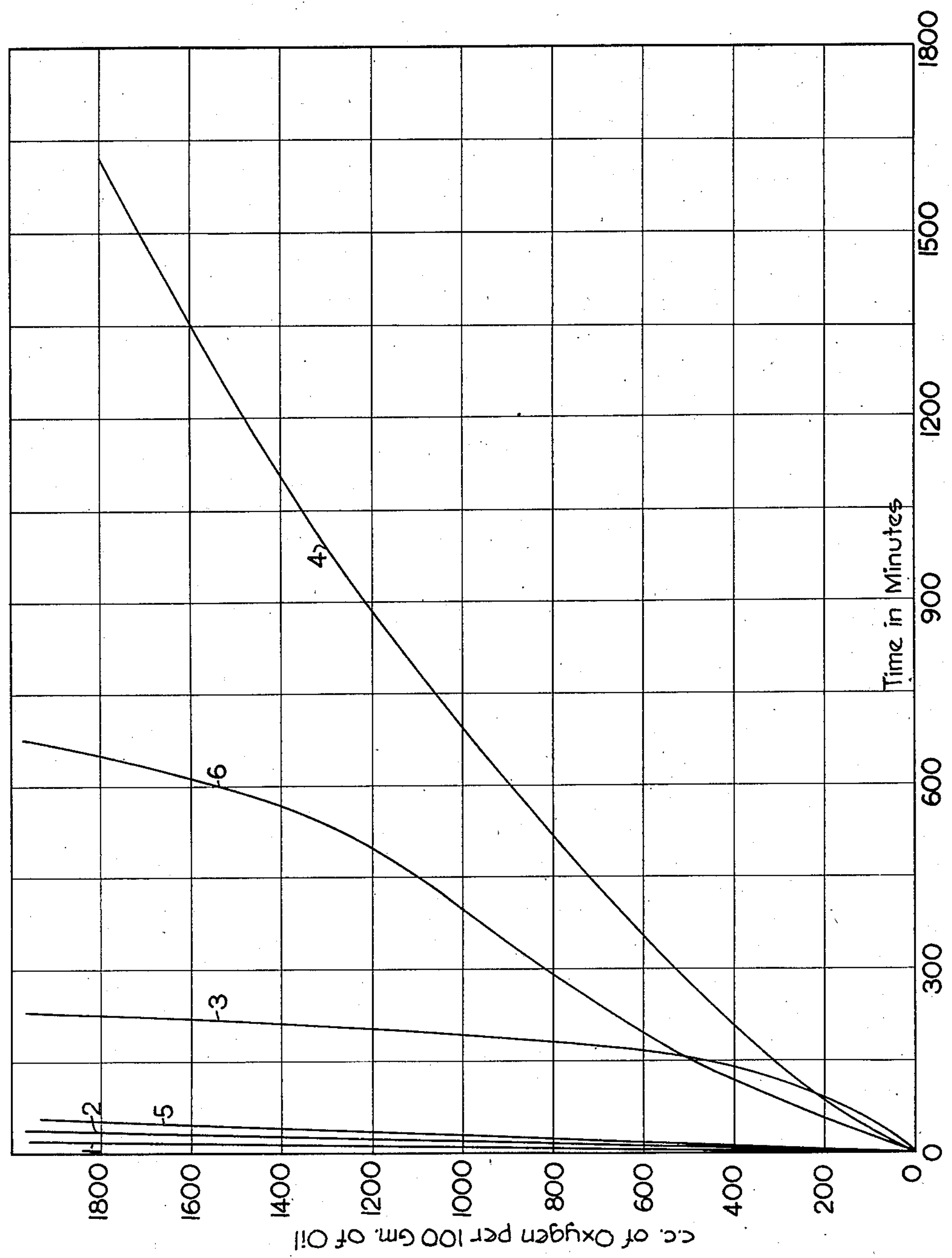
Sept. 23, 1947. H. DIAMOND 2,427,766

COMPOUNDED LUBRICATING OIL

Filed Aug. 5, 1944



Inventor: Hyman Diamond

By his Attorney:

Patented Sept. 23, 1947

2,427,766

UNITED STATES PATENT OFFICE

2,427,766

COMPOUNDED LUBRICATING OIL

Hyman Diamond, Berkeley, Calif., assignor to
Shell Development Company, San Francisco,
Calif., a corporation of Delaware

