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3,843,533

LUBRICANT COMPOSITION CONTAINING SULFURIZED AND CHLORINATED ALKYLENE POLYAMINE REACTION PRODUCT

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U.S. Cl. 252—47.5 3 Claims

ABSTRACT OF THE DISCLOSURE

Sulfurized and chlorinated alkylene-polyamine reaction product effective as an ashless lubricant additive and a mineral lubricating oil composition containing same.

BACKGROUND OF THE INVENTION

Mineral lubricating oils by themselves cannot meet the lubrication needs of modern internal combustion engines and it is customary to incorporate additives in formulated lubricating oil compositions in order to enhance the dispersant, detergent, corrosion inhibiting and antiwear properties of the composition. The difficulties of providing a satisfactory motor oil are increased because these oils are subjected to a wide range of operating conditions. In particular, it is extremely difficult to formulate a motor oil composition which will be effective under both high temperature, high speed operating conditions as well as under low temperature stop and go driving conditions. This problem is compounded when the motor oil is employed in different types of engines, such as diesel and gasoline engines both of which put very severe but greatly different stresses on the motor oil composition.

Nitrogen-containing and sulfurized nitrogen-containing ashless lubricating oil additives are well known and are effective for reducing varnish and sludge deposits in an internal combustion engine. The dispersant effectiveness of these lubricant additives is attributed primarily to the nitrogen content of the additive. However, there appears to be a limit to the amount of nitrogen which can be incorporated in the nitrogen-containing and in the sulfurized-nitrogen-containing ashless lubricant additives.

PRIOR ART

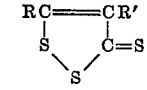
U.S. 3,459,664 discloses a class of trithione polyamine reaction products which are sulfurized ashless lubricant additives.

SUMMARY OF THE INVENTION

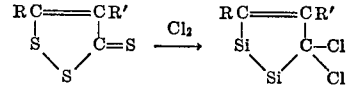
A novel ashless lubricating oil additive is provided which comprises oil-soluble sulfurized and chlorinated polyalkylene polyamine reaction product as well as a lubricating oil composition containing same.

The additive of the invention is obtained by reacting a known trithione compound, which is obtained from the reaction of a polyalkylene compound and sulfur as described in U.S. 3,459,664, with chlorine under suitable conditions to effect chlorination of the trithione compound. This product is then reacted with an alkylene polyamine, i.e. an alkylene diamine or a polyalkylene polyamine to produce the sulfurized and chlorinated polyalkylene-polyamine ashless lubricating oil additive of the invention. This reaction product is characterized by consisting of from about .10 to 5.0 weight percent sulfur, .10 to 5.0 weight percent chlorine and 1.0 to 5.0 weight percent nitrogen.

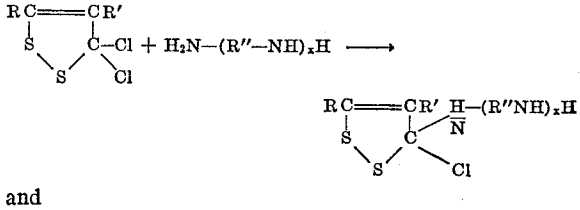
More specifically, a trithione represented by the formula:



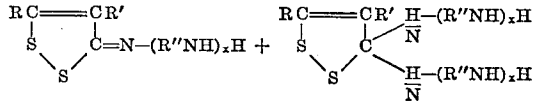
in which R and R' represent hydrogen or a hydrocarbyl radical preferably a saturated aliphatic hydrocarbon radical having from about 50 to 125 carbon atoms, at least one of R and R' representing an aliphatic hydrocarbon radical, is reacted with chlorine under conditions effective to cause chlorination of the trithione. This reaction can be generally expressed as follows:



where R and R' have the values noted above. The intermediate product which may include some other chlorinated compounds, is then reacted with an alkylene diamine or a polyalkylene polyamine generally represented as follows:



and



in which R'' is a divalent alkylene radical having from 2 to 6 carbon atoms and x is an integer ranging from 1 to 6. In the preferred trithione compounds, R and R' are derived from polyisobutylene and polypropylene.

