

UNITED STATES PATENT OFFICE

2,235,860

HALOGENATED EXTREME PRESSURE
LUBRICANTNorman D. Williams, Chicago, Ill., assignor to The
Pure Oil Company, Chicago, Ill., a corporation
of OhioNo Drawing. Application October 19, 1938,
Serial No. 235,775

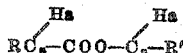
22 Claims. (Cl. 252-54)

This invention relates to lubricants and to the method of preparing and using the same, and is more particularly concerned with lubricants having extreme pressure characteristics.

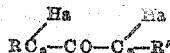
It is well known that mineral lubricating oils can be improved by adding thereto halogenated aromatic hydrocarbons and compounds in which hydrogen in the aromatic nucleus is substituted by chlorine. Many halogenated aliphatic hydrocarbons and compounds in general have been found to be unsatisfactory because such compounds hydrolyze readily in contact with water forming acid which corrodes the metal surfaces.

I have discovered that certain chlorinated esters and ketones, where the chlorine is attached to a carbon which is located between or protected by non-acidic, stable, aromatic or other carbocyclic nuclei, are not only not corrosive but are more active than the halogenated aromatics. Such compounds have the ability to impart to mineral lubricating oils increased oiliness, film strength and extreme pressure characteristics.

The compounds which I have discovered to be suitable are those of the type



and

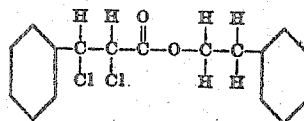


in which R and R' are non-acidic, stable, aromatic or other carbocyclic nuclei either the same or different, COO is the characteristic group found in esters, CO is the bivalent ketone group found in ketones, C represents an aliphatic carbon radical either saturated or unsaturated having any number (n) of carbon atoms and Ha represents a halogen united to one or more aliphatic carbon atoms which are linked between the carbocyclic nuclei. These compounds are similar to those disclosed in the co-pending application of William A. Whittier, Ser. No. 180,487, but distinguish from the compounds therein disclosed by containing the characteristic COO ester group or CO ketone group.

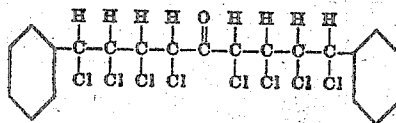
Examples of compounds which are suitable for use are dichlorophenyl ethyl cinnamate, tetrachlorocinnamyl cinnamate, dichlorocinnamyl acetophenone, tetrachlorodibenzylidene acetone and octachlorodibenzylideneacetone. The halogen may be added directly to the carbon in those compounds which are unsaturated or may replace the hydrogen in those compounds which are saturated. In the case of unsaturated compounds, halogen may be linked to the carbon by direct

addition and by substitution of the hydrogen. Generally speaking, the greater the number of chlorine atoms linked to the carbon, the greater is the effectiveness of the compound as an E. P. agent.

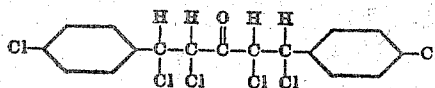
To illustrate more clearly the nature of the compounds with which this invention is concerned, the following graphic formulae are shown:



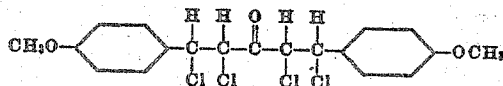
Dichlorophenylethyl cinnamate



Octachlorodibenzylidene acetone



Tetrachlor derivative of para para dibenzylidene acetone



Tetrachloro dianisylidene acetone

The halogenated compounds may be used in connection with straight mineral lubricating oils or in connection with oils which have been blended with other reagents to improve the lubricating characteristics thereof as for example, phosphorized or sulfurized and phosphorized lubricants. One method of preparing a phosphorized lubricant is as follows: No. 1 lard oil is heated with 10% of phosphorous oxychloride at 170° F., to 200° F. for 15 minutes. During this time only a slight darkening of the oil occurs. The temperature is then slowly increased to 275° F. in order to drive off any remaining phosphorous oxychloride. A black sludge forms in the amount of approximately 25%. 5% of the oil, after it has been decanted from the sludge, is blended with 95% of lubricating oil having the following characteristics:

Gravity	----- A. P. I.	21-23
Flash	----- °F.	530-540
Fire	----- °F.	600-610
Viscosity, Saybolt at 210° F.	-----	155-165
Four	----- °F.	20-25

I have found that when small quantities of halogenated compounds of the nature of those above described are incorporated in a blend of mineral lubricating oil with a sulfurized and phosphorized fatty oil base such as that disclosed in the application of Whittier et al, Ser. No. 55,200, the extreme pressure characteristics of such lubricants can be materially improved. A number of tests have been made on straight lubricants blended with halogenated compounds of the nature of those above set forth and on lubricants blended with sulfurized and phosphorized base together with halogenated compounds, the results of which are given in Table III. In these tests the straight mineral oil used was a blend to approximately S. A. E. 90 viscosity of the following oils:

Table I

	Oil No. 1	Oil No. 2
A. P. I. gravity.....	21.5-23	17-19
Flash, °F.....	345-365	510-520
Fire, °F.....	385-405	590-600
Vis. at 130° F. (Say. Univ.).....	98-102	1750-2100
Vis. at 210° F. (Say. Univ.).....	43-45	150-165
Pour point, °F.....	-20	25
Color N. P. A.....	2-3	8

In those tests in which a mineral oil was blended with sulfurized-phosphorized base and/or chlorinated compound, the lubricating oil before blending had the following characteristics:

Table II

A. P. I. gravity.....	18-20
Flash..... ° F.....	380-400
Fire..... ° F.....	430-450
Vis. at 130° F. (Say. Univ.).....	460-500
Vis. at 210° F. (Say. Univ.).....	90-95
Pour point..... ° F.....	0

This oil was blended with sulfurized phosphorized base in the proportion of 82% of oil to 18% of base. The sulfurized-phosphorized base was made in

the following manner: A homogeneous mixture of 570 pounds of Gulf Coast pale oil having a Saybolt Universal viscosity at 100° F. of 200 seconds and a pour point of -20° to -25° F. and 55 pounds of sulfur chloride was prepared in a cold state. This mixture was added to 9,581 pounds of prime lard oil contained in an enclosed steam jacketed kettle. The mixture was heated to 275° F. while being vigorously agitated. At this point the steam was shut off and 814 pounds of flowers of sulfur were sifted into the contents of the kettle over a period of approximately two hours. The contents of the kettle were vigorously agitated during this entire period. At the end of the two-hour period the temperature had dropped to 265° F. The steam was again turned on and the contents of the kettle heated to approximately 300° F. when the steam was turned off. Agitation was continued for a period of approximately 7½ hours after the addition of the sulfur. During this period the temperature rose from 300° to 344° F. during the first three hours indicating that an exothermic reaction was taking place. The temperature during the 7½-hour period was not permitted to drop below 320° F. and it was found that it was unnecessary to use any further heat to maintain this temperature after the mixture had been initially heated to 300° F.

The sulfurized material was then cooled to a temperature of 220° to 230° F. by circulating the material through cooling coils and back to the kettle. When this temperature had been reached, 44 pounds of phosphorous sesqui-sulfide was added slowly over a period of ½ hour of continuous agitation. The steam was again turned on at such times as was necessary to maintain the temperature at 220° to 230° F. After the addition of phosphorous sesqui-sulfide, agitation was continued for a period of approximately five hours while the temperature was maintained at 220° to 230° F. At the end of this period the contents of the kettle were immediately cooled to 130° F. by circulation through the exteriorly located cooling coils and pumped to storage.

