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LUBRICANT

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The present invention relates to mineral lubri-
cating oils, particularly those oils containing addi-
tives in the nature of detergents, rust preventives
and extreme pressure agents. More particular-
ly, the invention is concerned with compounded
mineral lubricating oils which are not subject to
or will not show additive separation in the pres-
ence of water.

It is known that internal combustion engines,
both of the Diesel type and of the spark ignition
type, which are subject to long and continuous
periods of use as, for example, in long-haul truck-
ing service, construction tractor service, high-
speed marine or railway service, certain types of
aeronautical service, etc., require special lubricat-
ing oils, commonly designated as heavy duty oils,
which are compounded especially for this type
of service. Mineral lubricating oils which are not
so expressly prepared deteriorate relatively rapid-
ly in service, depositing sludge, carbonaceous ma-
terials, or varnish-like coatings on such surfaces
as cylinder walls, piston skirts, piston ring grooves,
etc. and creating an otherwise unclean condition
within the engine. For the purpose of counter-
acting to as great an extent as possible the tend-
ency of mineral lubricating oils to form these de-
posits, materials of a detergent nature are in-
corporated into mineral oils destined for heavy
duty uses. Generally speaking, these additives are
metallic derivatives of organic compounds, but
regardless of their exact chemical configuration,
they all exhibit the property of reducing or pre-
venting the deposition of carbonaceous or gummy
residues and varnish-like films resulting from the
deterioration of the lubricating oil. The more
common of the detergent additives present in
heavy duty oils in amounts ranging from 0.5% to
5% are such compounds as metal naphthenates,
metal phenates, metal phenol sulfides, and poly-
sulfides, reaction products of metal phenol sul-
fides with phosphorus sulfides, metal carboxyl-
ates, metal sulfonates, metal alcoholates, metal
salts of esters of acids or thio acids of phosphorus,
etc. where the metal ion is a polyvalent metal ion,
such as calcium, barium, tin, aluminum, zinc,
magnesium, strontium, lithium, nickel, etc. Cer-
tain non-metallic organic compounds are also
employed on occasion.

Detergent additives used for improving mineral
lubricating oils for heavy duty service are often
somewhat hydrophilic and as a result they tend
to form emulsions in the presence of water and
to drop out of the oil solution, which action results
in a heavy duty oil of impaired effectiveness. Nor-
mally, mineral lubricating oils used in internal
combustion engines are not expected to come in
contact with water. However, situations beyond
the control of the oil refiner do arise where the
prepared lubricating oil does come in contact with
water and these occurrences present themselves

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with sufficient regularity that additive loss
through contact with water becomes a serious
problem. One instance where loss of additives
through contact with water occurs is during ship-
ment of the oil in large size drums or tank cars.
Either through atmospheric condensation or leak-
age of rain water, or because, through oversight,
it is left in the drum after cleaning, water is per-
mitted to mix with the oil and precipitate out the
detergent additive. Water may also come into
contact with the oil in normal automotive opera-
tion, particularly during the winter, when low
temperatures cause moisture to condense in the
crankcase. Another instance where the dele-
terious action of water on compounded heavy duty
oils has been noted is in connection with certain
large Diesel installations where, after installation
or after the engine has been given a general over-
hauling, the whole lubricating system including
the oil reservoir is washed out with water and
then flushed with some of the lubricant intended
to be used for normal lubrication. After the flush-
ing operation, the oil is centrifuged to dispose of
the water and the oil is then put back into the oil
reservoir. If the additive in the oil is hydrophilic
in nature, this method of removing water from
the oil also removes some of the detergent addi-
tive, and thus the oil returned to the system is
not of the quality desired for such use. It is ob-
vious from the foregoing that some means of re-
taining detergent additives in the oil even in the
presence of water would be very beneficial.

The same phenomenon of additive removal re-
sulting from water contamination and emulsifi-
cation is encountered with certain soap-contain-
ing rust preventive agents and in other petroleum
products containing metallo organic materials.

The principal object of the present invention
resides in the provision of a compounded lubri-
cant for use in the capacity set forth which, when
accidentally or otherwise placed in contact or
mixed with water, will not lose any substantial
amount of the compounding agent. This and
other objects to be attained by the use of the
present invention will be apparent to those
skilled in the art upon reading the following
description.

