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COMPOUNDED OIL

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This invention relates to new and useful com-
positions of matter and involves more particularly
a composition comprising a hydrocarbon oil and
an alkaline earth metal phenate of high mo-
lecular weight.

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. Gen-
erally speaking, the compounding of hydrocarbon
oils to obtain desired characteristics involves em-
pirical phenomena, and the action of untested
types of compounding agents cannot be predicted.

A characteristic which has been the subject of
extensive investigation is the tendency of hydro-
carbon oils to deteriorate or partially decompose
when subjected to high temperatures. This de-
terioration is evidenced by the deposition of ad-
hesive deposits on hot metallic surfaces over
which the hydrocarbon oil may flow. It is im-
portant 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.
Compounds which render hydrocarbon oils more
resistant to deterioration by heat at high tem-
perature levels usually, though not always, impart
to the oil the ability to inhibit piston ring stick-
ing in internal combustion engines and permit
longer periods of operation of such engines with-
out the necessity of major overhauls heretofore
occasioned by stuck piston rings.

It has been discovered that dispersion of alka-
line earth metal phenates in hydrocarbon oils
such as mineral lubricating oil imparts new and
unpredictable properties thereto. These new
properties render the compounded oil particu-
larly useful for various purposes. For example,
oil-soluble alkaline earth phenates like calcium
lauryl phenates, calcium cetyl phenates, calcium
di-amylyl phenate and calcium heptyl phenate are
capable of inhibiting piston ring sticking when
incorporated in crankcase lubricants for internal
combustion engines such as Diesel engines.

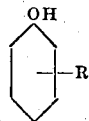
In general, it has been discovered that the new
compositions herein disclosed are more stable to
heat than is the hydrocarbon oil from which the
compositions are compounded. The alkaline
earth metal phenates are capable of imparting to

mineral lubricating oils the property of resistance
to sludge formation and to the deposition of lac-
quer or gum-like materials on metal surfaces at
high temperatures, such as 425° F. to 550° F., en-
countered in the ring belt zone of Diesel engines.
The new compositions of this invention are there-
fore particularly useful where resistance to heat is
important. In addition to having outstanding
advantages as a lubricant for pistons and piston
rings of internal combustion engines, the present
composition is useful as a heat transfer fluid
where it may be desirable to inhibit or prevent
the formation of a deposit on the metal surface
from or to which heat is being conveyed.

It has also been discovered that calcium phe-
nates in particular have a combination of proper-
ties heretofore unknown and particularly desir-
able in compounded lubricating oils, namely, the
ability to impart resistance to deterioration by
heat or the ability to inhibit piston ring sticking,
the ability to reduce wear on cylinder walls and
piston rings of internal combustion engines as
compared with the wear produced by conven-
tional un-compounded mineral oils, and non-cor-
rosivity of the compounded oil as respects its
chemical action on bearing metals such as cad-
mium-silver alloys. Although various compound-
ed mineral oils are known which are capable of
inhibiting piston ring sticking, the discovery of
specific compounding agents capable of imparting
the above combination of properties to hydro-
carbon oils represents an unobvious and im-
portant discovery.

Examples of alkaline earth metal phenates
which may be added to hydrocarbon oils such as
mineral oils to provide a new composition of mat-
ter of the type herein involved comprise mag-
nesium phenates, barium phenates, strontium
phenates and calcium phenates.

The phenates of this invention are preferably
formed from high molecular weight alkyl phenols
of the type formula—



in which R is an alkyl group containing at least
five carbon atoms. Although alkyl substituents
in the phenolic radical of the present compounds
are preferred, oil-soluble alkaline earth phenates
of other substituted phenols may be utilized. The
invention does not preclude substitution of aryl,
aralkyl, alkaryl or cyclic non-benzenoid groups,

either alone or together with an alkyl group, in the aromatic nucleus to which the phenolic hydroxyl group is directly attached. In general, the phenolic radical of the alkaline earth metal phenates should contain more than ten carbon atoms and preferably sixteen or more carbon atoms. It is to be understood that the term high molecular weight phenols is intended to designate phenols having a molecular weight greater than 100. Compounds containing one or more alkyl groups are contemplated. For example, either mono-alkyl phenolic or di-alkyl phenolic radicals may be utilized in the present invention.