The following is a table of results obtained:

Table III

Halogenated compound added	Added	Lubricant used for blend	Timken test		S. A. E. test at 1,000 R. P. M.
			Beam load	Pressure	
	Percent		Pounds	Lbs. per sq. in.	Pounds
Mineral oil.....			12	7,000	15-50
Sul.-phos. base blend ¹			86	35,750	90
Do. ²			86	35,750	335
Dichlor phenylethyl cinnamate.....	5.0				315
Do. ³	2.5				310
Do. ⁴	1.25				330
Dichlor cinnamyl acetophenone.....	5.0		96	31,500	300
Do. ²	1.25				465
Chlorinated dibenzylidene acetone ¹	5.0		86	30,250	325
Do. ²	1.2				320
Do. ³	0.6				340
Do. ⁴	5.0		86	33,750	310
Do. ¹	2.5				Failed to hold starting load.
Do. ¹	2.0	Mineral oil.....	51	15,750	90
Do. ²	2.0	do.....	59	16,500	320
Do. ³	5.0	do.....			350
Do. ⁴	10.0	do.....			

¹ 33.5N chlorine.

² 35.0N chlorine.

³ 43.0N chlorine.

⁴ All of the lubricants named "Sul.-Phos. base blend" are composed of 82% mineral oil and 18% of sulfurized and phosphorized fatty oil.

The tests were made on the machine recommended as a tentative standard by the Society of Automotive Engineers for testing extreme pressure lubricants and on the "Timken wear and lubricant tester." Both of these machines are widely recognized as extreme pressure type lubricant testing devices.

As shown above, the sulfurized-phosphorized lubricant without the addition of a chlorine compound, withstood a load of only 90 pounds on the S. A. E. machine but when small amounts of the chlorinated compounds were added, the load could be increased to over 300 pounds, although the chlorinated compounds when blended in small quantities with straight mineral oil tested only approximately 16,000 lbs. per sq. in. on the Timken machine and 90 lbs. on the S. A. E. machine. The E. P. characteristics of a phosphorized or a sulfurized-phosphorized lubricant as determined by the Timken machine, are not appreciably altered by addition of the halogen compound while greatly increasing the film strength and E. P. characteristics of the lubricant as measured by the S. A. E. machine. The Timken test results of the sulfurized-phosphorized lubricant blended with a chlorine compound are the same as the unblended material within the limit of accuracy of the testing machine. Corrosion tests made in the presence of water indicate that the halogenated compound may be introduced into the lubricant without rendering it corrosive.

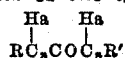
Although I do not wish to be limited to the addition of any particular amount of the halogenated compound to the lubricant, I prefer to use from approximately 1% to 10% in connection with lubricants to be used where E. P. characteristics are important. Where the compound is added to improve the oiliness and film strength, as for example, in motor oil, the amount added may range from a fraction of 1% to approximately 5%. The upper limit of 10% has been fixed only because with the methods of testing now available, it has been found that maximum results can be obtained by adding this amount. There is no reason, however, why quantities in excess of 10% may not be used.

Instead of adding the halogenated compound directly to the oil, it may be separately fed into the particular mechanism to be lubricated and mixed in situ with the lubricating oil.

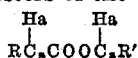
It has also been found that materials within the scope of this invention containing a phosphorized or sulfurized and phosphorized lubricant and chlorinated ester or ketone of the class previously described, are excellent cutting fluids and are also well adapted to be used in drawing, grinding and burnishing operations. They may be used straight, blended with mineral oil and/or emulsified with water.

What I claim is:

1. A lubricant comprising mineral lubricating oil and a compound selected from the group of halogenated ketones of the type

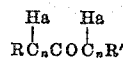


and halogenated esters of the type

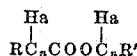


in which R and R' are non-acidic, stable, carbocyclic radicals either the same or different, CO and COO are the characteristic ketone and ester groups, C is an aliphatic chain having any number (n) of carbon atoms and the halogen (Ha) is linked to carbon in the aliphatic chain.

2. Method of lubricating relatively moving metallic surfaces which comprises maintaining between the surfaces and chemically reacting therewith a quantity of a compound selected from the group of halogenated ketones of the type



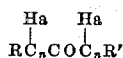
and halogenated esters of the type



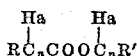
in which R and R' are non-acidic, stable, carbocyclic radicals either the same or different, CO and COO are characteristic ketone and ester groups, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain.

