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3,284,355

LUBRICATING COMPOSITIONS

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This invention relates to lubricating compositions and more particularly to improved extreme pressure lubricating compositions.

In various metal cutting and working operations as well as in certain types of modern machinery such as hypoid gears used in motor vehicles, the engaging pressure between the contacting elements are so high that ordinary lubricating oils alone are incapable of supplying proper lubrication, since these abnormally high pressures generally cause rupture of the oil films on the surfaces to be lubricated. To overcome this problem, extreme pressure lubricants have been developed. These lubricants are generally prepared by incorporating into relatively high viscosity natural or synthetic lubricating oils, additives which will form a lubricating film capable of withstanding high pressures. Additives of this character are known as extreme pressure (E.P.) additives and lubricating compositions compounded with minor proportions of these additives are known as E.P. lubricants.

A variety of compounds particularly halogen-containing compounds have been proposed for use as E.P. additives. Thus, for example, chlorine and/or bromine-containing partially halogenated carboxylic acid compounds and low molecular weight perhalogenated polymers have been incorporated in oils to be used under extreme pressure conditions.

These known types of halogen-containing compounds have not, however, been completely satisfactory as extreme pressure additives. The chlorine and/or bromine-containing partially halogenated carboxylic acids are unstable at high temperatures thus liberating corrosive HCl or HBr and promoting sludge formation and the degradation of the base oils. The perhalogenated polymers, on the other hand, are quite limited in their ability to impart improved extreme pressure characteristics.

It is therefore the main object of the present invention to provide extreme pressure lubricating compositions possessing improved E.P. characteristics, high thermal stability and non-corrosive characteristics under extreme operating conditions. Other objects of the invention and some advantages thereof will become apparent hereinafter.

It has now been found that the addition of a specific type of halogen-containing carboxylic acid or derivative thereof to certain high viscosity base oils, results in the production of improved E.P. lubricants possessing the aforementioned desirable characteristics.

These specific halogen-containing carboxylic acid compounds are:

(1) perhalogenated aliphatic carboxylic acids, such as the perfluorinated, perchlorinated, perbrominated, perfluorochlorinated, perfluorobrominated, etc., carboxylic acids or their derivatives and,

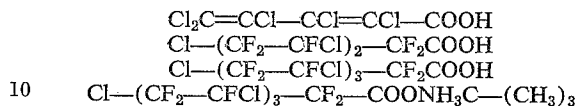
(2) polyfluorinated aliphatic carboxylic acids or derivatives thereof.

Either saturated or unsaturated carboxylic acid compounds of this type are suitable. Suitable acid derivatives include the corresponding esters, amides and amine salts of the acids. For example, perhalogenated or polyfluorinated carboxylic acid derivatives containing $-\text{COO}-\text{R}$, $-\text{CONH}_2$ or $-\text{COONH}_3-\text{R}$ groups, wherein R is an alkyl, cycloalkyl, aryl, arylalkyl or alkaryl radical containing preferably from 1 to about 20 carbons are effective E.P. agents according to the present invention.

A preferred group of compounds are perhalogenated

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or polyfluorinated aliphatic carboxylic acids or derivatives containing from 2 to about 40 carbon atoms, especially from 5 to 9 carbon atoms. Some specific compounds which are particularly suitable as E.P. agents according to the present invention, include:



and $\text{H}-\text{CF}_2(\text{CF}_2)_7-\text{COOH}$. Pentachlorodienic acid ($\text{Cl}_2\text{C}=\text{CCl}-\text{CCl}=\text{CCl}-\text{COOH}$) due to its high solubility in mineral oils and low cost is a particularly desirable E.P. agent.

Although the above acid compounds possess a carboxylic acid group or acid derivative to promote the chemisorption of the lubricant to the metal surfaces, they are, because of the particular nature and relative location of the halogens in the acid molecule, stable and non-corrosive under extreme pressure operating conditions.