To guide those skilled in the art in the preparation of the compositions of this invention, the following specific examples of methods of preparing alkyl phenols are submitted:

Example 1.—An alkyl phenol desirable for present purposes may be prepared as follows: Phenol and a butene polymer, having an apparent molecular weight of 194 and obtained by polymerization of a mixture of butenes containing butene-1, butene-2, and iso-butene, were mixed. To this mixture, containing 237 grams of phenol and 500 grams of the above mentioned butene polymers, 140 cubic centimeters of 94% sulfuric acid were added slowly with agitation. The temperature was kept below 65° F. during addition of the acid. The mixture was agitated for two hours after the addition of acid was completed and permitted to come to room temperature. The reaction product was then diluted with an equal volume of water and placed in a sealed autoclave where it was heated at 350° F. for an hour with agitation. The product was washed with water, 5% sodium carbonate solution and again with water in order to free it of sulfuric acid, sulfonates and unreacted phenol. A 93% yield of high molecular weight water-insoluble alkyl phenol having an acetyl number of 181 was obtained.

Example 2.—511 grams of crude cresylic acid, 900 grams of olefine polymers containing an average of 14 carbon atoms per molecule, and 475 grams of 98% sulfuric acid were utilized in preparing an alkylated cresol. These ingredients were combined and treated in the manner described above for preparation of cetyl phenol. The product was vacuum-distilled at 10 mm. and a 50 to 90% cut of an alkyl phenol obtained which had a molecular weight of 291 and was used to prepare the calcium salt hereinafter described in Example 6.

It is to be understood that the above examples are given by way of illustration only and that other condensation reactions utilizing alcohols, alkyl chlorides and the like, rather than olefines, may be adopted as a starting material for introducing the alkyl group into the aromatic nucleus. Also other known condensation agents, such as aluminum chloride, zinc chloride, etc., may be adopted for effecting the alkylation reaction. A mixture of sulfuric and glacial acetic acids may be used with advantage as a condensing agent. A suitable mixture comprises 100 parts by weight 98% H₂SO₄ to 60 parts by weight of glacial acetic acid. The presence of the acetic acid facilitates temperature control and gives a softer, easier handled reaction product.

The following comprise illustrative examples of the preparation of alkaline earth metal phenates of this invention:

Example 3.—247 grams of an alkylated phenol having an apparent molecular weight of 247 were agitated for six hours at 500° F. with 64 grams

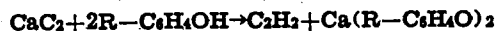
of powdered calcium carbide. A gaseous reaction product containing acetylene was formed and removed. The product remaining in the reaction zone was a dark-colored brittle solid at room temperature and comprised a calcium salt of the alkylated phenol. 94% of the theoretical yield of calcium phenate was obtained as shown by an analysis of a sample of the reaction product freed from calcium carbide by filtration of its petroleum ether solution.

Example 4.—685 grams of an alkylated phenol having an apparent molecular weight of 290 were agitated for six hours at from approximately 500° F. to 540° F. with 90 grams of calcium carbide. A gas containing acetylene was formed and removed. The product remaining in the reaction zone was a dark-colored brittle solid at room temperature. A yield of calcium phenate, representing 96% of that theoretically possible, was obtained.

Example 5.—44 grams of p-cyclohexyl phenol and 20 grams of powdered calcium carbide were heated together at 350° F. for one hour. The product was a tan-colored powder insoluble in petroleum ether, soluble in benzene, and comprising the calcium salt of p-cyclohexyl phenol.

Example 6.—234 grams of an alkyl cresol (molecular weight 291) and 25 grams of powdered calcium carbide were heated at 530° F. with stirring for four hours. The product obtained comprising the calcium salt of alkyl cresol was a hard brittle solid, soluble in mineral oil.

It is believed that the reaction occurring in the above examples may be represented by the following equation:



The other alkaline earth metal carbides give this type reaction which may be utilized in their preparation.

Additional examples of methods of preparing alkaline earth metal phenates useful in the compositions of this invention comprise the following:

Example 7.—500 grams of an alkyl phenol (molecular weight 290) was heated to 520 to 540° F. and a crystal of iodine was added. 30 grams of magnesium turnings were then incorporated in small increments to maintain a rapid but safe evolution of hydrogen. Before the entire quantity of magnesium has been added, the reaction mixture became too viscous to stir even at 600° F. This mixture was dissolved in acid treated S. A. E. 30 Western lubricating oil and topped to 480° F. at 5 mm. pressure in a still.

Example 8.—7.6 grams of barium hydroxide were dissolved in 7 cc. of water at 212° F. To this was added, with agitation, about 5 grams of cetyl phenol and 7 cc. of ethyl alcohol to promote solution of the cetyl phenol and facilitate reaction. The mixture was boiled for about three minutes, extracted with a hydrocarbon thinner, the extract filtered and the thinner evaporated. The product obtained was an amber, brittle semi-solid containing approximately 65% of the barium salt of cetyl phenol. The reaction product as obtained was dissolved as a 1% solution in lubricating oil and found by engine test to satisfactorily inhibit piston ring sticking.

