United States Patent [19]

Malec

[11] **3,900,410**

[45] **Aug. 19, 1975**

[54] **LUBRICATING OIL COMPOSITIONS CONTAINING TRIALKYL-SUBSTITUTED PHENOLS AND BENZOTRIAZOLE**

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[22] Filed: **Apr. 23, 1973**

[21] Appl. No.: **353,394**

[52] **U.S. Cl.**..... **252/51.5 R;** 252/50; 252/392

[51] **Int. Cl.**..... **C10m 1/32**

[58] **Field of Search**..... 252/51.5 R, 50, 42.7, 392

[56] **References Cited**

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Attorney, Agent, or Firm—Donald L. Johnson; Robert A. Linn; Joseph D. Odenweller

[57] **ABSTRACT**

Lubricating oil is protected against oxidative degradation by inclusion of a 2,6-di-C_{4-20}-tert-alkyl-4-n-C_{8-24} alkylphenol, e.g., 2,6-di-tert-butyl-4-n-dodecylphenol, and benzotriazole.

9 Claims, No Drawings

LUBRICATING OIL COMPOSITIONS CONTAINING TRIALKYL-SUBSTITUTED PHENOLS AND BENZOTRIAZOLE

BACKGROUND

Alkylphenols have been used to provide antioxidant protection for a broad range of organic materials. For example, 2,6-di-tert-butyl-4-methylphenol is a known commercial antioxidant used in polymers, rubber and as a food additive. Polyolefin use of 2,6-di-tert-butyl-4-dodecylphenol is disclosed in Neth. Pat. No. 64/**08010.** The dodecyl group appears to be a branched-chain secondary or tertiary alkyl because there is no method given for the preparation of the 4-n-alkyl derivative. In U.S. Pat. No. 3,717,611 the antioxidant use of 2,6-di-tert-butyl-4-dodecyl anisole and 2,6-di-tert-butyl-4-octadecyl anisole is disclosed. The anisole derivatives are made from the corresponding phenol. The dodecyl and octadecyl groups appear to be secondary or tertiary since those compounds in which the alkyl is normal are so specified.

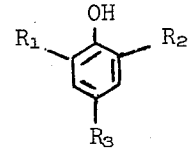
Synthetic ester lubricants containing benzotriazole in addition to other constituents are disclosed in U.S. Pat. No. 2,971,912. Lubricating oils containing phenylborate esters are reported in Br. Pat. No. 1,287,444 to give increased undercrown and piston skirt deposit which is said to be largely eliminated by inclusion of a heterocycle such as benzotriazole.

SUMMARY

According to the present invention, mineral lubricating oils are stabilized against oxidative degradation by the addition of a small antioxidant amount of a 2,6-di-tert-alkyl-4-C_{8-24}-n-alkylphenol and a small promoter amount of benzotriazole.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The phenolic additives of this invention are compounds having the formula:



wherein R_1 and R_2 are tert-alkyl groups containing 4 to about 20 carbon atoms and R_3 is a straight chain primary alkyl group containing 8 to about 24 carbon atoms.

Representative examples of these compounds are: 2,6-di-tert-amyl-4-n-decylphenol, 2,6-di-tert-octyl-4-n-tetracosylphenol, 2,6-di-tert-eicosy-4-n-dodecylphenol, and the like.

In a preferred embodiment, R_1 and R_2 are tert-butyl groups. These are represented by: 2,6-di-tert-butyl-4-n-decylphenol, 2,6-di-tert-butyl-4-n-dodecylphenol, 2,6-di-tert-butyl-4-n-tetradecylphenol, 2,6-di-tert-butyl-4-n-hexadecylphenol, 2,6-di-tert-butyl-4-n-octadecylphenol, 2,6-di-tert-butyl-4-n-eicosylphenol, 2,6-di-tert-butyl-4-n-docosylphenol and 2,6-di-tert-butyl-4-n-tetracosylphenol.