The prescribed trithione is reacted with chlorine gas at a moderately elevated temperature to effect chlorination. In general, chlorine gas is contacted with or bubbled through the trithione while maintaining a temperature ranging from about 20 to 95° C. While the foregoing temperature range is effective and is not considered critical, a preferred temperature range is from about 45° to 80° C. With the most preferred temperature range being from about 50 to 70° C. Sufficient chlorine is employed so that the reaction produces an intermediate reaction product which contains an average of two atoms of chlorine per molecule as indicated by the formula above. While an excess of chlorine can be employed, the reaction takes place between about 1 mole of trithione and 1 mole of chlorine.

The chlorinated trithione or chlorinated intermediate reaction product is then reacted with an alkylene diamine or polyalkylene polyamine to produce the lubricant additive of the invention. In general, one to five moles of an alkylene diamine or a polyalkylene polyamine are reacted with the chlorinated trithione as indicated by the formulas above, with the preferred ratio being one to two moles of the amine per mole of trithione.

The diamine or polyamine reactants which can be employed in this reaction include alkylene diamines such as ethylenediamine, 1,2-, and 1,3-propylene diamine, 1,4-butylenediamine, 1,5 - amylenediamine, 1,6 - hexylenediamine and the like.

The polyalkylene polyamines which can be employed include diethylene triamine, tetraethylene pentamine, pentaethylene hexamine and hexaethylene heptamine. The diamine and polyamine reactants can be represented by the formula $H_2N—(R''NH)_xH$ in which R'' is a divalent alkylene radical having from 2 to 6 carbon atoms and x

has a value from 1 to 6. Additionally, ring containing nitrogenous materials, such as piperazine, aminethyl piperazine, aminoethylpiperidine etc. may also be employed.

In general, the reaction between the chlorinated intermediate product and the alkylenediamine or polyalkylene polyamine is conducted at a temperature ranging from about 100 to 275° C., and preferably from about 150 to 225° C. in the presence of an alkali or halide acceptor. Any alkali or alkaline earth metal salt which is alkaline reacting or is effective as a halide acceptor can be employed to facilitate the above reaction.

The product resulting from the foregoing reactions starting from a trithione which represents a mixture of compounds taken with the step of chlorination and reaction with an alkylene diamine or polyalkylene polyamine is a very complex reaction product characterized by its method of preparation and the sulfur, chlorine and nitrogen content.

The following examples illustrate the preparation of the reaction product of the invention.

EXAMPLE I

Sulfurization of Polyisobutylene

Polyisobutylene of about 1200 average molecular weight (496 g., 0.41 m.) and sulfur (80 g., 2.5 m.) were heated at 250° C. for 4 hours with stirring and nitrogen purge. The reaction mixture was cooled, dissolved in isooctane and chilled in an ice bath. Filtration followed by stripping under aspirator pressure afforded 504 g. product which contained 4.32% S (theory 6.9).

EXAMPLE II

Chlorination of Sulfurized Polyisobutylene

Sulfurized polyisobutylene from Example I above (288 g., .19 m.) was charged to a 500 ml. flask fitted with gas inlet tube, thermowell and thermocouple, stirrer and condenser. Chlorine was bubbled through the sulfurized material at 60° C. until net weight gained was approximately 8–10 g. The mixture was purged with nitrogen for 1 hour. Elemental analysis found: percent S, 3.75; percent Cl, 4.20.

EXAMPLE III

Reaction of Chlorinated Sulfurized Polyisobutylene With Pentaethylenehexamine

To a 500 ml. 3 necked flask fitted with gas inlet tube, thermowell and couple, stirrer and condenser was charged chlorinated sulfurized polyisobutylene from Example II (218 g., 0.18 m.), pentaethylenehexamine (138 g., 0.6 m.) and sodium carbonate (63 g., 0.6 m.). The mixture was heated at 200° C. for 5 hours, cooled, dissolved in isooctane, filtered and extracted three times with methanol. The isooctane solution was stripped under aspirator pressure to 100° C. Elemental analysis found: percent N, 1.1; percent S, 2.3 percent Cl, 1.1.

The following example is of a reaction product prepared without the intermediate chlorination step.

