United States Patent Office 3,368,975 Patented Feb. 13, 1968

3,368,975

ANTIOXIDANTS

Thomas G. Davis and John W. Thompson, Kingsport, Tenn., assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

No Drawing. Filed June 2, 1966, Ser. No. 554,673
8 Claims. (Cl. 252—51.5)

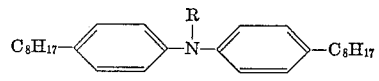
ABSTRACT OF THE DISCLOSURE

N-(C_1–C_{14} alkyl)-p,p'-dioctyl-diphenylamines as antioxidants for lubricating oils, especially synthetic lubricants such as jet lubricants.

DISCLOSURE

This invention relates to the use of C_1–C_{14} N-alkyl-substituted-p,p'-dioctyldiphenylamines as antioxidants for lubricating oils, especially synthetic lubricants such as jet lubricants.

U.S. 2,691,632 discloses p,p'-dioctyldiphenylamine as an oil antioxidant. N-alkyl-substituted-diphenylamines of no specified use are disclosed in U.S. 2,558,285. By use of such amines as antioxidants in jet lubricants, which are subjected to extremely high temperatures, sludging tendencies or antioxidant inactivity is sometimes encountered. We have found surprisingly that N-alkyl-p,p'-C_1–C_{14} dioctyldiphenylamines minimize such sludging tendencies in jet lubricants, especially in ester-type lubricating oil formulations for aircraft turbine engines, and cause a high degree of lasting antioxidant effect and high-temperature resistance. Also, our novel N-alkyl-p,p'-dioctyldiphenylamines give low coking values when in contact with air and hot metal surfaces. Their structural formula can be represented as follows:



R is a C_1–C_{14} alkyl. The octyl group C_8H_{17} can be either straight or branched-chain. Preferred are N-methyl-p,p'-dioctyldiphenylamine, N-ethyl-p,p'-dioctyldiphenylamine and N-dodecyl-p,p'-dioctyldiphenylamine.

The concentration of the arylamine to be used will depend on the ester base oil in which used and the degree of stability desired to be imparted thereto. A general range is about 0.10% to 5.0% by weight, and a preferred range is about 0.5% to 3.0% by weight.

The following examples are illustrative of our invention.

Example I.—Preparation of N-ethyl-p,p'-dioctyldiphenylamine

N-ethyl-p,p'-dioctyldiphenylamine is prepared by the following procedure.

980 g. (2.5 m.) p,p'-dioctyldiphenylamine + 1820 g. (15 m.) triethylphosphate + 50 g. p-toluene-sulfonic acid were combined in a 5-liter flask, heated between 190–200° C., with stirring, for 5 hrs. The mixture was then cooled to 100° C. and poured into 4 liters of 88% isopropanol and stirred until the temperature reached 30° C. The solution was then chilled in a cold bath, and the solids filtered out. After standing approximately 72 hrs. the solid material was recrystallized twice from ethanol to yield 738 g. of tan colored crystals with a melting point of 66–67° C., 71% yield.

Example II.—Preparation of N-methyl-p,p'-dioctyldiphenylamine

N-methyl-p,p'-dioctyldiphenylamine is prepared by the procedure of Example I using trimethylphosphate as the alkylating agent.

Example III

Table 1 illustrates use of our N-alkyl-p,p'-dioctyldiphenylamine as antioxidant in a pentaerythritol mixed ester. A modified version of the Wright Air Development Division (WADD) oxidation test was used. The results recorded in Table 1 demonstrate the improved oxidative stability of the high-temperature antioxidants of this invention over related prior art additives. Our antioxidants are also shown in Table 1 to be cleaner than those of the prior art. The original test is described in a paper entitled "Materials for High Temperature Jet Engine Lubricants" (H. E. Adams) in Wright Air Development Command (WADC) Technical Report 59–244 (U.S. Air Force, 1959). In the instant test a 250-ml. sample of lube oil was heated to 500° F. in a Pyrex test tube while 5 liters of air per hour were blown through the oil. Freshly polished 1" x 1" x 1/32" coupons of steel, aluminum, titanium and silver were assembled in accordance with method 5308.4 of Federal Test Method Standard 791 and immersed in the oil. The tube was capped with a Pyrex fitting which allows volatile products to escape. The oil was heated in 20 hour cycles. At the end of each cycle the tube was cooled, a 10-ml. oil sample withdrawn for analysis and the oil lost by evaporation replaced. The test was continued to approximately a 100% increase in viscosity. The 10-ml. sample was analyzed for viscosity in centistokes at 100° F., acid number and sludge in the oil. The sludge was determined by filtereing 2 ml. of the 10-ml. sample through Whatman No. 2 filter paper and washing with naphtha to remove the oil. The sludge on the pad was then rated according to a rating schedule where 0 is clean, 2= trace, etc. for increasing amounts of sludge. The results of this test are recorded in Table 1, which follows. Increase in antioxidant potency is shown by longer time to 100% viscosity increase.

