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COMPOUNDED LUBRICATING OIL

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This invention relates to compounded lubricating oils and to addition agents, to lubricants for improving lubrication. Chlorinated compounds, such as the chlorinated esters of monohydric and dihydric alcohols in U. S. Patent 1,944,941, granted to Lincoln et al., January 30, 1934, constitutes one of the various types of oiliness agents which have been proposed in the prior art. Sulfo-chlorinated glyceryl esters are also disclosed in the early literature as addition agents for thickening and improving hydrocarbon lubricants. See for example, British Patent 12,795 of 1888 to Sommer, and U. S. Patent 461,513, issued to Sommer, October 20, 1891.

All chlorine containing compounds possess a definite tendency to liberate hydrochloric acid, especially at high temperatures. The liberation of hydrochloric acid in high temperature service, for instance, in internal combustion engine crankcase lubrication, increases the corrosion of engine parts such as copper-lead and cadmium-silver connecting rod bearing metals. Chlorinated glycerides which have not been treated according to the principles of the present invention are particularly offensive in this respect and are so corrosive as to render them unsuitable for continuous use in modern internal combustion engines.

Likewise sulfo-chlorinated glyceryl esters, such as disclosed in the above mentioned Sommer patents, impart highly corrosive properties to internal combustion engine crankcase lubricating oils compounded therewith. It has also been found that if chlorine is added to an unsaturated fat, such as lard oil, soya bean oil, or the like, the bulk of the chlorine is taken up at the double bond. This reaction produces a compound with chlorine atoms on adjacent carbon atoms which is a particularly unstable and corrosive group.

Accordingly, an object of the invention is to reduce the corrosivity of lubricants containing chlorinated compounds as oiliness agents.

A further object of the invention is to provide a hydrocarbon lubricant containing a chlorinated glyceryl ester which produces the minimum amount of corrosion consistent with maximum increased oiliness.

A further object of the invention is to provide an addition agent for petroleum lubricating oils comprising a chlorinated ester of a 3 to 6 carbon atom polyhydric alcohol, free from loosely combined and highly corrosive chlorine.

Another object of the invention is to provide a method of reducing the corrosivity of lubricating oils containing chlorinated glyceryl esters of saturated fatty acids.

Inasmuch as unsaturated glyceryl esters give chlorinated compounds which are more corrosive than glyceryl esters of saturated acids, the ester to be treated according to the present invention should preferably be that of a fatty acid of the saturated type and should have an iodine number of 15 (Wijs) or less.

Cocoanut oil is a saturated fat containing esters particularly suitable for the purposes of this invention. This material may be readily chlorinated by treatment with a slow stream of gaseous chlorine. During chlorination, hydrochloric acid is formed as a product of the reaction. Blowing with air at ordinary temperature or washing with water will remove this free hydrochloric acid. The product is still corrosive, however, due to the presence of loosely combined chlorine which is slowly liberated at high temperatures. Blowing with air or inert gases, such as carbon dioxide or nitrogen, at elevated temperatures (e. g., 300° F.) serves to partially remove this corrosive loosely combined chlorine, but the process still does not produce a non-corrosive product. It has been discovered that washing with dilute sodium hydroxide solution at ordinary temperatures removes the loosely combined and corrosive chlorine to the point where the resulting chlorinated cocoanut oil is no longer corrosive. This method has the additional advantage that the dilute caustic treatment will remove any chlorinated free fatty acids which are also extremely corrosive.

For the purpose of determining the relative stability of chlorine containing materials, there has been developed in the trade a test known as the "tin can" corrosion test. This test is made by placing 25 grams of a sample in a bright one-pound tin can, covering the can tightly and heating the same to 240° F. At intervals of thirty minutes the cans are opened and the samples inspected for the odor of hydrochloric acid. Chlorinated addition agents for lubricating oils should give no odor of hydrochloric acid in this test for a minimum of 90 minutes if undue corrosivity is to be avoided.

Four samples of chlorinated cocoanut oil were prepared by various processes to illustrate relative corrosivity and oiliness effects. The starting material in each case was a cocoanut oil of low neutralization value. Sample No. 1 was chlorinated to a content of 17% chlorine and then washed with water to remove free hydrochloric acid. Sample No. 2 was prepared in the same

manner as sample No. 1 with the added step of blowing at a temperature of 300° F. for one hour with a stream of carbon dioxide. Sample No. 3 was prepared like sample No. 1 with the added step of washing with dilute caustic soda solution. This caustic soda solution should be strong enough to remove loosely combined corrosive chlorine yet not so strong as will effect any substantial amount of saponification of the ester at the temperature of treatment. A solution containing 1 to 2% of caustic soda is in general satisfactory. Sample No. 4 was prepared in the same manner as sample No. 3 except that only 10% of chlorine was incorporated in the cocoanut oil.

