

# UNITED STATES PATENT OFFICE

2,472,503

## LUBRICATING OIL COMPOSITIONS

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5 Claims. (Cl. 252—37)

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This invention relates to lubricating oil compositions containing added ingredients which improve their properties in one or more important respects. The invention also pertains to the addition of certain oil-soluble agents to undoped or doped mineral oils to produce lubricating oils of improved oxidation stability and having excellent anti-wear and anti-corrosion properties for internal combustion engines. More particularly, the invention covers the addition to lubricating oils of detergent and anti-oxidant metal salts of organic acidic materials together with oxidation products of synthetic lubricating oils and other high molecular weight hydrocarbons, said additive combination having the property of preventing the sticking of piston rings when engines are being operated for long periods of time, and which in addition have the ability of adding the lubricating oil to properly lubricate the cylinders, pistons and other engine parts, under severe operating conditions.

It is known that in modern internal combustion engines, such as high-speed Diesel engines, aviation gasoline engines, etc.; which due to their high power output operate at relatively high temperatures, piston rings have a tendency to become stuck in the grooves. Lacquer, varnish and/or carbon formation appears to be the principal reasons for this occurrence. Piston rings have a tendency to become stuck in grooves and become worn when fuel is incompletely combusted, resulting in carbon formation which at elevated temperatures is baked on to the metal surfaces.

Lacquer, varnish and carbon formation results from the deterioration and oxidation of lubricants at elevated temperatures and pressures. Under these conditions highly acidic resinous materials form which up to a degree are rather soluble in petroleum hydrocarbons. However, they are exceedingly unstable and have a marked tendency toward polymerization, the resulting oil being high in sticky oil-insoluble residues which have a pronounced affinity for hot metal surfaces, coating said surfaces with a gummy, sticky material which causes ringsticking. Other oil-insoluble resinous-like materials thus formed also have a tendency to act as a binding agent for carbonaceous materials formed during oxidation of oils, resulting in a metal coating that causes engine wear. The resinous acidic bodies formed during oxidation of oils also readily attack and corrode or pit alloyed bearings.

Carbonaceous deposits formed in oils under conditions described above usually consist of brittle carbon which is generally deposited above

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the top piston ring and on the piston crown. A softer and more granular carbon deposits in the ring grooves, and it is this type of deposit, together with the lacquer which act as a binder for the carbon particles, which leads to ringsticking and its attendant evils. Lacquers as they build up a coating on the metal surface ultimately causes seizure between the piston and cylinder, since engine parts are machined to close tolerances. Also, such coatings prevent free oil circulation and distribution to various engine parts, resulting in excessive wear and corrosion.

The addition of small amounts of certain oil-soluble carboxylic acid salts, such as polyvalent metal salts of fatty acids, naphthenic acid, etc., is known to reduce the ringsticking tendencies. The addition of small amounts of such salts or soaps, however, has the disadvantage that newer type bearings such as those containing copper-lead, cadmium or silver alloys are corroded. A further disadvantage of such soaps is that many of them tend to settle out of the oil in use. For example, salts of hydroxy aromatic compounds in which the metal is held by a hydroxy group tend to decompose when exposed to the action of water and carbon dioxide under conditions of lubrication in internal combustion engines, thereby precipitating oil-insoluble carbonates.

In accordance with this invention it has been found that the combination of polyvalent metal salts of organic acidic materials together with oxidation products of synthetic lubricating oils and other high molecular weight hydrocarbons, when added to mineral oils in suitable quantities, produces effective anti-ringsticking lubricants which are stable, non-corrosive and prevent engine wear.

As stated above, it is a known fact that oxidation products occurring in lubricating oils are largely the cause of ringsticking, engine wear, corrosion and the like. However, contrary to such teaching it has been found that oxidation products formed from oxidized synthetic lubricating oils and other high molecular weight hydrocarbons when combined with metal salts of organic acids inhibit deterioration of lubricating oils and very little if any sludge, carbonaceous and other foreign materials form. These oxidation products derived from synthetic lubricating oil and the like also have a marked activating or synergistic effect on metal salts, increasing the detergent properties, thus keeping the engine clean. The presence of oxidation products derived from synthetic lubricating

oils also activates the anti-oxidant properties of salts, thus inhibiting the deterioration of the base oil even under the most adverse operating conditions. The functions performed by oxidation products derived from synthetic lubricating oils and the like are unique in view of the fact that oxidation product occurring in natural oils are rather detrimental to engine lubrication.

