United States Patent Office 2,695,273 Patented Nov. 23, 1954

2,695,273

LUBRICATING OIL COMPOSITIONS

Edwin O. Hook, New Canaan, and William D. Thomas, Jr., Cos Cob, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application April 8, 1952, Serial No. 281,226

4 Claims. (Cl. 252—33.4)

This invention relates to hydrocarbon lubricating oil compositions and to improvement agents to be incorporated therein, and includes methods of producing the same. More particularly, this invention relates to hydrocarbon lubricating oil compositions for use as crankcase oils in passenger automobiles and especially heavy-duty truck, bus, aeroplane, marine and diesel engines which operate for long periods of time at high temperatures.

When conventional lubricating oils are subjected to high operating temperatures for extended periods of time, such as in heavy-duty service, they tend to deteriorate with the formation of complex and objectionable oxidation and decomposition products of an acidic nature. These acidic oxidation products which are developed in the oil create serious problems inasmuch as they attack and corrode metallic parts and particularly alloy bearings commonly used in internal combustion engines. As a consequence, alloy bearing-metals, such as copper-lead, silver-cadmium, nickel-cadmium, and the like are corroded and require replacement in a relatively short period of time.

Additionally, these acidic oxidation and decomposition products tend to polymerize under the high temperature conditions prevailing in an engine to form lacquer-like deposits on the cylinder walls or other stationary parts of the engine and on or between the relatively moving parts of the engine causing them to stick or to wear rapidly. Even larger quantities of these polymerization products remain dispersed in the partially oxidized crankcase oil and are rapidly precipitated to form a heavy mayonnaise-like sludge when the engine cools or when fresh oil is added to the engine. These precipitated sludges become caked on heated metal surfaces and reduce the effective life of the engine by reducing the effectiveness of the lubrication system.

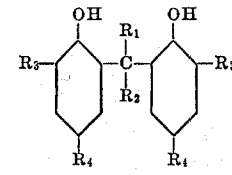
A number of oil-soluble anti-oxidants have been developed to inhibit or retard such oxidational changes to reduce the deterioration of the lubricating oil and obviate these undesirable effects. For example, substituted and unsubstituted alkylidene bis-(4,6-dialkylphenols) have been employed in such a capacity and have greatly improved the resistance of hydrocarbon lubricating oil compositions to oxidational changes and have substantially inhibited or retarded deterioration of the oil and the development of undesirable decomposition products. One consequence of this has been to reduce the corrosion of metallic parts such as alloy bearings in the engine and to thus minimize the deleterious effects of oil deterioration on cylinders, pistons and other relatively moving engine parts.

Although the lubricating oils containing these alkylidene bis-phenols are extremely resistant to oil oxidation and sludge formation under conditions of heavy-duty service, we have found that a lacquer-like formation has developed on metallic engine parts during use of such lubricating oils which has detracted to some extent from the value of the inhibitors and from the satisfactory operation of the engine. Without being bound to any theory on the formation of such a lacquer-like deposit, it is believed that such deposition is a result of decomposition of the inhibitor, alone or with certain components of the oil, rather than that of the lubricating oil alone.

Various compounds which normally have detergent properties have been added to these hydrocarbon lubricating oil compositions containing alkylidene bis-phenols in efforts to improve such conditions but none has heretofore proved sufficiently successful in inhibiting such lacquer-like formation. For example, neutral salts of petroleum sulfonates, metal salts of alkyl substituted phenol sulfides, metal phenates, and the like, have been utilized but have not sufficiently inhibited such lacquer-like formation.

It is a principal purpose of the present invention to provide hydrocarbon lubricating oil compositions containing alkylidene bis-phenols which possess superior anti-oxidant and corrosion inhibitor characteristics and do not develop any lacquer-like formation during use.

For the purposes of this invention, these substituted and unsubstituted alkylidene bis-phenols may be represented by the following structural formula:



in which R_1 and R_2 are substituents selected from the class consisting of aliphatic, cycloaliphatic and aromatic groups and hydrogen; and R_3 and R_4 are alkyl radicals.

Examples of these hydrocarbon lubricating oil compositions including alkylidene bis-phenols and their methods of preparation are set forth in U. S. Letters Patent 2,515,906–8 and 2,570,402 and it is a principal purpose of the present invention to improve the operating characteristics of such oil compositions containing the alkylidene bis-phenols set forth therein.