Application August 5, 1944, Serial No. 548,217

14 Claims. (Cl. 252—42.7)

This invention relates to improved normally liquid or solid predominantly hydrocarbon compositions and more particularly to compounded oils such as mineral lubricating oils for internal combustion engines and turbines, transformer oils, etc., which are used under conditions which tend to cause oxidation through contact with atmospheric oxygen and/or metallic catalysts such as copper, iron, etc. surfaces. It comprises compounded lubricating oils which are of a highly refined character and substantially free of olefinic hydrocarbons which oils contain two stabilizing additives selected from the classes of oil-soluble organic sulfides and polynuclear aromatic compounds.

Highly refined lubricating oils have certain desirable characteristics, but the modern "high-output" aircraft engines and Diesel engines tax or exceed the capabilities of such oils. One defect of highly refined oils is that they tend to absorb oxygen at the elevated temperatures encountered in the above-mentioned types of engines, particularly when in contact with metals which catalyze the oxidation reaction. The oils thus deteriorated tend to form acidic components which render the oil corrosive and necessitate their replacement or purification within a relatively short time.

It is known that certain organic sulfur compounds can be added to lubricating oils in small amounts to impart to the oil improved stability against atmospheric oxidation. It has been discovered, however, that some of these sulfur compounds are relatively ineffective in stabilizing the more highly refined lubricating oils. This ineffectiveness, I have found, is traceable to a deficiency of aromatic hydrocarbons in these more highly refined oils.

It is a purpose of this invention to improve the oxidation stability of highly refined lubricants. Another purpose is to increase the effectiveness of sulfur compounds in stabilizing highly refined oils. A further purpose is to decrease the rate of absorption of oxygen by such oils and retard the catalytic action of metals with which the oil comes in contact.

In carrying out my invention a highly refined mineral oil is rendered singularly stable against oxidation by the combined use of an organic sulfide, preferably an aromatic polysulfide, and a (preferably alkyl-substituted) polynuclear aromatic hydrocarbon. The useful life of such oils can be improved to a degree which cannot be approached with similar quantities of either of the two types of addition agents alone.

By the term "highly refined mineral oil," I mean mineral oils that have been drastically treated to improve such properties as viscosity index, stability against sludging, etc. Oils of such character are produced by extracting them with such selective solvents for aromatic hydrocarbons as sulfur dioxide, furfural, phenol, nitrobenzene, Chlorex, aniline, antimony trichloride, etc., or through treatments with such refining agents as sulfuric acid, aluminum chloride; also by hydrogenation; or by a combination of such treatments, etc.

These highly refined oils are in general identifiable through their relatively high viscosity index and the fact that they have a low aromatic content. The latter is indicated by specific dispersions of not over 110 and often below 105 when measured by the method of von Fuchs and Anderson described in Industrial & Engineering Chemistry, vol. 29, page 319, March 1937. Another method of determining aromatic content of petroleum fractions is by Waterman analysis as described in J. Inst. Petroleum Tech. 18:735 (1932) and 21:661 (1935). Oils having aromatic contents of up to about 6% according to this method respond to the present addition of aromatic hydrocarbons and sulfur-containing inhibitors.

The organic sulfur inhibitors may be either monosulfides or polysulfides. Among the organic sulfides useful for my purpose are the organic disulfides such as di-alkyl, di-aryl, di-aryl-substituted alkyl, di-alkyl-aryl, thiuram and thiazo disulfides, etc., illustrated respectively by di-isoamyl disulfide, di-benzyl disulfide, di-phenylethyl disulfide, di-tertiary butyl-phenyl disulfide, tetramethyl thiuram disulfide and benzo-thiazole disulfide. Other examples are hydroxy- and amino-substituted aromatic and aromatic-alkyl disulfides such as dipropyl diphenol disulfides, dinaphthol disulfides (alpha-alpha, beta-beta or alpha-beta), tetramethyl-dianilino disulfide, di-tertiary-butyl-di-anilino disulfide, etc.; esters of disulfides such as fatty-acid-esterified alkyl diphenol disulfides, e. g., acetic ester of di-tert.-butyl diphenol disulfide, stearic ester or diphenol disulfide, etc.; corresponding mono-, tri-, and tetra-sulfides; certain alkyl pentasulfides such as butyl pentasulfide, etc. Of the above, aromatic disulfides are preferred. Excellent polysulfide anti-oxidants may also be prepared by the reaction of sodium polysulfide with polychlorinated waxes. It is believed the compounds thus obtained consist of several long hydrocarbon chains linked by multiple disulfide or polysulfide bridges.