EXAMPLE IV

Reaction of Sulfurized Polyisobutylene With Pentaethylenehexamine

Sulfurized polyisobutylene (120 g., 0.10 m.) from Example I above and pentaethylenehexamine (116 g., 0.5 m.) were charged to a 500 ml. 3 neck flask and heated with stirring at 250° C. for 6 hours. The mixture was cooled, dissolved in isooctane and triply extracted with methanol. The isooctane solution was stripped under aspirator pressure to 100° C. Elemental analysis found: percent N, 0.4; percent S, 1.09.

It can be seen that the nitrogen content of the reaction product of Example IV is only about 36 percent of the nitrogen content of Example III of the invention. Since the nitrogen content of these additives governs their effectiveness as lubricating oil dispersants, it is evident that the same amount of the reaction product of the invention is much more effective as a dispersant or that a substantially smaller quantity of the reaction product of the invention can be used to realize an equivalent level of effectiveness. In either case a surprising improvement is obtained.

The hydrocarbon mineral base oil employed in preparing the lubricating oil composition of the invention can be a paraffinic base, naphthene base or mixed paraffin-naphthene base distillate or residual oil. Paraffin base distillate lubricating oil fractions are preferred for the formulation of the highest quality engine or motor oils. The lubricating oil base generally will have been subjected to solvent refining to improve its lubricity and viscosity temperature relationship as well as to solvent dewaxing to remove waxy components and to improve the pour of the oil. Generally, mineral lubricating oils having an SUS viscosity at 100° F. between 50 and 1000 may be used in the formulation of the improved lubricants of this invention with the preferred base oils having a viscosity range from 70 to 300 SUS at 100° F. A blend of base oils can be employed to provide a suitable base oil for either a single or multigrade motor oil.

The effectiveness of the reaction product of the invention was determined by formulating a motor oil composition and testing this in the MS–VB Engine Test.

The MS–VB Engine Test is conducted in accordance with the detailed procedures found in ASTM Special Technical Publication No. 315–D, "Engine Test Sequences for Evaluating Automatic Lubricants for API Service MS," published by the American Society for Testing Materials, 1916 Ruse Street, Philadelphia, Pa. The test is cyclic in nature alternating between operating and "soak" periods. At test termination engine inspection according to standard procedures is conducted in the completely dissembled engine and the results of various lubricants compared accordingly.

The base oil employed for preparing the motor oil was a paraffinic mineral oil having an SUS viscosity at 100° F. of about 450. Seven (7.0) weight percent of the reaction product of Example III illustrative of the present invention was incorporated in the base oil and the motor oil composition tested in the MS–VB Engine Test. The results of this test are set forth in Table I below:

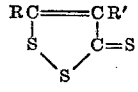
TABLE I.—MS-VB ENGINE TEST

Sludge	Varnish	PSV	Oil ring	Oil screen	PCV value at 4" Hg, percent
45.6	41.7	9.50	0	0	0.0

In addition to providing outstanding detergency, the reaction product of this invention is expected to possess outstanding anti-oxidant activity.

We claim:

1. A lubricating composition comprising a major proportion of a mineral oil of lubricating viscosity containing a minor detergent amount of an oil-soluble ashless sulfurized and chlorinated alkylene polyamine reaction product prepared by chlorinating a reaction product of sulfur and a polyolefin containing a trithione using at least a mole of chlorine per mole of trithione at a temperature ranging from about 20 to 95° C. to form a chlorinated intermediate product, said trithione being represented by the formula:



in which R and R' represent hydrogen or a hydrocarbyl radical having from about 50 to 125 carbon atoms, at least one of R and R' representing an aliphatic hydrocarbon radical, and, reacting said intermediate product with a polyamine in the proportion of 1 to 5 moles of said polyamine per mole of said intermediate product at a tempera-

ture in the range of 100 to 275° C., said polyamine being represented by the formula

$$H_2N—(R''—NH)_xH$$

in which R'' is a divalent alkylene radical having from 2 to 6 carbon atoms and x is an integer ranging from 1 to 6.

2. A lubricating composition according to Claim 1 in which R is a radical derived from polyisobutylene and R' is hydrogen.

3. A lubricating composition according to Claim 1 in which said polyamine is tetraethylenepentamine.

References Cited

UNITED STATES PATENTS

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HELEN M. S. SNEED, Primary Examiner

U.S. Cl. X.R.

252—47; 260—327 C