Additives of this invention are made by heating a 2,6-di-tert-alkylphenol with a straight chain primary alcohol of the desired chain length in the presence of potassium hydroxide and a cupric oxide catalyst. The alcohol is generally employed in stoichiometric excess. An amount of about 3–20 moles of alcohol per mole of phenol is satisfactory. Good results are obtained using about 0.5–0.2 mole of KOH per mole of alcohol. About 0.005–0.05 mole of cupric oxide per mole of 2,6-di-tert-alkylphenol gives good results. Reaction temperatures of about 200°–250°C. are preferred. Product can be recovered by distillation. In a highly preferred embodiment the reaction mixture is distilled to remove 2,6-di-tert-alkylphenol and other more volatile components and the residue used as the phenolic antioxidant of this invention.

The following example illustrates the manner by which the phenolic additives are prepared.

EXAMPLE 1

In a pressure reaction vessel was placed 326.1 grams of 2,6-di-tert-butylphenol, 1000 grams of n-decanol, 32.8 grams of 86 per cent KOH and 0.95 gram of cupric oxide. This mixture was stirred and heated to 225°C. and held at that temperature for 24 hours. Following this, the mixture was cooled, diluted with 250 ml toluene and washed with aqueous sodium bicarbonate. It was then washed with water until neutral and distilled under vacuum to isolate the product 2,6-di-tert-butyl-4-n-decylphenol (b.p. 155°C., 0.25–0.3 mm Hg).

EXAMPLE 2

In a pressure reaction vessel was placed 247.5 grams of 2,6-di-tert-butylphenol, 894 grams of n-dodecanol, 26.9 grams 86 per cent KOH and 1.2 grams cupric oxide. The vessel was flushed with hydrogen and pressurized to 100 psig with hydrogen. While stirring, it was heated to 235°C. and maintained at this temperature for 24 hours. Following this, it was cooled and discharged into dilute hydrochloric acid. Discharge was completed by adding 200 ml of toluene and 300 ml of hot water to the reaction vessel, which was combined with the discharged reaction mixture. The organic phase was washed with water until almost neutral (pH 6) and then dried over magnesium sulfate. Toluene and unreacted n-decanol was distilled from the reaction mixture, leaving 403 grams of residue which assayed 90 per cent 2,6-di-tert-butyl-4-n-dodecylphenol by VPC.

Other additives can be similarly prepared by substituting different straight chain alcohols containing from 8–24 carbon atoms.

The amount of antioxidant blended with the oil should be sufficient to impart the required degree of stability. Good results are achieved using about 0.01–3 weight per cent and, preferably, 0.05–1.5 weight per cent. The amount of benzotriazole should be an amount such that when used with the 2,6-di-tert-alkyl-4-C_{8-24}-n-alkylphenol good overall performance is obtained. A useful range is from about 0.01–0.5 weight per cent. Optionally, simple lower alkyl-substituted benzotriazoles can be used such as the C_{1-8} alkyl-substituted benzotriazoles, e.g., 3-methylbenzotriazole, 1,2,3-trimethylbenzotriazole, 6-sec-butylbenzotriazole, 4-tert-octylbenzotriazole, 4-sec-hexylbenzotriazole, and the like.

Other additives normally included in oil compositions can be beneficially used together with the additives of this invention. These include zinc dialkyldithiophosphates, calcium aryl sulfonates, overbased calcium aryl sulfonates, magnesium aryl sulfonates, barium phe-

nates, calcium phenates, barium polybutenyl ph phonates, V.I. improvers such as polybutene, ethylene-propylene copolymer, polylauryl methacrylate, dispersants such as polybutenyl succinimides of alkylenepolyamines, and the like.

The following example illustrates the preparation of a typical oil composition of this invention.