The metal salts employed in accordance with the invention may be the salts of polyvalent metals with petroleum naphthenic acids, petroleum sulfonic acids, fatty acids having at least 10 carbon atoms, such as oleic and stearic acids, equivalent hydroxy fatty acids, aromatic fatty acids and other aromatic carboxylic acids, such as benzoic, naphthoic, alkyl benzoic, alkyl naphthoic, phenyl acetic, hydrogenated rosin acids, rosin acid, and carbonic, oxalic, succinic, alkyl succinic, sebacic, aspartic, and like acids. In addition other acids can be used, such as phenyl stearic acid, naphthyl stearic acid, resinic acids, acids obtained by oxidation of solid paraffin wax or sweating oils, alkylated oxycarboxylic acids such as resorcylic acids, salicylic acids such as diisopropyl salicylic acid, and the like. Any of the above acids, if desired, may contain polar neutral or basic substituents. Such substituents are, for example, OH, NH<sub>2</sub>, halogen, sulfur, etc., radicals, examples of these substituted acids being lactic, hydroxystearic, ricinoleic aminostearic, hydroxy or amine benzoic or naphthoic, hydroxy or amino phenyl stearic, carbamic, allophanic, thiocarbamic, thiocarbamic or -allophanic, chlorinated or sulfurized fatty acids.

Anti-oxidant metal salts which are very effective anti-ring-sticking agents when in combination with oxidation products derived from synthetic lubricating oils and other hydrocarbons may be salts of polyvalent metals with mononuclear or polynuclear aromatic hydroxy compounds such as phenol, naphthol, anthrol etc., and derivatives thereof.

If desired the aromatic hydroxy compounds may contain additional polar substitution radicals, such as carboxylic, alkoxy, aryloxy, hydro-sulfide, amino, imino, halogen, etc., radicals. While, in general these polar radicals reduce the solubility in hydrocarbon oils considerably rather than enhance it, some of them frequently are advantageous in further reducing corrosiveness.

Examples of compounds that may be used to form the polyvalent metal salts are alkyl phenols, alkyl naphthols, alkyl amino phenols, alkyl polyhydroxy phenols, such as alkylated catechol, alkylated resorcinol, alkylated pyrogallol, and the like.

Mixtures of these metal salts may be used advantageously also in combination with oxidation products of this invention. Thus, a salt of anti-oxidants enumerated above may be added to a detergent salt and the mixture combined with the oxidation products of this invention so as to enhance detergency properties and inhibit corrosion of the lubricating oils.

Of the polyvalent metal salts which are valuable for our purpose are beryllium magnesium, calcium, strontium, barium, zinc, cadmium, aluminum, and tin, and of these calcium, magnesium and zinc appear to be especially effective.

The salts may be either the basic or normal salts. Methods of dispersing the salts in solution may vary. Some can be dissolved while in a cold state; others are best added to the lubricating oil at an elevated temperature, for example, in

the range of 100° C. to 350° C. Still others can only be formed in the oil, preferably at elevated temperatures for example by methods described in U. S. Patent No. 2,228,500. Once they have been dissolved at elevated temperatures, many of the solutions thus obtained tend to remain substantially stable even at normal temperatures.

In general, it is preferred to use about 0.3 to 1.5% by weight of the salts in a lubricating oil, however, suitable amounts may be varied from approximately 0.15 to 2% by weight. Under certain operating conditions as high as 3% by weight of a salt may be used, but excessive amounts (about 3%) are to be avoided because of their tendency to increase oil viscosity as well as cause gelling of the oil.

The second additive used in combination with any of the above salts and/or their mixtures is the oxidation product derived from the oxidation of synthetic lubricating oils and other hydrocarbons. Synthetic lubricating oils and other hydrocarbons which are subjected to oxidation, and the oxidation fraction removed therefrom and used as additives, are obtained by polymerization and/or condensation of unsaturated, lower molecular hydrocarbons or hydrocarbon mixtures. Starting materials for producing synthetic lubricating oils and the like can be gases as utilized by the Fischer-Tropsch process. This process consists in subjecting carbon monoxide and hydrogen to controlled conditions in order to cause the oxygen molecules to split and combine with hydrogen, and then polymerizing the unsaturated hydrocarbon fraction to lubricating oil in the presence of a catalyst. The starting material for the Fischer-Tropsch process, namely, carbon monoxide and hydrogen can be obtained from various sources such as gas works coke or coke-oven gas, natural gas, carbonaceous materials such as coal, lignite, peat, etc., vegetable matter, petroleum residuum matter and the like.

