This invention relates to non-corrosive compounded mineral lubricating oils and more particularly deals with lubricating oils containing non-corrosive oil-soluble organic detergents which possess the property of softening carbon, preventing or retarding sticking of piston rings and deposition of lacquer in internal combustion engines when running these engines for long periods of time under severe conditions of loading.

It is known that in modern internal combustion engines, such as aviation gasoline engines operating at relatively high temperatures due to their high power output, or in high-speed Diesel engines due to incomplete combustion, piston rings have a tendency to become stuck in the grooves. Lacquer and/or carbon formation appear to be the principal reasons for this occurrence.

Moreover, scuffing of top lands due to the formation of hard carbon particularly when using high viscosity index oils may cause serious damage to the engine.

To eliminate or reduce the lacquer deposition, ring-sticking, and hard carbon forming characteristics of oils it is necessary to compound them with additives normally metal soaps which improve the oils in one or more of its properties. Now, I have found purely organic compounds of excellent solubility in lubricating oils which are both detergents and carbon softeners.

In accordance with my invention, I have found that well refined lubricating oils which contain oil-soluble carboxylic acid esters of tri- and tetra hydroxy alcohols having a neo-carbon atom are remarkably stable, in addition to having the valuable property of positively retarding or preventing piston ring sticking as well as being carbon softeners.

These esters are derived by esterifying at least one and preferably all of the hydroxy radicals of a tri or tetra hydroxy alcohol having a neo-carbon atom. A neo-carbon atom is one that is attached directly to four other carbon atoms. Alcohols containing such a neo-carbon atom are represented by the formula:

\[
(CH)\_x\_OH
\]

\[
R-C\left(CH)\_y\_OH\right)
\]

\[
(CH)\_z\_OH
\]

wherein \(x\), \(y\), and \(z\) are whole numbers preferably 1, and the \(R\) radical is a hydrocarbon radical which may be aliphatic, alicyclic, aromatic or heterocyclic, examples being methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl and higher alkyl groups; cyclohexyl, methyl cyclohexyl and other alkyl cyclohexyl and di- and poly-alicyclic radicals, such as may be obtained by hydrogenation of alkyl phenols, alkyl naphthols, or of cyclic polymerization products of acetone, methyl ethyl ketone, methyl oxide, etc.; phenyl, naphthyl and their alkyl derivatives, such as methyl phenyl, ethyl phenyl, methyl naphthyl, etc. The hydrocarbon radicals may contain a polar substitution group, preferably not more than one, of high thermal stability, in particular, hydroxy, carbonyl ester, ether, thio-ether, chlorine and nitro radicals, as well as nitrogen in heterocyclic aromatic ring structures such as in pyridine, quinoline, etc. Radicals of lesser stability such as aliphatic amino, imino, hydroxyimide, etc., radicals are less desirable.

The preferred type of alcohol is one in which \(x\), \(y\), and \(z\) are 1 and the \(R\) group is a carbonyl group as in penta-erythritol, the latter having the formula \(C\left(CH)\_3\_OH\right)\). Symmetrical alcohols having short, equal length carbon chains linking hydroxy radicals to the neo-carbon atom appear to be most effective carbon softeners.

These alcohols may be prepared by reacting hydrocarbon trihalogenes of the general formula \(R-C-Hal\) with hydrogen or a metal-cyanide, e. g. silver, potassium, etc. cyanide to form the nitrile \(R-C-(CNMe)\), hydrogenating the nitrile to the amine and converting the amine to the corresponding alcohol by treating the former with nitrous acid. Some alcohols, especially penta-erythritol and o-tertiary-trihydroxy butyl pyridine are readily and cheaply prepared by the specific reaction of acetaldehyde or o-methyl pyridine, respectively, with formaldehyde. This reaction is, however, not applicable generally.

Poly-hydroxy alcohols of the above types are normally insoluble in mineral oils. It is therefore necessary to esterify at least some and preferably all of the hydroxy groups with mono carboxylic acids of sufficient carbon atoms to impart solubility. Acids suitable for esterifying these alcohols are carboxylic acids having 8 or more carbon atoms per molecule, and preferably between 12 and 24 carbon atoms. These acids may be saturated or unsaturated aliphatic or cycloaliphatic mono carboxylic acids preferably having not more than one olefinic double bond such as fatty acids, e. g. lauric, myristic, palmitic, stearic, arachidic, behenic, oleic, erucic acids, etc., higher petroleum naphthenic acids; aromatic acids, such as alkyl benzoic, alkyl phenyl acetic, phenyl stearic alkyl pyridine carboxylic acids, etc. Saturated carboxylic acids, in general, are prefer-
ferred. If desired these acids may contain chlorine or bromine preferably in a position other than in alpha position to the carboxyl radical.

Some specific examples of esters derived from the above-mentioned alcohols and acids are penta-erythritol tri- and tetra-laurate, palmitate, stearate, oleate, napthenate, phenyl stearate, etc., 2-methyl-2-methylo1, 3-propanediol di- or tri-palmitate, oleate, napthenate, phenyl acetate, phenyl stearate; benzo trimethylol di- and tri-stearate, oleate, napthenate, isopropyl benzolate, phenyl stearate, etc., corresponding esters of 3-methyl-2,2,2-dimethylol-1-butanol, 2-amino-2-methylo1,3-propanediol, 2,2-dimethylol-3-hydroxy n-propyl benzene, benzo trimethylol, o-tertiary-tri-hydroxy butyl pyridine, etc.

Suitable amounts of organic detergent ester which an anti-ring-sticking and soft carbon forming oil should contain range from about 0.5% to 10.0% and preferably from 2% to 5.0%.