It will be noted, that except for the polyfluorinated carboxylic acid compounds, the E.P. additives of the present invention are perhalogenated acid compounds, i.e., no hydrogen atoms are present in the carbon chain of acid compound. This is important since it has been found that the presence of both hydrogen atoms and chlorine or bromine atoms in the carbon chain of the acid compound promotes the thermal instability of the acid with the liberation of corrosive HCl or HBr. However, no corresponding corrosion problem has been found to exist in the case of polyfluorinated carboxylic acids wherein both fluorine and hydrogen are present. It is thought that this lack of corrosiveness is due to the fact that the carbon-fluorine bond is much stronger than the hydrogen-fluorine bond and therefore no HF is formed. This is particularly the case in omega-hydro polyfluorinated carboxylic acid compounds where only one hydrogen is present and this hydrogen is located in the omega position with respect to acid group, i.e., on the carbon atoms most remote from the acid group.

It is therefore critical that both hydrogen and chlorine or bromine atoms not be present in the carboxylic acid compounds of this invention. The co-existence of these halogen atoms and hydrogen atoms results in the liberation of corrosive HCl or HBr, thereby promoting undesirable sludge formation and the degradation of the base oils and, in general, tends to detract from the E.P. effectiveness of the additive. A consideration of the following comparative test will demonstrate this point.

Two oil compositions, one containing a partially halogenated carboxylic acid possessing both chlorine and hydrogen atoms (chlorinated lauric acid containing about 29% by weight of chlorine) and the other containing a carboxylic acid of the present invention (pentachloropentadienoic acid) were subjected to the SAE 1000 r.p.m. test.

This test, which is commonly accepted in the art as a standard, is used to determine the extreme pressure effectiveness of a lubricant. The test procedure is described in SAE Journal 39, 23-4 (1936). In general, the oil sample to be tested is placed in an SAE machine wherein the shaft rotates at 1000 r.p.m. and the rubbing ratio is 14.6 to 1. The test is continued until scoring occurs. The values obtained are expressed as pounds of scale reading. Straight mineral oil fail at about 20 lbs. and this scale reading is taken as the break in point. Two readings are taken for each oil composition tested.

The results obtained are reported in the following Table I.

TABLE I

Halogenated Compound	Concentration (Weight, Percent)	SAE Machine Reading ^b (lbs.)
Chlorinated Lauric Acid (29% chlorine)-----	1.1	75, 85
Pentachloropentadienoic-----	1.0	375, 380

^a Equal molar concentrations of each acid were used.

^b In each case the base oil was composed of a blend of (a) 70% of a solvent refined stock having an S.U.V. at 210° F. of 150-160, an A.P.I. gravity of 25 and a Flash Point of 550° F. with (b) 30% of a furfural-refined neutral stock having an S.U.V. at 210° of 46, and A.P.I. gravity of 29-31, and a Flash Point of 415° F., and 3.0% of di-t-butyl disulfide.

It will be noted from the results reported in Table I that the pentachloropentadienoic acid was about five times more effective (375 lbs. and 380 lbs.) in improving the extreme pressure characteristics of the oil than chlorinated lauric acid (75 lbs. and 80 lbs.)

Another demonstration of the superiority of the particular E.P. additives of the present invention is given in the following Table II, wherein the SAE 1000 r.p.m. extreme pressure test results obtained using oil compositions containing a partially chlorinated paraffin wax containing about 40% chlorine (Anglamol 40), chlorinated lauric acid containing 29% chlorine and pentachloropentadienoic acid respectively are given.

TABLE II
[SAE 1000 r.p.m. test]

Composition ^a No.	Halogenated Compound	Conc. (Weight Percent)	Cl (Weight Percent)	SAE Machine Reading (lbs.)
1-----	Chlorinated paraffin wax (40% chlorine)	1.7	0.68	75, 80
2-----	Pentachloropentadienoic Acid-----	1.0	0.64	375, 380
3-----	do-----	0.5	0.32	290, 305
4-----	Chlorinated Lauric Acid (29% chlorine)	1.1	0.32	75, 85

^a Same base oil as that of Table I but containing 1.08% di-t-butyl disulfide.

