United States Patent Office 3,462,367 Patented Aug. 19, 1969

3,462,367

LUBRICATING OILS CONTAINING AN ANTIOXIDANT MIXTURE OF ZINC AND ANTIMONY DIALKYL DITHIOCARBAMATES

Russell L. Booher, Edwardsville, Ill., assignor to Shell Oil Company, New York, N.Y., a corporation of Delaware

No Drawing. Filed Oct. 31, 1966, Ser. No. 590,498
Int. Cl. C10m 1/40
U.S. Cl. 252—33.2 8 Claims

ABSTRACT OF THE DISCLOSURE

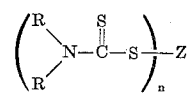
Lubricating oil compositions containing zinz diamyl dithiocarbamate and antimony amyl dithiocarbamate exhibit good anti-oxidation properties. The lubricating oil may also contain a pro-oxidant material selected from the group consisting of copolymers of lauryl methacrylate and N-vinyl pyrrolidone, copolymers of laurel methacrylate, stearyl methacrylate and 2-methyl-5-vinyl pyridine, an imide of mono C_{20-300} polymeric hydrocarbyl succinic anhydride, a calcium salt of a high molecular weight sulfonic acid and mixtures thereof.

This invention relates to improved lubricating compositions, and more particularly to lubricating compositions which exhibit increased oxidation stability even when the compositions contain relatively large amounts of pro-oxidant additives.

At one time straight mineral oils were able to meet all normal lubrication requirements of automotive and industrial practice. As these requirements became more severe with the progressive development of engines and machinery, it became necessary firstly to improve the quality of lubricating oils by new methods of refining and eventually to use additives to either reinforce existing qualities or to confer additional properties. These additives, e.g., dispersant polymers, pour depressants, viscosity index improvers, anti-wear and anti-rust inhibitors, etc., some of which contain metals, when added in large amounts to lubricating oil, act as catalysts or accelerators in promoting oxidation of the oil. These additives may appropriately be referred to as "pro-oxidant" additives. To further complicate the oxidation stability problem of lubricating oils, many of the oils are derived from crudes containing compounds which are readily attacked by oxygen, e.g., aromatics and olefins. Oil oxidation results in deterioration of the oil and formation of sludge deposits. Sludge is used to identify all types of engine deposits ranging from varnish-like films to baked carbon accumulations. Sludge causes engine wear, loss of lubricating properties of the oil and generally loss of overall engine efficiency. In the past, therefore, it has been necessary to establish a proper balance between oxidation inhibitor and, for example, detergent or dispersant in order to secure optimum oxidation resistance of the oil.

It has now been discovered in accordance with the present invention that lubricating oil compositions containing a minor amount of zinc N,N-dialkyl dithiocarbamate and a minor amount of antimony N,N-dialkyl dithiocarbamate in solution therewith are inhibited against oxidation even in the presence of pro-oxidant materials.

According to the present invention, the carbamates which are incorporated into oil compositions are of the formula:



wherein R is an alkyl radical having from 1 to 10 carbon atoms, preferably from 4 to 6 carbon atoms; Z is either antimony or zinc; and n is an integer corresponding to the valence of Z. Both R's attached to the nitrogen atom may be the same or different, branched or straight-chained, e.g., wherein R is an ethyl, isobutyl, n-butyl, n - amyl, n - hexyl, heptyl radical, and the like. Preferred compounds of the above formula include antimony and zinc N,N-dibutyl dithiocarbamates, antimony and zinc N,N-diamyl, N,N-dihexyl dithiocarbamates, and antimony and zinc N,N-dioctyl dithiocarbamates.

Base oils to which the zinc and antimony N,N-dialkyl dithiocarbamates described herein are added may be selected from a variety of natural oils such as paraffinic, naphthenic, and mixed base mineral oils having a viscosity range, e.g., from 30 SUS up to 250 SUS and higher at 100° F. Moreover, the oils may result from crudes which have or have not been highly refined. In addition to mineral lubricating oils, the carbamates may be added to synthetic lubricating oils such as polymerized olefins, silicone polymers, esters and ethers. Mixtures of natural and synthetic oils can also be employed.