A compound of this type is referred to in Example II as wax polysulfide.

The organic sulfur-containing anti-oxidants may also contain metallic constituents. In general, salts of the alkaline-earth metals (calcium, barium, magnesium and strontium) are preferred although other polyvalent metals such as Cu, Zn, Al, Pb, Fe, Ni, Co, Mn, Cr and Sn may be employed. Salts of the alkali metals (sodium, potassium and lithium) may also find application. Illustrative salts are metallic phenates, carboxylates, phosphates, thiophosphates, etc. Such salts also have detergent properties in lubricating compositions for internal combustion engines. However, when the sulfur-containing anti-oxidants are employed only for their anti-oxidant properties, it is preferred to use the non-metallic rather than the metallic compounds. So as not to be corrosive, the sulfides should be free from halogen substituents.

Aromatics useful in combination with the above-illustrated organic sulfides are the oil-soluble, relatively high-molecular weight polynuclear hydrocarbons. Those containing one or more short alkyl chains and/or having a condensed-ring structure are preferred. Such aromatics may be obtained by synthesis, i. e. alkylating naphthalene or anthracene with such low-carbon alkyl radicals as methyl, ethyl, normal- and iso-propyl, primary, secondary, and tertiary butyl and amyl, etc., radicals; or they may be obtained from highly cracked hydrocarbon oils such as purified relatively high-boiling fractions of so-called coking cycle stock, blow-down oils, or aromatic fractions of vapor-phase-cracked fuel oils; or they may be obtained from lubricating oils by extraction and subsequent purification.

Coking cycle stock, as herein defined, is a highly aromatic liquid obtained by operating a liquid-phase petroleum cracking unit under conditions to produce coke instead of residual fuel oil. The vapors leaving the coking chamber are fractionated to remove fixed gases and gasoline and the remaining relatively heavy liquid fraction is the coking cycle stock.

Blow-down oil, as herein defined, is a highly aromatic liquid condensed from the vapors obtained by blowing out a coking chamber with steam after discontinuance of oil circulation through it.

It is to be understood that all of these fractions from hydrocarbon oils should be highly aromatic and have initial boiling points above about 500° F. They may be further separated into fractions of different aromaticities as by solvent extraction, fractional precipitation, etc. For example, the cracked distillates may be extracted with a solvent for aromatics, such as liquid sulfur dioxide, furfural, nitrobenzene, phenol, aniline, acetone, dichlordiethyl ether, etc. alone or if desired, in counter-current with liquid propane, butane, pentane, etc.

All of the aromatic hydrocarbon mixtures prepared as above, to be useful, should have a specific dispersion of at least 200. It is preferable that the specific dispersion be above 250 and the preferred limits are specific dispersions between 250 and 400. Moreover, they should be well refined and have negligible contents of olefins and other impurities. Suitable refining may be achieved by treatment with sulfuric acid, aluminum chloride, or hydrogenation under conditions to remove olefins without substantially attacking the aromatics. It will be observed that all of these aromatic hydrocarbons are substantially free of inorganic and polar substituents.

Amounts of organic sulfides suitable for use in the compositions of this invention range from about 0.001% to 1% and preferably from about 0.01% to 0.2%. In combination with such amounts of organic sulfides, amounts of polynuclear aromatic hydrocarbons up to about 15% are used, although amounts ranging between about 1% and 10% usually impart good stability to the oil composition. In oils containing some residual aromatics, as little as 0.2% added aromatics may show some effect. It will be seen that the aromatic hydrocarbons have limited anti-oxidant properties by themselves and even in the present combination the amount added is considerably in excess of quantities usually applicable for conventional anti-oxidants. In other words, the present effect is not simply that of using a multiplicity of inhibitors, each of which is specific for different components of the oil. The exact mechanism by which the organic sulfides and the aromatic hydrocarbons interact is not known.

