

UNITED STATES PATENT OFFICE

2,280,474

LUBRICATING OIL

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No Drawing. Application July 18, 1938,
Serial No. 219,818

14 Claims. (Cl. 252—35)

Our invention relates to methods for the production of lubricating oils and specifically comprises such products as new compositions of matter.

The general trend in the development of internal combustion engines and particularly Diesel engines has imposed increasing demands upon lubricating oils. These demands have required lubricants of greatly increased load carrying capacity, lubricants which may be used satisfactorily at higher temperatures of operation and lubricants more stable to the effect of high temperatures and pressures under an oxidizing condition. The operating difficulties encountered with Diesel engines now being used represent these increased demands and the increasing requirements being placed on lubricants. Other types of internal combustion engines encounter the same difficulties in some duties and when employed for some services have encountered troubles similar to or identical with those occurring with Diesel engines.

Some of these difficulties are sludge formation, stuck piston rings and the like. The term sludge as used in this specification includes various types of materials which are objectionable and some of which preclude continuous normal operation. Others are objectionable only under abnormal operating conditions. Some of these sludge materials are objectionable under one set of certain operating conditions but not under another set of operating conditions. We do not limit our invention to any theory of the action of these sludges and various conditions. We do know that some sludges are hard, adhesive, coherent and damaging to normal engine operation while others are soft, pilable, easily disintegrated and do not materially affect normal engine operation.

Probably the most serious damage is caused by that type of sludge which results in piston ring sticking. This in turn causes inadequate lubrication of the piston and cylinder walls and hence increased cylinder wear. Mild and severe scoring of the cylinder walls may occur and under severe conditions there may be actual seizure of the piston and cylinder by welding. Another consequence of ring sticking is blow-by which causes loss of power, increased consumption of fuel and lubricant for the same output and overheating of the piston and cylinder walls. Permanent distortion of the latter is a result of this overheating.

These difficulties cannot be overcome by changing the character of the hydrocarbon oil

itself. Mineral lubricating oils of one type, however, may not cause as much difficulty as oils of another type. In some cases, changes in refining processes will reduce the difficulties to a certain extent, but it is commercially impractical and uneconomical to manufacture and distribute special lubricants from oil of a particular type and refined by a special and often expensive refining process. Generally speaking, the more highly paraffinic lubricants which are usually conceded to be superior lubricants are not as satisfactory as the naphthenic type lubricants for this specific purpose.

At least two special lubricants have been offered to solve the foregoing difficulties, but they have been found unsatisfactory and inadequate in many respects. One of these is a hydrocarbon lubricating oil to which has been added halogen bearing metal soaps, while the other is a blend of mineral oil with a small quantity of calcium soaps of aromatic substituted fatty acids. Both of these types of special lubricants have been found inadequate in the following respects:

1. *Solubility*.—Many of these addition agents are not sufficiently soluble in hydrocarbon oils to give stable solutions containing the requisite amount of additive material. This causes difficulty in the manufacture and distribution of these lubricants. If the amount of addition agent be reduced to that which will remain permanently in solution, it is insufficient to produce an appreciable improvement in the behavior of the oil even in normal use. This difficulty is sometimes partially overcome by the addition of a mutual solvent for both the soap and the hydrocarbon oil.

2. To overcome this lack of solubility, free organic acids such as oleic, phenylstearic and the like may be added which increase the solubility of the soap in the oil. The added acid may be the same or different from the acid combined as soap. The addition of free acid to lubricants, however, precludes their use with many of the now common bearing metals especially those containing lead and cadmium because of the rapid corrosion of these metals by organic acids.

3. *Effectiveness*.—Neither of the two types of additive materials has satisfactorily reduced the ring sticking difficulty. This failure may be due to lack of stability or lack of solubility in sufficient amounts to accomplish the purpose or both.

One object of our invention is to provide lubricants which will greatly reduce or substantially

eliminate ring sticking in internal combustion engines, particularly those of the Diesel type.

Another object of our invention is to provide materials which when added to hydrocarbon oils will accomplish the same result.

A further object of our invention is to provide addition agents for lubricants which accomplish the above purposes and which are at the same time noncorrosive to the various metals encountered in internal combustion engines.