It has now been discovered that compounded
oils and lubricants having dissolved therein ap-
preciably hydrophilic detergent additives may be
stabilized against emulsification and additive
separation by the incorporation of certain oil-
soluble organic hydrophilic compounds. The
use of the term "oil-soluble organic hydrophilic
compounds" implies those organic materials
which are miscible in oil and have, by virtue of
certain substituent groups, an affinity for water.
These materials are exemplified by aliphatic and
cycloaliphatic alcohols having from 4-10 carbon
atoms to the molecule, which may or may not

contain substituent ester, ether, ketone, or hydroxyl groups. Oil-soluble phenols, esters, ether esters, etc. exhibit lesser degrees of effectiveness. Specific examples of suitable materials are amyl alcohols, mixed amyl alcohols, methyl cyclohexanol, trimethyl cyclohexanol, 2-ethylhexyl alcohol, phenoxy ethanol, phenoxy isopropanol, tert. amyl phenoxy ethanol, and 2-ethylbutyl mono ether of ethylene glycol. Tertiary amyl phenol, iso-octyl phenol, diamyl oxylate and monomethyl ether of diethylene glycol acetate may also be employed with advantage.

The oils in such compounded oils and lubricants range in viscosity from 90–1800 S. U. S. at 100° F. with pour points usually from +25° F. to –10° F. and contain from 0.5% to 5% of additives such as metal phenates, metal phenol sulfides, reaction products of metal phenol sulfides with phosphorus sulfides, metal carboxylates, metal sulfonates, metal naphthenates, metal alcoholates, metal salts of the esters of acids or thio acids of phosphorus, etc. or mixtures of the foregoing additives. In general the metallo organic compounds utilizable as detergent additives contain ions of polyvalent metals, specific examples being calcium, barium, aluminum, tin and zinc. The non-metallic detergent additives include materials such as the naturally occurring phosphatides. The usual method of blending compounded oils is to use an oil concentrate of the additive which is dissolved in the mineral oil in the required amount to give the desired product, which solution may be hastened by means of agitation and heat. These detergent additives are frequently made "in situ" in oil solutions so that after removal of the by-products of the reaction, an oil concentrate of the desired additive is obtained directly and this is then used later to make the finished oil by blending it with the proper amount of the base stock.

A specific and preferred detergent additive is a mixture of an alkaline earth metal sulfonate and an alkaline earth metal alkylated phenol sulfide reacted with a sulfide of phosphorus such as P_2S_5 . Thus an improved lubricating oil composition may consist of a mineral lubricating oil containing between 0.5 and 5% of a mixture of calcium sulfonate and the reaction product of a barium tertiary octyl phenol sulfide with P_2S_5 and from 0.1 to 1% of mixed amyl alcohols. As a further specific example, the oil may contain about 2% of a mixture of calcium sulfonate and the reaction product of barium tertiary octyl phenol sulfide with phosphorus pentasulfide and 0.5% of mixed amyl alcohols. If desired, however, the calcium salt of mineral oil soluble sulfonic acids may be used alone as the detergent additive, in which case the oil composition might consist of a mineral lubricating oil containing between 0.5 and 5% of the calcium salt of mineral oil soluble sulfonic acids with 0.1 to 1% of mixed amyl alcohols as an oil soluble organic hydrophilic compound.

According to the present invention, oil soluble organic hydrophilic compounds will, when present in compounded heavy duty oil and other lubricants in amounts ranging from .05–4% by weight and preferably 0.1–1% by weight, reduce to negligible proportions the additive separation caused by emulsification of the oil with water. The oil-soluble organic hydrophilic compounds may be blended into previously compounded oils by means of heat sufficient to hasten solution. If desired the hydrophilic compounds can be incorporated in the oil concentrate of additives

at the time that the concentrates are prepared, in which case the hydrophilic compounds will be incorporated in amounts ranging from 1–40% by weight based upon the weight of the detergent additives present in the oil concentrate, depending upon the concentration of oil-soluble hydrophilic compounds desired in the final compounded oil. Also if desired, the stabilizing agent may be incorporated in concentrates of other additives, such as anti-oxidant bearing corrosion inhibitors, film strength agents, thickeners, pour depressants and the like. However, if the stabilizing agent is incorporated in the concentrate for the purpose of stabilizing that concentrate against the action of water, then the former or lesser concentration of stabilizing agents should be used. The various detergent additives differ somewhat in their reactions toward water and the amount of detergent additive present is also influential in determining the amount of stabilizing agent required to effectively induce additive stabilization; however, the preferred range of 0.1–1% by weight of oil-soluble hydrophilic compound will, in most instances, be found sufficient to give adequate protection against emulsification and additive separation.