Mineral lubricating oils which are particularly desirable for use in compositions of this invention are obtained from West Texas Ellenburger crudes, East Texas crudes, Oklahoma crudes, California crudes. Useful refined oils therefrom include oils which have properties within the following ranges:

Gravity, ° API	min.	26.5
Pour point, ° F.	max.	10
Flash, COC, ° F.	min.	390
Viscosity, SUS at 100° F.		120—160
Viscosity index	min.	95

Other oils, which include a SAE 30 mineral oil, have the following property ranges:

Gravity, ° API	min.	24.5
Pour point, ° F.	max.	—5
Flash, COC, ° F.	min.	415
Viscosity, SUS at 210° F.		58–63
Viscosity index		50–60

The dithiocarbamate combination is particularly suitable for lubricating oil compositions which contain large amounts of pro-oxidant additives or compositions which are less susceptible to inhibitors such as low viscosity oils prepared from crudes which are not highly refined. Thus, by using the combination of carbamates described herein, it is possible to formulate oil compositions which can contain relatively large amounts (up to 10% or higher) of numerous other additives such as corrosion inhibitors, pour point depressants, wear and corrosion inhibitors, viscosity index improvers, anti-foaming agents, blooming agents, detergents, and the like and yet have a lubricating life equal to or greater than present lubricating compositions which contain only moderate amounts of these additives. The lubricating life of an oil is that period of time in which the oil is an effective lubricant for its intended purpose.

Specific examples of the pro-oxident materials include (1) nitrogen-containing polymeric additives such as the copolymers of lauryl methacrylate and N-vinyl pyrrolidone; copolymers of lauryl methacrylate, stearyl methacrylate and 2-methyl-5-vinyl pyridine; an amide-imide of a mono C_{20-300} polymeric hydrocarbyl succinic anhydride, and the like, (2) basic additives such as, calcium salts of high molecular weight sulfonic acids, e.g., calcium naphtha sulfonates which are treated with calcium hydroxide to form the basic salts, and the carbonated calcium sulfonates, and (3) metal ions and acid-forming materials, as well as unsaturated organic compounds, but are not limited to these materials.

The amount of additive combination incorporated into the lubricating oil compositions may vary over a wide

range, i.e., 0.01% to 20%, depending upon pro-oxidant materials present as well as the conditions under which the compositions are used. Ordinarily, the amount of additive combination present will be from 0.01% to 10% by weight based upon the weight of the base oil, and preferably from about 0.1% to about 5%. Preferably, the zinc and antimony dialkyl dithiocarbamates are present in weight ratios of from 9:1 to 1:9, and most preferably from 7.5:2.5 to 2.5:7.5. Usually the carbamates are present in equal weight ratios. However, beneficial coaction between the carbamates is obtained even when one of the carbamates is present in only trace amounts, although to a lesser degree.

The following examples are for purposes of illustrating the invention and are not intended to limit the invention to the particular compounds and compositions described. Unless otherwise specified, "percent by wt." has reference to percent by weight based upon the weight of the base stock. In illustrating the invention, the following base stocks, compounds and compositions are referred to.

BASE STOCKS

Base stock A:

HVI[a] 250 N (neutral) 228.4 SUS at 100° F.; 49.2 SUS at 210° F.

Base stock B:

20% spray base 60[b]

15% HVI 250 N; 228.4 SUS at 100° F.; 49.2 SUS at 210° F.

10% LVI[c] 65 N; 64.2 SUS at 100° F.; 34.9 SUS at 210° F.

4.5% of a mineral oil[d] containing 36% by weight of a lauryl methacrylate/N-vinyl pyrrolidone copolymer (Acryloid 917)

5% carbonated calcium sulfonates

Balance HVI 100 N; 95.3 SUS at 100° F.; 39.2 SUS at 210° F.

[a] HVI has reference to high viscosity index corresponding to 85 or higher.

[b] A base oil having the following properties:

Gravity, ° API	30.4
Color, ASTM	<0.5
Pour point, ° F.	−70
Flash, COC ° F.	300
Viscosity SUS at ° F.—	
100	63.5
210	34.8

[c] LVI has reference to low viscosity index corresponding to less than 40.

[d] A solvent refined 150 SUS at 100° F. neutral oil.

Compounds

Compound *a* ____ Zinc diamyl dithiocarbamate.
Compound *b* ____ Antimony diamyl dithiocarbamate.
Compound *c* ____ Zinc di-n-butyl dithiocarbamate.
Compound *d* ____ Antimony di-n-butyl dithiocarbamate.
Compound *e* ____ Zinc di-n-hexyl dithiocarbamate.
Compound *f* ____ Antimony di-n-hexyl dithiocarbamate.

The following compositions are prepared from the above base stocks and compounds.