Without limiting the scope of the present invention, the following alkylidene bis-phenols are listed, primarily for purposes of illustration and such is not to be construed as limitative in any way of the scope of the inventive concept: 2,2′-methylene bis(4-methyl-6-t-butylphenol); 2,2′-methylene bis(4-methyl-6-t-octylphenol); 2,2′-methylene bis(4-methyl-6-t-dodecylphenol); 2,2′-methylene bis(4-t-octyl-6-methylphenol); 2,2′-methylene bis(4-t-butyl-6-methylphenol); 2,2′-methylene bis(4,6-di-t-butylphenol); 2,2′-ethylidene bis(4-methyl-6-t-octylphenol); 2,2′-ethylidene bis(4-methyl-6-t-butylphenol); 2,2′-isopropylidene bis(4-t-butyl-6-amylphenol); 2,2′-isopropylidene bis(4-t-butyl-6-methylphenol); 2,2′-isopropylidene bis (4,6-di-t-dodecylphenol); 2,2′-propylidene bis-(4-methyl-6-t-octylphenol); 2,2′-isobutylidene bis(4,6-dimethylphenol); and others set forth in the above mentioned U. S. patents.

The alkylidene bis-phenols may be used in such proportions as to stabilize the lubricating oil composition and retard or inhibit the oxidation or deterioration thereof. It has been found that the addition of from about 0.01 up to about 3.0 per cent by weight of these compounds to a lubricating oil subject to oxidational changes will substantially inhibit or greatly retard the formation of objectionable oxidation or decomposition products which are injurious or corrosive to metallic engine parts. The exact amount of inhibitor employed in any particular case, however, will depend upon the nature of the base oil stock used, as well as upon the severity of the operating conditions to which it is intended to be subjected, upon the presence of any other lubricating oil additives which may be utilized in the composition, and so forth.

We have now discovered that this lacquer-like formation in hydrocarbon lubricating oil compositions containing alkylidene bis-phenols as anti-oxidants and anti-corrosive agents may be substantially inhibited or retarded by the addition to such compositions of a small amount of an oil-soluble basic organic sulfonate.

Among the various oil-soluble basic organic sulfonates which are effective to produce the compositions of the present invention are the basic petroleum or mahogany sulfonates which are well-known products in the oil industry and are produced by methods well-known in the art. These are preferable to use because of their availability and relatively inexpensive nature. Other basic oil-soluble organic sulfonates, however, may be employed. We may use, for example, any basic alkyl or aryl sulfonate, provided it is sufficiently oil-soluble for its in-

tended purposes and does not contain any chemical group which could react with alkali to prevent the over-neutralization required to supply the required basicity.

In accordance with the principles of the present invention, we use these oil-soluble surface-active organic sulfonates in the form of their basic metal salts, preferably the basic alkaline earth metal salts. Among the various metal salts which may be employed are those of the salt forming radicals, calcium, barium, strontium, magnesium, lead and other polyvalent metals such as zinc, cobalt, tin and aluminum.

As used herein, the term "basic" organic sulfonate includes those sulfonates which are sufficiently over-neutralized so as to contain a minimum of 20% metal in excess of the amount theoretically required to form the ordinary neutral organic sulfonate. This excess of metal may be introduced into the sulfonic acid by methods disclosed in U. S. Patent 2,501,731–2 and 2,585,520. For example, the desired excess of metal may be introduced and held by the organic sulfonates by employing an alcohol as the carrying medium for the metal in the reaction with the sulfonic acid. For example, in the case of the basic barium salt, methanol may be reacted with barium oxide to form what is believed to be barium methylate or perhaps a hydroxy-methoxy barium compound. This, in turn, may be reacted with a petroleum sulfonic acid or an oil-soluble organic sulfonic acid to produce a complex containing a substantial amount of barium over and above that which is present in an ordinary neutral sulfonate. In preparing the barium methylate, barium oxide may be reacted with the methanol in a quantity sufficient to provide at least about 20% of excess barium when reacted with the sulfonic acid to form the final product. If a greater excess is desired, such as up to 100% excess or greater, such may be accomplished by using a greater quantity of barium oxide with respect to the sulfonic acid. However, in order to accomplish the desired objects of the present invention, the excess of barium must not be lower than about 20%. Therefore, as used herein, the term "basic" as applied to a petroleum sulfonic acid salt or an oil-soluble organic sulfonic acid salt includes only those sulfonates having at least about 20% or greater excess metal over that found in the corresponding neutral sulfonic acid salt.

