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COMPOUNDED HYDROCARBON OIL

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This invention relates to a new and useful composition of matter and involves a composition comprising a hydrocarbon oil and a new combination of stabilizing ingredients.

This application is a continuation-in-part of our copending application Serial No. 241,649, filed November 21, 1938, issued as United States Patent No. 2,344,988 on March 28, 1944.

The production of improved hydrocarbon oils, and particularly of lubricating oils having desired characteristics, has been the subject of extensive research and investigation in recent years. Generally speaking, the compounding of hydrocarbon oils to obtain desired characteristics involves empirical phenomena, and the action of untested combinations of different types of compounding agents cannot be predicted.

A characteristic which has been the subject of extensive investigation is the tendency of hydrocarbon oils to deteriorate or partially decompose and oxidize when subjected to high temperatures. This deterioration is evidenced by the deposition of adhesive deposits on hot metal surfaces over which the hydrocarbon oil may flow. It is important that resistance to such deterioration be imparted to hydrocarbon oils, particularly to lubricating oils, in order that such compositions may be relatively free from the tendency to form such deposits even under high temperatures and severe operating conditions. A direct result of this type of deterioration during lubrication of internal combustion engines, such as engines of the Diesel type, is the tendency of the oil to cause or permit the sticking of piston rings.

The crankcase lubricant in internal combustion engines is subjected to extremely severe operating conditions, and in engines of the Diesel type the lubricant encounters in the piston ring zone temperatures of from approximately 425° to 650° F. and pressures from the oxidizing combustion gases as high as 750 to 1150 pounds per square inch. In its more specific aspects the present invention is directed to the improvement of hydrocarbon lubricating oils by imparting thereto increased resistance to deterioration by heat at high temperature levels in the order of those above mentioned.

We have discovered that aromatic compounds having at least two polar substituents on the aromatic nucleus, when used in combination with metal phenates, impart to hydrocarbon lubricating oils a number of highly desirable properties and improve the lubrication and operation of internal combustion engines. More particularly, it has been discovered that a lubricating oil containing both a metal phenate and a polypolar

substituted aromatic compound having antioxidant properties permits longer periods of operation of engines without the necessity of major overhauls heretofore occasioned by stuck pistons, wear of pistons and cylinder walls, or corrosion of bearing metal alloys.

The broader aspects of the invention involve the discovery that polypolar substituted aromatic compounds and metal phenates cooperate to give new results in hydrocarbon oil compositions. Hydrocarbon oils containing this combination of ingredients have greater stability under various operating conditions than do oils containing either of these types of ingredients alone. For example, the same stability is not obtainable with 1% of a metal salt of a phenol or with 1% of the polypolar aromatic antioxidant in a lubricating oil as is obtained with $\frac{3}{4}$ % of the metal phenate and $\frac{1}{4}$ % of the antioxidant in the same lubricating oil.

Metal phenates, which may be added to hydrocarbon oils such as mineral lubricating oils to provide one component of the new composition of matter herein claimed, comprise the alkali, alkaline earth and other metal phenates. Examples of such metal phenates are sodium phenates, potassium phenates, beryllium phenates, calcium phenates, strontium phenates, barium phenates, magnesium phenates, zinc phenates, cadmium phenates and aluminum phenates.

The metal phenates are preferably formed from high molecular weight phenols of the type formula:



in which u , v , w , x and y are selected from the group consisting of hydrogen, hydrocarbon, oxy and hydroxy radicals. The phenol preferably contains at least one alkyl group having at least four carbon atoms. The term "hydrocarbon radicals" used in the above connection is intended to include alkyl, aryl, alkaryl, aralkyl and cyclic non-benzenoid groups; and the term "oxy radicals" refers to a group in which the hydrogen of a hydroxy radical has been replaced by esterification, neutralization, or the like. Although phenols containing at least one alkyl substituent are preferred, the invention does not preclude compounds containing no alkyl groups and embodies the substitution of aryl, alkaryl, aralkyl and cyclic non-benzenoid groups as well as conjugated rings

in the aromatic nucleus to which the phenolic hydroxy group is directly attached.

Examples of specific metal phenates which may be utilized comprise sodium lauryl phenate, sodium cetyl phenate; calcium lauryl phenate, calcium cetyl phenate, calcium di-amy l phenate, calcium heptyl phenate, calcium p-tertiary amy l phenate, calcium monochloramy l phenate, calcium p-cyclohexanol phenate; aluminum lauryl phenate, aluminum di-cetyl phenate; magnesium cetyl phenate, barium cetyl phenate; and calcium cetyl cresylate.

