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CHLORINATED ESTERS OF ACIDS DERIVED
FROM PETROLEUM

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This invention relates to a new composition of matter and to methods for producing the same. More particularly, it relates to the chlorinated esters of certain acids derived from petroleum.

It is known (see the Alleman Patent No. 1,694,461) that there may be obtained from the alkali precipitate formed during the refining treatment of petroleum lubricating oil certain acids, belonging chiefly to the series $C_nH_{2n-4}O_2$ and $C_nH_{2n-6}O_2$. It is likewise known (see Angstadt Patent No. 1,931,880) that there are present in the asphaltic still bottoms obtained in the distillation of topped crude to produce lubricating oils (see the Pew Patent 1,761,153) certain similar acids. These latter acids were first erroneously supposed to be substantially identical with those described in the Alleman Patent No. 1,694,461, but it is now known that while similar thereto they are specifically different, belonging chiefly to the series $C_nH_{2n-8}O_2$ and $C_nH_{2n-10}O_2$. Since the method of distillation described in the Pew Patent No. 1,761,153 has eliminated the necessity of refining the lubricating oil fractions, the former group of acids is not commercially available today in any great quantity, but the latter group of acids is produced commercially, for example, in accordance with the method of the Terrell et al. Patent No. 2,056,913.

Now we have found in accordance with the present invention that the chlorinated esters of these acids, more particularly of the latter group of acids referred to above, are extremely valuable compounds possessing many and varied uses in the industrial arts. In particular these chlorinated esters, and especially those containing three or more atoms of chlorine, when added to lubricating oils produce an "extreme pressure" lubricant possessing an exceedingly high film strength.

The chlorinated esters may best be produced in accordance with our invention by first esterifying the acids, either in crude or refined form, with an alcohol, as, for example, methyl, ethyl, isopropyl, isobutyl, amyl alcohols, etc., or with polyhydric alcohols such as, for example, glycol, glycerin, etc.; and then chlorinating the esters so formed, for example, by suitable treatment with chlorine gas. However, if desired, the acids may be first chlorinated, and the resulting chlorinated acids esterified with the desired alcohol.

The esterification of the acids may be carried out either with the crude acids containing some petroleum oil, directly as obtained, for example, from the process of the Terrell et al. Patent No. 2,056,913; or the crude acids may first be refined,

for example, by the method described in Alleman Patent No. 1,931,855, or by heating the sodium soap of the crude, oil-containing acids with water, under superatmospheric pressure at all times to prevent boiling. The process, which causes the oil and acid soaps to separate into layers, is analogous in details to that described in the Alleman Patent No. 1,694,463. In any event, the acid number of the mixture of acids will be determined, and using this value as a basis for calculations, a quantity of the desired alcohol, preferably from 3 to 8 times that theoretically required to combine with the acids, will be added, and the mixture heated and permitted to reflux until repeated tests show that the reaction is substantially complete. Ordinarily an esterification catalyst such as, for example, sulphuric acid, or anhydrous hydrogen chloride, etc., will be used to increase the rate and completeness of the reaction.

Following the completion of the esterification, the excess alcohol will be removed by distillation, and the product washed and dried, and, if desired, distilled in vacuo. The esters so obtained will then be treated with chlorine gas (the reaction progresses rapidly at ordinary temperatures and cooling of the reaction mixture may be required), until the desired quantity of chlorine has been absorbed, which may be determined by following the increase in weight of a weighed amount of the ester.

The following examples are illustrative of practical procedure in accordance with this invention.

Chlorinated methyl esters

The petroleum acids used were of the series $C_nH_{2n-8}O_2$ and $C_nH_{2n-10}O_2$. They had been purified and contained about 3 per cent of hydrocarbon oil. They had the following characteristics:

Acid number	167
Saponification No.	170
Average molecular weight	316

The following quantities of reactants were placed in a 12 liter Pyrex flask having three necks and provided with a stirrer and two condensers:

	Cc.
Petroleum acids	4,000
Methyl alcohol	4,000
Sulphuric acid	100

This reaction mixture was stirred, heated to refluxing temperature, and kept refluxing. In order to follow the progress of the reaction,

samples were removed from the flask at various times, washed with water in order to remove the sulphuric acid, the sulphuric acid reaction products such as sulphates of the alcohol, and the alcohol, dried, and the acid number determined. The results were as follows:

After refluxing	Acid number
8 hours.....	7.7
20 hours.....	2.0
32 hours.....	1.4

After the reaction was completed (as indicated by substantial constancy of the acid number) the excess of methanol was recovered by distillation, the residue washed with water in order to remove the remaining sulphuric acid and the sulphuric acid reaction products such as sulphates of the alcohol, dehydrated, and distilled in vacuo. Two fractions were collected.