3. A lubricant in accordance with claim 1 to which has been added sulfurized and phosphorized fatty oil.

4. A lubricant comprising a compound selected from the group of halogenated ketones of the type



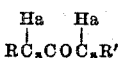
and halogenated esters of the type



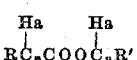
in which R and R' are non-acidic, stable, carbocyclic radicals either the same or different, CO and COO are the characteristic ketone and ester groups, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain, to which has been added sulfurized and phosphorized fatty oil.

5. A lubricant in accordance with claim 1 to which has been added phosphorized fatty oil.

6. A lubricant comprising a compound selected from the group of halogenated ketones of the type

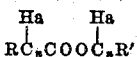


and halogenated esters of the type



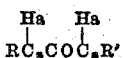
in which R and R' are non-acidic, stable, carbocyclic radicals of either the same or different, CO and COO are the characteristic ketone and ester groups, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain, to which has been added phosphorized fatty oil.

7. A lubricant comprising mineral lubricating oil and a halogenated ester of the type



in which R and R' are non-acidic, stable, carbocyclic radicals, COO is the characteristic carbon and oxygen group found in esters, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain.

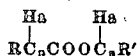
8. A lubricant comprising mineral lubricating oil and a halogenated ketone of the type



in which R and R' are non-acidic, stable, car-

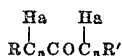
bocyclic radicals, CO is the characteristic carbon and oxygen group found in ketones, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain.

- 5 9. Method of lubricating relatively moving metallic surfaces which comprises maintaining between the surfaces and chemically reacting therewith a quantity of a halogenated ester of the type



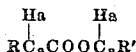
- 15 in which R and R' are non-acidic, stable, carbocyclic radicals, COO is the characteristic carbon and oxygen group found in esters, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain.

- 20 10. Method of lubricating relatively moving metallic surfaces which comprises maintaining between the surfaces and chemically reacting therewith a quantity of a halogenated ketone of the type



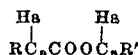
- 25 in which R and R' are non-acidic, stable, carbocyclic radicals, CO is the characteristic carbon and oxygen group found in ketones, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain.

- 30 11. A lubricant comprising a halogenated ester of the type



- 40 in which R and R' are non-acidic, stable, carbocyclic radicals, COO is the characteristic carbon and oxygen group found in esters, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain, to which has been added sulfurized and phosphorized fatty oil.

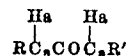
- 45 12. A lubricant comprising a halogenated ester of the type



- 50 in which R and R' are non-acidic, stable, carbocyclic radicals, COO is the characteristic carbon and oxygen group found in esters, C is an

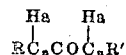
aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain, to which has been added phosphorized fatty oil.

- 5 13. A lubricant comprising a halogenated ketone of the type



- 10 in which R and R' are non-acidic, stable, carbocyclic radicals, CO is the characteristic carbon and oxygen group found in ketones, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain, to which has been added sulfurized and phosphorized fatty oil.

- 15 14. A lubricant comprising a halogenated ketone of the type



- 20 in which R and R' are non-acidic, stable, carbocyclic radicals, CO is the characteristic carbon and oxygen group found in ketones, C is an aliphatic chain having any number (n) of carbon atoms and the halogen is linked to carbon in the aliphatic chain, to which has been added phosphorized fatty oil.

- 25 15. A lubricant comprising mineral lubricating oil and tetrachlorocinnamyl cinnamate.

- 30 16. A lubricant comprising mineral lubricating oil and dichlorocinnamyl acetophenone.

- 35 17. A lubricant comprising mineral lubricating oil and chlorinated dibenzylidene acetone.

18. A lubricant in accordance with claim 15 and containing sulfurized and phosphorized fatty oil.

19. A lubricant in accordance with claim 16 and containing sulfurized and phosphorized fatty oil.

20. A lubricant in accordance with claim 17 and containing sulfurized and phosphorized fatty oil.

21. A lubricant according to claim 7 in which R and R' are non-acidic, stable aryl radicals and in which the hydrogen in the benzene ring is either substituted or unsubstituted.

22. A lubricant according to claim 8 in which R and R' are non-acidic, stable aryl radicals and in which the hydrogen in the benzene ring is either substituted or unsubstituted.

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