EXAMPLE 3

In a blending vessel place 10,000 pounds of SAE-30 neutral mineral oil. To this add 100 pounds of zinc dialkyldithiophosphate (7 weight per cent zinc), 50 pounds of 2,6-di-tert-butyl-4-n-dodecylphenol, 50 pounds calcium aryl sulfonate (overbased with colloidal calcium carbonate), 250 pounds ethylene-propylene copolymer and 400 pounds of a 50 per cent oil solution of a C_{70} polybutenyl succinimide of tetraethylenepentamine. Stir the mixture until homogenous to obtain an oil composition suitable for use in internal combustion engines.

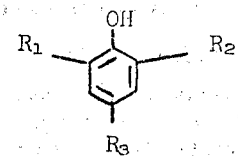
Tests have been carried out to demonstrate the effectiveness of the present compositions. These are oxidationcorrosion tests in which oil samples are prepared containing the test additive, 0.1 per cent lead bromide and a copper-lead bearing. These are heated to 300°F. and air bubbled through them for 48 hours at 48 liters per hour. Criteria of the additive effectiveness are the increase in acid number, increase in viscosity and bearing weight loss. The results obtained were as follows:

Additive	Acid No. Increase	Percent Viscosity Increase	Bearing Wt. Loss
None	5.4	63	37 mg
2,6-di-tert-butyl-4-n-dodecylphenol (1%)	4.2	35	164 mg
2,6-di-tert-butyl-4-n-dodecylphenol (1%) plus benzotriazole (0.05%)	0.4	10	11 mg
2,6-di-tert-butyl-4-n-decylphenol (1%)	1.0	16	64 mg
2,6-di-tert-butyl-4-n-decylphenol (1%) plus benzotriazole (0.05%)	0.3	11	12 mg
2,6-di-tert-butyl-4-n-octylphenol (1%)	0.5	12	28 mg
2,6-di-tert-butyl-4-n-octylphenol (1%) plus benzotriazole (0.05%)	0.2	14	11 mg

As the above results show, the phenolic additives are effective in preventing oxidative degradation but cause a large increase in bearing weight loss. Inclusion of benzotriazole not only greatly reduces the bearing weight loss but, in addition, sharply reduces the acid number increase and viscosity increase, thus contributing to the overall effectiveness of the antioxidant.

I claim:

1. A mineral lubricating oil composition containing an antioxidant amount of a compound having the formula:



wherein R_1 and R_2 are tert-alkyl groups containing 4 to about 20 carbon atoms and R_3 is a straight chain primary alkyl group containing 8 to about 24 carbon atoms and an antioxidant promoter amount of a benzotriazole.

2. A lubricating oil composition of claim **1** wherein said antioxidant compounds are 2,6-di-tert-butyl-4-n-C_{8-24}-alkylphenols.

3. A lubricating oil composition of claim **2** wherein said antioxidant compound is 2,6-di-tert-butyl-4-n-octylphenol.

4. A lubricating oil composition of claim **2** wherein said antioxidant compound is 2,6-di-tert-butyl-4-n-decylphenol.

5. A lubricating oil composition of claim **2** wherein said antioxidant compound is 2,6-di-tert-butyl-4-n-dodecylphenol.

6. A lubricating oil composition of claim **2** wherein said antioxidant compound is 2,6-di-tert-butyl-4-n-tetradecylphenol.

7. A lubricating oil composition of claim **2** wherein said antioxidant compound is 2,6-di-tert-butyl-4-n-hexadecylphenol.

8. A lubricating oil composition of claim **2** wherein said antioxidant compound is 2,6-di-tert-butyl-4-n-octadecylphenol.

9. A lubricating oil composition of claim **2** wherein said antioxidant compound is 2,6-di-tert-butyl-4-n-eicosylphenol.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,900,410

DATED : August 19, 1975

INVENTOR(S) : Robert E. Malec

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, in Claim 1, at lines 13-14, insert "about 0.01-0.5 weight per cent of" before "a benzotriazole"

Signed and Sealed this

fourteenth Day of *October 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

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