For the purpose of demonstrating the effectiveness of oil soluble organic hydrophilic compounds as emulsification preventives and as stabilizers against additive separation, 50 cc. of a rust preventive composition comprising 18% lead oleate, 12% petroleum oil bright stock, and .5% sodium sulfonate in a solvent naphtha was violently agitated with 2% of water for a few minutes and a gray emulsion resulted. When 2% of mixed amyl alcohols was added to the rust preventive composition and the experiment repeated it was found that 6% of water could be agitated with the rust preventive composition without the formation of an emulsion.

In a test somewhat similar to the above, a highly refined S. A. E. 30 paraffinic lubricating oil was compounded with 1.5% of calcium sulfonate. 100 cc. of this compounded oil was violently agitated with 1% by volume of water for several minutes. After standing overnight, 25% of the volume of the oil was precipitated as large curds. The supernatant oil by analysis showed a loss of 48% of the original concentration of the detergent additive. When this test was repeated with various stabilizing agents blended in the sulfonate-oil composition, the following results were obtained:

Table

Blend	Per Cent Sediment by Volume
(1) S. A. E. paraffinic lubricating oil + 1.5% calcium sulfonate.....	25
(2) (1) + .5% methyl cyclohexanol.....	0
(3) (1) + .1% methyl cyclohexanol.....	12
(4) (1) + .5% mixed amyl alcohol.....	0
(5) (1) + .1% mixed amyl alcohol.....	0
(6) (1) + .5% monobutyl ether of ethylene glycol.....	3
(7) (1) + .5% monomethyl ethre of ethylene glycol acetate.....	3
(8) (1) + .5% iso-octyl phenol.....	5
(9) (1) + .5% trimethyl cyclohexanol.....	0
(10) (1) + .5% tertiary amyl phenoxy ethanol.....	0
(11) (1) + .5% 2-ethylhexyl alcohol.....	1
(12) (1) + .5% diamyl oxylate.....	10
(13) (1) + .1% monomethyl ether of ethylene glycol acetate.....	9
(14) (1) + .1% phenoxy ethanol.....	0
(15) (1) + .1% phenoxy isopropanol.....	0
(16) (1) + .5% mono 2-ethylbutyl ether of ethylene glycol.....	0

¹ Hazy solution.

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The above data clearly show that the agents of this invention, the oil-soluble organic hydrophilic compounds, are very effective in counteracting additive separation resulting from water contamination of compounded lubricants.

It is to be understood that the crankcase oil, extreme pressure lubricant, rust preventive, etc., compositions of the invention may, and frequently will, contain other constituents than those mentioned above. For instance, the use of viscosity-index improvers, pour point depressants, oiliness agents, extreme pressure agents, bearing corrosion inhibitors, dyes, emulsifiers, organic bases, fatty materials, esters, polymers, sulfur containing compounds, halogen bearing substances, phosphorus oxide and sulfide reacted materials, sulfur chloride treated compounds, and the like is contemplated.

What is claimed is:

1. An improved lubricating oil composition consisting essentially of a mineral lubricating oil containing from 0.5 to 5.0% by weight based on the total composition of an alkaline earth metallo-organic detergent composition having a tendency to form emulsions and drop out of oil solution in the presence of water, and 0.05 to 4% of an oil soluble hydrophilic agent selected from the group which consists of phenoxy ethanol and phenoxy isopropanol for stabilizing said detergent in solution in said oil.

2. An improved lubricating oil composition consisting essentially of a mineral lubricating oil

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containing from 0.5 to 5.0% by weight based on the total composition of an alkaline earth metallo-organic detergent composition having a tendency to form emulsions and drop out of oil solution in the presence of water, and 0.1 to 1% of an oil soluble hydrophilic agent selected from the group which consists of phenoxy ethanol and phenoxy isopropanol for stabilizing said detergent in solution in said oil.

3. A composition according to claim 1 wherein said hydrophilic agent is phenoxy ethanol.

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