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LUBRICATING OIL COMPOSITION

Franklin M. Watkins, Chicago, Ill., assignor to
Sinclair Refining Company, New York, N. Y., a
corporation of Maine

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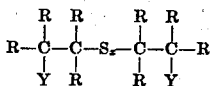
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This invention relates to lubricating oil compositions and more particularly to lubricating oil compositions, consisting principally of a petroleum lubricating oil fraction, with which there has been compounded a calcium organic compound and an olefin sulfide, and having improved characteristics especially with respect to oxidation and corrosion.

It has previously been recognized that oxidation of many petroleum lubricating oil compositions is materially accelerated by contact with certain bearing metals or alloys, notably copper-lead alloys. It has also been recognized that the presence of various metallo-organic substances, included in the oil composition, for improving the characteristics of the lubricant in various respects, may ultimately detrimentally affect oxidation and corrosion characteristics of the lubricant. Copper-lead alloys, for example, are known materially to catalyze the oxidation of the oil. Various metal compounds, notably calcium organic compounds, for instance the calcium salt of octyl salicylates, used in lubricating oil compositions as detergents and oxidation inhibitors, have been found actually to effect an increase over the normal rate of corrosion of copper-lead bearing alloys by the lubricant and the normal rate of oxidation of the lubricating oil composition at the termination of the induction period.

I have discovered that the corrosion and oxidation characteristics of lubricating oil compositions in the presence of pro-oxidant metals or such detergent materials may be substantially improved by the inclusion therein of relatively small proportions of certain olefin sulfides, the detrimental activity of the metal and metallo-organic materials present being thereby substantially inhibited. Also, when used in larger proportions, these sulfides have been found favorably to affect the film strength of the composition.

The olefin sulfide, used in accordance with my present invention, may be represented by the structural formula:



wherein R is hydrogen or a hydrocarbon radical, S is sulfur, x is either 1 or 2 and Y is a radical selected from the group consisting of —SH, —SR' and amino radicals, the R' representing a hydrocarbon radical.

Examples of my improved addends which have been used with particular advantage include:

Mercapto olefin sulfides, i. e., where Y of the above structural formula is —SR, R being either a hydrogen atom or a hydrocarbon radical. Mercapto olefin disulfides, i. e., where x is 2 and Y is —SH, have been found particularly effective. Suitable mercapto olefin sulfides include those

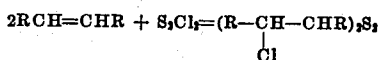
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wherein Y is either aromatic or aliphatic or a mixture of such sulfides prepared from a mixture of mercaptans of five carbon atoms per molecule such as that extracted from gasoline.

Amino olefin sulfides, i. e., where Y of the foregoing structural formula is —NR²R², where R² may be hydrogen or aromatic or aliphatic hydrocarbon. For instance, diamyl olefin disulfide, i. e., where each R² is an amyl group, and anilino olefin disulfide, where one R² is hydrogen and the other is —C₆H₅, may be used with particular advantage.

These olefin sulfides have in common the characteristic that at least one and usually two adjacent carbon atoms of each original olefin molecule is substituted by an electronegative sulfur atom. This type of substitution appears to serve to activate the carbon-sulfur bonds thereby changing their normal reactions. Further, these sulfides have been found to be soluble in lubricating oil fractions in effective amounts and to be compatible with conventional detergents.

The olefin sulfides used in accordance with my present invention may be prepared by reacting an olefin or a mixture of olefins boiling in the gasoline range with either sulfur dichloride, SCl₂, or sulfur monochloride, S₂Cl₂, by known methods to introduce sulfur and chlorine at the double bonds, in accordance with the formula



and thereafter treating the product of the reaction with an alkali metal sulfide, mercaptide or amino compound to replace the chlorine, as more fully hereinafter described.

Various olefins or olefin mixtures may be used in the preparation of my olefin sulfides. It is desirable to use olefins or mixtures of olefins having a boiling range within that of cracked naphtha, say 200 to 300° F. However, some olefins lend themselves more readily than others to the preparation of the olefin sulfides of my present invention. Upon sulfo-chlorination, some olefins have a stronger tendency than others to lose the chlorine as hydrochloric acid. Accordingly, the substitution of other radicals for the chlorine of the sulfo-chlorinated olefin is more difficult with such olefins and the product of the reaction less stable.

The olefin mixtures resulting from thermal cracking are available at low cost and in adequate quantities and may be used in the preparation of my olefin sulfides. However, this thermally cracked product frequently consists largely of tertiary olefins, i. e., unsymmetrically di-alkylated ethylene or tri-substituted ethylene. These tertiary olefins form, on sulfo-chlorination, tertiary chlorides which lose HCl rather readily during sulfo-chlorination and subsequent treatment in the preparation of my olefin sulfides,

and, after substitution for the chlorine, have a tendency to split to re-form olefins. Though the thermally cracked olefin mixtures have this disadvantage, they afford a convenient and economic source of raw materials for the preparation of my improved olefin sulfides.

I may, with advantage, use as the olefin constituent, olefins or mixtures of olefins having from five to ten carbon atoms per molecule, whether they be produced by dehydrogenation, thermal or catalytic cracking or olefin polymerization. Higher molecular weight olefins may frequently be less desirable because of the lower proportion of active sulfur groups in the resultant addend.

However, I prefer to use the more stable secondary olefins, for instance symmetrically disubstituted ethylene from which the more stable secondary chlorides may be formed by sulfochlorination. Using these secondary olefins, the chlorine in the sulfo-chlorinated product may be more completely replaced by organic radicals and consequently there is less splitting out of the chlorine and resultant re-formation of the olefins. Secondary olefins, such as cyclohexane, octene-1, oleone and wax olefins, have been found to produce stable inhibitors and may be used with particular advantage.

The sulfo-chlorination of thermally cracked naphtha has with advantage been effected by the following process:

In this operation there was used as the olefin constituent a thermally cracked naphtha boiling in the range of 200–300° F., and including the C₈ and C₉ fractions. This naphtha had an A. P. I. gravity of 56.4 and contained 48% by weight of olefins, as shown by the bromine number determination. There was charged to a flask, equipped with a stirrer and a cooling bath, 2333 grams of this naphtha, containing 10 moles of olefin, and 675 grams (5 moles) of sulfur monochloride, S₂Cl₂, was slowly added over a period of 5½ hours at a maximum temperature of 100° F. An addition rate of above 3 drops per second was found to cause excessive temperature rise and a loss of HCl. During this addition of the sulfur chloride, the mixture was stirred and the stirring was continued for 1½ hours thereafter to complete the reaction. Following the completion of the reaction the product was washed to remove HCl and thereafter topped to a final bottom temperature of 210° F. at 30 mm. of mercury to remove the paraffins present. There was obtained from this operation 975 grams of a dark liquid product containing 23.1% sulfur and 12.9% chlorine.

Mercapto olefin disulfide was prepared from the sulfo-chlorinated olefin, produced as above described, by the following method:

A solution containing 400 cc. of 95% alcohol and 30 grams of NaOH (0.75 mole) was saturated with H₂S to form an NaHS solution. 110 grams (0.31 mole) of the sulfo-chlorinated olefin was then added and the mixture refluxed for 7 hours and stored for 66 hours at room temperature. The reaction product was then dissolved in benzol and the benzol layer washed with water, dried and topped to remove the solvent. The resultant mercapto olefin disulfide was found by analysis to contain 26.8% sulfur and 0.88% chlorine.

Diamylamino olefin disulfide was successfully prepared as follows: A mixture of 150 c. c. benzene, 90 grams (0.25 mole) of the sulfo-chlorinated olefin, 157 grams (1 mole) of diamylamine, 30 grams (0.75 mole) of caustic soda and 150

c. c. of water were refluxed for 13 hours until the organic layer gave a negative Bellstein copper oxide test for chlorine. The organic layer was then separated from the aqueous layer, filtered and topped to remove excess amine solvent. By this operation, a residue of 67.2 grams was obtained. This residue was filtered free of amine hydrochloride and was found by analysis to contain 20.85% sulfur, 1.66% nitrogen and 3.17% chlorine. The product was found to be readily soluble in lubricating oil fractions to an extent of at least 5%.

This analysis indicates that the substitution of amine for chlorine had not gone to completion. Upon standing at room temperature, dechlorination continued, forming traces of oil insoluble amine hydrochloride. Though this product was useful in accordance with my present invention, it is desirable particularly in the preparation of olefin sulfides containing nitrogen for use in accordance with my present invention that all or substantially all of the chlorine be replaced by the amine.

Anilino olefin disulfide has been successfully prepared as follows:

227 grams (0.63 mole) of the sulfo-chlorinated olefin, 119 grams (1.28 moles) of aniline, 216 grams (4 moles) of sodium bicarbonate and 200 c. c. of toluene were admixed and the mixture refluxed for 14 hours at approximately 220° F. The organic layer thus obtained was at the end of this period found to be halogen-free. It was thereafter thoroughly washed with water and topped to remove the solvent toluene. By this operation, there was obtained 187 grams of the anilino olefin disulfide, equivalent to 63% of the theoretical yield. This material contained some oil insoluble crystals which appeared to be aniline hydrochloride, although, by analysis, the halogen content of the mixture was found to be only .06%. These crystals were removed by diluting with naphtha, filtering and distilling the naphtha from the filtrate. This purified product was found to be soluble in oil at room temperature to an extent of 5% and to contain 2.31% nitrogen, 21.5% sulfur and 0.12% chlorine.

As the lubricating oil constituent of my improved lubricating oil compositions, various petroleum lubricating oil fractions may be used. For instance, solvent-treated Mid-Continent neutral or a blend of such neutrals with bright stock or a solvent-refined lubricating oil fraction from a Pennsylvania crude or various blends of such lubricating oil fractions may be employed. In the compounding of the lubricating oil composition of my present invention I have with advantage used a solvent-treated Mid-Continent 250 neutral refined by the so-called Chlorex process and having the following characteristics:

Gravity, A. P. I.	29.5
Flash, °F.	405
Fire, °F.	480
Viscosity at 100° F., S. U. S.	249.6
Viscosity at 210° F., S. U. S.	49.0
Viscosity index	92.8
Pour, °F.	5
Carbon residue	.039
Ash	0.0
Acid number	.025
Saponification number	.16
Sulfur, per cent.	.20

The proportion of the olefin sulfide addend used in the compounding of my improved lubricating oil composition may be varied somewhat but in

any case only a minor proportion is used. Concentrations as low as 0.1% by weight may frequently be used with advantage. Usually concentrations of about 0.5% to 1% are desirable. The optimum concentration will depend to a considerable extent upon the nature and amount of the metallo-organic detergent used and also upon the nature of the base oil and other addends present. Concentrations as high as 10% and even somewhat higher of these sulfur-rich olefin sulfides may, with advantage, be incorporated in my lubricating oil composition for the purpose of improving the film strength or imparting extreme pressure qualities to the lubricant.

The lubricating oil composition of my present invention may consist solely of the lubricating oil constituent, a calcium organic compound detergent and the olefin sulfide inhibitor. However, the addends of my present invention have been found to be compatible with other desirable lubricating oil addends and the inclusion of such other addends is within the contemplation of my present invention.

The inclusion of said so-called calcium salt detergents, for instance, in internal combustion engine lubricants, has been previously proposed and been found highly advantageous. An especially effective lubricating oil composition for the lubrication of internal combustion engines, and the like, contemplated by my present invention, is one comprising, in addition to the lubricating oil constituent and my olefin sulfide inhibitor, a minor proportion of the calcium salt of an octyl salicylate, particularly iso-octyl salicylate or capryl salicylate. These calcium salts have been found particularly effective as detergents in lubricating oil composition, as more fully described in the Willard L. Finley Patents Nos. 2,339,692 and 2,347,547 issued on January 18, 1944 and April 25, 1944, respectively.

The invention also contemplates lubricating oil composition containing my olefin sulfide inhibitor and other known calcium organic compound detergents, for example such as calcium cetyl phenolate, calcium petrolatum sulfonates, soaps and the like.

When used in conjunction with these detergents, particularly the calcium compounds such as previously mentioned, my olefin sulfide inhibitors and such detergents have been found to complement each other so that the effectiveness of each is promoted. The tendency of the detergent to promote oxidation of the oil and corrosion of bearing metal, at the termination of the oxidation induction period, is minimized by the presence of my olefin sulfide inhibitor without destroying the effectiveness of either the detergent or the inhibitor.

My improved lubricating oil composition will be further illustrated by the following specific examples in which the base oil used was the solvent-treated Mid-Continent neutral previously described. The oxygen absorption rate of this base oil in the presence of copper-lead bearing metal was 25.6 cubic centimeters, at normal temperature and pressure, per minute per 100 grams of oil. This same base oil compounded with 1% by weight of calcium iso-octyl salicylate, previously referred to, had, in the absence of copper-lead bearing metal, an oxygen absorption rate of 48.8 c. c. per minute per 100 grams of oil and, in the presence of copper-lead bearing metal, an oxygen absorption rate of 50 c. c. per minute. The oxygen absorption rate of the base oil containing the calcium iso-octyl salicylate is that

following the induction period of 167 minutes, in the absence of the bearing metal, and 107 minutes in the presence of the bearing metal.

The copper-lead bearing metal corrosion loss, due to the uncompounded base oil, was 5.8 milligrams and the bearing metal corrosion loss occasioned by the base oil compounded with 1% of the calcium iso-octyl salicylate was 11 milligrams.

The advantages of my present invention, with respect to oxidation and corrosion characteristics of my improved lubricating oil compositions are illustrated by their mean oxygen absorption rates, as compared with the oxygen absorption rate of the base oil and the corrosion losses of bearing metals in contact with the respective lubricants.

Example I

By the addition of 0.5% of the mercapto olefin disulfide, prepared as described herein, to the base oil, the oxygen absorption rate was decreased from 25.6 to 10.8 c. c. per minute per 100 grams of oil. By the addition of the same amount of this olefin sulfide inhibitor to a blend of the base oil with 1% of the calcium iso-octyl salicylate, the oxygen absorption rate of the composition, in the absence of copper-lead bearing metal, was reduced from 48.8 to an average of 1.9 c. c. per minute. The oxygen absorption rate of this blend, in the presence of copper-lead bearing metal, was reduced from 50 c. c. to an average of 3.1 c. c. per minute. The bearing corrosion loss occasioned by the compounding of 0.5% of the mercapto-olefin disulfide with the base oil alone was reduced from 5.8 to 0.6 milligram and, where 1% of the calcium iso-octyl salicylate was also present, the bearing corrosion loss was entirely eliminated.

Example II

By the addition of 0.5% of the anilino olefin disulfide, prepared as described herein, to the base oil, the oxygen adsorption rate was reduced to 4.8 c. c. at normal temperature and pressure per minute per 100 grams of oil. By the addition of the same amount of the anilino olefin disulfide to a blend of the base oil and 1% of calcium iso-octyl salicylate, the oxygen absorption rate, in the absence of the bearing metal, was found to average 2.5 c. c. per minute throughout the test and, in the presence of the copper-lead bearing metal, was reduced to an average of 2.9 c. c. per minute. When using the blend containing 1% of the calcium iso-octyl salicylate, the bearing corrosion loss was only 0.4 milligram.

Example III

By the addition of 0.5% of diamylamino olefin disulfide, prepared as described herein, to the base oil, the oxygen absorption rate was reduced to an average of 7 c. c. per minute. By the addition of 0.5% of the diamyl-amino olefin disulfide to a blend of the base oil with 1% calcium iso-octyl salicylate, the average oxygen absorption rate, in the absence of bearing metal, was found to be 3.3 c. c. per minute. In the tests of the compounds thus prepared, the copper-lead bearing corrosion loss was completely eliminated.

In each instance the proportions of the addends used are based on the weight of the lubricating oil constituent. The tests of the base oils and of my improved lubricants of the foregoing examples were carried out under identical conditions. The oxygen absorption tests were carried out at a temperature of 360° F. and the

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results, in each instance, are reported as cubic centimeters of oxygen, measured under normal temperature and pressure conditions, absorbed per minute per 100 grams of the lubricant during the conventional oxygen absorption test.

I claim:

1. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil fraction, a minor proportion of calcium iso-octyl salicylate, effective as a detergent, and a mercapto olefin disulfide in an amount sufficient substantially to deactivate the calcium of the detergent.

2. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil fraction, a minor proportion of calcium iso-octyl salicylate, effective as a detergent, and an olefin sulfide in an amount sufficient substantially to deactivate the calcium of the calcium iso-octyl salicylate, said olefin sulfide being selected from the group consisting of mercapto olefin sulfides, diamylamino olefin sulfides and anilino olefin sulfides.

3. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil

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fraction, a minor proportion of calcium iso-octyl salicylate, effective as a detergent, and a diamylamino olefin disulfide in an amount sufficient substantially to deactivate the calcium of the calcium iso-octyl salicylate.

4. A lubricating oil composition comprising a major proportion of a petroleum lubricating oil fraction, a minor proportion of calcium iso-octyl salicylate, effective as a detergent, and an anilino olefin disulfide in an amount sufficient substantially to deactivate the calcium of the calcium iso-octyl salicylate.

FRANKLIN M. WATKINS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,230,966	Reid	Feb. 4, 1941
2,282,710	Dietrich	May 12, 1942
2,304,623	Berchet	Dec. 8, 1942
2,347,547	Finley	Apr. 25, 1944
2,361,043	McCleary	Oct. 24, 1944