In addition to their use in petroleum fractions, the present additives may be employed in numerous other predominantly hydrocarbon compositions such as synthetic hydrocarbons produced by Fischer-Tropsch synthesis, or the products of condensation or polymerization of unsaturated compounds such as olefins and the like, which are reacted to produce synthetic lubricating oils. The hydrocarbon mixtures may be either liquid (as lubricating oil) or solid (as waxes or plastics) or the liquid may be soap-thickened to form a grease.

My invention is further illustrated by the following non-limiting examples.

Example I

A highly refined mineral oil having a Saybolt Universal Viscosity at 100° F. of 354.5 seconds, and at 210° F. of 53 seconds, a viscosity index of 78, and a specific dispersion of 96.5 was divided into six samples and to each sample the following materials in per cent by weight were added:

	Sample					
	1	2	3	4	5	6
Dibenzyl Disulfide........per cent..	----	.1	----	.1	----	.1
Diamylanthracene..............do....	----	----	10	10	----	------
Polyamylnaphthalene..........do....	----	----	----	------	10	10

Each of the above samples was subjected to the following stability test:

An 18-gram sample of oil was placed in a glass container and an iron wire of 90 sq. cm. surface was immersed in the oil. The oil was heated to and maintained at a temperature of 313° F. Oxygen was then passed through the oil at a rate of 6 liters per hour and the amount of oxidation measured by the quantity of oxygen absorbed.

The effect of the addition of the various additives on the oxidation stability of the oils is illustrated by the attached drawing which is a graph wherein the range of time in minutes of oxidation is plotted as abscissa and cubic centimeters of oxygen absorbed per 100 grams of oil is plotted as ordinate. Six curves are shown. Each curve represents the rate of oxygen absorbed for each oil sample having the corresponding number above. It will be seen that the combination of dibenzyl disulfide with an aromatic hydrocarbon has far more effect than the sum of the effects produced by the two additives alone, giving an increase in stability (e. g., as measured by time required to absorb 1800 cc. of oxygen per 100 g. of oil) far greater than the sum of the increases obtained with the two additives separately.

Example II

The effect of the combination of organic sulfide and aromatic hydrocarbon on the oxidation stability of an oil similar to that used in Example I, in the absence of metallic catalyst at 150° C. may be seen from the following data:

Sulfides	Aromatics						
	None	10% Monoamyl naphthalene	10% Polyamyl naphthalene	10% Retene	10% Refined Aromatic Blowdown Oil	10% Propylated Terphenyl	5% Anthracene
None	(0.7) 1.6	(4.2) 6.3	(4.1) 5.1	(1.0) 2.0	(3.5) 5.1	(0.5) 1.4	(4.0) 6.5
0.1% Diphenyl disulfide	(0.6) 2.5	(44.0) 46.9	(111) 115	>300	(*) 33.0	(*) 8.5	(*) 130
0.2% Wax Polysulfide	(16) 19.9	(59) 61					
0.2% Dodecyl disulfide	(6.5) 9.0	(37) 41.2					
0.1% Ethylene bis (p-tolyl sulfide)	(10.6) 12.0	(159) 161					
0.1% Sulfurized wax olefin	(5.3) 6.6			(12) 15.7			

NOTE: Numbers given are time in hours required to absorb 1800 ml. O_2/100 g. of oil. Numbers in parentheses are induction periods or time in hours before oxidation becomes rapid. An asterisk (*) indicates that principal effect was to retard the rate of rapid oxidation rather than to increase the induction period.

Example III

The effect of the present combination of additives on the oxidation stability of a refined turbine lubricating oil (150 vis. at 100° F.) in the presence of copper and iron oxidation catalysts, respectively, may be seen from the following:

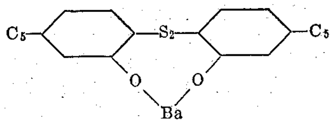
Additives	Catalyst	Induction Period, hours	Hrs. to Absorb 1800 ml. O_2/100 g.
None	1 sq. cm. Cu surface/g. oil.		1.6
0.1% Diphenyl disulfide			3.2
10% Monoamylnaphthalene			2.3
10% Refined aromatic blowdown oil.			3.2
0.1% Diphenyl disulfide and 10% monoamyl naphthalene.		[1]	47.2
0.1% Diphenyl disulfide and 10% refined aromatic blowdown oil.		[1]	34.0
None	3.5 sq. cm. Fe surface/g. oil.	1.5	2.9
0.1% Diphenyl disulfide		[1]	7.3
10% Monoamylnaphthalene		3	5.8
0.1% Diphenyl disulfide and 10% Monoamyl naphthalene.			157

[1] Principal effect was to retard the rate of rapid oxidation rather than to increase the induction period.

