PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in or relating to Lubricating Protective Oils having Anti-Corrosive Properties

We, C. C. WAKEFIELD & COMPANY LIMITED, a British Company, of 46, Grosvenor Street, London, W.1, do hereby declare the nature of this invention to be as follows:—

The present invention comprises improvements in or relating to lubricating or protective oils having anti-corrosive properties, and it is one object of the invention to produce a lubricating composition which is not only suitable for lubrication purposes but which also protects metal surfaces against corrosion or rusting, especially surfaces of iron and steel. It is another object of the invention to produce additives which may be incorporated in a mineral oil to impart such anti-corrosive or anti-rusting properties thereto.

Wherever water is likely to contaminate a mineral oil used for lubrication or protective purposes, iron and steel parts in contact therewith can easily become rusted. Following such undesirable corrosion the oil itself is likely to be adversely affected, e.g. by contamination and increase of the rate of oxidation thereof catalytically. Turbine oils and extreme pressure lubricants for hypoid gears represent important examples of oils which are likely to become affected in this way in use and other examples are referred to in the specification of co-pending Patent Application No. 10074/44.

The use of acid phthalates and other acid esters in lubricants has already been proposed, but the alcohols from which such materials are prepared are in general less readily available and more costly than the materials necessary for the production of the compounds the use of which is proposed by the present invention.

According to the invention a lubricating or anti-corrosive composition comprises a mineral oil containing a proportion of an acid ester of a di-basic or poly-basic organic carboxylic acid derived from a fatty, naphthenic or abietic acid ester of a di- or poly-hydric alcohol.

The acid esters of di-basic acids the use of which is proposed by the present invention may be represented by the following general formula:—

$$(R.COO)_xR_1.(OOC.R_2 \begin{matrix}(-OH)_z \\ \cdot \\ COOH)_y\end{matrix}$$

in which R represents a fatty or naphthenic acid residue preferably having at least ten carbon atoms, R_1 is a polyhydric alcohol residue, containing no free hydroxyl substituent, which may represent $(CH_2)_n$ where n is at least 2 or the group

$$—CH_2—\underset{|}{CH}—CH_2—$$

or the group

$$(—CH_2—O—CH_2—)_n.$$

CH_2CH_2 where n is 1 or more, and R_2 is any organic radicle. In the above general formula x, y and z are small integers, x and y being at least 1, whereas z may be zero.

Similarly, general formulæ quoted below represent acid esters of a tri-basic acid which it is proposed to employ (a) in the case where R_1 is a dihydric alcohol residue and (b) in the case where R_1 is a tri-hydric alcohol residue.

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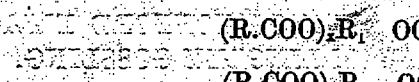
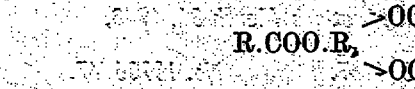
(a) 

(b) 

R, R_2, x and z in these formulæ have the same significance as that previously assigned to them.

Preferably a composition in accordance with the invention includes a proportion of from about 0.05% to about 1.0% of the acid ester, the proportion actually employed depending on the acid ester used and also on the intended use of the composition. Thus in a turbine oil 0.05% to 0.2% by weight of the acid ester may conveniently be employed, more especially in the case of the first two of the following examples of acid esters which may be incorporated in a mineral oil in accordance with the present invention.

EXAMPLE 1.

Ethylene glycol mononaphthenate acid phthalate.

EXAMPLE 2.

Ethylene glycol monostearate acid phthalate.

EXAMPLE 3.

Diethylene glycol mononaphthenate acid maleate.

EXAMPLE 4.

Glyceryl distearate acid tartrate.

EXAMPLE 5.

Acid phthalate from mixed glyceryl mono-, di- and tri-stearate.

The compounds affording Examples 1 and 2 are capable of preparation very simply by heating equi-molecular proportions of ethylene glycol mononaphthenate or monostearate and phthalic anhydride to a temperature of about 130 to 135° C. for about 5 hours. The reaction product is then boiled with water several times to dissolve out all unreacted phthalic anhydride, and the washed product is then dried. Yields of about 95% of the theoretical value have been obtained in this way including a residue of about 5% of the original unreacted ester. The stearic compound so produced (Example 2) has been found to be solid at ordinary temperatures but has not been produced in a pure state. The naphthenate compound (Example 1) has been found to be liquid at ordinary temperatures.

The invention will be understood as including a process for producing the acid ester additives specified above as well as the lubricating or anti-corrosive compositions which may incorporate such additives either alone or in conjunction with other known additives such as known anti-oxidants.

It is a particular object of one form of this invention to provide a marine turbine oil comprising a mineral lubricating oil, an anti-rusting additive of the nature described above and an anti-oxidant which may be of the aromatic amine or alkylated phenol type.

Surprisingly it has been found that such lubricants have superior anti-rusting properties to compositions, otherwise similar, from which the anti-oxidant has been omitted.

Dated this 23rd day of April, 1947.

BOULT, WADE & TENNANT,
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London, E.C.1,
Chartered Patent Agents.

COMPLETE SPECIFICATION

Improvements in or relating to Lubricating Protective Oils having Anti-Corrosive Properties

We, C. C. WAKEFIELD & COMPANY LIMITED, a British Company, of 46, Grosvenor Street, London, W.1, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention comprises improvements in or relating to lubricating or protective oils having anti-corrosive properties, and it is one object of the invention to produce a lubricating composition which is not only suitable for lubrication purposes but which also protects metal surfaces against corrosion or rusting, especially surfaces of iron and steel. It is another object of the inven-

tion to produce additives which may be incorporated in a mineral oil to impart such anti-corrosive or anti-rusting properties thereto.

Wherever water is likely to contaminate a mineral oil used for lubrication or protective purposes, iron and steel parts in contact therewith can easily become rusted. Following such undesirable corrosion the oil itself is likely to be adversely affected, e.g. by contamination and increase of the rate of oxidation thereof catalytically. Turbine oils and extreme pressure lubricants for hypoid gears represent important examples of oils which are likely to become affected in this way in use and other examples are referred to in the specification of British Patent No. 588,864.

The use of acid phthalates and other acid esters in lubricants has already been proposed, but the alcohols from which such materials are prepared are in general less readily available and more costly than the materials necessary for the production of the compounds the use of which is proposed by the present invention.

According to the invention a lubricating or rust-preventing oil composition having anti-corrosive properties comprises a lubricating or other type of mineral oil containing a minor proportion of an acid ester of a di-basic or polybasic organic carboxylic acid and derived also from a fatty, substituted fatty or naphthenic acid hydroxy or partial ester of a di- or polyhydric alcohol. The term naphthenic acid as used in this specification includes mixtures of naphthenic acids, similarly, the term fatty acid includes mixtures of fatty acids.

The acid esters of di-basic acids the use of which is proposed by the present invention may be represented by the following general formula:—

$$(R.COO.)_xR_1.(OOC.R_2\overset{(-OH)_z}{.}COOH)_y$$

in which R represents a naphthenic acid residue or a group having at least eight carbon atoms in a straight chain and consisting of a fatty or substituted fatty acid residue; R_1 is a polyhydric alcohol residue containing no free hydroxyl substituent, which may represent $(-CH_2-)_n$ where n is at least 2 or the group

$$-CH_2-\overset{|}{C}H-CH_2-$$

or the group

$$(-CH_2-O-CH_2-)_n.$$

CH_2CH_2 where n is 1 or more, and R_2 is any organic radical wherein the two carboxyl groups shown in the formula are spaced from one another in the radicle R_2 preferably by two carbon atoms. In the above general formula x, y and z are small integers, x and y being at least 1 whereas z may be zero. The fatty acid radicle R may contain as substituents alkyl or aryl groups but is preferably free from hydroxyl groups unless such hydroxyl groups are in close proximity to the carboxyl group.

Similarly, general formulæ quoted below represent acid esters of a tri-basic acid which it is proposed to employ, (a) and (b) in the case where R_1 is a dihydric alcohol residue and (c) in the case where R_1 is a tri-hydric alcohol residue.

(a) $$\begin{matrix}(R.COO)\,R_1 & OOC\diagdown & & (-OH)_z \\ & & R_2\diagdown & \\ (R.COO)\,R_1 & OOC\diagup & & COOH\end{matrix}$$

(b) $$\begin{matrix}(R.COO)R_1 & OOC\diagdown & & (-OH)_z \\ & & R_2\diagdown & \\ & HOOC\diagup & & COOH\end{matrix}$$

(c) $$R.COO.R_1\begin{matrix}\diagup OOC\diagdown & & (-OH)_z \\ & R_2\diagdown & \\ \diagdown OOC\diagup & & COOH\end{matrix}$$

R, R_2 and z in these formulæ have the same significance as that previously assigned to them and the qualifying remarks already made in this connection again apply.

Preferably a composition in accordance with the invention includes a proportion of from about 0.01% to about 1.0% of the acid ester, the proportion actually employed depending on the acid ester used

and also on the intended use of the composition. Thus in a turbine oil 0.02% to 0.2% by weight of the acid ester may conveniently be employed.

Specific examples of acid esters (or intermediate di- or polyhydric alcohol hydroxy-esters) from which the compounds employed in accordance with the present invention may be derived, are those produced from the following di- or polyhydric alcohols (which have a formula of $R_1.(OH)_{x+1}$ when expressed in terms of the symbols employed and defined above):

Ethylene glycol, di-ethylene glycol, tri-ethylene glycol, propylene glycol and glycerol,

and from the following acids (which have a formula of R.COOH when expressed in terms of the symbols employed and defined above:

Stearic acid, oleic acid, phenyl stearic acid and a naphthenic acid.

Specific examples of di-basic or poly-basic organic carboxylic acids which may be employed in the production of the final acid ester (and which have a formula of:—



when expressed in terms of the ~~symbols~~ Symbols employed and defined above) are:—

Phthalic acid, succinic acid, malic acid, tartaric acid, citric acid and maleic acid.

General methods suitable for the preparation of the intermediate di- or polyhydric alcohol hydroxy-esters are those of Hilditch and Rigg given in the Journal of the Chemical Society for 1935, page 1774, and given in U.S. Patent Specifications Nos. 2,293,265 (Standard Oil Development Company) and 2,151,185 (Carbide and Carbon Chemicals Corporation). The use of phenol in the reaction described by Hilditch and Rigg was, however, found to be unnecessary in the case of the preparation of naphthenic acid esters. A further method available for the preparation of the intermediate hydroxy-ester is by the reaction of an alkylene chlorhydrin (e.g. ethylene chlorhydrin) employed in excess, with the sodium salt of the desired acid.

Suitable methods for the preparation of the final acid ester to be incorporated in the oil composition provided in accordance with the invention are afforded by:—

(A) direct heating of the intermediate di- or polyhydric alcohol hydroxy-ester with the acid anhydride of the desired di-basic or polybasic organic carboxylic acid where such anhydride is available, and

(B) the method of Hilditch and Rigg referred to above with the use of an excess of the selected di-basic or poly-basic organic carboxylic acid.

Specific examples are given below in some detail of the preparation of one intermediate hydroxy-ester (Example 1) and of the respective preparation of final acid esters (Examples 2 and 3) by the methods (A) and (B) last referred to above.

EXAMPLE 1.

Preparation of ethylene glycol mono-naphthenate represented by the formula

$$R.COOCH_2CH_2OH$$

where R represents a naphthenic acid residue.

900 grams of naphthenic acids, of molecular weight about 320, were mixed in a five-litre three-necked organic reaction flask with 521 grams of ethylene glycol and 4.5 grams of *p*-toluene sulphonic acid employed as a catalyst.

The flask was connected through a constant water separator to a reflux condenser and the mixture heated at 160° C. to 180° C. for four and a half hours while a steady stream of carbon dioxide was passed through the reaction flask. Water was given off during the reaction and trapped in the separator, about 70 cubic centimetres being so collected.

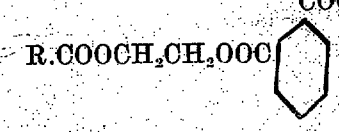
The reaction product was twice boiled with water to extract excess glycol and dried by heating in a current of carbon dioxide. This crude product was shown to contain approximately:—

78% ethylene glycol mononaphthenate
4% naphthenic acid
18% ethylene glycol di-naphthenate.

An 88% yield of 896 grams of the crude product was obtained.

EXAMPLE 2.

Preparation of ethylene glycol mono-naphthenate acid phthalate, represented by the formula:—



where R is a naphthenic acid residue.

230 grams of ethylene glycol mono-naphthenate and 59.2 grams of phthalic anhydride were placed in a 500 c.c. round-bottomed flask, heated to 135° C. in an oil-bath and stirred gently for about 1 hour, with the temperature maintained roughly constant.

The product of this reaction was freed from excess phthalic anhydride by stirring for 5 minutes with 2 litres of water at 80° C. and decanting the water, this pro-

cess being repeated a second time and followed by washing with cold water until the effluent (or decanted cold water) was neutral to methyl orange. The washed product was dried by dissolving in benzene and refluxing under a constant water separator until no more water was eliminated, the solvent then being removed by distillation.

The final product so obtained was a dark reddish-brown viscous liquid, quite easily soluble in oil and having an acidity equivalent to a content of about 53% of ethylene glycol mononaphthenate acid phthalate. Since the ethylene glycol mononaphthenate employed for this preparation contained only 63% of the true mono-ester, 75% of the latter was converted to the acid phthalate to provide the yield quoted. Other materials present in the crude acid ester obtained included ethylene glycol dinaphthenate, di(ethylene glycol mononaphthenate) phthalate, and a very small amount of naphthenic acid.

EXAMPLE 3.

Preparation of ethylene glycol mononaphthenate acid malate, represented by the formulæ:—

$$\begin{array}{l} CH_2COOCH_2CH_2OOC\ R \\ | \\ (OH)\,CH\ COOH \end{array} \quad \text{and} \quad \begin{array}{l} (OH)CH\ COOCH_2CH_2OOC\ R \\ | \\ CH_2COOH \end{array}$$

where R is a naphthenic acid residue.

11.6 grams of ethylene glycol mononaphthenate were mixed with 3.0 grams of malic acid and 0.3 grams of *p*-toluenesulphonic acid employed as a catalyst in a 100 c.c. round-bottomed flask, and 15 grams of phenol were added to act as a mutual solvent.

The flask was fitted with a short air condenser and a thermometer and a slow stream of carbon dioxide was passed through the flask for 4 hours at such a rate that water was eliminated from the sphere of action through the condenser while the bulk of the phenol was refluxed. The temperature of the reaction mixture was maintained at 170° C.

The reaction product was then washed and dried in a manner similar to that adopted for the reaction product in Example 2. The resulting material was a dark reddish-brown viscous liquid containing about 72% of actual ethylene glycol mononaphthenate acid malate.

Further specific examples of materials employed in accordance with the present invention are referred to hereinafter and are in most cases derived from the specific examples already quoted of the alcohols and acids (from which the intermediate hydroxy esters may be prepared) and of the di-basic or polybasic organic carboxylic acids from which the final acid ester may be prepared. Acid succinates and acid maleates are conveniently prepared by methods similar to that described in Example 2 for the preparation of an acid phthalate, while acid tartrates and acid citrates are conveniently prepared by methods similar to that described in Example 3 for the preparation of an acid malate.

Physical properties of the final acid esters employed in accordance with the present proposals resemble the physical properties of the acids from which the intermediate di or polyhydric alcohol hydroxy esters are produced. For example, acid esters of glycol stearates and glyceryl stearates are white waxy solids, acid esters of corresponding oleates are yellow or brown liquids and said esters of corresponding naphthenates are dark viscous liquids.

All of the acid esters employed in accordance with the present proposals are readily soluble in oil in the proportions referred to above in which such compounds are intended to be incorporated in a mineral oil. In addition such acid esters have very little effect on the demulsification value of the oils in which the acid esters are incorporated, and have, furthermore, an extremely low solubility in water so that they are not removed from an oil solution on contact or mixture with water. From the examples given above of the methods by which the acid esters may be prepared, it will be seen that the acid esters may in practice be incorporated in a mineral oil while associated with appreciable quantities of unobjectionable neutral esters produced as by-products during preparation of the acid esters. If desired, however, more pure acid esters may be separated from such by-products and employed in an oil in the purified condition. These crude acid esters may, for example, be purified by forming the sodium salts, dissolving them in water, removing the neutral esters by filtration or extraction and regenerating the original acid esters by acidifying the aqueous solution. The acid esters are incorporated with advantage in any mineral oil lubricating composition and more

especially in turbine oils and in extreme pressure lubricating compositions. The acid esters may, however, also be incorporated in protective oils employed for application to metal surfaces to prevent wetting of the latter so as to avoid corrosion that would occur as a consequence of such wetting or to avoid adhesion and accumulation of ice which may result from such wetting at a suitable temperature.

Various examples of compounds employed in accordance with the present proposals have been subjected to a test to show the effectiveness of such compounds in use. The test employed was a modified form of the well-known A.S.T.M. D.665—44T test described in the British Admiralty Specification O.M.88. In carrying out the test polished mild steel rods were immersed in a rapidly stirred mixture of oil and an artificially produced equivalent of Sea water, the immersion being for a period of 48 hours at a temperature of 140° F. The rods were examined after the completion of the period of immersion for signs of rusting.

The tests were conducted with a mineral oil blend consisting of 70% of a solvent refined naphthenic base oil of viscosity approximately 170 seconds Redwood at 140° F., and 30% of solvent refined paraffinic oil of viscosity approximately 60 seconds Redwood at 140° F. The oil blend had a demulsification value of about 2 minutes (I.P. Standard method) which, in most cases was not appreciably increased by the incorporation of a small proportion of an acid ester the effectiveness of which was undergoing test. To obtain comparable results from the test the latter were conducted on oil compositions including acid esters added in such proportions as to impart a definite similar fixed acidity to the compositions.

TEST 1.

The oil blend (free from any added acid ester) subjected to the test described above produced extremely severe corrosion of the test specimen which became covered in rust in a few hours.

TEST 2.

Samples of the oil blend with the following examples of acid esters incorporated in the oil in a concentration such as to impart an acidity of 0.02 mgs. of KOH per gram of oil composition, resulted on test in the complete elimination of any rust formation on the steel test specimens.

It is to be noted in this connection that British Admiralty Specification O.M.88 permits an acidity of 0.10 mgms. of KOH per gram of final oil composition.

EXAMPLE 4.

Ethylene glycol mononaphthenate acid succinate.

EXAMPLE 5.

Ethylene glycol mononaphthenate acid maleate.

EXAMPLE 6.

Ethylene glycol monophenylstearate acid phthalate.

EXAMPLE 7.

Glyceryl distearate acid phthalate.

EXAMPLE 8.

Ethylene glycol mononaphthenate acid tartrate.

TEST 3.

Samples of the oil blend with the following examples of acid esters incorporated in the oil in a concentration similar to that employed in Test 2 resulted on test in the production of only slight rusting in the form of a few small spots.

EXAMPLE 9.

Ethylene glycol mono-oleate acid phthalate.

EXAMPLE 10.

Diethylene glycol mononaphthenate acid phthalate.

EXAMPLE 11.

Glyceryl mononaphthenate di-acid phthalate.

EXAMPLE 12.

Triethylene glycol mononaphthenate acid phthalate.

TEST 4.

Samples of the oil blend with the following examples of acid esters incorporated in the oil in a concentration such as to impart an acidity of 0.04 mgs. of KOH per gram of oil composition, similarly resulted in the complete elimination of any rust formation on the steel test specimens.

EXAMPLE 2.

Ethylene glycol mononaphthenate acid phthalate.

EXAMPLE 13.

Glyceryl monostearate di-acid phthalate.

EXAMPLE 3.

Ethylene glycol mononaphthenate acid malate.

TEST 5.

Samples of the oil blend with the following examples of acid esters incorporated in the oil in a concentration similar to that employed in Test 4 resulted on test in the production of only slight rusting in the form of a few small spots.

EXAMPLE 14.

Ethylene glycol monostearate acid phthalate.

EXAMPLE 15.

Ethylene glycol mononaphthenate acid citrate.

Further examples of acid esters which may be employed in accordance with the present proposals are:—

EXAMPLE 16.

Diethylene glycol monolaurate acid phthalate.

EXAMPLE 17.

Acid phthalates of ethylene glycol mono-ester of coconut oil acids.

EXAMPLE 18.

Propylene glycol mononaphthenate acid phthalate.

EXAMPLE 19.

Diethylene glycol mononaphthenate acid maleate.

EXAMPLE 20.

Glyceryl distearate acid tartrate..

EXAMPLE 21.

Acid phthalate of mixed glyceryl mono- and di-stearate with some glyceryl tristearate.

It will be appreciated that the acid esters employed in accordance with the present proposals vary slightly in their effect of inhibiting corrosion, but as seen from the information given above the group of acid esters employed are surprisingly effective. The said group of acid esters are also superior to corresponding derivatives of monohydric straight or branched chain alcohols and, for example, cetyl acid phthalate employed in the oil blend referred to above in a proportion similar to that indicated in Tests 2 and 3 resulted in rusting of about 15% of the surface of the test specimen while octadecyl acid phthalate employed in the oil blend in a proportion similar to that indicated in Tests 4 and 5 resulted in the rusting of the test specimens after 21 hours.

It is preferred that the acid residue represented by the group R in the formulæ hereinbefore quoted when consisting of a fatty or substituted fatty acid residue also be such as to include at least 8 carbon atoms in a straight chain, less satisfactory results otherwise being secured as, for example, in the case of ethylene glycol monoabietate acid phthalate. It is preferred also that any hydroxyl group present in the acid residue is disposed very close to the —COOH group, less satisfactory results otherwise again being secured as for example in the case of ethylene glycol monoricinoleate acid phthalate in which a hydroxyl group exists in the acid residue widely spaced from the carboxyl group. Further it is preferred that the carboxyl groups of the di-basic or polybasic acid are not widely spaced or separated by a carbon chain as in ethylene glycol mononaphthenate acid sebacate since less satisfactory results are then again obtained. A satisfactory disposition of the carboxyl groups of the di-basic or polybasic acid is found to be one in which the groups are separated by 2 carbon atoms.

In the application of the present invention to certain oil compositions, and particularly in the case of a turbine oil it is found possible and desirable to include in the oil an anti-oxidant in addition to the anti-corrosive acid ester now proposed. Such an anti-oxidant may be an aromatic amine and particularly a secondary aromatic amine such as phenyl-α-naphthylamine, phenyl-β-naphthylamine, diphenylamine and the like, or may be an alkylated phenol such as tertiary butyl cresol, 2:4 dimethyl 6-tertiary butyl phenol, 2:6 ditertiary butyl-4-methyl phenol, or may be any other well known anti-oxidant compound such as β-naphthol or tetramethyldiaminodiphenyl methane. The effect of such anti-oxidants is not adversely influenced by the presence of the acid esters and in some cases the joint use of the two compounds results in an improved resistance to rust formation as compared with that secured by the use of the acid ester alone. Corrosion resistance secured by the use of an acid ester is enhanced for example, by the conjoint use of 2:6 ditertiary butyl-4-methyl phenol as an anti-oxidant, the further incorporation of 0.5% by weight of which in an oil blend similar to that referred to above but composed of oils from different sources was found completely to eliminate the slight rusting which occurred on testing the oil blend with 0.05% by weight of ethylene glycol mononaphthenate acid phthalate incorporated in the oil.

The use with the acid esters of anti-oxidants containing components which hydrolyse to give water soluble alkaline materials is, however, to be avoided.

Lubricating or protective oil compositions provided in accordance with the present invention may include also other materials such as those known as extreme pressure agents, pour-point depressants, V.I. improvers and the like. An extreme pressure lubricating composition containing organic sulphur and halogen compounds such as those described in British Patent Specifications Nos. 455,235, 561,898 and 561,941 may, for example, include also an acid ester in accordance with the present proposals. Any desired or available type of mineral oil may have the acid ester incorporated therein although the effect of the acid esters may vary for different oils so that larger amounts of acid esters may be required to be incorporated in some oils than in others to secure the best possible results.

Having now particularly described and

ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A lubricating or rust preventing oil composition having anti-corrosive properties and comprising a lubricating or other type of mineral oil in which there is incorporated a minor proportion of an acid ester of a di-basic or polybasic organic carboxylic acid derived also from a fatty, substituted fatty, or naphthenic acid hydroxy or partial ester of a di- or polyhydric alcohol.

2. An oil composition as claimed in Claim 1 wherein the acid ester includes a group which consists of a fatty or substituted fatty, acid residue and which has at least eight carbon atoms in a straight chain.

3. An oil composition as claimed in Claim 1 or Claim 2 wherein the acid ester includes a group which consists of a fatty, substituted fatty or naphthenic acid residue and which is free from hydroxyl groups or has any such hydroxyl groups very close to the carboxyl group.

4. An oil composition as claimed in any of the preceding claims wherein the acid ester includes a di- or polyhydric alcohol residue containing no free hydroxyl substituent.

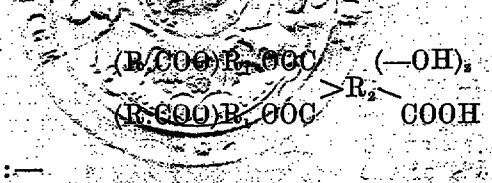
5. An oil composition as claimed in any of the preceding Claims wherein the acid ester includes a group which consists of the dibasic or polybasic organic carboxylic acid radical and which has the carboxyl groups spaced apart by two carbon atoms.

6. An oil composition as claimed in Claims 1 to 5 wherein the acid ester is derived from a di-basic acid and has the general formula:—

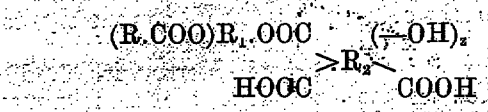
$$(R.COO)_x.R_1.(OOC.R_2.COOH)_y \quad (-OH)_z$$

in which R represents a fatty, substituted fatty or naphthenic acid residue, R_1 is a di- or polyhydric alcohol residue, R_2 is any organic radical and x, y and z are small integers of which x and y are at least one while z may be zero.

7. An oil composition as claimed in Claims 1 to 5 wherein the acid ester is derived from a tri-basic acid, and an acid ester of a dihydric alcohol to have a general formula:—

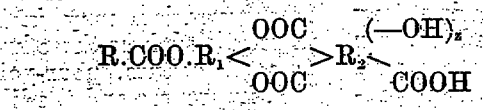


or:—



where R, R_1, R_2, and z have the significance assigned to them in Claim 6.

8. An oil composition as claimed in Claims 1 to 5 wherein the acid ester is derived from a tri-basic acid and an acid ester of a tri-hydric alcohol to have a general formula of:—



where R, R_1, R_2 and z have the significance assigned to them in Claim 6.

9. An oil composition as claimed in any one of Claims 6, 7 and 8, wherein R_1 is a di- or polyhydric alcohol residue which contains no free hydroxyl substituent and which represents $(-CH_2-)_n$ where n is at least 2 or the group $-CH_2-CH-CH_2-$ or the group $(-CH_2-O-CH_2-)_n$. CH_2CH_2- where n is 1 or more.

10. An oil composition as claimed in any of the preceding Claims wherein a proportion of from 0.01% to 1.0% of the acid ester is incorporated in the composition.

11. A turbine oil comprising an oil composition as claimed in any of the preceding Claims in which is incorporated from 0.02% to 0.2% by weight of the composition of the acid ester.

12. A turbine oil comprising an oil composition as claimed in any of the preceding Claims having a mineral lubri-

ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A lubricating or rust preventing oil composition having anti-corrosive properties and comprising a lubricating or other type of mineral oil in which there is incorporated a minor proportion of an acid ester of a di-basic or polybasic organic carboxylic acid derived also from a fatty, substituted fatty, or naphthenic acid hydroxy or partial ester of a di- or polyhydric alcohol.

2. An oil composition as claimed in Claim 1 wherein the acid ester includes a group which consists of a fatty or substituted fatty, acid residue and which has at least eight carbon atoms in a straight chain.

3. An oil composition as claimed in Claim 1 or Claim 2 wherein the acid ester includes a group which consists of a fatty, substituted fatty or naphthenic acid residue and which is free from hydroxyl groups or has any such hydroxyl groups very close to the carboxyl group.

4. An oil composition as claimed in any of the preceding claims wherein the acid ester includes a di- or polyhydric alcohol residue containing no free hydroxyl substituent.

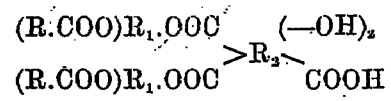
5. An oil composition as claimed in any of the preceding Claims wherein the acid ester includes a group which consists of the dibasic or polybasic organic carboxylic acid radical and which has the carboxyl groups spaced apart by two carbon atoms.

6. An oil composition as claimed in Claims 1 to 5 wherein the acid ester is derived from a di-basic acid and has the general formula:—

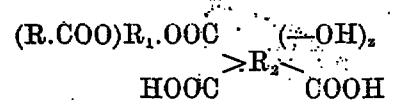
$$(R.COO)_x.R_1.(OOC.R_2.COOH)_y^{(-OH)_z}$$

in which R represents a fatty, substituted fatty or naphthenic acid residue, R_1 is a di- or polyhydric alcohol residue, R_2 is any organic radical and x, y and z are small integers of which x and y are at least one while z may be zero.

7. An oil composition as claimed in Claims 1 to 5 wherein the acid ester is derived from a tri-basic acid, and an acid ester of a dihydric alcohol to have a general formula:—

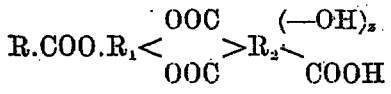


or:—



where R, R_1, R_2, and z have the significance assigned to them in Claim 6.

8. An oil composition as claimed in Claims 1 to 5 wherein the acid ester is derived from a tri-basic acid and an acid ester of a tri-hydric alcohol to have a general formula of:—



where R, R_1, R_2 and z have the significance assigned to them in Claim 6.

9. An oil composition as claimed in any one of Claims 6, 7 and 8, wherein R_1 is a di- or polyhydric alcohol residue which contains no free hydroxyl substituent and which represents $(-CH_2-)_n$ where n is at least 2 or the group $-CH_2-CH-CH_2-$ or the group $(-CH_2-O-CH_2-)_n$. CH_2CH_2- where n is 1 or more.

10. An oil composition as claimed in any of the preceding Claims wherein a proportion of from 0.01% to 1.0% of the acid ester is incorporated in the composition.

11. A turbine oil comprising an oil composition as claimed in any of the preceding Claims in which is incorporated from 0.02% to 0.2% by weight of the composition of the acid ester.

12. A turbine oil comprising an oil composition as claimed in any of the preceding Claims having a mineral lubri-

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cating oil base and including in addition to the acid ester a minor proportion of an anti-oxidant material which may be an aromatic amine, alkylated phenol or other known anti-oxidant compound.

13. An extreme pressure lubricant comprising an oil composition as claimed in any of the preceding claims and including in addition to the acid ester a known extreme pressure agent such as organic sulphur and halogen compounds known as extreme pressure agents.

14. A lubricating or protective oil composition as claimed in any of the preceding Claims wherein is incorporated an acid phthalate of glycol of glycerol naphthenate or stearate.

15. A lubricating or protective oil composition as claimed in any of the preceding claims wherein is incorporated an acid ester as set forth in any of the Examples 2 to 21 quoted herein.

Dated this 31st day of March, 1948.
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* C L M S *