Table No. 1 shows the results obtained in the "tin can" corrosion test on these chlorinated compounds. It is noted that samples 1 and 2 failed and samples 3 and 4 passed the test.

TABLE 1

"Tin Can" Corrosion Test

Addition agents

Chloro-cocoanut Oil No. 1—Failed 30 minutes.
Chloro-cocoanut Oil No. 2—Failed 60 minutes.
Chloro-cocoanut Oil No. 3—O. K. 90 minutes (slight odor, 150 minutes).
Chloro-cocoanut Oil No. 4—O. K. 90 minutes (slight odor, 150 minutes).

The above test is, of course, actually a test of comparative stability of the chlorinated compounds and therefore indicates only in an indirect manner the corrosivity to be expected when these oiliness agents are added to lubricating oils. As a more direct measure of corrosion of bearing metals a lubricating oil containing the chlorinated addition agents in 1% concentration is tested by suspending strips of cadmium-silver and copper-lead bearing metals in 300 cc. samples of the oil contained in large test tubes. The samples are placed in an oil bath at 300° F. and blown with air at the rate of 10 liters per hour for a period of 90 hours. The loss of weight from the metal strips constitutes an accurate measure of corrosion.

Table 2 shows the results of these tests on the above four samples of chlorinated cocoanut oil and also on methyl dichlorostearate, an oiliness agent which is regarded as one of the least corrosive of the chlorinated type so far produced in the lubricating oil industry.

TABLE 2

Strip Corrosion Test

	Weight loss at 90 hours mg. per sq. cm.	
	Cadmium-silver	Copper-lead
Motor oil, S. A. E. 20	0	3
+1% chloro-cocoanut oil No. 1	130	12
+1% chloro-cocoanut oil No. 2	120	16
+1% chloro-cocoanut oil No. 3	0	5
+1% chloro-cocoanut oil No. 4	0	4
+1% methyl dichlorostearate	74	2

Attention is directed to the fact that methyl dichlorostearate is decidedly corrosive to cadmium-silver bearing materials in this test, whereas samples 3 and 4 of the chlorinated cocoanut oils show no corrosion to this material and negligible corrosion within experimental error to copper-lead bearings as does the methyl dichlorostearate.

A General Motors testing machine shows that lubricating oils containing ¾% of methyl dichlorostearate increase corrosion of copper-lead bearings to three times that of the same uncompounded motor oil. Three-fourths percent chlorinated cocoanut oil sample No. 3 in the same motor oil and on the same testing machine under the same conditions gave practically no increase in corrosion of copper-lead bearings over that of the original uncompounded oil. The results of this test are as follows:

TABLE 3

Corrosiveness

*General Motors machine**

[300° F., 2,460 R. P. M.]

	Bearing weight loss—grams copper-lead
Motor oil, S. A. E. 30	0.45
+ ¾% methyl dichlorostearate	1.41
+ ¾% chloro-cocoanut oil No. 3	0.48

*Described in section III, page 76 of A. P. I. Proceedings of 1931. Published by American Petroleum Institute.

The above data indicate that the chlorinated esters of glycerin prepared according to the process of this invention are superior from the standpoint of corrosivity to other chlorinated esters known in the prior art. However, mere reduction in corrosivity is not the only factor involved since this effect could be produced by omitting the chlorinated compounds altogether. It is also essential that the oiliness or lubricity of the compounded oil be increased adequately to meet the demands placed upon lubricating oils in new high speed machinery. Chlorinated cocoanut oil is also superior to the chlorinated ester methyl dichlorostearate in these latter respects. Comparative data of straight mineral oil and the same oil compounded with ¾% of methyl dichlorostearate and compounded with ¾% chlorinated cocoanut oil of sample No. 3 is given in the Tables 4, 5, 6 and 7 hereinbelow.

TABLE 4

Film Strength

Weeks machine—Steel on steel surfaces*

	Total load at failure—Pounds	
	600 R. P. M.	800 R. P. M.
Motor oil, S. A. E. 30	120	80
+¾% methyl dichlorostearate	400	320
+¾% chloro-cocoanut oil No. 3	400	300

*Similar to Timken machine described in the S. A. E. Journal, vol. 28, page 53 (1932).

TABLE 5

Oiliness

Kinetic machine—Model B—Bronze on steel surfaces*

[5½ feet/minute, 175° F.]

