

[54] **TETRA-T-DODECYLAMARCAPTO-P-BENZOQUINONE**

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76,835 12/1954 Netherlands

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[52] **U.S. Cl.**..... **252/48.2, 260/396 R**

[51] **Int. Cl.**..... **C10m 1/42**

[58] **Field of Search**..... **252/48.2, 393; 260/396 R**

[57] **ABSTRACT**

A lubricating oil composition of improved corrosion, wear and oxidation inhibiting properties consisting of a hydrocarbon lubricating oil composition comprising a major amount of hydrocarbon lubricating oil and between about 0.1 and 10 wt. percent of tetra-t-dodecylmercapto-p-benzoquinone and optionally including additional automotive lubricating oil additives such as VI improvers, detergent-dispersants, anti-foamants and supplementary corrosion, wear and oxidation inhibitors.

[56] **References Cited**

UNITED STATES PATENTS

3,328,301 6/1967 Thompson et al..... 252/48.2 X

FOREIGN PATENTS OR APPLICATIONS

566,055 12/1944 Great Britain

2 Claims, No Drawings

**TETRA-T-DODECYLAMARCAPTO-P-
BENZOQUINONE**

BACKGROUND OF INVENTION

Lubricating oils employed in the lubrication of internal combustion engines normally contain additives imparting desired properties thereto such as detergent-dispersancy, oxidation resistance, corrosion resistance, wear resistance, antifoaming, etc. Since the demands on the automotive lubricating oil compositions have been becoming increasingly severe, a greater number and a greater quantity of additives in the lube oil formulations have been required. Many of the additives employed are metal containing, and therefore, the increased requirements result in undesirably increased metal deposits in the engines which in turn result in decreased engine efficiency. There is, therefore, a continuing need in the lube oil additive art to develop superior ashless, i.e., non-metal containing additives, in order to eliminate or reduce engine deposits caused by additive residues. Further, there is a continuing need in the interest of economy and in the interest of decreasing the chance of inter additive incompatibility to develop additives which have a multiplicity of functions.

One class of ashless lube oil additives are the tetraalkylmercapto-p-benzoquinones which are broadly known as dopes and extreme pressure agents in lubricating oils (Dutch Pat. No. 76,835). However, the tetraalkylmercapto-p-benzoquinones specifically described in the art such as tetra-n-dodecylmercapto-p-benzoquinone are in many respects undesirable additives for lube oils in that they increased wear and substantially contributed to the undesirable thickening of the lubricating oil during use.

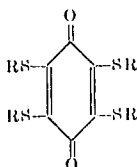
SUMMARY OF INVENTION

Surprisingly, I have discovered and this constitutes my invention that when one of the previously unrecognized members of the tetra-alkylmercapto-p-benzoquinone class, namely, tetra-t-dodecylmercapto-p-benzoquinone is incorporated in a hydrocarbon lubricating oil it unexpectedly imparts thereto improved wear and oil thickening resistant properties and further imparts thereto unexpectedly superior corrosion and oxidation resistant properties.

DETAILED DESCRIPTION OF THE INVENTION

More specifically, I have found when tetra-t-dodecylmercapto-p-benzoquinone is incorporated in a hydrocarbon lubricating oil in amounts between about 0.1 and 10 wt. percent, it not only does not have the negative properties of accelerating oil thickening and contributing to wear attributed to members of its class, but actually inhibits oil thickening, promotes wear resistance and in addition is many times superior in promoting resistance to corrosion and oxidation than closely related members of its class.

The tetra-t-dodecylmercapto-p-benzoquinone additive can be characterized by the formula:



where R is tertiary dodecyl group characterized by the formula:



where R¹, R² and R³ are alkyl groups such that R¹ + R² + R³ equal 11 carbon atoms. Specific examples are where R² and R³ are methyl and R¹ is a trimethylhexyl group and where R² and R³ are ethyl and R¹ is heptyl. Hereinbefore and hereinafter the term "t-dodecyl" denotes a single isomeric form as well as isomeric mixtures.

The tetra-t-dodecylmercapto-p-benzoquinone additive is incorporated in the lubricating oil base by standard means such as by direct addition to the base accompanied with agitation, e.g., stirring, to insure uniform distribution throughout or may be incorporated as a lube oil concentrate, e.g., 50-50 weight mixture of the benzoquinone and a light lubricating oil (100 SUS at 100° F.) with the concentrate being added to the lubricating oil base accompanied by agitation.

Suitable base oils useful in the compositions of the invention as well as diluent to form the tetra-t-dodecylmercapto-p-benzoquinone lube oil concentrate include a wide variety of hydrocarbon lubricating oil such as naphthenic base, paraffinic base mineral oils or other hydrocarbon lubricants, e.g., lubricating oils derived from coal products and synthetic hydrocarbons, e.g., polyalkylene such as polypropylene and polybutylene of a molecular weight between about 250 and 2,500. Advantageously, the base oils have an SUS viscosity at 100° F. between about 50 and 2,000 and constitute between about 90 and 99.9 wt. percent of the lube oil composition.

In the finished lubricating oil compositions other additives may be included. These other additives in addition to supplementary wear, oxidation and corrosion additives, may be any of the standard suitable additives such as detergent-dispersants, e.g., calcium carbonate overbased calcium petroleum sulfonates having a total base number of about 200 to 500 or more as set forth in U. S. Pat. No. 3,537,996 utilized in an amount of between about 1 and 6 wt. percent and/or ethoxylated inorganic phosphorus acid free, steam hydrolyzed polybutene (1,000-5,000 m.w.)-P₂S₅ reaction product as set forth in U. S. Pat. No. 3,087,956 utilized in an amount between about 2 and 6 wt. percent, VI improvers such as the polymethacrylates, e.g., the copolymers of dodecyl and octadecyl methacrylates having an intrinsic viscosity in benzene at 77° F. of between about 0.1 and 1 and utilized in an amount of between about 0.05 and 1 wt. percent and antifoamants such as the polysilicones in amounts of 10 to 1,000 ppm. Exactly what other additives are included in the finished oil compositions and the particular amounts employed depends on the particular use and severity to which the finished oil product is to be subjected.

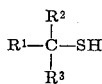
The following examples further illustrate the compositions of the invention but are not to be construed as limitations thereof:

EXAMPLE I

This example illustrates a method of preparing the tetra-t-dodecylmercapto-p-benzoquinone additive.

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To a reactor there was charged 101 grams (0.5 mole) of t-dodecylmercaptan wherein the mercaptan is composed principally of an isomer of the chemical structure characterized by the formula:



where R² and R³ are methyl and R¹ is trimethylhexyl, 113 grams of naphthenic lubricating oil of an SUS viscosity of about 100 at 100° F. and 200 mls. of methanol. The resultant mixture was stirred and there was added to the stirred mixture 21 grams (0.5 mole) of sodium hydroxide at a temperature of 37° C. The resultant reaction mixture was cooled to room temperature and there was added 32 grams (0.125 mole) of chloranil (tetrachloroquinone) over 1-2 hours, the temperature rising to 60° C. Then the resultant mixture was refluxed for 1 hour at 72° C. followed by atmospheric distillation to 100° C. and thence cooled to room temperature. The mixture was diluted with pentane, filtered and stripped. The resultant solid product was analyzed and the following found: wt. percent sulfur 6.7 (calc. 7 percent), wt. percent sulfur as mercaptan 0.16, wt. percent metal 0.16 (0 percent calc.), wt. percent chlorine 0.11 (0 percent calc.).

EXAMPLE II

This example illustrates the surprising effectiveness of the tetra-t-dodecylmercaptan-p-benzoquinone in lubricating oil compositions.

Three test lubricant compositions were prepared. In Composition A representative of the lubricant compositions of the invention tetra-t-dodecylmercaptan-p-benzoquinone was employed. In comparative Composition B there was substituted tetra-n-dodecylmercaptan-p-benzoquinone. Comparative Composition C was identical to Compositions A and B but contained no benzoquinone ingredient. In both Compositions A and B the formulation was as follows: 89.67 wt. percent paraffinic lube oil of an SUS viscosity of about 130 at 100° F., 0.93 wt. percent of the benzoquinone, 6 wt. percent of lube oil concentrate containing 44 wt. percent of ethoxylated, inorganic phosphorus acid free, steam hydrolyzed polybutene (1,200 m.w.)-P₂S₅ reaction product, 2.9 wt. percent lube oil concentrate containing about 50 wt. percent of an overbased calcium petroleum sulfonate having a total base number of about 300 and 0.5 wt. percent of a lube oil concentrate containing 40 wt. percent of a copolymer of dodecyl and octadecyl methacrylate in approximately a 4 to 1 weight ratio, said copolymer having an intrinsic viscosity of about 0.58 in benzene at 77° F. The finished oil formulations of A and B had a sulfur content of 0.13 wt. percent contributed by the tetraalkylmercaptan-p-benzoquinone, a 0.06 wt. percent phosphorus content contributed by the polybutene-P₂S₅ reaction product and 0.35 percent calcium contributed by the overbased calcium sulfonate. Composition C consisted of 90.6 wt. percent of the lube oil, 6 wt. percent of the ethoxylated concentrate, 2.9 wt. percent of the sulfonate concen-

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trate and 0.5 wt. percent of the polyacrylate concentrate.

Compositions A, B and C were subjected to three lubrication tests:

5 The MacCoull Corrosion Test outlined in U. S. Pat. No. 3,549,534 which measures the corrosion in terms of bearing weight loss, the greater the weight loss the greater the degree of corrosion. The MacCoull test further measures the degree of oxidative thickening under the MacCoull test conditions, the greater the kinematic viscosity the greater the thickening.

10 The second test employed was the Four Ball Wear Test described in U. S. Pat. No. 3,384,588 which is the measure of the amount of wear the lubricating oil permits under engine test conditions. The greater amount of wear, the poorer the ability of the test oil composition to prevent such wear. This wear is measured in terms of millimeter wear.

20 The final test was the Oxygen Absorption Test. It measures the number of hours that it takes for a 25 gram test sample at 340° F. to absorb 500 mls. of oxygen. The longer the time that is required for oxygen absorption, the greater the resistance of the test composition to oxidation.

25 Composition A and comparative Compositions B and C were tested and the test data and results are reported below in Table I:

TABLE I

30 Composition	A	B	C
Tetra-alkylmercapto-p-benzoquinone additive MacCoull Corr. Test, 20 hrs. Bearing wt. loss, mg. at 10 hours at 20 hours	Tertiary Dodecyl	Normal Dodecyl	None
Used Oil Tests (20 hrs.)			
Neut. No.	9.2	Too thick to determine	10.4*
Kin. Visc. at 100°, cs.	131.4		179.8*
Oxygen Absorption Test, 340° F. Hrs. to absorb 500 mls. O ₂ per 25 g. sample	7.8	4.3	2.0
4-Ball Wear Test, mm. (2 hr./40 kg., 200° F., 600 rpm) *at 10 hours	0.33	0.51	0.38

I claim:

- 45 1. A lubricating oil composition comprising a major amount of a hydrocarbon lubricating oil containing between about 0.1 and 10 wt. percent of tetra-t-dodecylmercaptan-p-benzoquinone
- 50 2. A lubricant composition comprising between about 2 and 6 wt. percent of an ethoxylated, inorganic phosphorus acid free, steam hydrolyzed polybutene (1,000-5,000 m.w.)-P₂S₅ reaction product, between about 1 and 6 wt. percent of a calcium carbonate overbased calcium petroleum sulfonate of a total base number between about 200 and 500, between about 0.05 and 1 wt. percent of a dodecyl methacrylate-octadecyl methacrylate copolymer having an intrinsic viscosity in benzene at 77° F. of between about 0.1 and 1.0, between about 0.1 and 10 wt. percent tetra-t-dodecylmercaptan-p-benzoquinone and the remainder being hydrocarbon lubricating oil of an SUS viscosity between about 50 and 2,000 at 100° F.

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