The metal phenates of this invention may be prepared by any suitable method. For example, the alkyl phenols may be obtained by alkylation of the phenols, in the presence of sulfuric acid, with an olefin or an olefin polymer, such as di, tri and tetra butylenes or di, tri and tetra isobutylenes. The alkylated phenol may then be reacted with the proper metal or metal ion, or the sodium or potassium salts of the alkyl phenol may be reacted with the proper metal ion to obtain the desired salt. The preparation of the metal phenates comprises no part of this invention and may be effected by those skilled in the art without undue difficulties.

Among the polypolar substituted aromatic compounds that may be used in accordance with the invention are the polyhydroxy phenols, aryl diamines, nitrosoamines, oxazines, benzothiazole and phenthiazine.

The polar substituted aromatic compounds used in combination with a metal phenate in accordance with the invention have, as stated, at least two polar substituents, and are herein frequently referred to for convenience as "polypolar substituted aromatic compounds" and as "polypolar compounds." These substituents may be attached to the same aromatic nucleus or to two or more different aromatic nuclei (as in diphenyl) but preferably at least two polar groups are attached to a single aromatic nucleus.

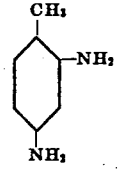
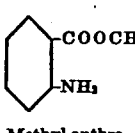
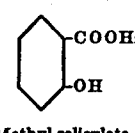
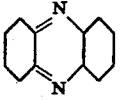
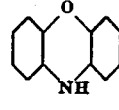
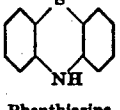
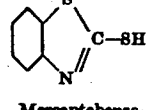
The following polar groups will serve to exemplify the types of polar substituents that may be present:

—OH	Hydroxyl
—OR	Alkoxy (aroxy, cycloalkoxy)
—NH ₂	Amino (including substituted amino)
—NHR	
—NR ₁ R ₂	
—NO	Nitroso
—NO ₂	Nitro
—CO	Carbonyl
—CO—R	Keto
—CHO	Aldehyde
—COOH	Carboxyl
—COOR	Carboxy ester
—CONH ₂	Amido
—SH	Mercapto
—SR	Alkyl thio (aryl thio, cycloalkyl thio)
—Cl	Chloro
—Br	Bromo

Preferably, aromatic compounds are used which, used by themselves in viscous mineral oil, do not promote bearing corrosion and oxidation, more particularly those which are themselves corrosion inhibitors and/or oxidation inhibitors in mineral oils. A class of aromatic compounds meeting these specifications, and which constitutes a preferred class of additives for purposes of the present invention, are aromatic compounds containing a plurality of substituents selected from the group consisting of hydroxyl, alkoxy, cycloalkoxy, aroxy, carboxy ester, amino (including

substituted amino), nitroso, nitro, mercapto, and organic substituted mercapto substituents. One or more of the polar substituents may form part of a ring, as in the benzothiazoles and phenthiazines. Preferably, the polar groups are directly connected to the aromatic nucleus, that is, are nuclear substituents, but one or more of the polar groups may be separated from the aromatic nucleus by one or even two carbon atoms. Thus, saligenin (ortho hydroxy benzyl alcohol) may be used, but pyrocatechin (1,2-dihydroxy benzene) is preferred.

In the table below are illustrated the preferred classes of polypolar substituted aromatic compounds, specific members of these classes, and the structures of these specific members:

Class of compounds	Specific members
Polyhydric phenols	 p-Hydroquinone
Aryl polyamines	 2,4-diamino toluene
Aminophenols	 p-Amino phenol
Nitroso and nitro amines and phenols	 p-Nitroso dimethylaniline
	 p-Nitrophenol
Polar substituted aryl carboxy esters	 Methyl anthranilate
	 Methyl salicylate
Phenazines, phenoxazines, phenthiazines and benzothiazoles	 Phenazine
	 Phenoxazine
	 Phenthiazine
	 Mercaptobenzothiazole

As has been previously pointed out, the present invention embraces the discovery that hydrocarbon oils containing both the metal salt of a phenol and a polypolar substituted aromatic compound have new and unpredictable advantages. The properties of hydrocarbon oils containing both a metal phenate and a polypolar compound are illustrated by the following discussion and data.