TABLE 1.—ANTIOXIDANT COMPARISON 500° F. IN WADC TYPE TEST [1]

Antioxidant at 2.0% w./w. in pentaerythritol tetra(octanoate/2-ethyl hexanoate 50/50	Hours to 100% viscosity increase	Varnish, deposits sludge rating
N-pheny-1-naphthylamine	45	Heavy.
p,p'-dioctyldiphenylamine	28	Do.
N-ethyl-p,p'-dioctyldiphenylamine	50	Light.
N-methyl-p,p'-dioctyldiphenylamine	40	Do.
Base oil, no antioxidant	25	Heavy.

[1] 250 ml. oil, 5 liters air/hr., Al, Fe, Ag, Ti, stainless steel.

Example IV

This example illustrates the use of our antioxidants where the oils have a tendency to form carbonaceous deposits or coke when in contact with a hot metal surface in the presence of air. This is an important factor in selection of antioxidants for oils to lubricate engines of a supersonic transport where heat rejection rates of the oil will be high due to increased engine temperatures at high speeds.

For this example a Model C panel coker was used with certain variations. The standard Model C panel coker test is outlined in the "Detailed Handbook on Test Procedures in Support of Turbojet and Turboprop Lubricants," WADC, March 1957. This procedure was varied to regulate the sump oil to a controlled 400° F. Briefly this test involved a sample of the lubricant splashed upon a stainless steel panel heated to 700° F., and controlled at that temperature for a period of 8 hours. The weight of solid decomposition products accumulated on the test panel over this period was determined. A visual rating of the oil sump and cover was made.

Table 2 below illustrates the benefits of use of our novel antioxidants in this type test. This example also shows the antioxidant utility of our compound in different

esters and at different concentrations. It is to be noted that in each instance the N-ethyl-p,p'-dioctyldiphenylamine gave less coke than N-phenyl-1-naphthylamine or p,p'-dioctyldiphenylamine. The compound N-methyl-p,p'-dioctyldiphenylamine also gave a cleaner lubricant in this test. Results are essentially the same as for the N-ethyl and N-methyl product in the other base stocks.

TABLE 2.—PANEL COKER TESTS AT 700° F. PANEL

Antioxidant at wt. percent	Coke on panel in grams	Sump and cover dirtiness rating
(A) Base-Pentaerythritol tetra(pelargonate/2-Ethyl hexanoate 75/25)+0.065% K(EDTA-Primene 81R Triamide)[1]		
2.5% N-phenyl-1-naphthylamine	0.398	Sump=Tr. dep., Cover=Light dep.
2.5% N-ethyl-p,p'-dioctyldiphenylamine.	0.052	Sump=Clean, Cover=Light.
B. Mixed ester base stock—Pentaerythritol tetra(pelargonate/2-Ethyhexanoate 75/25)+25% Bis(2,2,4-trimethylpentyl)azelate+0.13% K(EDTA-Primene 81R Triamide)		
1.0% N-phenyl-1-naphthylamine	0.254	Sump=Light, Cover=Moderate.
1.0% p,p'-dioctyldiphenylamine (Vanlube 81).	0.255	Sump=Moderate, Cover=Moderate.
1.0% N-ethyl-p,p'-dioctyldiphenylamine.	0.155	Sump=Moderate, Cover=Light.
C. Base stock—Bis(2-ethylhexyl)sebacate "Plexol 201"		
2.5% N-phenyl-1-naphthylamine	0.482	Sump=Heavy, Cover=Heavy.
2.5% p,p'-dioctyldiphenylamine (Vanlube 81).	0.243	Sump=Clean, Cover=Moderate.
2.5% N-ethyl-p,p'-dioctyldiphenylamine.	0.062	Do.
2.5% N-methyl-p,p'-dioctyldiphenylamine.	0.066	Do.