	Relative friction	Relative wear
Motor oil, S. A. E. 30	100	100
+¾% methyl dichlorostearate	70	33
+¾% chloro-cocoanut oil No. 3	71	10

*Described in section III, page 60 of A. P. I. proceedings (Midyear 1932), published by American Petroleum Institute.

TABLE 6

OILINESS

Kinetic machine—Model A—Bronze on steel surfaces*

	Coefficient of friction					
Rubbing speed, feet/minute	4.5	9	18	35	81	135
Motor oil, S. A. E. 30	.59	.54	.48	.36	.31	.29
+¼% methyl dichlorostearate	.35	.29	.26	.22	.19	.17
+¼% chloro-cocoanut oil No. 3	.22	.21	.20	.17	.15	.12

* Described section III, page 60 of A. P. I. proceedings (Midyear 1932), published by American Petroleum Institute.

TABLE 7

OILINESS

*Almen machine**—Bronze on steel surfaces*

	Mg. wear		Temp. °F., Max.
	Bronze	Steel	
Motor oil, S. A. E. 30	11.5	-------	650
+¼% methyl dichlorostearate	2.5	1.6	387
+¼% chloro-cocoanut oil No. 3	1.4	0.6	362

** Described in Automotive Industry, November 19, 1932, at page 650.

It will be apparent to those skilled in the art that other saturated oil soluble glyceryl esters may be substituted for the cocoanut oil specifically herein described. For example, equivalent results are obtainable with palm kernel oil chlorinated and treated according to the present invention.

Similarly, synthetic as well as naturally occurring glycerides may be utilized in this invention. Chlorinated glycerides of monobasic fatty acids having three or more carbon atoms (propionic, butyric, valeric, caproic, oenanthylic, caprylic, capric, lauric, myristic, palmitic, stearic and arachadic acids, for example) are operative for the purposes of this invention. Experiments indicate that acids suitable for the purposes of this invention should be of the carboxyl type but that they need not necessarily be entirely aliphatic in nature. Such suitable fatty acids may be represented by the general formula: $R—(CH_2)_n—COOH$ where n is no less than 1 and R is an alkyl, aryl, aralkyl or cyclic nonbenzenoid (as, for instance, naphthenic) group The esters of these acids should have an iodine number of 15 or less prior to chlorination and may be incorporated either singly or as mixtures in the lubricating oil after chlorination and removal of corrosive loosely combined chlorine.

The invention in its broader aspects is not limited to the tri-glycerides but includes chlorinated mono-glycerides and di-glycerides of the above types of acids which are sufficiently oil soluble to remain in oil solution in the required proportions. Also the invention is not limited to glycerides but includes esters of polyhydroxy alcohols having 3 to 6 carbon atoms. Erythritol, arabitol and mannitol comprise examples of such polyhydroxy alcohols. The glycerides are, however, preferred to the esters of these higher polyhydroxy alcohols.

The proportion of chlorinated compounds to be added to the oil varies depending upon the type of mineral oil to which it is added and upon the service demands to be met. For general industrial uses where the service is not severe ½ to 5% by weight of the chlorinated ester is adequate. For gear oils and particularly for lubrication of worm gears where the service requirements are more severe, up to approximately 10% of the chlorinated compound will be found necessary. Likewise, where the lubricant is to be used as a cutting lubricant, for drawing wire, and the like, these higher percentages of the addition agent are necessary. In internal combustion engines approximately 1% by weight represents a suitable proportion. It is also apparent that concentrates of the chlorinated addition agents in mineral oil or other solvents may be prepared for addition in the proper proportion to the lubricating oil at the place of use.

The percentage of chlorine present in the ester itself also may be varied according to the uses intended. The proportion of chlorine which may be incorporated in a compound of the type involved in the present invention without rendering that compound corrosive varies with the nature of the compound and with its molecular weight. It has been found, however, that for the most part the esters themselves should contain from 5 to 25% by weight of chlorine.

As previously acknowledged, chlorinated compounds have been proposed in the prior art as addition agents to increase the oiliness and load carrying capacity of mineral lubricating oils. The corrosivity of prior known compounds on various bearing materials, particularly on copper-lead and cadmium-silver bearing metals, has been one of the principal difficulties encountered relative to the use of these compounds. It has been the general experience of petroleum engineers and chemists that corrosivity is essential to adequate increased oiliness and load-carrying capacity and that non-corrosive chlorinated compounds are decidedly inferior if not entirely ineffective oiliness agents. The present invention provides a class of chlorinated compounds for addition to lubricating oils which are non-corrosive and at the same time equal to or superior to previously proposed compounds in imparting increased oiliness and load-carrying capacity to mineral lubricating oils. The discovery of materials having this unexpected and unpredictable combination of properties is regarded as the substance of the present invention.

