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3,492,234

ORGANIC COMPOSITIONS CONTAINING
POLYALKYLATED NAPHTHOL

Harry J. Andress, Jr., Pitman, and Albert L. Williams,
Princeton, N.J., assignors to Mobil Oil Corporation, a
corporation of New York

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10 Claims

ABSTRACT OF THE DISCLOSURE

Organic compositions containing polyalkylated naphthols having up to 30 carbon atoms per alkyl group possess high temperature antioxidant properties at temperatures of 600° F. and higher. These polyalkylated naphthols are produced by reacting an olefin with a naphthol in the presence of a boron trifluoride type catalyst.

CROSS-REFERENCES TO RELATED
APPLICATIONS

The present application is a continuation-in-part of U.S. Ser. No. 603,138 filed Dec. 20, 1966, now abandoned, which in turn is a continuation-in-part of U.S. Ser. No. 358,375 filed on Apr. 8, 1964, now abandoned.

BACKGROUND OF THE INVENTION

Field of the invention

As is well known in the art, many organic industrial fluids, such as lubricating oils, are subject to oxidative deterioration under conditions of modern use. As a result, acidic oxidation products are formed which exert a corrosive effect on metal parts and which produce formations of varnish and sludge on engine surfaces; thus, lowering the operating efficiency of the engine. Such oxidative deterioration is a severe problem under the high temperature conditions prevailing in higher powered modern engines. With the development of more powerful engines including free piston and gas turbine engines for trucks and autos as well as turbine engines for high speed jet aircraft, the need for lubricants possessing good high temperature stability has greatly increased.

Description of the prior art

The following patents may be referred to: U.S. Patent Nos. 2,191,499, 2,194,312, 2,691,634 and 2,831,898.

The first reference relates to wax petroleum phenols and a process for making it. The second reference relates to producing wax phenol and naphthols. The third reference relates to forming resinous compounds produced from chlorinated paraffin wax and resinified hydroxy aromatic compounds. The fourth reference relates to the product of reaction between a phenol (including naphthol) and an olefin under the catalytic influence of a metal phenolate, which may be the same as or different from the phenol being alkylated.

SUMMARY OF THE INVENTION

In accordance with the present invention it has been found that the foregoing and additional objects can be accomplished by incorporating into organic fluid compositions minor amounts of certain polyalkylated naphthols. We have found that the polyalkylated naphthols hereinafter described are surprisingly capable of imparting oxidation resistance particularly under high temperature conditions, from 500° F. and above, to lubricating oil compositions.

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DESCRIPTION OF THE PREFERRED
EMBODIMENTS

In general, these polyalkylated naphthols are either alpha or beta-naphthols containing at least two alkyl groups attached to the naphthol nucleus, the alkyl groups being selected so that the sum total of carbon atoms for all the alkyl groups present is at least twelve.

The alkyl groups which supply the minimum of twelve carbons may, in general, possess straight chain or branched chain structures. Some examples of suitable groups include hexyl, heptyl, nonyl, dodecyl, pentadecyl, hexadecyl, octadecyl, eicosyl, tetracosyl, heptacosyl, triacontyl etc. or mixtures thereof. Thus, alkyls containing from 6 to about 30 carbon atoms, derived from olefinic hydrocarbons, are used.

While the naphthols nucleus must contain a minimum of two alkyl groups, the maximum number of alkyl groups present is seven which is the limit of available positions on the nucleus. A preferred class of polyalkylated naphthols contain from 2 to 4 alkyl groups.

As some further examples of the polyalkylated naphthols of the invention there may be mentioned: di-(hexyl)-1-naphthol, di-(octadecyl)-1-naphthol, tri-(dodecyl)-1-naphthol, tetra-(hexadecyl)-1-naphthol, tri-(tetrapropyl)-1-naphthol, tri-(hexadecyl)-2-naphthol, di-(dodecyl)-2-ethyl-1-naphthol, tri-(C₁₂-C₂₀)-1-naphthol, and the like.

According to another and preferred aspect of the invention, we have found that polyalkylated naphthols of the general type herein described exhibit especially superior anti-oxidant properties at high temperatures when the alkyl groups present are primary or secondary alkyl groups. As used herein the terms primary or secondary alkyl groups refer to alkyl groups wherein the carbon atom of the alkyl group adjacent to and directly attached to the naphthol nucleus is derived from a primary or secondary carbon atom. These primary or secondary alkyl groups may contain branched chains and tertiary carbon atoms elsewhere in the alkyl group, the important factor is that the carbon directly attached to the naphthol nucleus be derived from a primary or secondary carbon.

The present antioxidants may be relatively pure compounds or mixtures of various polyalkylated naphthols containing different alkyl groups or combinations of alkyl groups attached to the naphthol nucleus. For example, the polyalkylated products prepared using a C₁₂-C₂₀ olefin fraction, are mixtures of different polyalkylated naphthols, the particular alkyl groups attached to the nucleus being generally dependent on the relative proportions of the different olefins in the C₁₂-C₂₀ fraction.

The polyalkylated 1- or 2-naphthols of this invention are prepared by reacting the naphthols with an olefin or a mixture of olefins, in the presence of a boron trifluoride catalyst, such as the boron trifluoride etherates.

The amount of polyalkylated naphthols employed in the organic compositions of this invention will depend on various factors such as the particular polyalkylated naphthol compound employed, the nature of the composition, the presence or absence of other additives, etc. In lubricating compositions, the polyalkylated naphthol may be employed in amounts from about 0.1 to about 10 wt. percent, preferably from about 1 to about 5 wt. percent.

The polyalkylated naphthols described herein are surprisingly effective antioxidants for lubricating compositions. These compounds are effective in lubricants which are subjected to elevated temperatures, particularly elevated temperatures such as in the range from about 500° to about 800° F. As a result, the instant polyalkylated naphthols may be used in a variety of lubricants such as automobile lubricants, marine oils, hydraulic fluids, industrial lubricants, etc. which may require good oxidation

resistance at high temperatures. The present antioxidants are excellent for use in jet engine lubricants and the like.

Further details of the invention will be apparent from the following specific embodiments.

EXAMPLE 1

A mixture of 96 grams (0.67 mol) 1-naphthol, 168 grams (2 mols) 1-hexene, and 30 grams boron trifluoride-ethyl etherate was stirred at 70° C. for nine hours. The reaction mixture was washed with hot distilled water until the washings were neutral to litmus. Topping at 225° C. under reduced pressure gave a yield of 236 grams of a product that was chiefly di-(hexyl)-1-naphthol.

closed system. A pump continuously circulated air through the oxidation chamber where the oil is oxidized in a thin film on the spinning disk. The oxygen consumed is replaced continuously and automatically from an oxygen reservoir. Upon leaving the disk the oxidation of the oil is stopped by passing it through a water jacket held at 90° F. After ten passes over the disk the test is stopped and the deposits on the disk are measured.

Test runs were also conducted on oil blends containing di-2-ethylhexyl sebacate oil.

Further details as to the test procedures are described in ASME paper No. 8 presented at the joint symposium of the ASME and ASLE at New York City, 1959.

The results are reported in the following Table I.

TABLE I.—THIN FILM OXIDATION TEST AT 575° F.

Test No.	Base oil	Antioxidant	Mol per kg. oil	Wt. percent	(ml. O ₂ per 5 min.)	Oxygen uptake Lacquer on disk
1	White oil+1	None				>500
2	do 1	1-naphthol	0.035	0.5	350	Heavy.
3	do 1	Di-(2-hexyl)-1-naphthol	0.035	1.2	35	Very light.
4	do 1	Tri-(tetrapropyl)-1-naphthol	0.035	2.25	30	Do.
5	do 1	Di-(2-octadecyl)-1-naphthol	0.035	2.25	30	Vo.
6	do 1	2-naphthol	0.035	0.5	470	Medium.
7	do 1	Tetra-(C ₁₂ -C ₂₀)-2-naphthol	0.035	3.7	20	Very light.
8	Di-2-ethylhexyl sebacate	None				>500
9	do	Di-(tetrapropyl)-2-ethyl-1-naphthol	0.035		30	Do.

¹ K.v. at 210° F.=8 cs.

EXAMPLE 2

A mixture of 200 grams (1.39 mols) of 1-naphthol, 700 grams, (4.17 mols) propylene tetramer, and 36 grams boron trifluoride-ethyl etherate was stirred at 90° C. for about 12 to 14 hours. The reaction mixture was washed with hot distilled water until the washings were neutral to litmus. The final product, a tri-(tetra-propyl)-1-naphthol, was obtained by topping at 230° C. under reduced pressure.

EXAMPLE 3

A mixture of 102 grams (0.17 mol) of 1-naphthol, 357 grams (1.42 mols) 1-octadecene, and 45 grams boron trifluorideethyl etherate was stirred at 95° C. for about 10 to 12 hours. The reaction mixture was washed with hot distilled water until the washings were neutral to litmus. The final product, a di-(octadecyl)-1-naphthol, was obtained by topping at 240° C. under reduced pressure.

EXAMPLE 4

A mixture of 120 grams (0.833 mol) of 2-naphthol, 767 grams (3.33 mols) Adecene A51, a commercial product, comprising 6% 1-dodecene, 14% 1-tetradecene, 42% 1-hexadecene, 33% 1-octadecene, 5% 1-eicosene and averaging about 230 molecular weight, herein referred to for convenience as the C₁₂-C₂₀ fraction and 35 grams boron trifluoride-ethyl etherate was stirred at 90° C. for about 10 hours. The reaction mixture was washed with hot distilled water until the washings were neutral to litmus paper. The final product, a tetra-(C₁₂-C₂₀)alkylated 2-naphthol, was obtained by topping at 225° C. under reduced pressure.

The effectiveness of the polyalkylated naphthol antioxidant of this invention is illustrated in the Thin Film Oxidation Test which simulates the conditions to which a lubricating oil is exposed at high temperatures.

THIN FILM OXIDATION TEST

According to this test each antioxidant is dissolved in a white oil (K.V. at 210° F.=8 cs.) at 0.035 mols per kg. of blend. The oil sample is pumped through a preheater where it is heated to the test temperature (575° or 600° F.) into a closed oxidation chamber where the oil is brought into contact with heated pure aluminum disk spinning at 2500 r.p.m. The contact time of the oil on the disk is about one second. The oxidation chamber is a

It will be seen from the above data that the oil compositions containing the non-alkylated 1- and 2-naphthols (tests 2 and 6) exhibited high oxidation rates of 350 and 470 (ml. O₂/5 min.) respectively. By contrast, the polyalkylated naphthols of the invention exhibit oxidation rates in all instances below 100 and in some cases as low as 20 (test 7).

As indicated in previous patents, it is known to employ certain alkylated phenols. It has been found in accordance with this invention, that such substituted phenols do not provide satisfactory antioxidant protection at the temperatures contemplated in this invention. Several of these phenols were tested by the Thin Film Oxidation Test described previously. The compositions tested in this series included the white oil used in the earlier tests alone and in the presence of alkylated phenols and naphthols prepared in accordance with the method described in this invention and illustrated in the examples. A naphthol or a phenol was reacted with the olefin in the presence of boron trifluoride etherate catalyst. The concentrations of each additive in the oil sample was 0.035 mol per kg. of oil.

The evaluations in this series of tests were made after one pass over the disk and after the tenth and last pass. The volume of the oxygen consumed during the 1-cycle and 10-cycle periods is regarded as indicating the ability of the additive to perform as an antioxidant. The temperature of the test is at 575° F. The results are tabulated below in Table II.

TABLE II

Compositions tested	Oxygen uptake (ml. O ₂ per 5 min.)	
	Cycle 1	Cycle 10
White oil	1,000	
White oil+tri-(C ₁₁₋₁₃)-phenol	230	335
White oil+tri-(C ₁₅₋₂₀)-phenol	130	130
White oil+di-(dodecyl)-p-phenyl phenol	230	280
White oil+tri-(dodecyl)-1-naphthol	25	20
White oil+di-(dodecyl)-2-ethyl-1-naphthol	30	30
White oil+tri-(C ₁₂₋₂₀)-1-naphthol	30	25

The results tabulated in Table II show that phenol additives provide unsatisfactory antioxidant protection at high temperatures whereas the naphthol derivatives of this invention provide as much as 3 to 10 times the improvement over that of the phenol.

Also, as indicated in a previous patent (U.S. 2,831,898), it is known to employ certain alkylated naphthols prepared from naphthol and an olefin using a metal phenolate, such as aluminum phenolate, as the catalyst. It has been found that alkylated naphthols prepared in this manner are not satisfactory antioxidants under the temperature conditions of this invention.

The unsatisfactory performance of alkylated naphthols prepared by using metal phenolates as catalyst is shown using a product made with the reactants of Example 3 above, but using reaction temperatures in accordance with Example 10 of 2,831,898. In particular, 102 grams (0.71 mol) of 1-naphthol was added to a suitable reactor and 1.5 gram of aluminum turnings was added thereto in small increments over about 1 hour at 170° C. The mixture was stirred for 1 hour at 170° C., and then cooled to 50° C. To the mixture was added 357 grams (1.42 mol) of 1-octadecene, and the resulting mixture was stirred at 300° C. for 2 hours. The mixture was cooled to 100° C. and 300 grams of water was added. The temperature was maintained at 100° C. for about 1 hour, whereupon the mixture was filtered and fractionated under high vacuum.

The resulting product, which was prepared using proportions of reactants sufficient to yield a disubstituted naphthol, was evaluated in the Thin Film Oxidation Test using the same white oil of the above tests. The product was present to the extent of 2.25% by weight of the oil. The test was run at 575° F. Results showed that the oxygen uptake of the oil, in ml. of O₂ per 5 minutes, was 123.

A comparison of the results obtained with the aluminum phenolate catalyzed product with the result using the product from the same reactants, but with a boron trifluoride catalyst (see page 9, Test No. 5) will show the unexpected superiority of the latter.

The polyalkylated naphthols of the invention may be employed to improve the high temperature oxidation stability of lubricating oils of various origins and characteristics. Such lubricating oils include both mineral oils as well as synthetic oils, e.g., synthetic esters, synthetic hydrocarbons, silicones, etc. Mineral oils include oils obtained from different crudes either naphthenic, paraffinic, mixed base, etc., solvent refined, acid refined, hydrocracked etc. Synthetic oils include alkylene polymers such as polymers of propylene, butylene, etc., alkylene oxide polymers, di-carboxylic acid esters, liquid esters of phosphorus, polypropylene glycol, di-(2-ethylhexyl) sebacate, di-(2-ethylhexyl) adipate, esters of pentaerythritol, neopentyl glycol, polyalkyl silicone polymers etc. The polyalkylated naphthols may also be used in grease compositions produced from the above fluids. Other base media aside from the lubricating oils include solid compositions such as natural and synthetic rubbers, including the GR-S type butadiene-styrene resins, polybutylene rubbers, polyisobutylene rubbers, polyvinyl resins, polyester resins and the like.

The organic compositions of the present invention may, of course, also contain effective quantities of typical additives normally used in said compositions such as detergents, rust inhibitors, pour point improvers, V.I. improvers, supplemental antioxidants etc.

It will be appreciated that many variations and modifications can, of course, be practiced without departing from the spirit and scope of the present invention.

Having thus described the present invention what we desire to secure by Letters Patent is:

1. A lubricating oil composition comprising a major proportion of a lubricating oil and a minor proportion sufficient to inhibit oxidative deterioration thereof under high temperature conditions of a product produced by reacting a naphthol with an olefin containing from 6 to about 30 carbon atoms in the presence of a boron trifluoride catalyst, at a mol ratio of at least 2 mols of olefin per mol of naphthol.

2. The composition of claim 1 wherein the amount of mols of olefin per mol of naphthol is from 2 to 4.

3. The composition of claim 1 wherein the olefine is hexene.

4. The composition of claim 1 wherein the olefin is octadecene.

5. The composition of claim 1 wherein the olefin is propylene tetramer.

6. The composition of claim 1 wherein the olefin is a mixture of olefins having from 12 to 20 carbon atoms.

7. The composition of claim 1 wherein the lubricating oil is a mineral oil.

8. The composition of claim 1 wherein the lubricating oil is a synthetic ester oil.

9. The composition of claim 8 wherein the synthetic ester oil is di-(2-ethylhexyl sebacate).

10. The lubricating oil composition of claim 1 wherein the said reaction product is a substantially neutral, topped reaction product.

References Cited

UNITED STATES PATENTS

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2,623,855	12/1952	Garner	252—404 X
2,831,898	4/1958	Ecke et al.	252—52 X

DANIEL E. WYMAN, Primary Examiner

W. CANNON, Assistant Examiner

U.S. Cl. X.R.

252—52, 404; 260—45.95, 624

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,492,234 Dated January 27, 1970

Inventor(s) HARRY J. ANDRESS, JR. and ALBERT L. WILLIAMS

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

In Table I, the headings of the last two columns thereof reading

(ml. O ₂ per 5 min.)	Oxygen uptake Lacquer on disk
should read	

Oxygen uptake (ml. O ₂ per 5 min.)	Lacquer on disk
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In Table II, under the heading "Cycle 10", the number "20" should read --25--.

In column 6, line 21, "olefine" should read --olefin--.

SIGNED AND
SEALED
JUL 7 1970

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents