(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 011 497**
A1

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **79302596.6**

(22) Date of filing: **15.11.79**

(51) Int. Cl.³: **C 10 M 1/24**
C 23 F 11/12

(30) Priority: **15.11.78 US 960764**

(43) Date of publication of application:
28.05.80 Bulletin 80/11

(84) Designated Contracting States:
BE DE FR GB IT NL

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(54) **Lubricating oil composition and additive concentrate for addition to lubricating oil.**

(57) A lubricating oil composition formulated to exhibit improved rust and corrosion-inhibiting properties and comprising, in addition to lubricating oil, an oxyalkylated sorbitan triester of a fatty acid and an oxyethylated alkylphenol.

The invention further includes an additive concentrate formulated for addition to lubricating oil and containing, for corrosion-inhibiting purposes, both an oxyethylated sorbitan triester of a fatty acid and an oxyethylated alkylphenol.

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LUBRICATING OIL COMPOSITION AND ADDITIVE CONCENTRATE FOR ADDITION TO LUBRICATING OIL

This invention relates to a lubricating oil composition and an additive concentrate for addition to lubricating oil; and the invention is concerned, in particular, with the provision of an improved oil for crankcase service for internal combustion engines. Oils for such service commonly contain various additives which serve different functions. Ashless dispersants are added to prevent deposition of engine sludge. Zinc dihydrocarbyldithiophosphate is added to inhibit wear and provide antioxidant protection. Alkaline earth metal alkylbenzene or petroleum sulfonates function as high temperature detergents. Over-based alkaline earth metal sulfonates or salicylates provide both detergent action and an alkaline reserve to protect engine parts against corrosion.

The use of certain surfactants for lubricating oil is discussed in U. S. Patents Nos. 3,509,052 and 3,928,219. These include certain oxyalkylated polyols, oxyalkylated ethylenediamine, nonylphenyl polyethylene glycol ethers and the like. Furthermore, U. S. Patents Nos. 2,681,315 and 2,833,717 disclose the use of oxyethylated alkylphenols in oil as corrosion inhibitors. In addition, U. S. Patent No. 2,921,027 discloses the use of oxyethylated sorbitan mono-esters. The actual products employed are "Tweens"

specifically Tween 80 and Tween 81, both being mono-esters which only differ in their degree of oxyethylation. Anticorrosion properties are demonstrated using the "static water-drop test" and it is made absolutely plain that only the polyoxyethylene sorbitan monooleates meet the requirements of this test. Indeed, the disclosure of this U. S. Patent is very definite in its teaching of the use of mono-esters, the only thing being varied being the degree of oxyethylation of such esters.

The present invention is founded upon the unexpected discovery that the rust and corrosion-inhibiting properties of lubricating oil are significantly improved by addition of the combination of an oxyalkylated sorbitan tri-fatty acid ester and an oxyalkylated alkylphenol, especially an oxyethylated alkyl phenol.

A preferred embodiment of the invention is a lubricating oil composition comprising a major amount of lubricating oil and a minor corrosion-inhibiting amount of the combination of (a) an oxyalkylated sorbitan triester of a fatty acid and (b) an oxyethylated C_{4-12} alkylphenol.

While the present invention is particularly suitably applied to crankcase oils, the invention is not limited to such use and can be applied whenever lubricating oils are used for lubrication.

The oxyalkylated sorbitan triester can be made by esterifying one mole of sorbitan with about three moles of fatty acid. Preferred fatty acids contain about 10-20 carbon atoms. Examples of these are decanoic acid, lauric

acid, palmitic acid, stearic acid, arachidic acid, tall oil acids and the like. The most preferred fatty acid is oleic acid or mixtures of fatty acids containing substantial amounts of oleic acid.

Esterification can be conducted by known methods such as by heating a mixture of sorbitan and fatty acid to distill out water. A distillation aid such as xylene can be used. The reaction forms a mixture in which the principal component is the triester although minor amounts of di- and tetraester might form. These will not interfere with the effectiveness of the product.

The sorbitan triester is then reacted with an alkylene oxide such as ethylene oxide, propylene oxide or butylene oxide. The alkylene oxide reacts mainly with the free hydroxyl group on the sorbitan triester to form an oxyalkylene chain with a terminal hydroxyl group. The length of the chain can be varied by adjusting the ratio of alkylene oxide to sorbitan tri-fatty acid ester. Some of the alkylene oxide can react with the ester bond to insert oxyalkylene units between the sorbitan and the fatty acid. Preferably, the reaction is conducted until about 4-50 moles of alkylene oxide are reacted per mole of sorbitan tri-fatty acid ester. A preferred range is about 10-30 moles of alkylene oxide and a most preferred coadditive is formed when an average of about 20 moles of alkylene oxide react per mole of sorbitan tri-fatty acid ester.

The preferred alkylene oxide is ethylene oxide which forms a chain of repeating ethyleneoxy units.

Suitable oxyalkylated sorbitan tri-fatty acid esters are available commercially. Atsurf 2822, a product of ICI United States, Inc., is an oxyethylated sorbitan trioleate containing an average of about 20 ethyleneoxy units per molecule. It is made by esterifying one mole of sorbitan with three moles of oleic acid followed by reaction with ethylene oxide. It is very effective in the present combination.

The other required component in the combination is an ethoxylated alkylphenol. Preferably, the alkylphenol contains about 4-12 carbon atoms in the alkyl group. More preferably, the alkyl group contains about 7-12 carbon atoms such as heptylphenol, 2-ethylhexylphenol, decylphenol and dodecylphenol. The most preferred alkylphenol is nonylphenol.

The coadditive is made by reacting alkylphenol with ethylene oxide until the desired number of ethylenoxy groups are reacted. Preferably there are an average of about 2-10 ethyleneoxy groups per each alkylphenol. More prefereably each alkylphenol has an average ofabout 3-5 ethyleneoxy groups per molecule. The most preferred additive is an ethoxylated nonylphenol containing an average of about 4 oxyethylene groups. Such additives are commercially available. One such additive is marketed by Monsanto Company under the name "Sterox ND"

The amount of each additive used need only be an amount such that the combination provide adequate corrosion and rust protection in, for example, an engine. A useful range is about 0.005-5.3 weight percent of the oxyalkylated sorbitan triester and 0.01-0.5 weight percent of the oxyethylated alkylphenol.

Coadditives may be included in a fully formulated crankcase lubricant. Examples of these are dispersants such as the polyisobutyl succinimide of ethylenepolyamine and polyisobutylphenol Mannich condensates with formaldehyde and ethylenepolyamine. Metal detergents such as calcium alkylbenzene sulfonate, magnesium petroleum sulfonate, calcium salicylates and calcium alkyphenate are conventionally included.

Of special importance in preventing rust are the overbased metal detergents. These include overbased alkaline earth metal alkylbenzene sulfonates, petroleum sulfonates, phenates, salicylates and the like. Examples of these are overbased calcium alkylbenzene sulfonate,

overbased calcium petroleum sulfonate, overbased magnesium alkylbenzene sulfonate, overbased calcium salicylate, overbased calcium alkylphenate, overbased magnesium alkylphenate sulfide and the like. Overbasing methods are well known. For example, alkylbenzene sulfonic acid having an equivalent weight of about 300-2,000 can be overbased by reaction with excess calcium oxide in the presence of water and methanol followed by carbon dioxide injection. The colloidal alkaline earth metal base in these additives serve to neutralize acids in blow-by gases formed in combustion.

Viscosity index improvers are generally added to improve viscosity property of the formulated oil. These include the polyalkylmethacrylate type and the olefin copolymer type. Examples of the latter are ethylene/propylene copolymer, styrene/butadiene copolymer and the like.

Phosphosulfurized olefins can be added such as phosphosulfurized terpenes or phosphosulfurized polybutenes. These may be further reacted by steam blowing or by neutralization with alkaline earth metal bases such as barium oxide.

Phenolic antioxidants are frequently added to the oil compositions. Examples of these are 4,4'-methylenebis-(2,6-di-tert-butylphenol); 2,6-di-tert-butyl-4-dimethylaminomethylphenol; 4,4'-thiobis-(2,6-di-tert-butylphenol) and the like

Zinc salts of dihydrocarbyldithiophosphoric acid are routinely added to provide both wear and antioxidant protection. A typical example is zinc di-(2-ethylhexyl)-dithiophosphate.

The following Example illustrates the preparation of a typical formulated oil suitable for use in an engine crankcase.

Example 1

In a blending vessel place 1,000 gallons 150 SUS solvent refined mineral oil. To this add 100 gallons 1-decene oligomer containing mainly trimers and tetramers. Add sufficient zinc isobutylamylthiophosphate to provide 0.07 weight percent zinc. Add overbased (TBN 300) calcium alkylbenzene sulfonate in an amount to provide 0.15 weight percent calcium. Add 30 gallons of a poly-laurylmethacrylate VI improver. Add sufficient polyisobutyl succinimide of tetraethylene pentamine to provide 3 weight percent active dispersant. Add 0.03 weight percent Atsurf 2822 and 0.3 weight percent Sterox ND. Blend the oil until homogenous and package for distribution.

In many cases the additive combination of this invention is first packaged in an additive concentrate formulated for addition to lubricating oil. Thus, the invention provides an additive concentrate formulated for addition to lubricating oil characterised by a content, for corrosion - inhibiting purposes, of both an oxyalkylated sorbitan triester of a fatty acid and an oxyethylated alkylphenol. These concentrates usually contain conventional additives such as those listed above in addition to the oxyalkylated sorbitan triester and ethoxylated alkylphenol described herein. The various additives are present in a proper ratio such that when a quantity of the concentrate is added to lubricating oil the various additives are all present in the proper concentration. The additive concentrate also contains mineral oil in order to maintain it in liquid form.

The following Example illustrates formulation of an additive concentrate formulated for addition to lubricating oil to provide an effective crankcase lubricant.

Example 2

In a blending vessel place 1199.5 lbs. of 100 SUS mineral oil, 748 lbs. of polyisobutyl succinimide of tetraethylene pentamine, 2352 lbs. of ethylene/propylene copolymer VI improver, 264.8 lbs. of zinc di-(2-ethylhexyl)dithiophosphate, 245 lbs. of over based calcium alkylbenzene sulfonate (300 TBN), 5.88 lbs. of Atsurf 2822 and 58.8 lbs. of Sterox ND. Blend until homogenous and then package. The addition of 2450 lbs. of the above concentrate to 1,000 gallons of 150 SUS mineral oil will provide an effective crankcase lubricant.

Standard multi-cylinder Sequence IId tests were carried out in a fully formulated oil containing a commercial succinimide ashless dispersant, a zinc dialkyldithiophosphate, a commercial viscosity index improver, a commercial 300 TBN overbased calcium alkylbenzene sulfonate and 0.3 weight percent Sterox ND and 0.03 weight percent Atsurf 2822. In this test a rust rating of 8.5 or above is a pass. The test was conducted using two different base oils. Ratings of 8.5 and 8.7 were obtained. Both oils passed.

CLAIMS:

1. A lubricating oil composition comprising a lubricating oil and a corrosion-inhibiting additive characterised in that the composition comprises as additives for corrosion-inhibiting purposes both an oxyalkylated sorbitan triester of a fatty acid and an oxyethylated alkylphenol.

2. A composition as claimed in claim 1 further characterised in that the oxyethylated alkylphenol contains about 3-5 ethyleneoxy units.

3. A composition as claimed in claim 1 or claim 2 further characterised in that the oxyalkylated sorbitan triester is an oxyethylated sorbitan trioleate.

4. A composition as claimed in claim 3 further characterised in that the oxyethylated sorbitan trioleate contains about 4-50 ethyleneoxy units.

5. A composition as claimed in claim 4 further characterised in that the oxyethylated sorbitan trioleate contains about 20 ethyleneoxy units.

6. A composition as claimed in any one of claims 1 to 5 further characterised in that the oxyethylated alkylphenol is an oxyethylated C_{4-12} alkylphenol.

7. A composition as claimed in claim 6 further characterised in that the oxyethylated alkylphenol is an oxyethylated nonylphenol containing an average of about 4 ethyleneoxy units.

8. A composition as claimed in any one of claims 1 to 7 further characterised in that the oxyalkylated sorbitan triester is present in the composition in an amount of from 0.005 to 0.3 weight percent and the oxyethylated alkylphenol is present in the composition in an amount of from 0.01 to 0.5 weight percent.

9. An additive concentrate formulated for addition to lubricating oil characterised by a content, for corrosion-inhibiting purposes, of both an oxyalkylated sorbitan triester of a fatty acid and an oxyethylated alkylphenol; the oxyalkylated sorbitan triester optionally being as defined in any one of claims 3 to 5, the oxyethylated alkylphenol optionally being as defined in any one of claims 2, 6 or 7 and the amounts of said triester and alkylphenol optionally being as defined in claim 8.

10. An additive concentrate formulated for addition to lubricating oil and containing an overbased alkaline earth metal detergent and an ashless dispersant characterised in that the concentrate also contains, for corrosion-inhibiting purposes, both an oxyalkylated sorbitan triester of a fatty acid and an oxyethylated C_{4-12} alkylphenol.

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European Patent Office

Application number
EP 79 30 2596

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	US - A - 2 968 621 (F.C. TEETER et al.) * Claim 1; column 2, lines 40-51; column 3, lines 1-10; column 5, lines 30-43 *	1-6
A	US - A - 3 872 048 (C.L. BROWN)	
A	US - A - 4 122 217 (R.J. STURWOLD et al.)	
A	FR - A - 2 275 546 (EDWIN COOPER)	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 10 M 1/24
C 23 F 11/12

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 10 M 1/08
C 23 F 11/12

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	20-02-1980	ROTSAERT