It is to be understood that modifications and variations falling within the terms and spirit of the appended claims are to be included within the scope of the invention which is not limited by the various details disclosed and described.

We claim:

1. A lubricating composition improved with respect to oiliness and simultaneously with respect to corrosivity comprising a lubricating oil containing an ester of a polyhydric alcohol having three to six carbon atoms per molecule and an organic acid of the type represented by the general formula $R—(CH)_n—COOH$, where n is no less than one and R is selected from the group consisting of alkyl, aryl, aralkyl and cyclic nonbenzenoid organic radicals, said ester being chlorinated but substantially free from loosely combined chlorine corrosive to cadmium-silver and copper-lead bearing alloys and removable by washing with dilute caustic alkali, and said ester having an iodine number less than approximately fifteen prior to chlorination.

2. A lubricating composition as defined in claim 1 in which said polyhydric alcohol is glycerine.

3. A lubricating composition as defined in claim 1 in which said organic acid is a fatty acid.

4. A lubricating composition as defined in

claim 1 in which said ester is a glyceride of a fatty acid.

5. A lubricating composition as defined in claim 1 in which said ester is present in the lubricating composition in the proportion of from about one-half to about ten per cent by weight based on said lubricating oil.

6. A lubricating composition as defined in claim 1 in which said ester contains from about five to about twenty-five per cent by weight of chlorine and comprises a glyceride of a fatty acid, said chlorinated ester being present in the lubricating composition in a proportion of from about one-half to about ten per cent by weight based on said lubricating oil.

7. A lubricating composition comprising a lubricating oil containing an ester of a polyhydric alcohol having three to six carbon atoms per molecule and an organic acid of the type represented by the general formula

$$R—(CH_2)_n—COOH$$

where n is no less than one and R is selected from the group consisting of alkyl, aryl, aralkyl and cyclic non-benzenoid organic radicals, said ester being chlorinated but substantially free from loosely combined chlorine corrosive to cadmium-silver and copper-lead bearing alloys and removable by washing with dilute caustic alkali, said ester having an iodine number less than about fifteen prior to chlorination, and said lubricating oil composition being substantially free from corrosive chlorinated esters resulting from the chlorination of esters having an iodine number greater than about fifteen.

8. A lubricating composition comprising a lubricating oil containing an ester of a polyhydric alcohol having three to six carbon atoms per molecule and an organic acid of the type represented by the general formula

$$R—(CH_2)_n—COOH$$

where n is no less than one and R is selected from the group consisting of alkyl, aryl, aralkyl and cyclic non-benzenoid organic radicals, said ester being chlorinated but substantially free from loosely combined chlorine corrosive to cadmium-silver and copper-lead bearing alloys and removable by washing with dilute caustic alkali, said ester having an iodine number less than about fifteen prior to chlorination, and said lubricating composition being substantially free from corrosive chlorinated esters resulting from chlorination of relatively highly unsaturated esters.

9. A lubricating composition comprising a lubricating oil containing an ester of a polyhydric alcohol having three to six carbon atoms per molecule and an organic acid of the type represented by the general formula

$$R—(CH_2)_n—COOH$$

where n is no less than one and R is selected from the group consisting of alkyl, aryl, aralkyl and cyclic non-benzenoid organic radicals, said ester being chlorinated but substantially free from loosely combined chlorine corrosive to cadmium-silver and copper-lead bearing alloys and removable by washing with dilute caustic alkali, said ester having an iodine number less than about fifteen prior to chlorination, and said lubricating composition being substantially free from corrosive chlorinated unsaturated organic esters having an iodine number greater than about fifteen prior to chlorination.

10. A lubricating composition as defined in claim 7 in which R is an organic radical containing a naphthenic group.

11. A lubricating composition comprising a lubricating oil containing an ester of a polyhydric alcohol having three to six carbon atoms per molecule and an organic acid containing a naphthenic group, said ester being chlorinated and substantially free from loosely combined chlorine corrosive to cadmium-silver and copper-lead bearing alloys and removable by washing with dilute caustic alkali, and said ester having an iodine number less than approximately fifteen prior to chlorination.

12. A lubricating composition comprising a lubricating oil containing a cocoanut oil which is chlorinated but substantially free from loosely combined chlorine corrosive to cadmium-silver and copper-lead bearing alloys and removable by washing with dilute caustic alkali, said cocoanut oil having an iodine number of less than about fifteen prior to chlorination.

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