Lubricating oil fractions utilizing the Fischer-Tropsch process can be increased by using Friedel-Crafts type catalysts and various other catalysts such as iron, nickel, and cobalt, supported on kieselguhr, silica-gel, or asbestos, and promoters of thorium and manganese. Preferred catalysts for this process for producing lubricating oil are the nickel-manganese-aluminum catalyst, and the cobalt-thoria-kieselguhr catalyst. Also various known fluid catalysts suitable for this process can be utilized.

Other methods of producing synthetic lubricating oils and high molecular weight hydrocarbons can be used, such as the Bergius process, which consists essentially in hydrogenating coal and various other carbonaceous materials in the presence of catalysts. Suitable synthetic hydrocarbons can be produced from olefinic hydrocarbons of lower molecular weight, for instance, by polymerizing olefins such as ethylene, propylene, butylene, isobutylene and the like and particularly heavier olefines having at least ten carbon atoms of straight chain type, although branched-chain or cyclic olefins may also be used, as well as cracked distillates containing such olefins and preferably obtained by vapor phase cracking of suitable hydrocarbons as kerosene, gas oil, paraffin wax; diolefins and hydrocarbons capable of addition of chlorine generally, in the presence of suitable polymerization catalysts, for instance aluminum chloride, boron fluoride, zinc chloride, ferric chloride and other Friedel-Crafts catalyst as well as clay, etc; or by condensation of diolefines with cyclic, particularly aromatic, hydro-

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carbons; or by some other means, as volatilization. Thus, lubricating oil fractions prepared by polymerizing alkenes or isoalkenes, or mixtures containing them, such as obtained by dehydrogenating or partially oxidizing mineral oils or paraffin wax, can be utilized as well as those obtained by condensation of cyclic alkenes or copolymerizing alkenes with straight chain alkenes or by condensing hydrocarbons with halogenated hydrocarbons. In general all methods of obtaining high-molecular hydrocarbons or hydrocarbon mixtures preferably of lubricating oil range by polymerization, condensation, hydrogenation or volatilization can be used as a source for obtaining oxidation product additives of this invention.

The oxidation of the synthetic lubricating oils may be effected by any known method, for instance by introducing into the synthetic product mixture of oxygen, air, or oxygen-containing gas, ozone, chromic acid, permanganate, hydrogen peroxide, nitric oxide and the like. If desired, the reaction may be carried out in the presence of catalysts such as alkali carbonates or hydroxides; or metals, oxides, and salts, preferably oil-soluble salts as oleates, stearates, sulfonates, naphthenates, resinates, etc; of copper, lead, vanadium, molybdenum, chromium, manganese, iron, nickel, cobalt, etc.

The temperature of oxidation treatment may vary depending upon the oxidation medium used. The temperature should be high enough to oxidize the product at a fair rate, but it should be low enough substantially to avoid breakdown of the synthetic hydrocarbon oils to compounds of lower molecular weights. In general, it is preferred to carry out the oxidation at an elevated temperature which is above atmospheric but below about 200° C.

A preferred method of producing the oxidized product comprises passing a stream of oxygen,

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added in quantity ranging between about 2% and about 6% by weight calculated on the lubricant

An illustrative example of a method of producing oxidation products of this invention follows. A cracked distillate boiling between about 100° C. and about 300° C. obtained by vapor phase cracking of paraffin wax was polymerized with aluminum chloride to produce a synthetic oil having an average molecular weight of 580 and a Saybolt Universal viscosity of 340 seconds at 50° C. This oil was oxidized at a temperature between about 170° to 190° C. by passing 200 liters of air per hour therethrough over a period of 216 hours. This period can be considerably reduced by carrying out the oxidation in the presence of a suitable catalyst, e. g. manganese resinate. The oxidized fraction was separated by refluxing the synthetic oil with an alcoholic solution of potassium hydroxide and pentane in order to separate the oily and alcoholic layers. At the end of the refluxing period water was added to effect a segregation of the layers. The aqueous alcoholic layer was separated and the alcohol evaporated whilst simultaneously adding water. The resulting aqueous solution was extracted with pentane to remove the oily non-saponified matter, and the de-oiled aqueous solution was then acidified with sulfuric acid to liberate the oxidation products.

The oxidation products derived from oxidized synthetic lubricating oils are entirely different from oxidation products derived from natural petroleum hydrocarbons. The synthetic oxygenated materials are much more potent lubricating oil improving agents and this can best be exemplified by references to the table which compares standard wear test results between two lubricating oils, one containing 1% of synthetic oxygenated products and the other oil containing 1% oxygenated products derived from natural paraffin wax.

Comparative standard test results as to changes in coefficient of friction with change in temperature

	50° C.	100° C.	150° C.	200° C.	250° C.
Undoped Oil.....	.120	.130	.163	.163	.163
Above oil containing 1% by wt. of Oxidized Fraction derived from natural hydrocarbons (paraffin wax).....	0.090	0.820	0.150	0.142	0.180
Above oil containing 1% by wt. of an Oxidized Fraction obtained by the above described method.....	0.100	0.085	0.085	0.086	0.088

air or other oxygen-containing gases through a synthetic hydrocarbon oil at a temperature between about 150° and 200° C., preferably in presence of a catalyst. The oxidized mass is then saponified and the unsaponifiable portion removed. The saponified fraction is acidified to release oxidized products or the oxidized product may be extracted with alcohol or ketone or the like, since these materials have a preferential solvent action for the saponifiable matter in the mass. If desired, the extraction may be carried out with a solvent pair of solvents which are only partially miscible, or substantially immiscible, with each other, such as phenol and light naphtha, the phenol being a selective solvent for the saponifiable matter and the naphtha for the non-saponifiable matter.

The oxidation product thus obtained is added in combination with the salt additives of this invention to lubricants to prevent ringsticking and to improve the lubricating properties of oils. The amount used varies from less than 1% up to about 10% by weight calculated on the lubricant. Preferably these oxidation products are

The following example further illustrates this invention:

About 1% by weight of calcium salt of diisopropyl salicylic acid was dissolved in a highly refined mineral lubricating oil at an elevated temperature. The resulting lubricating oil composition was found to be suitable for lubricating Diesel engines; it materially retarded corrosion of bearing metals and ringsticking, although the first piston ring groove showed signs of ringsticking.

About 1% by weight of calcium salt of diisopropyl salicylic acid was again dissolved in highly refined mineral lubricating oil at an elevated temperature and to this mixture was added about 4% by weight of an oxidized synthetic oil fraction obtained by the method fully described in column 6 on lines 3 to 29. The lubricating oil composition thus prepared was used in Diesel engines and aviation gasoline engines and it was observed that the piston, piston rings and grooves, cylinder as well as other engine parts remained perfectly clean and no corrosion was noted on any of the bearing metals.

Besides the additives mentioned above it is possible to incorporate in the lubricants other substances which contingently may impart thereto special properties. Among them may be detergents, pour points, reducing agents, anti-oxidants, extreme pressure agents, anti-foaming agents, thickening agents, viscosity index improvers, pigments, organic solvents and the like. Thus detergents other than those mentioned above may include oil-soluble salts of various bases with detergents which include oil-soluble salts of various bases with detergent forming acids. Such bases include metal as well as organic bases. Metallic bases include those of the alkali metals Cu, Mg, Ca, Sr, Ba, Zn, Cd, Al, Sn, Pb, Sr, Mn, Fe, Ni, Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary and quaternary amines.

Examples of specific types of detergent forming acids are chlorinated high molecular weight fatty acids, aromatic keto acids, aromatic ether acids, paraffin wax benzoic acids; diphenols as di-(alkyl phenol) sulfides and disulfides, methylene bis alkyl phenols; esters, phosphoric, arsenic and antimony acids mono and diesters, including the corresponding thiophosphoric, arsenic and antimony acids; phosphoric and arsenic acids and the like.

Additional detergents are the alkaline earth phosphate diesters, including the thiophosphate diester; the alkaline earth diphenolates, specifically the calcium and barium salts of diphenol mono and poly sulfides.

Non-metallic detergents include compounds such as phosphatides such as lecithin and cephalin, certain fatty oils as rapeseed oils, volatized fatty or mineral oils and the like.

An excellent metallic detergent for the present purpose is the calcium salt of oil-soluble petroleum sulfonic acids. This may be present advantageously in the amount of about 0.025% to 0.2% sulfate ash. Also alkaline metal salts of alkyl phenol-aldehyde condensation reaction products are excellent detergents.

Anti-oxidants comprise several types, for example, alkyl phenols such as 2,4,6 trimethyl phenol, penta methyl-phenol, 2,4 dimethyl-6-tertiary-butyl phenol, 2,4-dimethyl-6-octyl phenol, 2,6-di-tertiary-butyl-4-methyl-phenol, 2,4,6 tritertiary-butyl phenol and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenyl amine, phenyl - beta - naphthylamine, phenyl-alpha-naphthylamine, dinaphthylamine.

Corrosion inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 and more carbon atoms; alkali metal and alkaline earth salts of sulfonic acids and fatty acids; organic compounds containing an acidic radical in close proximity to a nitrile, nitro or nitroso group (e. g. alpha cyano stearic acid).

Extreme pressure agents which may be used comprise: esters of phosphorus acids such as tri-aryl, alkyl hydroxy aryl, or aralkyl phosphates, thiophosphates or phosphites and the like; neutral aromatic sulfur compounds or relatively high boiling temperatures such as diaryl sulfides, diaryl disulfides, alkyl aryl disulfides, e. g. diphenyl sulfide, diphenol sulfide, dicresol sulfide, dixylenol sulfide, methyl butyl diphenol sulfide, dibenzyl sulfide, corresponding di- and tri-sulfides, and the like; sulfurized fatty oils or esters of fatty acids and monohydric alcohols, e. g. sperm oil, jojoba oil, etc.; in which the sulfur is strongly bonded; sulfurized long chain olefins

such as may be obtained by dehydrogenation or cracking of wax; sulfurized phosphorized fatty oils or acids, phosphorus acid esters having sulfurized organic radicals, such as esters of phosphoric or phosphorus acids with sulfurized hydroxy fatty acids; chlorinated hydrocarbons, such as chlorinated paraffin, aromatic hydrocarbons, terpenes, mineral lubricating oil, etc.; or chlorinated esters of fatty acids containing the chlorine in position other than alpha position.

Additional ingredients may comprise oil-soluble urea or thiourea derivatives, e. g. urethanes, allophanates, carbazides, carbazones, etc.; polyisobutylene polymers, unsaturated polymerized esters of fatty acids and monohydric alcohols and other high molecular weight oil-soluble compounds.

Depending upon the additive used and conditions under which it is used, the amount of additive used may vary from 0.01 to 2% higher. However substantial improvement is obtained by using amounts ranging from 0.1 to 0.5% in combination with phosphorous sulfide-unsaturated cyclic ketone reaction products of this invention.

It is to be understood that while the features of the invention have been described and illustrated in connection with certain specific examples, the invention, however, is not to be limited thereto or otherwise restricted except by the prior art and the scope of the appended claims.

I claim as my invention:

1. A mineral lubricating oil having incorporated therein, in an amount sufficient to inhibit oxidation and corrosion, an oil-soluble polyvalent metal salt of an acidic aromatic compound selected from the group consisting of phenols and aromatic carboxylic acids and a saponifiable oxidation product of a polymeric olefin of lubricating oil viscosity, said oxidation product being obtained as follows: polymerizing an olefinic hydrocarbon material of boiling range of from about 100° C. to about 300° C. to produce a synthetic polymeric olefin hydrocarbon oil of lubricating oil viscosity and oxidizing said synthetic hydrocarbon oil at a temperature between about 150° C and 200° C. with an oxygen-containing gas for sufficient time to partially oxidize the synthetic hydrocarbon oil while avoiding breakdown thereof.

2. A mineral lubricating oil in accordance with claim 1 wherein said oil-soluble polyvalent metal salt of an acidic aromatic compound is an oil-soluble polyvalent metal salt of diisopropyl salicylic acid.

3. A mineral lubricating oil in accordance with claim 1 wherein said oil-soluble polyvalent metal salt of an acidic aromatic compound is an oil-soluble calcium salt of diisopropyl salicylic acid.

4. A mineral lubricating oil in accordance with claim 1 wherein said oil-soluble polyvalent metal salt of an acidic aromatic compound is an oil-soluble polyvalent metal salt of an alkyl phenol.

5. A mineral lubricating oil having incorporated therein from about 0.15% to 3% of a calcium salt of diisopropyl salicylic acid and from about 1% to about 10% of a saponifiable oxidation product of a polymeric olefin of lubricating oil viscosity, said product being obtained as follows: a cracked distillate boiling between about 100° C. and about 300° C. obtained by vapor phase cracking of paraffin wax is polymerized with aluminum chloride to produce a synthetic oil having an average molecular weight of 580 and

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a. Saybolt Universal viscosity of 340 seconds at 50° C., and said oil is oxidized at a temperature between about 170° to 190° C. by passing air therethrough for sufficient time to partially oxidize said oil while avoiding breakdown thereof. 5  
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**REFERENCES CITED**

The following references are of record in the file of this patent: 10

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**UNITED STATES PATENTS**

Number	Name	Date
2,128,574	Van Peski et al. ....	Aug. 30, 1938
2,227,149	Murphree .....	Dec. 31, 1940
2,230,228	Frey .....	May 25, 1943
2,379,290	Finley .....	June 26, 1945