A still further object of our invention is to provide addition agents for lubricants which accomplish the above purposes and which are at the same time stable under the conditions of use and which do not accelerate the formation of any objectionable type of sludge.

Still another object of our invention is to provide addition agents for lubricants which will cause any sludge resulting from changes of the mineral oil during use to be of a soft, pliable, noncohesive and noncoherent type which will not interfere with normal operation.

Briefly, our invention consists of the addition to lubricants of small amounts, usually not over 5.0 percent, and more often of from 0.5 to 2.0 percent of certain metal salts or soaps of organic acids containing, in addition to the acid group, also an ester grouping in the molecule. Most of the salts or soaps of the suitable metals with acids of the type described, namely acids having an ester group elsewhere in the molecule, are characterized by their ready solubility in mineral oils. This is a distinct advantage in that blending of the additive agent with hydrocarbon oils is particularly easily accomplished and also in that there is no possibility of any separation of the added salt during storage or use. Calcium and other metal salts of fatty acids such as stearic and the like are not generally soluble to any appreciable extent in mineral oils and are thus not suitable for the present use. Even the salt of substituted fatty acids, while somewhat better in this respect than the unsubstituted compounds, are still far from being adequately soluble. The introduction of one or more ester groups greatly increases solubility in hydrocarbon oils.

Some lubricating oils exhibit better solvent power for these salts than others though the greater solubility obtained by changing the base oil is still small compared to the introduction of an ester group into the soap radical. In general, naphthenic base oils are better salt solvents than mixed or paraffin base oils of the same viscosity.

By oil having lubricating characteristics in the appended claims, we mean to include the so-called mineral oils and various hydrogenated, polymerized and otherwise synthetically treated oils such as volatilized oils and the like. Furthermore, the lubricating oil may consist in whole or in part of animal or vegetable oils such as castor oil, lard oil, shale oil, corn oil, cottonseed oil and the like.

The addition of organic acids to improve the solubility of metal soaps as disclosed in the prior art is not nearly as effective as we obtain by introducing an ester group or groups into the molecule itself. It is a distinct improvement to have a soluble soap with the solubilizing agent a non-acidic group in the molecule of the soap itself.

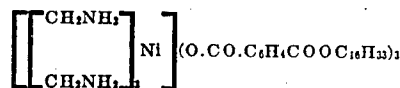
The metals which we use to prepare our addition agents from the ester-acids include calcium, strontium, barium, zinc, cadmium, beryllium, aluminum, gallium, indium, thallium, iron, lead, copper, tin, germanium, molybdenum, bis-

muth, antimony, manganese, cobalt, nickel, chromium, and others. Some of the suitable metals listed above may form two or more types of salts or soaps depending on the valence of the metal.

For example, we may use stannous or stannic salts. The salts of the same metal in different valence states are often quite different in solubility and suitability for special purposes. Thus salts of stannic tin appear to be better oxidation inhibitors than the corresponding stannous soaps. Plumbic lead soaps are more effective anti-knock agents when added to gasoline than the divalent lead soaps.

Some of these metals form salts or soaps which are more suitable than others for some purposes. Thus iron, lead, and copper soaps in general are found to be accelerators of oxidation in crankcase lubricants. While these are effective in reducing ring sticking, their other effect of accelerating oxidation renders them somewhat less desirable than other metal soaps in this particular service. On the other hand, the soluble lead soaps, for example, are quite desirable in the manufacture of mild and violent types of hypoid lubricants. Here the value of the extreme pressure characteristics of the soap far overshadows its oxidation accelerating ability. This is especially the case when we use a refined oil relatively difficult to oxidize or add an oxidation inhibiting material or both.

In some cases, we may use metal salts of our ester-acids in which the metal is present as a complex ion. Thus the cobalt and nickel ions (trivalent) form complexes with the diamines such as ethylene and propylene diamines which may be used for preparing our salts. For example, tri (ethylene diamine) nickelic cetyl phthalate:

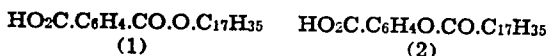


and chloropentammine cobaltic cetyl amylen succinate:



may be used.

The ester-acids which we use to prepare our addition agents are of two general types, both of which contain a carboxyl group (available for the preparation of the metal soap) and also an ester group. These are the partial esters of polybasic acids and the esters of hydroxyacids. These two types are characterized by the formulas: (a) $\text{HO}_2\text{C.R.CO.O.R}'$ and (b) $\text{HO}_2\text{C.R.O.CO.R}'$ respectively, in which R is a divalent group and R' is a monovalent group. The salts derived from esterified hydroxyacids of the type designated by formula (b) above constitute the subject matter of our copending application Serial 344,734, filed July 10, 1940, which is a continuation-in-part of the present application. Compounds of these types are closely related and may even be isomeric, as in the case of monoheptadecyl phthalate (1) and stearoyl salicylic acid (2):



both of which have the formula, $\text{C}_{25}\text{H}_{40}\text{O}_4$.

We may also use salts or soaps of the partial esters of polybasic organic acids and of polyhydroxy compounds. Examples of these are shown later.

The character of R and R' in the above gen-

eral formulas may vary within wide limits since the solubilizing effect of the ester group is so powerful that it overcomes any difficult solubility effect of R and R'. Even radicals commonly thought to be insoluble in hydrocarbon oils may in some cases be used. The products, however, in which R and R' contribute to solubility are particularly advantageous. R and R' may be carbocyclic, heterocyclic or open chain and may or may not carry substituting groups such as nitro- gen, halogens, sulfur, or phosphorus containing groups. Examples of these are shown below. It is to be understood that any of these substituting groups may be inserted in any of the specific compounds mentioned.

Dibasic acids and their derivatives, particularly the anhydrides, are used to prepare the half esters to be converted into metal soaps. Phthalic anhydride is an aromatic acid derivative suited to our purpose. Other satisfactory acids and their derivatives are terephthalic, naphthalic and the like. The condensation products of the Diels and Alder type are particularly useful. For example, we may condense, by the method of Diels and Alder, maleic anhydride with a terpene hydrocarbon such as alpha-terpinene or the like to obtain a carbocyclic dibasic acid anhydride. Such a product is known to the art as 3-isopropyl-6-methyl-3,6-endoethylene-Δ4-tetrahydrophthalic anhydride. Other materials which may be substituted for maleic anhydride in the Diels and Alder condensation include acrylic, methacrylic, cinnamic and crotonic acids and their derivatives among others. Acrolein is also useful. Other materials which may be substituted for the terpene in the above example include cyclopentadiene, cyclohexadiene, anthracene, furane, fulvene, acids of drying and semidrying oils such as tung, linseed, cottonseed, corn, soy bean, rapeseed and the like, fish oil acids and partially hydrogenated fish oil acids, turpentine and any other materials containing conjugated double bonds such as dienes present in cracked gases and gasolines.

In preparing these condensation products from mono-basic acids such as acrylic or from non-acids such as acrolein, we choose an acid for the other addend so that the product will have at least two carboxyl groups or one carboxyl and one hydroxyl group. In this way, we may prepare our ester-acid for conversion into the metal soap.

Some examples of the acids we may use in making our metal salts or soaps are:

I. Partial esters of polybasic acids

A. Cyclic polybasic acids

1. With aliphatic alcohols, e. g.:

- a. Mono-octadecyl phthalate:
(o) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{CO}_2\text{C}_{18}\text{H}_{37}$
- b. Monocetyl phthalate:
(o) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{CO}_2\text{C}_{21}\text{H}_{43}$
- c. Monotetradecyl 3-chlorophthalate
(o) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{Cl.CO}_2\text{C}_{14}\text{H}_{29}$
- d. Monolauryl naphthalate:
(1) $\text{HO}_2\text{C.C}_{10}\text{H}_{19}.\text{CO}_2\text{C}_{12}\text{H}_{25}$ (8)
- e. Monocetyl ester of the Diels-Alder condensation product of maleic anhydride with a terpene hydrocarbon:
 $\text{HO}_2\text{C.C}_{12}\text{H}_{23}.\text{CO}_2\text{C}_{18}\text{H}_{33}$
- f. Ditetradecyl pyromellitic acid
(1, 2) $(\text{HO}_2\text{C})_2\text{C}_6\text{H}_2(\text{CO}_2\text{C}_{14}\text{H}_{29})_2$ (4, 5)
(1, 4) $(\text{HO}_2\text{C})_2\text{C}_6\text{H}_2(\text{CO}_2\text{C}_{14}\text{H}_{29})_2$ (2, 5)
(1, 5) $(\text{HO}_2\text{C})_2\text{C}_6\text{H}_2(\text{CO}_2\text{C}_{14}\text{H}_{29})_2$ (2, 4)
- g. Phosphite of mono-β-hydroxyethylphthalate:
 $(\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{CH}_2\text{CH}_2\text{O})_2\text{P}$
- h. Monolauryl 3-nitrophthalate:
 $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{NO}_2.\text{CO}_2\text{C}_{12}\text{H}_{25}$

2. With cyclic alcohols, e. g.:

- a. Monobenzyl phthalate:
(o) $\text{HO}_2\text{C.C}_6\text{H}_5.\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$
- b. Mono-β-phenylethyl terephthalate:
(p) $\text{HO}_2\text{C.C}_6\text{H}_4.\text{CO}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$
- c. Monofurfuryl naphthalate:
(1) $\text{HO}_2\text{C.C}_{10}\text{H}_8.\text{CO}_2\text{CH}_2\text{C}_4\text{H}_7\text{O}$

B. Aliphatic polybasic acids:

1. With aliphatic alcohols, e. g.:

- a. Monomyricyl maleate:
 $\text{HO}_2\text{C.CH}=\text{CH.CO}_2\text{C}_{30}\text{H}_{61}$
- b. Monodecyl amylenesuccinate:
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_{10}\text{H}_{21}$
- c. Monolauryl malate:
 $\text{HO}_2\text{C.CH}_2\text{CHOH.CO}_2\text{C}_{12}\text{H}_{25}$
- d. Mono-β-hydroxyethyl chlorosuccinate:
 $\text{HO}_2\text{C.CH}_2\text{CHCl.CO}_2\text{CH}_2\text{CH}_2\text{OH}$
- e. Monotetradecyl adipate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_{14}\text{H}_{29}$
- f. Monododecyl mercaptosuccinate
 $\text{HO}_2\text{C.CH}_2\text{CHSH.CO}_2\text{C}_{12}\text{H}_{25}$

2. With cyclic alcohols, e. g.:

- a. Monobenzyl succinate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{C}_6\text{H}_5$
- b. Mono-β-phenylethyl thiodiglycolate
 $\text{HO}_2\text{C.CH}_2\text{S.CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5$
- c. Monocinnamyl oxalate
 $\text{HO}_2\text{C.CO}_2\text{CH}_2\text{CH}=\text{CHC}_6\text{H}_5$

C. Substituted polybasic acids:

1. With aliphatic alcohols, e. g.:

- a. Mono (2-ethyl hexyl) phenylsuccinate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_5$
- b. Mono-octadecyl phenylglutarate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_{18}\text{H}_{37}$
- c. Monocetyl p-nitrophenylsuccinate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_6\text{H}_4\text{NO}_2$

2. With cyclic alcohols, e. g.:

- a. Mono-hydrocinnamyl o-tolylsuccinate
 $\text{HO}_2\text{C.CH}_2\text{CH}(\text{C}_6\text{H}_4\text{CH}_3)\text{CO}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{CH}_3$
- b. Mono-tetrahydrofurfuryl phenylsuccinate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_4\text{H}_7\text{O}$
- c. Mono-β-phenylethyl o-aminophenylsuccinate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{NH}_2$
- d. Mono-cyclohexyl p-chlorophenylglutamate
 $\text{HO}_2\text{C.CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_6\text{H}_{11}\text{Cl}$

II. Esters of hydroxyacids

A. Cyclic hydroxyacids

1. With aliphatic acids, e. g.:

- a. Stearoyl salicylic acid:
(o) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{O.CO.C}_6\text{H}_4\text{OH}$
- b. Trimyristoyl pyrogalllic acid:
(1) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{O.CO.C}_6\text{H}_3(\text{OH})_3$ (3,4,5)

2. With cyclic acids, e. g.:

- a. Furoyl mandelic acid:
 $\text{HO}_2\text{C.CH}(\text{C}_6\text{H}_5).\text{O.CO.C}_4\text{H}_7\text{O}$
- b. Hydrocinnamoyl salicylic acid
(o) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{O.CO.CH}_2\text{CH}_2\text{C}_6\text{H}_4\text{OH}$

B. Aliphatic hydroxyacids

1. With aliphatic acids, e. g.:

- a. Trimolecular self-condensation product of 12-hydroxystearic acid
 $\text{HO}_2\text{C}(\text{CH}_2)_{10}\text{CH}_2\text{C}_6\text{H}_{13}$
 $\text{O.CO}(\text{CH}_2)_{10}\text{CH}_2\text{C}_6\text{H}_{13}$
 $\text{O.CO}(\text{CH}_2)_{10}\text{CHOHC}_6\text{H}_{13}$
- b. Stearoyl 12-hydroxystearic acid
 $\text{HO}_2\text{C}(\text{CH}_2)_{10}\text{CH}_2\text{C}_6\text{H}_{13}$
 $\text{O.CO.C}_{17}\text{H}_{35}$

2. With cyclic acids, e. g.:

- a. Monophthalyl amyl lactate
(o) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{CO}_2\text{OCH}(\text{CH}_3)\text{CO}_2\text{C}_5\text{H}_{11}$
- b. Monophthalyl amyl citrate
(o) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{CO}_2\text{O.C}(\text{CO}_2\text{C}_5\text{H}_{11})_2$
 $(\text{CH}_2\text{CO}_2\text{C}_5\text{H}_{11})_2$
- c. Diphtalyl amyl tartrate
(o) $(\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{CO}_2\text{O.C}_6\text{H}_4\text{CO}_2\text{C}_5\text{H}_{11})_2$
- d. Monotriphthalyl β-chloroethylmalate
(p) $\text{HO}_2\text{C.C}_8\text{H}_{17}.\text{CO}_2\text{OCH}(\text{OO}_2\text{CH}_2\text{CH}_2\text{Cl})\text{CH}_2\text{CO}_2\text{CH}_2\text{CH}_2\text{Cl}$

Some examples of the metal salts or soaps which we prepare from these acids and blend with hydrocarbon oils to obtain our improved lubricants are:

1. Calcium octadecyl phthalate
2. Nickelous octadecyl phthalate
3. Chromic (III) octadecyl phthalate
4. Mercurous octadecyl phthalate
5. Mercuric octadecyl phthalate
6. Magnesium octadecyl phthalate
7. Manganese (II) octadecyl phthalate
8. Stannous octadecyl phthalate
9. Lead (II) amyl-3-isopropyl-6-methyl-3,6-endoethylene-Δ4-tetrahydrophthalate
10. Lead (II) cetyl-3-isopropyl-6-methyl-3,6-endoethylene-Δ4-tetrahydrophthalate
11. Stannic cetyl-3-isopropyl-6-methyl-3,6-endoethylene-Δ4-tetrahydrophthalate
12. Barium soap of the monodecyl ester of the Diels and Alder condensation product of methacrylic acid with corn oil fatty acids.

13. Calcium cetyl-3-isopropyl-6-methyl-3,6-endoethylene- Δ 4-tetrahydrophthalate
14. Stannous dilauryl pyromellitate
15. Chromic cetyl naphthalate
16. Stannic benzyl phthalate
17. Magnesium betaphenylethyl terephthalate
18. Aluminum octadecyl phthalate
19. Strontium myricyl maleate
20. Beryllium decyl succinate
21. Cobalt lauryl malate
22. Iron (III) tetradecyl adipate
23. Germanium benzyl succinate
24. Zinc cinnamyl oxalate
25. Cadmium 2-ethylexyl phenylsuccinnate
26. Gallium octadecyl phenylglutarate
27. Indium (I) hydrocinnamyl o-tolylsuccinate
28. Indium (II) tetrahydrofurfuryl phenylsuccinnate
29. Indium (III) stearoyl salicylate
30. Thallous trimyristoyl pyrogallate
31. Thalic furoyl mandelate
32. Molybdenum hydrocinnamyl salicylate
33. Manganous tris-hydroxystearate
34. Manganic stearoyl 12-hydroxystearate
35. Nickel phthalyl amyl lactate
36. Calcium cetyl p-aminophenylsuccinate
37. Stannic tetradecyl mercaptosuccinate
38. Lead Δ -hydroxyethyl phthalate phosphite
39. Copper lauryl 3-nitrophthalate
40. Calcium mono-octadecyl chlorophthalate
41. Stannic monochloro-octadecyl phthalate
42. Lead p-chlorobenzyl phthalate
43. Stannous o-chlorobenzyl succinate
44. Mercuric monocetyl chlorophthalate

The quantities of our metal salts or soaps to be used may vary within wide limits depending on their relative effectiveness in accomplishing a certain desired result. As oxidation inhibitors in crankcase oils from 0.01 to 1.0 percent are generally effective. A blend of this composition has some beneficial effect on ring-sticking as compared with a hydrocarbon oil, but in order to obtain a sufficient effect to be satisfactory more is usually required. Thus we may employ from 0.5 to ten percent in order to prevent ring sticking. It is obvious that this will vary depending on the ring sticking tendency of the base oil, the efficiency of the addition agent, temperature and other conditions of operation and the like.

We are not limited to a blend of hydrocarbon oil and a single metal soap but we may use more than one soap in the same blend. These mixed soaps may be heterogeneous with respect to the acid or metal or both. Thus we may use a blend of hydrocarbon oil, a small quantity of tin cetyl phthalate and a small quantity of calcium cetyl phthalate. In this case the mixed soaps are heterogeneous with respect to metals. Another blend may contain besides the hydrocarbon oil small quantities of nickel octadecyl phthalate and nickel stearoyl-12-hydroxystearic acid. This blend is heterogeneous with respect to acid radicals in the soaps. One blend consists of hydrocarbon oil, stannic cetyl 3-isopropyl-6-methyl-3, 6-endoethylene- Δ 4-tetrahydrophthalic anhydride, calcium stearoyl salicylate and lead (II) amyl 3-isopropyl-6-methyl-3, 6-endoethylene- Δ 4-tetrahydrophthalic anhydride. This blend is heterogeneous with respect to both acids and metals.

Our metal soaps may be used advantageously in combination with lubricants of all kinds including those designed for use in automotive

crankcases, Diesel oils and any other oils of lubricating viscosity. Furthermore our addends are advantageously blended in gasoline and other petroleum fuels either directly or after being blended first in a lubricating oil and then added to the fuel. Soap thickened lubricants, that is greases, are modified by the incorporation of varying amounts of our metal soaps. The ordinary soaps used in making greases may be replaced in whole or in only small part by certain of our metal soaps. These addends modify considerably the tackiness, penetration, resistance to breakdown by working or heat, and other properties of the greases. In making these greases, the usual soaps such as sodium stearate, aluminum stearate, calcium soaps of beta fat and the like may be used to form the large part of the necessary soap. Various other thickening ingredients or materials for other purposes may be added. These include yarn, hair, graphite, glycerol, water, lamp black, mica, zinc dust, etc.

It may be desirable to include in one and the same blend, in addition to the addends here described, other addends for specific purposes. Thus we may add a pour point depressor such as a naphthalene-clor-wax condensation product and a viscosity index improver such as certain resins or polymerized hydrocarbons in addition to our metal soaps of ester-acids. Furthermore, various other metallic compounds may be added to the blend without interfering with the action of our ingredients. Indeed, in some cases, it is advantageous to combine with our addends here described in a lubricating oil blend, such materials as calcium dichlorostearate, chromium oleate, aluminum stearate and other metallic soaps. We may also add various halogenated oxygen-bearing ring or chain compounds including methyl dichlorostearate, lauryl trichloroacetate, chlorodiphenylene oxide, chlorodiphenyl ether and the like. Furthermore, sulfur-bearing materials may be added in the form of sulfurized methyl esters of corn oil acids, benzyl disulfide, alkyl polysulfides and the like. Examples of these are shown below.

The following examples of the preparation and use of the products of our invention are given for the purpose of illustration and not limitation:

Example 1

A mixture of 148 parts by weight of phthalic anhydride and 270 parts of octadecanol was heated at about 140° C. for about two hours. The product was taken up in petroleum ether, filtered at room temperature, and the solvent evaporated from the filtrate. The resulting half ester of phthalic acid required 22 ml. of N/10 alkali to neutralize one gram. Theory, 24 ml.

Example 2

Alcoholic potash was used to neutralize exactly the above product dissolved in 50 percent alcohol. The calcium soap was precipitated by the addition of a slight excess over the calculated amount of calcium chloride solution. The soap was taken up in petroleum ether and the solution washed, dried and evaporated to obtain the clear, sticky, very viscous, liquid calcium soap. The product was very soluble in oil.

Example 3

A blend of 98.7 parts of a naphthenic base oil and 1.3 parts of the calcium octadecyl phthalate was tested in a Lauson engine which has been

described in the literature of the art. While the oil alone showed two stuck rings at the end of fifteen hours, the blended oil showed no stuck rings and a much cleaner piston. After thirty hours with the blended oil, one ring was partly stuck.

Example 4

A mixture of 702 parts of the condensation product of maleic anhydride with alpha-terpinene and 768 parts of commercial cetyl alcohol at about 140° C. was heated for twenty hours. A considerably shorter time is probably ample. The resulting oil was honey-like in color and viscosity and soluble in mineral oils. It was less viscous, however, than the original dibasic acid.

Example 5

The acid-ester of Example 4 was vigorously stirred with water to which sufficient ammonia was added to neutralize the acid when a thick paste resulted. An excess of neutral calcium acetate solution was added with vigorous stirring. The oily product was washed thoroughly with water by decantation and then taken up in petroleum ether. The solution was dried and evaporated to obtain the calcium cetyl 3-isopropyl-6-methyl-3, 6-endoethylene- Δ^4 -tetrahydrophthalate. This was an oil somewhat darker and more viscous than the acid ester of Example 4. It was miscible in all proportions with hydrocarbon oils.

Example 6

A blend of 15 parts of the calcium cetyl 3-isopropyl-6-methyl-3, 6-endoethylene- Δ^4 -tetrahydrophthalate of Example 5 and 985 parts of Mid-Continent paraffin base oil, S. A. E. 30, was tested in the Lauson engine and showed at the end of a fifteen hour run a much cleaner piston and engine free of sludge as compared with a comparable run using the base oil without the soap.

Example 7

The mono-octadecyl phthalate of Example 1 was neutralized with alcoholic potash and the tin soap precipitated by the addition of stannic chloride. The soap was taken up in petroleum ether and this solution washed, dried and evaporated.

Blends of the tin octadecyl phthalate of Example 7 and others of our metal salts of ester-acids were made in a well-refined Mid-Continent paraffin base oil of S. A. E. 30 and treated in the well known Indiana oxidation test. The results are compared in the following table with the base oil and a corresponding blend of tin oleate and mercury phenyl stearate for comparison.

Addend	Amount	Indiana test—hours to form					
		Sludge		Neut. No.		True color	
		10 mg.	100 mg.	0.5	1.0	1,000	2,000
	Percent						
None (base oil).....		15	80	10	24	13	33
Mercuric phenyl stearate.....	0.3	15	53	11	22	13	44
Mercuric octadecyl phthalate.....	0.1	15	52	8	22	16	25
Chromic octadecyl phthalate.....	0.2	21	53	10	22	21	39
Nickelous octadecyl phthalate.....	0.2	11	64	8	20	23	42
Manganous octadecyl phthalate.....	0.2	13	49	7	15	27	54
Barium octadecyl phthalate.....	0.2	20	56	17	34	27	51
Stannic oleate.....	0.2	18	51	11	26	25	49
Stannic octadecyl phthalate.....	0.2	33	54	21	31	29	49

Example 8

	Percent
Mid-Continent paraffin base S. A. E. 40.....	98.0
Stannic octadecyl 3-isopropyl-6-methyl-3, 6-endoethylene- Δ^4 -tetrahydrophthalate.....	0.2
Chlorodiphenylene oxide.....	1.8

Example 9

	Percent
California naphthenic oil S. A. E. 20.....	97.5
Calcium cetyl phthalate.....	1.3
Chlorwax-naphthalene condensation product.....	0.8
Sulfurized methyl esters of corn oil acids....	0.4

Example 10

For the manufacture of a grease, we may use:

	Percent
Oleic acid.....	8.0
Lime.....	1.1
Water.....	0.3
Distillate (460 seconds at 100° F.).....	77.1
Bright stock.....	12.0
Calcium cetyl 3-isopropyl-6-methyl-3, 6-endoethylene- Δ^4 -tetrahydrophthalate.....	1.5

It will be observed from these data that in the case of the mercuric soaps, 0.1 percent of the octadecyl phthalate produced approximately the same improvement in the base oil as was produced by 0.3 percent of the phenylstearate. Similarly the stannic octadecyl phthalate produced considerably greater improvement than the stannic oleate. The other metal soaps of octadecyl phthalate showed appreciable improvement in the oxidation characteristics of the mineral oil.

It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and is within the scope of our claims. It is further obvious that various changes may be made in details within the scope of our claims without departing from the spirit of our invention. It is, therefore, to be understood that our invention is not to be limited to the specific details shown and described.

Having thus described our invention, we claim:

1. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of an organic acid containing an ester group elsewhere in the molecule.

2. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a partial ester of a polybasic organic acid.

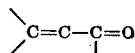
3. A lubricant comprising in combination a

major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a half ester of a dibasic organic acid.

4. A lubricant comprising in combination an oil of lubricating characteristics and from 0.01 to 10 per cent of a metal salt of an organic acid containing an ester group elsewhere in the molecule.

5. A lubricant comprising in combination an oil having lubricating characteristics and from 0.1 to 5 per cent of a metal salt of an organic acid containing an ester group elsewhere in the molecule.

6. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a partial ester of a polybasic acid which is prepared by condensing a polybasic acid containing conjugated double bonds with a material having the structure:



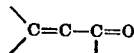
7. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a partial ester of a polybasic acid, which is prepared by condensing a material containing conjugated double bonds with a dibasic acid having a double bond alpha, beta to the carboxyl group.

8. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a partial ester of a polybasic acid, the anhydride of which is prepared by condensing a material containing conjugated double bonds with an anhydride of a dibasic acid having a double bond alpha, beta to the carboxyl group.

9. A lubricant comprising in combination a

major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a half ester of a dibasic acid formed by condensing a monobasic acid containing conjugated double bonds with a monobasic acid having a double bond alpha, beta to the carboxyl group.

10. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a partial ester of a polybasic acid anhydride which is prepared by condensing a polybasic acid anhydride containing conjugated double bonds with a material having the structure:



11. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of calcium cetyl 3-isopropyl-6-methyl-3,6-endoethylene-Δ4-tetrahydrophthalate.

12. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of tin octadecyl 3-isopropyl-6-methyl-3,6-endoethylene-Δ4-tetrahydrophthalate.

13. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a partial ester of a polybasic aromatic acid.

14. A lubricant comprising in combination a major proportion of an oil having lubricating characteristics and a minor proportion of a metal salt of a partial ester of a polybasic aliphatic acid.

GORDON D. BYRKIT.
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CERTIFICATE OF CORRECTION.

Patent No. 2,280,474.

April 21, 1942.

GORDON D. BYRKIT, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 52, for that portion of the formula reading " $(CO_2CH_2CH_2Cl)$ " read $--(CO_2CH_2CH_2Cl)--$; page 4, first column, line 70, for "tetrahyrophthalic" read --tetrahydrophthalic--; and second column, line 31, for "bend" read --blend--; page 5, second column, line 29, for "imprevement" read --improvement--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 7th day of July, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.