The above organic addition agents may be combined with other detergents, e.g. oil-soluble metal salts of carboxylic and sulfonic acids, such as soaps of fatty acids, chlorinated fatty acids, aromatic fatty acids, alpha aromatic amino monocoxylic acids, napthenic acids, rosin acids, mohogany acids. Salts of polyvalent metals are, in general, most active, e.g. Mg, Ca, Sr, Ba, Zn, Cd, Sn, Sb, Cr, Mn, Co, Ni, etc.

Crackcase lubricating oils containing the esters of the instant invention may contain additional compounds of the type such as oxidation inhibitors, pour point depressors, blooming agents, extreme pressure compounds, anti-sludging agents, etc.

The following example further illustrates my invention:

**Example**

An SAE-30 grade refined West Texas lubricating oil was divided into 4 portions. To one portion was added 2% by weight of penta-erythritol tetra-stearate. To a second portion was added 2% by weight of a mixture of napthenic and stearic tri-ester of o-tertiary-tri-hydroxy butyl pyridine. To a third portion was added 2% by weight of di-cetyl-phthalate. The doped and undoped oils were tested individually. In a Fairbanks-Morse Diesel engine having a four-stroke cycle operating at 900 R. P. M. with the lubricating oil temperature of 15° to 10° F. The duration of the test was 40 hours.

Examination of the pistons as they were removed from the engine after the runs showed that the oil alone gave a piston that had a medium coating of lacquer and a somewhat abrasive carbon deposit which had most of the piston rings stuck tight in the grooves. Oil containing di-cetyl-phthalate gave pistons in practically the same condition as the oil alone. The oils containing penta-erythritol tetra-stearate or the mixed napthenic and stearic tri-ester of o-tertiary-tri-hydroxy butyl pyridine left much less lacquer on the piston and the carbon was relatively soft and there was practically no ring sticking.

I claim as my invention:

1. A compounded mineral lubricating oil suitable for internal combustion engines containing dissolved a small amount sufficient to retard piston ring sticking of an oil-soluble mono-carboxylic acid ester of an alcohol selected from the group consisting of tri and tetra hydroxy alcohols having a neo-carbon atom, said carboxylic acid having a minimum of 8 carbon atoms and having not more than one olefinic double bond.

2. The composition of claim 1 in which the ester content is from about 0.5% to 10%.

3. The composition of claim 1 in which the ester content is from about 7% to 5.0%.

4. A compounded mineral lubricating oil containing dissolved a small amount sufficient to retard piston ring sticking of an oil-soluble mono-carboxylic acid partial ester of an alcohol having a minimum of 3 and a maximum of 4 hydroxy groups centered around a neo-carbon atom, said carboxylic acid having a minimum of 8 carbon atoms and having not more than one olefinic double bond.

5. A compounded mineral lubricating oil containing dissolved a small amount sufficient to retard piston ring sticking of an oil-soluble mono-carboxylic acid ester of an alcohol having a neo-carbon atom and the general formula

\[
R - C(\text{CH}_2\text{O})_n \text{OH}
\]

wherein R is a hydrocarbon radical and x, y, and z are whole numbers not less than 1, said carboxylic acid having a minimum of 8 carbon atoms and having not more than one olefinic double bond.

6. A compounded mineral lubricating oil suitable for internal combustion engines containing dissolved a small amount sufficient to retard piston of an oil-soluble saturated mono-carboxylic acid ester of penta-erythritol, said carboxylic acid having a minimum of 8 carbon atoms and having not more than one olefinic double bond.

7. A compounded mineral lubricating oil suitable for internal combustion engines containing dissolved a small amount sufficient to retard piston of an oil-soluble fatty acid ester of an alcohol selected from the group consisting of tri and tetra hydroxy alcohols having a neo-carbon atom, said fatty acid having from 12 to 24 carbon atoms and having not more than one olefinic double bond.

8. A compounded mineral lubricating oil suitable for internal combustion engines containing dissolved a small amount sufficient to retard piston ring sticking of an oil-soluble penta-erythritol stearate.

9. A compounded mineral lubricating oil suitable for internal combustion engines containing dissolved a small amount sufficient to retard piston ring sticking of penta-erythritol tetra-stearate.

10. The composition of claim 5 wherein the hydrocarbon radical R contains a polar substitution radical selected from the group consisting of -OH, -COOR', -OR', -SR', -Cl, -NO₂, and -N= in heterocyclic aromatic ring structure, R' being a hydrocarbon radical.

11. A compounded mineral lubricating oil suitable for internal combustion engines containing dissolved a small amount sufficient to retard piston ring sticking of an oil-soluble mono-carboxylic acid ester of o-tertiary trihydroxy butyl pyridine, said carboxylic acid having a minimum of 8 carbon atoms and having not more than one olefinic double bond.

12. A compounded mineral lubricating oil containing dissolved a small amount sufficient to retard piston ring sticking of an oil-soluble mono-
carboxylic acid ester of an alcohol having a neo-
carbon atom and the general formula

wherein R is a radical selected from the group

comprising hydrocarbon radicals and hydrocar-
bon radicals containing a polar substitution radi-
cal of high thermal stability, said carboxylic acid
having a minimum of 8 carbon atoms and hav-
ing not more than one olefinic double bond.

A compounded mineral lubricating oil con-
taining dissolved a small amount sufficient to re-
tard piston ring sticking of an oil-soluble mono-
carboxylic acid ester of an alcohol having a neo-
carbon atom and the general formula

wherein x, y, and z are equal and R is a hydroxyl
substituted aliphatic hydrocarbon radical having
x number of carbon atoms, said carboxylic acid
having a minimum of 8 carbon atoms and having
not more than one olefinic double bond.

14. The composition of claim 1 in which the
ester is a saturated compound.

15. The composition of claim 1 in which the
ester is derived from a carboxylic acid having
from 12 to 24 carbon atoms.

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