Base stock A

	Percent by wt.
Composition I:	
Compound *a*	0.5
Composition II:	
Compound *b*	0.5
Composition III:	
Compound *b*	1.0
Composition IV:	
Compound *a*	0.5
Compound *b*	0.5

Base stock B

Composition V:	
Compound *a*	0.5
Composition VI:	
Compound *b*	0.5
Composition VII:	
Compound *a*	0.5
Compound *b*	0.5

In order to illustrate the effectiveness of the carbamate combination to impart unexpected oxidation stability to lubricating oils, air oxidation tests were conducted. In these tests, a stream of air (30 ml./min.) was bubbled through a 20-gram sample of lubricant (oil composition) in the presence of 20 p.p.m. each of copper and iron (as octoates) catalysts. The induction period, which is the length of time elapsed before a substantial increase in the rate of oxygen-uptake occurs, is a standard measure of oxidation stability and is tabulated below for each lubricant. In some instances the blotter spot life is also recorded. In the blotter spot life test, a drop of lubricant is placed on a blotter at regular intervals and a spot is formed; the time required for undispersed insolubles to appear in the spot is recorded.

These air oxidation tests were developed to simulate engine operating conditions under which sludge forms. The tests were conducted at 350° F.

OXIDATION TEST RESULTS

Lubricant	Induction period, hours	Blotter spot life, hours
Base stock A	0	
Composition I	3	
Composition II	4	
Composition III	7	
Composition IV	14	
Base stock B	0	
Composition V	4	
Composition VI	2	6
Composition VII	12	15

The above test results illustrate the effectiveness of the combination of a zinc dialkyl dithiocarbamate and antimony dialkyl dithiocarbamate to impart oxidation stability to oils, and particularly to oils containing pro-oxidant materials (Compositions V–VII), whereas any of the individual carbamates per se is relatively ineffective. By reason of this effectiveness, it is possible to reduce the concentration of oxidation inhibitor presently required in lubricating formulations on the one hand or to improve other properties of the formulations on the other hand by maintaining the present oxidation inhibitor concentration while increasing the concentration of pro-oxidant additives.

Other additives may also be incorporated into the lubricating compositions according to the invention, for example, anti-foam agents, viscosity index improvers, rust inhibitors, and the like, as well as other anti-oxidants. As demonstrated by the tests (in particular Compositions V–VII), the inhibitor combination is effective even in the presence of pro-oxidant additives.

Moreover, particularly favorable results are obtained when phenyl-alpha-naphthylamine is added to the compositions of the present invention. In an air oxidation test carried out under exactly the same conditions as those employed in testing Compositions I–VII, it was found that when 0.2% phenyl-alpha-naphthylamine was added to Composition VII, the induction period was increased to 20 hours and the blotter spot life to 22 hours.

Compositions of this invention can be used as engine lubricants, hydraulic fluids, industrial lubricants, and the like.

I claim as my invention:

1. A lubricating oil composition comprising a major amount of lubricating oil and from 0.01% to about 10% each based upon the weight of the lubricating oil of (1) zinc di-C_{1-10}-alkyl dithiocarbamate and (2) antimony di-C_{1-10}-alkyl dithiocarbamate.

2. A lubricating oil composition comprising a major amount of lubricating oil, a minor amount of a pro-oxidant material, selected from the group consisting of copolymers of lauryl methacrylate and N-vinyl pyrrolidone, copolymers of lauryl methacrylate, stearyl methacrylate and 2-methyl-5-vinyl pyridine, an imide of mono C_{20-300} polymeric hydrocarbyl succinic anhydride, a calcium salt of a high molecular weight sulfonic acid and mixtures thereof and from 0.01% to about 10% each by

weight based upon the weight of the lubricating oil of (1) zinc di-C_{1-10}-alkyl dithiocarbamate and (2) antimony di-C_{1-10}-alkyl dithiocarbamate.

3. A composition according to claim 2 wherein the pro-oxidant material includes a lauryl methacrylate/N-vinyl pyrrolidone copolymer.

4. A composition according to claim 2 wherein the pro-oxidant material includes a basic calcium salt of a high molecular weight sulfonic acid.

5. A composition according to claim 2 wherein the pro-oxidant material includes a compound selected from the group consisting of a basic calcium salt of a high molecular weight sulfonic acid, a lauryl methacrylate/N-vinyl pyrrolidone polymer and a combination thereof.

6. A composition according to claim 5 wherein the oil is a mineral oil.

7. A composition according to claim 6 wherein the dithiocarbamates are zinc diamyl dithiocarbamate and antimony diamyl dithiocarbamate.

8. A composition according to claim 7 which contains from 0.01% to about 10% by weight of phenyl-alpha-naphthylamine.

References Cited

UNITED STATES PATENTS

2,794,781	6/1957	Diamond et al.	252—33.6
2,820,008	1/1958	Woods et al.	252—33.6 XR
2,916,450	12/1959	Miller	252—33.6 XR
2,947,695	8/1960	Leshin et al.	252—33.6
3,030,303	4/1962	Ryan	252—33.6
3,239,462	3/1966	Bergstrom et al.	252—33.6

PATRICK P. GARVIN, Primary Examiner

W. CANNON, Assistant Examiner

U.S. Cl. X.R.

252—33.6, 42.7