[1] Primene 81R is a tert-alkyl primary amine (C 12–15).

Example V

This example gives antioxidant data for N-dodecyl-p,p'-dioctyldiphenylamine. Tests for Table 3 were made as for Table 1 of Example III and tests for Table 4 as for Table 2 of Example IV. Table 3 shows a comparison of this antioxidant with N-phenyl-1-naphthylamine and p,p'-dioctyldiphenylamine. Table 4 shows a similar comparison.

TABLE 3.—ANTIOXIDANT COMPARISON 500° F. IN WADC TYPE TEST[1]

Antioxidant at 2.0% W/W in Pentaerythritol Tetra(Octanoate/2-Ethyl Hexanoate 50/50)	Hours to 100% Viscosity Increase	Varnish, Deposits Sludge Rating
N-phenyl-1-naphthylamine	45	Heavy.
p,p'-Dioctyldiphenylamine	28	Do.
N-dodecyl-p,p'-dioctyldiphenylamine	56	Moderate.

[1] 250 ml. oil, 5 ls air periter hr., Al, Fe, Ag, Ti, stainless steel.

TABLE 4.—PANEL COKER TESTS AT 700° F. PANEL

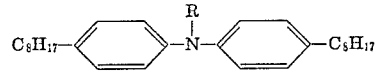
(C) Base stock—Bis(2-Ethyl Hexyl) Sebacate "Plexol 201"

Antioxidant, Wt. percent	Coke on Panel, g.	Sump and Cover Dirtiness Rating
2.5% N-phenyl-1-naphthylamine	0.482	Sump=Heavy, Cover=Heavy.
2.5% p,p'-dioctyldiphenylamine	0.243	Sump=Clean, Cover=Moderate.
2.5% N-dodecyl-p,p'-dioctyl-diphenylamine.	0.079	Sump=Clean, Cover=Heavy.

Although the invention has been described in detail with reference to preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined by the appended claims.

We claim:

1. A lubricating composition comprising a synthetic ester-type lubricant selected from the group consisting of a pentaerythritol mixed ester and bis (2-ethylhexyl) sebacate and about 0.10% to about 5.0% by weight of an N-alkyl-p,p'-dioctyldiphenylamine having the formula



wherein R is a C_1–C_{14} alkyl group.

2. The composition of claim 1 wherein the N-alkyl-p,p'-dioctyldiphenylamine is N-ethyl-p,p'-dioctyldiphenylamine.

3. The composition of claim 1 wherein the N-alkyl-p,p'-dioctyldiphenylamine is N-ethyl-p,p'-dioctylphenylamine.

4. The composition of claim 1 wherein the N-alkyl-p,p'-dioctyldiphenylamines is N-dodecyl-p,p'-dioctyldiphenylamine.

5. The composition of claim 1 wherein the lubricant is a pentaerythritol mixed ester.

6. The composition of claim 5 wherein the pentaerythritol mixed ester is a 50/50 by weight pentaerythritol tetra-(octanoate/2-ethyl hexanoate).

7. The composition of claim 5 wherein the pentaerythritol mixed ester is a 75/25 by weight pentaerythritol tetra (pelargonate 2-ethyl hexanoate).

8. The composition of claim 1 wherein the lubricant is bis (2-ethylhexyl) sebacate.

References Cited

UNITED STATES PATENTS

3,090,753 5/1963 Matuszak et al. ..... 252—56
3,282,840 11/1966 Foster et al. ..... 252—50

FOREIGN PATENTS

1,296,478 5/1962 France.

OTHER REFERENCES

Barnes et al.: "Synthetic Ester Lubricants," Lubrication Engineering, August 1957, pp. 454–458.

DANIEL E. WYMAN, *Primary Examiner.*

PATRICK P. GARVIN, *Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,368,975 February 13, 1968

Thomas G. Davis et al.

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

Column 4, line 30. "N-ethyl-" should read -- N-methyl- --; line 33, "dioctylphenylamine" should read -- dioctyl-diphenylamine --; line 44, "(pelargonate 2-ethyl hexanoate)" should read -- (pelargonate/2-ethyl hexanoate) --.

Signed and sealed this 19th day of August 1969.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents