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LUBRICATING OILS CONTAINING AN ACYLOXYACETIC ACID AS A RUST INHIBITOR

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4 Claims. (Cl. 252—56)

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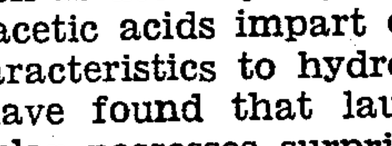
My invention relates to the production of improved turbine oils and other lubricants having valuable rust preventing characteristics. The character of a lubricant in terms of protection against rusting of ferrous parts it contacts in the presence of water is an important one. It is particularly important with respect to lubricant oil compositions designed for use as steam turbine oils. These oils undergo severe conditions of use, and mixing of oil with both fresh and sea water, depending upon the installation of the turbine, is likely to occur with resulting corrosive damage to exposed ferrous operating parts of the turbine unless the oil possesses the capacity of rust prevention under the conditions of service. My invention provides new lubricating oil compositions containing small quantities of an alpha-acyloxycarboxylic acid which possess valuable rust preventing characteristics in the presence of water.

I have found, for example, that higher acyloxyacetic acids such as decanoyloxy- or lauroyloxy- or stearoyloxyacetic acids impart excellent rust preventing characteristics to hydrocarbon mineral oils. I have found that lauroyloxyacetic acid in particular possesses surprising capacity for imparting rust preventing properties. These compositions are disclosed and claimed as such in my application Serial No. 140,550, filed January 25, 1950.

I have also found that higher acyloxycarboxylic acids in general impart rust preventing characteristics to hydrocarbon lubricants provided the acyloxy group is positioned in alpha relationship to the carboxyl group. In all of these compounds, the total number of carbon atoms should be sufficient to provide oil solubility and it appears that there must be at least 10 carbon atoms in the molecule for effectiveness in rust prevention. The generally useful alpha-acyloxy acids may be characterized by the following type formula in which R is an aliphatic group, R′ is an aliphatic group or hydrogen and the total number of carbon atoms in R and R′ is at least 7:



According to my invention a small amount of an alpha-acyloxycarboxylic acid is added to a hydrocarbon mineral oil or lubricant. The hydrocarbon lubricant contemplated ordinarily comprises a conventionally or solvent refined petroleum fraction of the lubricating oil range. Turbine oils according to my invention ordinarily

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comprise a highly refined, solvent extracted neutral oil. In general the amount of acyloxy acid incorporated will be below about 1 per cent. One of the difficult problems in compounding high quality commercial turbine oils is that the neutralization values are closely limited by specification. For example, the Navy Bureau of Ships Specification 14–0–15 for a marine turbine oil limits the neutralization number to 0.1 mg. KOH. The maximum concentration of acyloxy acid permissible by specification for such oils therefore is slightly below 0.1 per cent; 0.06 per cent by weight for stearoyloxyacetic acid, for example. One of the important advantages of turbine oils produced according to my invention is that they provide effective rust protection in these low concentration ranges. As little as about 0.005 per cent provides protection in some instances.

A selected acyloxycarboxy acid or a mixture of suitable acids may be employed according to my invention. Other lubricating oil additives such as oxidation inhibitors, detergents, viscosity index improvers, pour depressors and oiliness agents may also be present in the finished oil. For example, a turbine oil composition according to my invention may include small amounts of 2,6-ditertiarybutyl-4-methylphenol and diphenylamine. The acyloxy acids of my invention may be prepared by several methods. In general I prefer to employ the method of preparation disclosed and claimed in application Serial No. 140,566, of Lester W. Kalinowski, filed January 25, 1950. According to the Kalinowski method, the desired product is produced by reaction of an alkali metal salt of an aliphatic acid with the alkali metal salt of a halo aliphatic acid followed by acidification with a mineral acid. The acyloxy acids may also be prepared by esterification of a hydroxy acid by an acid chloride by the method described in Gilman, Organic Syntheses, volume 1, pages 12 to 13, although in certain instances the yields may be very low due to competing side reactions.

The acyloxy acids of my invention differ both in effective capacity for imparting rust inhibiting properties to lubricants and in the concentration in which they are tolerable in lubricants in terms of such considerations as solubility and effect upon neutralization value. Thus I consider that decanoyloxy-, lauroyloxy- and stearoyloxy-acetic acids have a specially good balance of properties for use in lubricants. They have good solubility and compatibility characteristics, low acid numbers and high capacity for imparting rust preventing properties. In particular, I have

found that lauroyloxyacetic acid has special superiority in providing effective rust protection. Of the alpha-acyloxy higher carboxylic acids, I have found that lauroyloxylauric acid has a specially good balance of desirable properties.

In the following examples, representative types of useful rust preventing acyloxy acids are illustrated. The materials represented, however, are merely illustrative of type, and other acids in which the acyloxy group is positioned alpha to the carboxyl group and in which the number of carbon atoms in the molecule is at least 10 are also useful. Thus caproyloxyacetic acid is useful but caproyloxyacetic acid, according to my tests, does not appear to have utility for this purpose. The acyloxy group may be an alicyclic acid group, such as a naphthenic acid radical of the type believed to constitute mixtures of alkylated cycloalkane rings to which there is attached a

$$(CH_2)_nCOOH$$

group. I have found that a substituted acyloxy acid such as alpha-hydroxydecanoyloxyacetic acid has value. However, I consider that acids in which the total number of carbon atoms in the molecule is as high as 36 such as alpha-stearoyloxy stearic acid, for example, and the acyloxy derivatives of acids produced by oxidation of microcrystalline wax, have value. Examples I to III illustrate typical preparations while tests of representative types in turbine oils are set out thereafter by way of further example.

Example I

In a 500 cc. 3 necked flask, equipped with condenser, agitator and thermometer, are placed 100 grams (0.5 mole) of lauric acid (acid number 280), 56.1 grams (1 mole) of potassium hydroxide and 250 cc. of ethyl alcohol. The mixture is heated to 65° C. with stirring until a homogeneous solution is obtained. Forty-seven and two-tenth grams (0.5 mole) of chloroacetic acid is then added and the reaction mixture is maintained at 80° C. for 16 hours. Upon filtering, there is obtained 37 grams of potassium chloride (37.5 grams potassium chloride represents 100% reaction). The alcohol is then distilled off; approximately 95 per cent of the alcohol is recovered. To the salt is added 200 cc. of water plus 43 cc. (2 per cent excess) of concentrated hydrochloric acid. Acidification of the salt is at 50° C. with stirring for 2 hours. The organic layer is isolated, washed twice with water, extracted with ether and dried over anhydrous sodium sulfate. The ether is removed, and 110 grams of crude lauroyloxyacetic acid (90 per cent of theoretical amount) is obtained. This product was recrystallized from n-pentane.

ANALYSIS OF CRUDE PRODUCT

	Calculated For	Found
Acid No.	217	210
Saponification No.	434	340

ANALYSIS OF PURE PRODUCT

Percent Carbon	65.2	65.2
Percent Hydrogen	10.0	10.4
Percent Oxygen	24.8	24.4
Acid No.	217	219
Melting Point °C.		65–66

Example II

In a 250 cc. round bottom flask provided with a condenser, are placed 21.6 grams (0.1 mole) of alpha-hydroxylauric acid (melting point 69–70° C.) and 23.4 grams (0.3 mole) acetyl chloride. A reaction sets in without the application of heat. As soon as a clear solution results, about 1 hour, the flask is gently heated to remove the excess acetyl chloride. The last trace of acetyl chloride is removed by vacuum distillation. The alpha-acetoxylauric acid then crystallizes after standing one day. The yield is 23 grams (85 per cent of the theoretical amount). Recrystallization from n-pentane gives a pure product.

ANALYSIS

Calculated:
Acid No. 229

Found:
Acid No. 225
Melting point ..... 42–42.5° C.

Example III

In a 500 cc. round bottom flask, equipped with a condenser, stirrer and thermometer, are placed 78 grams (0.39 mole) lauric acid (acid No. 293, melting point 30–33° C.), 43.65 grams (0.78 mole) potassium hydroxide and 250 cc. of ethyl alcohol. The reaction is heated until a homogeneous solution is obtained and then 109 grams (0.39 mole) of alpha-bromolauric acid (acid No. 180) is added. The reaction is then allowed to proceed for 16 hours at 80° C. Upon filtering, 35 grams of potassium bromide (76 per cent of theoretical) is recovered. The alcohol is removed by distillation, 200 cc. of water plus 35 cc. of concentrated hydrochloric acid are added and acidification of alpha-lauroyloxy potassium laurate proceeds at 50° C. with stirring for 2 hours. The organic layer is isolated, washed several times with water, extracted with ether and dried over anhydrous sodium sulfate. Upon removal of the ether, a crude product, 122 grams (78 per cent of theoretical amount) is obtained. The crude acid was vacuum topped at 1 mm. of mercury and the portion boiling below 130° C. discarded.

ANALYSIS OF PURE PRODUCT

	Calculated For	Found
Acid No.	141	139
Saponification No.	282	258

A number of the useful acyloxy acids were evaluated as rust inhibitors in a turbine oil composition based upon a solvent treated, highly refined Mid-continent neutral oil. The base oil composition contained 0.4 per cent by weight Paranox 441 (2,6 - ditertiarybutyl - 4 - methylphenol) and 0.15 per cent of diphenylamine. The base oil employed has the following characteristics:

Gravity	29.0
Flash	460
Fire	505
Viscosity at 100° F., SUS	338.0
Viscosity at 210° F., SUS	54.6
Viscosity index	98
Color, NPA	2½—
Neutralization number	0.00
Specific dispersion	107.0
Carbon residue	0.036
Steam emulsion number	141
Demulsibility at 130° F.	780
Navy emulsion test:	
Distilled water	OK (6 minutes)
1% NaCl	OK (1 minute)

Varying proportions of the acyloxy compounds tested were blended into the oil as indicated in the following table and the finished oil blends were tested according to ASTM turbine oil rust test D665–47T for effectiveness under procedure A for distilled water and procedure B for synthetic sea water. The tabulated data show that of the compounds illustrated, decanoyloxy-, lauroyloxy- and stearolyl-oxyacetic acids have the greatest effectiveness. Of the three, the first two are the most effective on a weight basis. All three rust inhibitors met the synthetic sea water rust test requirement of the Navy Bureau of Ships Specification 14–0–15 for a marine turbine oil. This specification limits the neutralization number of such an oil to 0.1 so that these three acids can be used in concentrations of 0.04, 0.045, and 0.06 per cent, respectively. Naphthenoyloxyacetic acid and alpha-acetoxylauric acid inhibited all corrosion in synthetic sea water and gave up to 95 per cent protection in distilled water at the concentrations tested. Alpha-hydroxy decanoyloxyacetic acid and alpha-lauroyloxylauric acid proved effective in distilled water but were not quite so effective in synthetic sea water, a more severe test. The test data follows:

Hence my invention provides hydrocarbon lubricant compositions having improved rust preventing characteristics in the presence of water. My invention particularly provides turbine oil compositions of specification grade with respect to the severe conditions of use required for turbine oils in the range of concentrations permissible for such oils. The rust inhibiting agents have the necessary compatibility and have good demulsibility properties. As indicated in the examples, the useful ranges of concentration do not adversely affect emulsion characteristics as measured by the Navy emulsion test F. S. 320.14.

I claim:

1. Lubricating oil compositions consisting essentially of a hydrocarbon mineral oil with a small amount, sufficient to impart rust preventing characteristics to said compositions, of an acyloxyacetic acid in which the total number of carbon atoms in the acyl group is at least 8.

2. The composition of claim 1 in which the acid is decanoyloxyacetic acid.

3. The composition of claim 1 in which the acid is lauroyloxyacetic acid.

4. The composition of claim 1 in which the acid is stearoyloxyacetic acid.

PROPERTIES OF THE ACYLOXYCARBOXYLIC ACIDS

	Acid No.	Melting Point, °C.	Distilled Water			Synthetic Sea Water			Neutralization No.	Navy Emulsion (F. S. 320.14)
			Rating[1]	Coating on Strip	Etching on Strip	Rating	Coating on Strip	Etching on Strip		
Decanoyloxyacetic acid	234	53–53.5								
0.04%			A	None	None	A	None	None	0.09	Passes.
0.02%			A	do	do	A	do	do	0.05	Do.
0.01%			B++	do	do	A−	do	do	0.02	Do.
Lauroyloxyacetic acid:										
Pure	219	65–66								
0.1%			A	Medium	None	A	Medium	Light	0.20	Do.
0.04%			A	None	do	A	None	None	0.08	Do.
0.02%			A	do	do	A	do	do	0.04	Do.
0.01%			A	do	do	B+	do	do	0.02	Do.
0.0075%			B++	do	do				0.01	Do.
Crude	210									
0.04%			A	None	None	A	None	None	0.08	Do.
0.03%			A	do	do	A	do	do	0.04	Do.
0.02%			A	do	do	B+	do	do	0.02	Do.
Stearoyloxyacetic acid	166	72–74								
0.05%			A	None	None	A	None	None	0.08	Do.
0.02%			A	do	do	B+	Trace	do	0.04	Do.
Naphthenoyloxyacetic acid	120									
0.07%			B+	None	None	A	None	None	0.08	Do.
Alpha-hydroxydecanoyloxy acetic acid.	213	108/1 mm. (B. P.).								
0.045%			A	Light	None	B+	Light	None	0.09	Do.
Alpha-acetoxylauric acid	225	42–42.5								
0.04%			B+	None	Slight	A	None	None	0.09	Do.
0.02%			B+	do	do	A	do	do	0.05	Do.
Alpha-lauroyloxylauric acid	139									
0.07%			A	None	Slight	B	None	None	0.08	Do.
Beta-lauroyloxypropionic acid	214	35–37								
0.04%			D	None	Slight	C	None	None	0.08	

[1] Rust test rating:
A—passes test.
B++—traces of rust on strip.
B+—up to 5% of surface rusted.
B—up to 25% of surface rusted.
C—25 to 50% of surface rusted.
D—50 to 75% of surface rusted.
E—75 to 100% of surface rusted.

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