Example IV

Samples of Mid-Continent, sulfuric acid treated, solvent extracted and percolated Turbo-Raffinate having a final viscosity of 500, a viscosity index of 95.5 and a specific dispersion of 100.4 were oxidized at 313° F. in the presence of 2.2 cm.^{2} of exposed copper per gram of oil. The uninhibited oil absorbed 2000 cc. of oxygen per 100 g. of oil in about 40 minutes. Another sample of the same oil containing 5% w. of diamylanthracene took about 100 minutes to absorb the same volume of oxygen. Another sample to which had been added 0.55% w. of para-tertiary-amyl-phenoldisulfide absorbed the same quantity of oxygen in about 300 minutes. A fourth sample of this oil containing both 5% w. diamylanthracene and 0.55% w. paratertiary amyl phenol sulfide did not absorb this volume of oxygen until 2500 minutes.

Analogous results were obtained when using the barium salt of the alkyl phenol disulfide



in place of the corresponding free phenolic inhibitor of the preceding paragraph, both in the preceding base oil and in a refined commercial aviation lubricating oil having an aromatic content of about 5% as determined by Waterman analysis. Substitution of the free phenol disulfide in the aviation oil gave like results.

This is a continuation-in-part of my copending application, Serial No. 461,801, filed October 12, 1942.

I claim as my invention:

1. A hydrocarbon lubricating oil composition initially having a content of less than about 6% of aromatic compounds, the oxidation stability of which has been increased by the addition of an antioxidant amount of the combination of an oil-soluble halogen-free organic sulfide and between about 0.2% and about 15% of a highly oil-soluble condensed ring polynuclear aromatic hydrocarbon.

2. The composition of claim 1 wherein the condensed ring polynuclear aromatic hydrocarbon is an alkylated compound.

3. The composition of claim 1 wherein the polynuclear aromatic hydrocarbon is retene.

4. The composition of claim 1 wherein the polynuclear aromatic hydrocarbon is an alkyl naphthalene.

5. The composition of claim 1 wherein the polynuclear aromatic hydrocarbon is an alkyl anthracene.

6. The composition of claim 1 wherein the oil composition is a petroleum lubricating oil composition.

7. The composition of claim 1 wherein the oil composition is a refined mineral lubricating oil.

8. The composition of claim 1 wherein the oil composition is a synthetic lubricant.

9. The composition of claim 1 wherein the halogen-free organic sulfide is a polysulfide.

10. The composition of claim 1 wherein the halogen-free organic sulfide is an aromatic disulfide.

11. The composition of claim 1 wherein the halogen-free organic sulfide is a wax polysulfide.

12. The composition of claim 1 wherein the

halogen-free organic sulfide is at the same time a metallic phenate.

13. A hydrocarbon lubricating oil lubricating composition of improved oxidation stability comprising predominantly a highly refined lubricating oil containing dissolved .001% to 1% of halogen-free organic polysulfide and .2% to 15% of an added highly oil-soluble alkyl-substituted halogen-free polynuclear aromatic hydrocarbon compound having a condensed-ring structure.

14. A hydrocarbon oil lubricating composition of improved oxidation stability comprising predominantly a lubricating oil having a specific dispersion of less than 110, containing dissolved therein small amounts each of halogen-free organic polysulfide and an added highly oil-soluble alkyl-substituted halogen-free condensed ring polynuclear aromatic hydrocarbon having a specific dispersion between 200 and 400.

HYMAN DIAMOND.

REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,856,700	Ford	May 3, 1932
2,000,105	Story	May 7, 1935
2,080,681	Wilson	May 18, 1937
2,117,602	Buckley	May 17, 1938
2,191,089	Barth	Feb. 20, 1940
2,363,880	Lieber	Nov. 28, 1944