These basic sulfonates may be used in such proportions as to substantially retard or inhibit the tendency of the oil composition containing the alkylidene bis-phenol to form objectionable lacquer-like deposits. We have found that the addition of from about 0.3 up to about 5.0 per cent by weight with respect to the base oil stock containing the customary quantities of alkylidene bis-phenols therein substantially inhibits or greatly reduces the formation of objectionable lacquer-like deposits. The percentages of these inhibiting amounts will naturally depend upon the nature of the base stock used, upon the amount of and the particular alkylidene bis-phenol used as an inhibitor therein, upon the severity of the operating conditions to which the oil composition is to be subjected, and so forth. It is also to be noted that these basic sulfonates, when in such combination with hydrocarbon lubricating oil and an alkylidene bis-phenol, are not corrosive to silver, copper, or similar metals used in alloy bearings for engines, which is a decided advantage over the usual sulfur-containing inhibitors.

The finished hydrocarbon lubricating oil composition may also contain other additives, such as oiliness and extreme pressure agents such as phosphorus or sulfur containing organic compounds; viscosity index improvers such as high molecular weight resins; pour point depressants such as high molecular weight polymers or wax-naphthalene condensation products; detergents such as metallic sulfonates or phenolates, foam inhibitors such as silicones; and other improvement agents, as desired.

The resistance of our improved lubricating oils to varnish and lacquer-like formation was demonstrated by the results of the following tests. The particular alkylidene bis-phenol selected for test purpose was 2,2'-methylene bis(4-methyl-6-t-butylphenol) but such was merely for illustrative purposes and is not to be considered limitative of the inventive concept. The particular test procedure employed was a Chevrolet L–4 test wherein the engine was operated continuously for 36 hours at 30 horsepower loading with a crankcase temperature of 280° F. and a water jacket outlet temperature of 200° F. The engine was then disassembled and the parts were inspected and rated.

The piston varnish ratings are reported on a scale of from 1 to 10, in which 1 means a piston which is very dirty with stuck piston rings and 10 means a perfectly clear piston. The overall rating is reported on a scale from 1 to 100 in which 100 means a clean engine with substantially no sludge deposits and with perfectly clean pistons.

The corrosion of the bearings is determined by determining the weights of a pair of whole bearings both before and after the test and then averaging the differences between these values, whereby the average weight loss per whole bearing is derived. The results of the tests were as follows:

Alkylidene bis-phenol	Basic Barium Petroleum Sulfonate	Piston Varnish	Overall Rating	Corrosion (mgms.)
0.50		5.3	86.8	3
0.30		6.8	92.5	119
0.35	1.00	8.9	94.6	55
0.30	2.85	9.6	98.0	145
	5.93	6.6	95.2	3,236

Alkylidene bis-phenol	Basic Lead Petroleum Sulfonate	Piston Varnish	Overall Rating
0.50		5.3	86.6
0.30		6.8	92.5
0.35	1.32	9.6	98.2
0.30	3.78	10.0	98.2
	4.70	10.0	98.6

Although we have shown but a few specific examples of our improved hydrocarbon lubricating oil compositions and have set forth the improved test results using a readily available particular alkylidene bis-phenol, we consider our inventive concept not to be limited thereto but to include other compounds of equivalent constitution as set forth in the claims appended hereto. It is understood that any suitable changes, variations and modifications may be made without departing from the spirit and scope of the invention.

We claim:

1. A hydrocarbon lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil, from about 0.01% to about 3% by weight of 2,2'-methylene bis(4-methyl-6-tertiary butyl phenol), and a basic petroleum sulfonate of a metal selected from the group consisting of alkaline earth metals and heavy metals in an amount sufficient to reduce the lacquer-forming propensities of the hydrocarbon lubricating oil composition.

2. The invention as defined in claim 1 wherein the metal is barium.

3. The invention as defined in claim 1 wherein the metal is calcium.

4. The invention as defined in claim 1 wherein the metal is lead.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,570,402	Stevens et al.	Oct. 9, 1951
2,585,520	Van Ess et al.	Feb. 12, 1952