The proportion of alkaline earth metal phenates added to mineral oils may vary widely depending upon the uses involved and the properties desired. As little as 0.1% by weight of the phenate gives measurable improvements, although from approximately 0.25 to approximate-

ly 2% phenate is preferred where the compounded oil is to be used as a crankcase lubricant for internal combustion engines. As much as 50% 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. Other solvents such as ethers, esters and the like may be used for preparing these concentrates. Such concentrates comprise a convenient method of handling the phenates and may be used as a compounding agent for lubricants in general, as well as for other purposes.

The advantages of the compounded mineral oil of this invention are shown by the following data:

in the same test with the same oil containing 1% calcium cetyl phenate, the wear was only 105 units. In the kinetic machine the wear at 400° F. was 193 units with the uncompounded oil, as against 15 units with the same oil containing 1% calcium cetyl phenate.

The alkaline earth metal phenates of this invention may be added to mineral oils containing other compounding ingredients, such as pour point depressors, oiliness agents, extreme pressure addition agents, corrosion inhibitors, blooming agents, compounds for increasing the viscosity index of the hydrocarbon oil, etc. The invention in its broader aspects embraces mineral lubricating compositions which have a thickened or grease-like consistency and which contain not

Oil	Time to stick rings		Relative corrosion Cd-Ag bearings	Relative ring slot carbon	Relative piston cleanliness	Used oil inspections			Remarks
	Hours	Comp. min. oil**				Vis. @ 100° F.	Vis. @ 210° F.	Neut. No.	
25 Acid refined, S. A. E. 30, Western oil—No. 1. Oil No. 1 plus 1% barium cetyl phenate.	45+	1.0	Very low..	Poor.....	Poor.....	906	64.3	0.72	Made by reaction with barium hydroxide. Made with calcium metal and cetyl phenol. Check run on above.
Oil No. 1 plus 1.1% calcium cetyl phenate.	90+	1.5+	Low.....	Good.....	Fair.....	1,045	67.1	0.99	
Oil No. 1 plus 1.0% calcium cetyl phenate.	165+	3.0+	Very low..	Excellent..	Very good..	1,490	76.7	3.87	
30 Oil No. 1 plus .88% calcium cetyl phenate.	135+	5.5+	do.....	Perfect.....	do.....	1,915	86.2	3.96	Made from calcium carbide and cetyl phenol. Made from calcium metal and cetyl phenol. Cetyl phenol made by aluminum chloride method.
Oil No. 1 plus 0.5% calcium cetyl phenate.	120+	4.5+	do.....	do.....	Good.....	1,576	79.7	3.63	
Oil No. 1 plus 0.96% calcium cetyl phenate.	120	4.0+	Low.....	Very good..	Fair.....	1,764	84.1	3.54	
35 S. A. E. 30, Western Oil—0.74% calcium cetyl phenate.	45+	4.0	Medium*	do.....	Good.....	1,480	57.9	3.45	Tests on compounding agent in different oil.
Oil No. 2 plus 1.22% calcium cetyl phenate.	105	1.5+	do.....	Fair.....	Poor.....	1,000	68.7	1.42	
Oil No. 1 plus 1% calcium di-amyly phenate.	60	3.5	Very low*	Good.....	Very good..	1,060	70.9	1.85	
40 Oil No. 1 plus 1% calcium "heptyl" phenate.	60+	2.0	do.....	do.....	Fair.....	1,250	72.5	2.06	Made with calcium metal and di-amyly phenol. Made with calcium metal and "heptyl" phenol. Made with calcium metal and lauryl phenol. Made with calcium metal and tertiary amyl phenol.
Oil No. 2 plus 1.55% calcium lauryl phenate.	120+	2.0+	High.....	do.....	do.....	1,425	75.7	3.01	
Oil No. 1 plus 1% calcium p-tertiary amyl phenate.	45	4.0+	Medium*	Excellent..	Good.....	1,107	72.2	0.81	
45	45	1.5	Very low*	Fair.....	Fair.....	1,150	69.2	1.87	

* Corrosion data not from engine test.