The strip corrosion test referred to in the table below was carried out as follows: Glass tubes 2 inches in diameter and 20 inches long were immersed in an oil bath, the temperature of which was automatically controlled to within plus or minus 1° F. of the test temperature, which was 300° F. Approximately 300 cc. of oil under test was placed in each tube and air was bubbled through it at the rate of 10 liters per hour. Strips of the different types of bearing metal were placed in the oils; in most cases the copper-lead and cadmium-silver bearing alloys were tested simultaneously in the same sample of oil. The weight loss of each strip was recorded. Before weighing, each strip was washed in petroleum ether and carefully wiped with a soft cotton cloth. The duration of the test was 72 hours. The oil at the end of each test was also inspected for viscosity and neutralization number, the results being noted in the table below along with the corrosion results.

The base oil was an SAE 30 solvent treated Pennsylvania (paraffinic) oil and the calcium cetyl phenate was the normal calcium salt of an alkylated phenol produced by alkylating phenol in the presence of sulfuric acid with a butylene polymer averaging C₁₆ per molecule (four butylene units), separating the alkylated phenol and forming the calcium salt.

desired. As little as 0.05% by weight of various of the polypolar compounds gives measurable improvements, particularly as respects the color stability of the compounded oil. From approximately 0.1% to 2% of the compound may be added to lubricants containing metal phenates where stability at high temperature comprises the principal property desired. Solutions containing more than 2% of the compounds in mineral oils may be utilized for various purposes, e. g., for preparing lubricating greases and concentrates capable of dilution with lubricating oils and the like. Likewise, the proportion of metal phenates present in compounded lubricants may vary widely depending on the uses involved and the properties desired. As little as 0.1% by weight of the phenate gives measurable improvement, although from approximately 0.25% to approximately 2% phenate is preferred where the compounded oil is to be used as a crankcase lubricant for internal combustion engines. As much as 50% or more by weight of various of the phenates may be dissolved in mineral oil for the purpose of preparing a concentrate capable of dilution with lubricating oils and the like. Concentrates containing high percentages of the phenate and a polypolar compound comprise a convenient method of handling the ingredients and may be used as addition agents for lubricants in general as well as for other purposes.

The combination of ingredients of this invention may be present in hydrocarbon oils containing other compounding agents such as pour point depressants, oiliness agents, extreme pressure addition agents, blooming agents and compounds for enhancing the viscosity index of the hydrocarbon oil. The invention in its broader aspects

Base oil	Additives	Strip corrosion test						Used oil inspections		
		Cu-Pb, hours			Cd-Ag, hours			Viscosity increase at 100° F.	(SSU) at 210° F.	Neutralization number
		24	48	72	24	48	72			
Penn. SAE 30...	Nil.....	1.9	6.0	22.0	0.0	0.2	0.2	88	5.2	1.39
Do.....	0.5% Ca cetyl phenate.....	12.6	52.1	100.5	1.1	20.1	103.5	159	7.3	1.80
Do.....	1% p-hydroquinone.....	5.5	13.9	60.5	0.2	0.3	0.3	135	5.2	1.13
Do.....	0.5% Ca cetyl phenate+1% p-hydroquinone.....	0.0	0.3	0.5	0.0	0.2	0.1	141	8.1	0.84
Do.....	1% diamino toluene.....	0.2	+1.7	+1.1	+0.1	+0.1	+0.1	60	2.2	0.54
Do.....	0.5% Ca cetyl phenate+1% diamino toluene.....	+0.5	0.5	1.2	0.0	0.0	0.0	62	2.3	0.23
Do.....	1% p-nitrosodimethylaniline.....	3.3	3.2	3.4	0.0	0.0	0.0	66	2.4	0.20
Do.....	0.5% Ca cetyl phenate+1% p-nitrosodimethylaniline.....	5.6	9.8	15.8	0.3	0.2	0.2	83	4.7	0.29
Do.....	1% methyl anthranilate.....	0.9	2.4	10.3	0.1	0.2	0.2	111	4.2	1.79
Do.....	0.5% Ca cetyl phenate+1% methyl anthranilate.....	1.1	1.0	22.0	0.0	0.0	20.9	91	4.3	0.72
Do.....	1% mercaptobenzothiazole.....	3.2	3.2	3.2	0.0	0.0	0.0	140	2.9	0.67
Do.....	0.5% Ca cetyl phenate+1% mercaptobenzothiazole.....	6.5	6.3	6.5	0.1	0.1	0.1	183	5.7	0.28
Do.....	1% phenthiazine.....	1.8	1.8	2.0	0.2	1.5	1.9	122	8.0	0.75
Do.....	0.5% Ca cetyl phenate+1% phenthiazine.....	6.3	32.0	94.7	2.8	31.6	80.1	131	6.0	0.81

Besides the above indicated and other advantages possessed by the combination in hydrocarbon lubricating oils of metal salts of phenols and the polypolar substituted aromatic compounds of the invention, a given amount of the combination also imparts to such oils a greater stability against oxidation than is imparted by an equal amount of either component alone.