It will be noted from the SAE 1000 r.p.m. test results, reported in Table II that the chlorine content of the oil compositions is less important than the type of compound which supplies the chlorine. Thus, it can be seen that although the chlorinated paraffin wax and perchlorinated dienoic acid each supply approximately the same amount of chlorine, the SAE 1000 r.p.m. test results for the oil composition containing the pentachloropentadienoic acid are markedly superior. Similarly, it is noted that although oil compositions Nos. 3 and 4 each containing 0.32% of chlorine, composition No. 3, which contains pentachloropentadienoic acid, gives high test results of 375 and 380 lbs. compared with the 75 and 85 lb. readings obtained when chlorinated lauric acid is the additive.

The perhalogenated and polyfluorinated carboxylic acid compounds of the present invention, when used either as the lone E.P. additive or in combination with other conventional E.P. additives, are capable of effecting substantial increases in the extreme pressure characteristics of lubricating compositions. When used in conjunction with other E.P. additives, the instant compounds are equivalent in effectiveness to about 2 to 10 times the amount of conventional E.P. additives and thus greatly increase the E.P. effectiveness of the combination.

The particular amounts of the halogen-containing car-

boxylic compounds employed in lubricating compositions will depend on various factors such as the type of base oil, the conditions of use, the presence of other additives, etc. In general, the instant compounds may be employed in amounts ranging from about 0.005% to about 10%, preferably from about 0.01 to about 5% by weight.

According to the present invention the instant acid compounds are employed to improve the extreme pressure characteristics of high viscosity petroleum as well as synthetic oils, having a Saybolt Universal viscosity at 210° F. of from at least 50 to 250 seconds, preferably from at least 50 to 90 seconds. The invention is therefore particularly advantageous in improving extreme pressure characteristics of high viscosity lubricating compositions useful as cutting oils, roll oils, gear oils, transmission oils and the like.

The oil compositions of the present invention may, of course, also contain effective quantities of various typical additives, normally used in lubricating oil compositions which additives are designed to improve the compositions in other respects, such as detergents, rust inhibitors, pour-point improvers, V.I. agents, etc.

The E.P. additives of the invention such as pentachloropentadienoic acid are very soluble even in petroleum base oils. However, when using other types of the present acid compounds with petroleum base oils it is advisable to insure that a polar compound is present in the lubricating

compositions in order to improve the solubility of the E.P. additive. This polar compound may be an additive normally used in extreme pressure lubricating compositions, or in the event that the use of a polar additive is not contemplated, a polar compound may be specifically added. Suitable polar compounds include any of the well-known polar materials such as aromatic hydrocarbons, alkyl-substituted aromatics, saturated aliphatic alcohols preferably containing 4-16 carbon atoms, esters of these alcohols with carboxylic acids preferably of from 1-20 carbons, amines either primary, secondary or tertiary containing 2-32 carbon atoms, sulfur-containing compounds including organic disulfides containing from 1-16 carbons, etc. The polar compound may be present in molar ratios of from about 0.01:1 to about 5:1 with respect to halogen-containing E.P. additive.

The following additional specific embodiments are given to further illustrate the present invention.

Examples 1-7

A perhalogenated carboxylic acid of the formula, $\text{Cl}-(\text{CF}_2-\text{CFCl})_3\text{CF}_2\text{COOH}$, was added to two base oils. These resulting compositions were then subjected to the SAE 1000 r.p.m. test and the results recorded as shown in Table III.