** Ratio of time required to stick rings with compounded oil as compared with uncompounded mineral oil.

In the above piston ring sticking tests, a single cylinder 2 5/8" bore, 2 1/2" stroke, Lauson gasoline engine was operated under extremely severe conditions for the purpose of developing fully piston ring sticking and piston gumming tendencies under circumstances simulating severe operating conditions encountered in the field. Operation of the motor during tests was continuous at 1600 R. P. M. except for periodic shut-downs at fifteen-hour intervals for inspection; the jacket temperature was maintained at 345° F. and sump oil temperature at 220° F. The corrosion data given, except where noted otherwise, were determined by measuring the loss of weight of metal from the bearings during runs with this type of engine under the above severe conditions.

The ability of the calcium phenates to reduce or prevent wear is illustrated by tests in a Weeks machine and a kinetic "B" machine. (The Weeks machine is similar to the Timken testing machine described in S. A. E. Journal, vol. 28, page 53, 1932, and the kinetic "B" testing machine is described section 3, page 60, of A. P. I. Proceedings, Mid-Year 1932, published by the American Petroleum Institute). In the Weeks machine an acid refined Western oil, S. A. E. 30, permitted a wear of 288 units at 300° F. where,

only metal phenates but thickening agents or metal soaps present either in grease-forming proportions or in amounts insufficient to form greases, as in the case of mineral castor machine oils.

While the character of this invention has been described in detail, and numerous examples of the preparation and application 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.

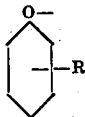
We claim:

1. A composition of matter comprising an oil and from approximately 0.1 to approximately 50% by weight based on the oil of an alkaline earth metal phenate dissolved therein, said phenate containing a substituted phenolic radical having more than ten carbon atoms.

2. A composition as defined in claim 1, in which the alkaline earth metal is calcium.

3. A composition of matter comprising a hydrocarbon oil and from approximately 0.1 to approx-

imately 50% by weight based on the oil of an alkaline earth metal phenate containing a radical of the type formula—



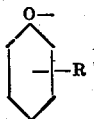
in which R is an alkyl group having at least five carbon atoms.

4. A composition as defined in claim 3, in which the alkaline earth metal is calcium.

5. A lubricating composition comprising a mineral oil and from approximately 0.1 to approximately 50% by weight based on the oil of an alkaline earth metal phenate dissolved therein, said phenate containing a substituted phenolic radical having more than ten carbon atoms.

6. A lubricating composition as defined in claim 5, in which said alkaline earth metal is calcium.

7. A lubricating composition comprising a mineral lubricating oil and a small amount sufficient substantially to inhibit deterioration of said lubricating oil at elevated temperatures of an alkaline earth metal phenate containing a radical of the type formula



in which R is an alkyl group containing at least five carbon atoms.

8. A lubricating composition comprising a mineral lubricating oil as defined in claim 7, in which the alkaline earth metal is calcium.

9. A liquid lubricating oil comprising a mineral oil and an alkaline earth metal phenate capable of inhibiting piston ring sticking in internal combustion engines when added to the crankcase lubricants thereof in an amount comprising from approximately 0.25 to 2% by weight of the lubricating oil, said phenate containing

a phenolic radical having a hydrocarbon substituent in the aromatic nucleus selected from the class consisting of alkyl, aryl, alkaryl, aralkyl and cyclic non-benzenoid groups.

10. A liquid lubricating composition as defined in claim 9, in which the alkaline earth metal is calcium.

11. A liquid lubricating oil comprising a hydrocarbon oil normally having the tendency to cause piston ring sticking in internal combustion engines, such as Diesel engines, and a small amount of an alkaline earth metal phenate having a phenolic radical containing a hydrocarbon substituent with at least five carbon atoms, said phenate being present in the oil in an amount sufficient substantially to inhibit piston ring sticking.

12. A liquid lubricating oil comprising a hydrocarbon oil normally having the tendency to cause piston ring sticking in internal combustion engines, such as Diesel engines, and a small amount of an alkylated phenate of an alkaline earth metal, said phenate being present in the oil in an amount sufficient substantially to inhibit piston ring sticking.

13. An anti-ring-sticking addition agent for lubricating oils comprising a concentrated solution in hydrocarbon oil of an alkaline earth metal phenate containing a substituted phenolic radical having more than ten carbon atoms, said phenate being effective to inhibit piston ring sticking in a crankcase lubricant of an internal combustion engine, said concentrate being capable of dilution with hydrocarbon lubricating oil to form a homogeneous mixture containing from approximately 0.25% to approximately 2% by weight of said phenate based on the lubricating oil.

14. An anti-ring-sticking addition agent for crankcase lubricating oils comprising an alkaline earth metal phenate containing a phenolic radical having an alkyl portion of at least five carbon atoms.

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