A variety of base oils may be employed for compounding with the additives of this invention; e. g., paraffinic, naphthenic and mixed base oils.

The proportion of polypolar substituted aromatic compound which may be added to mineral lubricating oils, according to the principles of the present invention, may vary widely depending upon the uses involved and the properties

embraces mineral hydrocarbon oils containing, in addition to the metal phenate and the polypolar compound, thickening agents and/or metal soaps in grease-forming proportions or in amounts insufficient to form grease, as in the case of mineral castor machine oils or other compounded liquid lubricants.

As used in the appended claims, the terms "amine" and "amino," unless otherwise qualified, include primary amine or amino, secondary amine or amino and tertiary amine or amino groups or radicals and the term "oxy," unless otherwise qualified, includes the free hydroxyl group and substituted hydroxyl groups (OR, where R is an etherifying group such as alkyl, aryl or cycloalkyl).

While the character of the invention has been

described in detail and numerous examples of the composition given, this has been done by way of illustration only and with the intention that no limitation should be imposed on the invention thereby. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be effected in the practice of the invention which is of the scope of the claims appended hereto.

We claim:

1. A lubricant comprising a major proportion of a hydrocarbon lubricating oil and a small amount each, sufficient to stabilize the oil against heat and oxidation, of a metal salt of a phenol and an oxidation inhibitor containing a benzene nucleus to which are directly attached at least two substituents selected from the group consisting of amino radicals and oxy radicals.

2. A lubricant comprising a major proportion of a hydrocarbon lubricating oil and a small amount each, sufficient to stabilize the oil against heat and oxidation, of an oil-soluble polyvalent metal salt of an alkylated phenol and an oxidation inhibitor containing a benzene nucleus to which are directly attached at least two substituents selected from the group consisting of amino radicals and oxy radicals.

3. A liquid lubricant comprising a major proportion of a hydrocarbon lubricating oil, about 0.1 to 2% by weight based on the oil of an oil-soluble polyvalent metal salt of an alkylated phenol and about 0.05 to 2% by weight based on the oil of an aromatic compound containing a benzene nucleus to which are directly attached a plurality of oxy radicals.

4. A liquid lubricant comprising a major proportion of a petroleum oil of lubricating viscosity, about 0.25 to 2% by weight based on the oil of a polyvalent metal salt of a phenol and about 0.05 to 2% by weight based on the oil of an oxidation inhibitor which is an aromatic compound containing a benzene nucleus to which are directly attached a plurality of substituents selected from the group consisting of amino substituents and oxy substituents.

5. A liquid lubricant comprising a major proportion of a petroleum lubricating oil and containing about 0.25 to 2% by weight based on the oil of an oil-soluble alkaline earth metal salt of an alkylated phenol and about 0.05 to 2% by weight based on the oil of a polyhydric phenol.

6. A lubricant comprising a major proportion of a petroleum lubricating oil containing about 0.25 to 2% by weight based on the oil of an oil-soluble alkaline earth metal salt of an alkylated phenol and about 0.1 to 2% by weight based on the oil of an aryl polyamine.

7. A liquid lubricant comprising a major proportion of a hydrocarbon lubricating oil, about 0.1 to 2% by weight of an oil-soluble polyvalent metal salt of an alkylated phenol and about 0.1 to 2% by weight of an aromatic compound containing in the aromatic nucleus at least two amino substituents.

8. The lubricant of claim 7 wherein said aromatic compound is an aryl diamine.

9. The lubricant of claim 4 wherein said polyvalent metal is an alkaline earth metal.

10. The lubricant of claim 4 wherein said polyvalent metal is calcium.

11. A concentrated dispersion in viscous hydrocarbon oil of a metal phenate and an oxidation inhibitor which is an aromatic compound containing a benzene nucleus to which are directly attached a plurality of substituents selected from the group consisting of amino substituents and oxy substituents.

12. A liquid lubricant comprising a major proportion of a hydrocarbon lubricating oil, about 0.1 to 2% by weight based on the oil of an oil-soluble polyvalent metal salt of an alkylated phenol and about 0.05 to 2% by weight based on the oil of an aromatic compound containing a benzene nucleus to which are directly attached two hydroxyl radicals.

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