TABLE III

Example No.-----	1	2	3	4	5	6	7
Conc. of Additive (wt. percent): Cl-(CF ₂ -CFCl) ₂ -CF ₂ COOH-----		1.0	0.5	2.0		2.0	1.0
Base Oil (wt. percent): Paraffinic oil ^a -----	100	99.0	99.5	98.0	100	98.0	99.0
Dodecyl Benzene Bottoms ^b -----							
SAE 1,000 r.p.m. test results (lbs.)-----	FBI., FBI. ^c	460+, 450	390, 370	460+460+	FBI., FBI.	460+, 460+	385, 420

^a 80% of Nujol (a commercially available, solvent refined paraffinic oil) plus 20% of oily dimer of xylene and styrene, S.U.S. at 210° F. > 50.

^b Viscous oily residue from the preparation of dodecyl benzene, S.U.S. at 210° F., 50-90.

^c Failure to break in. Break in reading=20 lbs.

It will be seen from Table III that while the oils containing no perhalogenated carboxylic acid failed to pass the break in, the oils containing acid exhibited superior E.P. characteristics.

Examples 8-13

To demonstrate the ability of the instant E.P. additives to improve the E.P. characteristics of an oil composition containing the conventional E.P. additives, six lubricating oil compositions, having the composition shown in Table IV, were subjected to the SAE 1000 r.p.m. test.

It will be noted upon comparing the SAE 1000 r.p.m. test results of Examples 9 and 10 with those of Example 8, that the substitution of 0.25% of the carboxylic acids of the invention for twice that amount (0.5%) of chlorinated paraffin wax resulted in greatly improved E.P. characteristics for the oil composition, i.e., readings of 330 and 320 lbs. compared with 210 and 230 lbs. for the oil of Example 8. Similarly, it can be seen that the use of

Examples 14-19

The oil compositions designated Examples 14-19 in Table V were prepared and subjected to the SAE 1000 r.p.m. test.

It is noted that composition of Example 17 containing 4% by weight of di-t-butyl disulfide exhibited low SAE test readings of 85 and 90 lbs. By contrast, the composition of Example 16 containing 3% of the disulfide and 0.25% of a halogenated carboxylic acid and thus wherein, in effect, 1% by weight of disulfide has been replaced by 0.25% of halogenated acid, exhibited high test readings of 300 and 295 lbs. A comparison of the test results obtained from the compositions of Examples 18 and 19 shows that the replacement of 0.75% zinc dihexyl dithiophosphate with only 0.25% halogenated carboxylic acid results in readings of 300 and 300 lbs. (Example 18) contrasted with readings of less than 20 lbs., i.e., failure to break in and 80 lbs. (Example 19).

TABLE V

Example No.-----	14	15	16	17	18	19
Additive (wt. percent): Cl-(CF ₂ -CFCl) ₂ -CF ₂ COOH-----	2	2	0.25		0.25	
Tricaprylamine-----	2					
Di-t-butyl disulfide-----		2	3	4		
Zinc dihexyl dithiophosphate-----					4.25	5.
Base oil ^a -----	96	96	96.75	96	95.50	95.0.
SAE 1,000 r.p.m. Test Results (lbs.)-----	356, 325	400, 385	300, 295	85, 90	300, 300	FBI, b80.

^a Same base oil as described in Table IV.

^b Failure to break in.

only 0.5% by weight of the instant additives (Examples 11 and 12) in place of 1.7% by weight of chlorinated paraffin wax (Example 13) significantly increased the extreme pressure characteristics of the oil.

Examples 20-25

Table VI shows the results obtained upon the addition of the perhalogenated acids to oils containing conventional E.P. agents such as chlorinated paraffin wax,

TABLE IV

Example No.-----	8	9	10	11	12	13
Additive (Wt. percent): Chlorinated paraffin wax (40% chlorine)-----	4.5	4	4			1.7
Pentachloropentadienoic Acid-----		0.25				
H-(CF ₂) ₅ -COOH-----			0.25			
Perfluorooctanoic Acid-----				0.5		
Perfluorocapric Acid-----					0.5	
Di-t-butyl-disulfide-----	2	2	2	3	3	3
SAE 1,000 r.p.m. ^a test Results (lbs.)-----	210, 230	330, 320	330, 320	250, 290	325-320	75, 80

^a Base oil was a blend of (a) 70% of a solvent refined stock having an S.U.V. at 210° F. of 150-160, an A.P.I. gravity of 25.7 and a Flash point of 550° F. with (b) 30% of a furfural-refined neutral stock having an S.U.V. at 210° F. of 46.5, an A.P.I. gravity of 29-31 and a Flash point of 415° F.

