxybenzyl) amine	0.9	12

It is clearly evident from the data shown in Table II that even under more stringent oxidizing conditions, the compounds of the most particularly preferred embodiment of this invention (as represented in this instance by N,N-dimethyl-N-(3,5-di-tert-butyl - 4 - hydroxybenzyl)amine) are outstanding antioxidants for oxygen-sensitive oils.

The compounds of this invention are particularly effective antioxidants for use in steam turbine oils. This is demonstrated by making use of the standard test procedure

of the American Society for Testing Materials bearing ASTM designation D-943-54. According to this test procedure, 300 milliliters of a suitable test oil is placed in contact with 60 milliliters of water and the resulting oil-water system is maintained at a temperature of 95° C. while passing oxygen therethrough at a rate of 3 liters per hour. Oxidation is catalyzed by the use of iron and copper wire. Periodically measurements are made of the acid number of the test oil and failure of an antioxidant is indicated by an acid number in excess of 2.0. It is found that when the various compounds of this invention are added in small antioxidant quantities to steam turbine oils, substantial resistance against oxidative deterioration results.

The compounds of this invention are very effective antioxidants for grease. The potency of the compounds of this invention in this respect is demonstrated by conducting the Norma Hoffman Grease Oxidation Stability Test, ASTM test procedure D-942-50. It is found that the presence of minor proportions of the compounds of this invention in conventional greases greatly inhibits oxidative deterioration. By way of example an initially antioxidant-free lithium base grease was modified to the extent that it contained 0.5 percent by weight of N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine and was subjected to the above oxidation stability test. It was found that the presence of N,N-dimethyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine greatly retarded oxygen absorption by the grease. Thus, after maintaining this grease composition in the oxygen bomb for 376 hours under the standard test conditions, the oxygen bomb pressure had been reduced from 110 p.s.i. to 104 p.s.i. This represents an extremely small diminution of oxygen pressure in the light of the severe test conditions employed and is indicative of a negligible amount of oxygen absorption.

The results described above are merely illustrative of the effectiveness of the compounds of this invention when employed as antioxidants. The compounds of this invention effectively inhibit oxidation in industrial lubricants of the hydrocarbon type, such as lubricating oil, turbine oil, transformer oil, transmission fluids, glass-annealing oil, gear and machine lubricants, hydraulic lubricants and other industrial oils, grease and the like. As pointed out above, the compounds of this invention as a class are effective antioxidants. Furthermore, the compounds of the various embodiments of this invention substantially differ in effectiveness from one embodiment to another. For example, the compounds of the preferred class of this invention are more effective antioxidants than the compounds of this invention as a class. Still more effective are the particularly preferred compounds of this invention. As brought out by the experimental results described in connection with Table I above, the compounds of the most particularly preferred embodiment of this invention possess still greater effectiveness as antioxidants. In short, the compounds of the most particularly preferred embodiment of this invention are superlative antioxidants.

The compounds of this invention are also very effective antioxidants for high molecular weight hydrocarbon polymers, such as polyethylene, polystyrene, polyisobutylene, polybutadiene, isobutylene-styrene copolymers, natural rubber, butyl rubber, GR-S rubber, GR-N rubber, methyl rubber, polybutene rubber, piperylene rubber, dimethyl butadiene rubber, and the like.

The compounds of this invention are also useful in protecting petroleum wax—paraffin wax and micro-crystalline wax—against oxidative deterioration. The compounds of this invention also find use in the stabilization of edible fats and oils of animal or vegetable origin which tend to become rancid especially during long periods of storage because of oxidative deterioration. Typical representatives of these edible fats and oils are linseed oil, cod liver oil, castor oil, soybean oil, rapeseed oil, coconut oil, olive oil, palm oil, corn oil, sesame oil, peanut oil, babassu oil, butter, fat, lard, beef tallow, and the

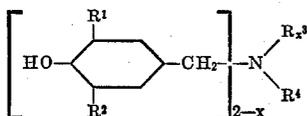
like. The compounds of this invention may also be used as antioxidants for gasolines containing lead alkyl anti-knock agents, such as tetraethyllead; concentrated formulations of tetraalkyllead compounds, such as pure tetraethyllead or tetraethyllead admixed with organic halogen scavengers, oxygen-sensitive diesel fuels, domestic heating oils, bunker and residual fuel oils, asphalt, and other organic material normally susceptible of oxidative deterioration.

The amounts of the compounds of this invention employed in the materials to be stabilized are dependent both upon the nature of the material itself and the oxidative conditions to be encountered. Generally speaking, amounts in the order of about 0.001 to about 3 percent by weight of the material to be protected are satisfactory. In some cases such as where the antioxidant is employed in an article normally subjected to severe oxidizing conditions, somewhat higher concentrations are useful.

The 2,6-dialkyl phenols which are employed as starting materials in the preparation of the compounds of this invention can be prepared by alkylating a phenol or an appropriate mono ortho alkyl phenol with an olefinic hydrocarbon in the presence of an aluminum phenoxide catalyst.

I claim:

1. A 3,5-dialkyl-4-hydroxybenzyl amine having the formula:



wherein R<sup>1</sup> is alkyl of from 1-12 carbon atoms, R<sup>2</sup> is alkyl of from 3-12 carbon atoms characterized by being branched on the alpha carbon atom, R<sup>3</sup> is selected from the group consisting of alkyl of 1-12 carbon atoms, cycloalkyl of 5-6 carbon atoms, hydrocarbon aralkyl of 7-11 carbon atoms, hydrocarbon aryl of 6-10 carbon

atoms and hydrocarbon alkaryl of 7-12 carbon atoms; R<sup>4</sup> is selected from the group consisting of hydrogen and R<sup>3</sup>, and x is 0 or 1.

2. N,N - dimethyl - N - (3,5 - di - tert - butyl - 4 -hydroxybenzyl)amine.

3. N - methyl - N,N - bis - (3,5 - di - tert - butyl - 4 -hydroxybenzyl)amine.

4. The compound of claim 1 where R<sup>3</sup> and R<sup>4</sup> are alkyl of 1-12 carbon atoms.

5. The compound of claim 1 wherein R<sup>3</sup> and R<sup>4</sup> are hydrocarbon alkaryl of 7-15 carbon atoms.

6. The compound of claim 4 wherein x is 1.

7. The compound of claim 5 wherein x is 0.

8. The compound of claim 6 wherein R<sup>1</sup> and R<sup>2</sup> are tertiary butyl groups.

9. N,N - dimethyl - N - (3,5 - diisopropyl - 4 -hydroxybenzyl)amine.

10. N - (2,6 - diethylphenyl) - N - (3,5 - di - tert - butyl - 4 -hydroxybenzyl)amine.

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