1. 150° to 200° C. at 2 mm.....per cent..	49
Saponification number.....	169
Acid number.....	0.9
Molecular weight.....	328.0
2. 200° to 230° C. at 2 mm.....per cent..	49
Saponification number.....	147
Acid number.....	1.4
Molecular weight.....	346.0

The color of these distillates, when exposed to light for 10 days, changed from a light yellow to a deeper yellow. The color remained unchanged in the dark.

Yields of about 99 per cent of the crude esters were obtained.

328 g. of the methyl ester (1st fraction) so obtained were then placed in a weighed flask provided with a thermometer and gas inlet and outlet connections, and the flask placed in an ice bath. Chlorine gas under atmospheric pressure was then passed through the ester, the temperature being maintained at about 20° C. for about 24 hours, at which time the weight of the contents of the flask had risen to 434 g., indicating that three atoms of chlorine had been taken up. The chlorinated ester so formed was freed from the small amount of hydrogen chloride present therein by the application of a high vacuum. The purification may also be accomplished less satisfactorily by washing the product with water or a Na_2CO_3 solution.

The final product had the following properties:

It is insoluble in water, but is soluble in methyl, ethyl and propyl alcohols, benzene, toluene, carbon tetra-chloride, acetone, gasoline and petroleum lubricating oils. The density at 25° C. is 1.15. The distillation range at 760 mm. is from 318° C. to 469° C.; at 2 mm., between 144° C. and 270° C.; at 20 mm., between 190° C. and 320° C.

The ethyl, isopropyl, and isobutyl esters of the acids may be made by methods substantially the same as that described above for the methyl esters.

The mixed ethyl esters boil at about 150° C.-230° C. at 2 mm. The average molecular weight is 343.

The mixed isopropyl esters boil at about 155° C.-235° C. at 2 mm., and have an average molecular weight of 356.

The mixed isobutyl esters have an average molecular weight of 399.

The amyl esters are more readily prepared using anhydrous hydrogen chloride as a catalyst rather than sulphuric acids, because of undesirable side reactions induced by the latter. Otherwise the procedure is similar to that described above.

A satisfactory product may also be formed by esterifying the acids with "Lorol," a trade-name for a mixture of primary alcohols containing from 8 to 18 carbon atoms.

All these various esters may be chlorinated to produce the desired final products in accordance with our invention by procedure similar to that described above in connection with the methyl esters.

The chlorinated esters in accordance with this invention, particularly those having at least three chlorine atoms, are extremely valuable as an ingredient of lubricating oil. Dissolved in ordinary lubricating oil in small quantity, 0.1 to 5% of the oil, these compounds greatly increase the "oiliness" and film strength of the oil, and make it a high pressure lubricant adapted for use under pressure conditions where the untreated oil would be entirely unsatisfactory.

No claim is made herein to the extreme pressure lubricants described, since these are the subject matter of, and are claimed in, our copending application Serial No. 295,050, filed September 15, 1939.

What we claim and desire to protect by Letters Patent is:

1. The method of producing a chlorinated ester which comprises reacting an acid selected from the group of acids consisting of those naturally occurring in petroleum and those formed in petroleum during the distillation thereof, said acids also having the generic formula $\text{C}_n\text{H}_{2n-x}\text{O}_2$, where x is an even number from 4 to 10, inclusive, with a monohydric, aliphatic alcohol, and subjecting the ester so formed to the action of chlorine gas.

2. The method of producing a chlorinated ester which comprises reacting an acid selected from the group of acids consisting of those naturally occurring in petroleum and those formed in petroleum during the distillation thereof, said acids also having the generic formula $\text{C}_n\text{H}_{2n-x}\text{O}_2$, where x is an even number from 4 to 10, inclusive, with an alcohol, and subjecting the ester so formed to the action of chlorine gas until the ester has absorbed an amount of chlorine equivalent to three atoms of chlorine per molecule of ester.

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