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di-t-butyl disulfide, triisooctylthionophosphate and tri-butyl-trithiophosphite.

It will be seen from a comparison of Examples 20 with 21 that the addition of only 0.1% of the additives of the invention substantially increases the extreme pressure characteristics of the oil composition.

In addition, a comparison of Examples 22 with 23, and 24 with 25 shows that replacement of a portion of the conventional E.P. agent with smaller proportions of the perchlorinated acids, produces oils exhibiting greatly enhanced E.P. characteristics.

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5. The composition of claim 1, wherein said carboxylic acid compound is a perchlorinated carboxylic acid.

6. The composition of claim 1, wherein said carboxylic acid compound is a perfluorochlorinated carboxylic acid.

7. The composition of claim 1, wherein said carboxylic acid compound has the formula,



8. The composition of claim 1, wherein said carboxylic acid compound has the formula,



TABLE VI

Example No.	20	21	22	23	24	25
Additive (wt. percent):						
Cl-(CF ₂ -CFCl) ₃ -CF ₂ COOH	0.1		1.33		0.1	
Di-t-butyl disulfide	2	2				
Chlorinated paraffin wax (40% chlorine)	4	4				
Tri-isooctylthionophosphate			2.67	4.4		
Tri-butyltrithiophosphite					2	3.
Base Oil ^a	93.9	94	96	95.6	97.9	97.
SAE 1,000 r.p.m. Test Results (lbs.)	280, 310	FBI, ^b 140	350, 300	FBI, FBI	210, 215	FBI, FBI.

^a Same base oil as described in Table IV.

^b Failure to breakin.

Although the present invention has been described with reference to certain preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of this invention, as those skilled in the art will readily understand.

Having thus fully described the invention, what I desire to secure and claim by Letters Patent is:

1. An extreme pressure lubricating composition comprising a major proportion of a mineral lubricating oil having a Saybolt Universal viscosity at 210° F. of at least 50 seconds and a minor proportion sufficient to improve the extreme pressure characteristics thereof, of a carboxylic acid compound containing from 5 to about 9 carbon atoms selected from the group consisting of perchlorinated aliphatic carboxylic acid compounds and perfluorochlorinated aliphatic carboxylic acid compounds.

2. The composition of claim 1 wherein there is present an organic disulfide containing from 1 to 16 carbon atoms, said disulfide being in a mole ratio of from 0.01:1 to about 5:1 of disulfide to said carboxylic acid compound.

3. The composition of claim 1 wherein there is present di-t-butyl disulfide in a molar ratio of from about 0.01:1 to about 5:1 of disulfide to said carboxylic acid compound.

4. The composition of claim 1 wherein there is present a member selected from the group consisting of tricaprylamine, zinc dihexyldithiophosphate, tri-isooctothionophosphate and tri-butyltrithiophosphite wherein said members are present in a molar ratio of from about 0.01:1 to about 5:1 of said member to said carboxylic acid compound.

9. The composition of claim 1, wherein said carboxylic acid compound has the formula,



10. The composition of claim 1, wherein the acid compound is present in an amount from at least about 0.005% by weight.

11. The composition of claim 1, wherein said oil is a high viscosity petroleum oil having a Saybolt Universal viscosity at 210° F. of from at least 50 to about 250 seconds.

12. The composition of claim 1, wherein said oil is a high viscosity petroleum oil having a Saybolt Universal viscosity at 210° F. of from at least 50 to about 90 seconds.

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