Patented Sept. 14, 1954

2,689,251

UNITED STATES PATENT OFFICE

2,689,251

POLYHALOMETHANE-UNSATURATED ACID REACTION PRODUCTS

Lyle A. Hamilton, Pitman, and Charles F. Feasley, Woodbury, N. J., assignors to Socony-Vacuum Oil Company, Incorporated, a corporation of New York

No Drawing. Original application June 23, 1948, Serial No. 34,827. Divided and this application December 23, 1949, Serial No. 134,842

6 Claims. (Cl. 260—408)

1

This invention relates to new chemical compositions or reaction products and is more particularly related to a novel group or class of reaction products which are especially valuable as extreme pressure addition agents in lubricating compositions. The new products are also useful chemical intermediates from which other extreme pressure lubricant assistants can be prepared.

It is well known to those familiar with the art that a lubricating oil such as a mere refined petroleum oil fraction is incapable of maintaining a lubricating film between engaged metallic surfaces where the unit load at the engaged surfaces exceeds a pressure of say 3000–4000 pounds per square inch. In various types of modern machinery, such as the hypoid gears used in motor vehicles, the engaging pressures between the gear teeth are so high that ordinary lubricating oils alone are incapable of properly lubricating them, the abnormally high pressures generally causing serious rupture of the oil film. To overcome this problem, special extreme pressure type lubricants have been developed. These lubricants are prepared by incorporating into a petroleum lubricating oil, or other suitable carrying agent, an additive ingredient which will form a lubricant film capable of withstanding these abnormally high pressures. Ingredients of this character are known as extreme pressure ingredients or extreme pressure (E. P.) lubricant bases and the lubricant compositions compounded with minor proportions of such ingredients are known as E. P. lubricants. Numerous materials have been proposed for use as E. P. bases. Among such materials are various types of halogen-containing compounds. The present invention is concerned with E. P. bases of this type.

It is an object of this invention to provide a novel class of compounds which are valuable base ingredients for extreme pressure lubricants. A further object is the provision of extreme pressure lubricants characterized by the presence therein of these ingredients, either alone or in combination with other ingredients. A still further object is the provision of a method for preparing these lubricants. Other objects and advantages will appear hereinafter.

This invention is based upon the discovery that novel lubricants, having exceptional ability to

2

lubricate effectively under conditions of extreme pressure loading may be produced by incorporating with a hydrocarbon lubricant oil a small proportion of a compound of the general formula

$$[R—CHA—CHB—(CH_2)_mCOO—]_nR'$$

where R is selected from the group consisting of hydrogen, alkyl and alkenyl radicals, R′ is selected from the group consisting of hydrogen, hydrocarbon, metal and basic ion, m is an integer from 4 to 13, n is an integer from 1 to 3, and where A and B together make up a polyhalomethane.

The polyhalogenated acids and esters contemplated by the invention are prepared by reaction of a polyhalomethane, such as carbon tetrachloride, chloroform or bromotrichloromethane, with an unsaturated organic acid or ester of the general formula

$$R—CH=CH—(CH_2)_mCOOR'$$

wherein R is selected from the group consisting of hydrogen, alkyl and alkenyl; R′ is selected from the group consisting of hydrogen and hydrocarbon radicals, and m is a whole number from 4 to 13. When R is hydrogen, A in the preceding general formula would be the carbon-containing fragment of the polyhalomethane (directive addition) and a single product would be formed. However, when R is alkyl, the carbon-containing fragment of the polyhalomethane would be partially A and partially B (random addition) and two isomeric products would be formed. If an ester is desired as the final product, an unsaturated ester may be used as the starting reactant in place of the acid, or the acid may be used and the product esterified.

Among the unsaturated acids which may be reacted with the polyhalomethanes to produce the new products of the invention the following may be mentioned as non-limiting examples: 6,7-heptenoic acid, 9,10-decenoic (caproleic) acid, 9,10-undecylenic acid, 10,11-undecylenic acid, 9,10-dodecenoic (lauroleic) acid, 9,10-tetradecenoic (myristoleic) acid, 9,10-hexadecenoic (palmitoleic) acid, 6,7-octadecenoic (petroselinic) acid, 9,10-octadecenoic (oleic) acid, 11,12-octadecenoic (vaccenic) acid, 13,14 - docosenoic (erucic) acid, 15,16-tetracosenoic (selacholeic) acid, 9,10,12,13-octadecenoic (linoleic) acid, and

9,10,11,12,13,14-octadecatrienoic (elaeostearic) acid.

Where it is desired to produce a polyhalogenated ester, the esters of any of the foregoing acids may be utilized in the reaction with the polyhalomethane compound. Specific examples of suitable esters are: octadecyl ester of 6,7-heptenoic acid, methyl ester of 9,10-decenoic acid, butyl ester of 9,10-dodecenoic acid, hexadecyl ester of 9,10-undecylenic acid, amyl ester of 10,11-undecylenic acid, octadecyl ester of 10,11-undecylenic acid, tetradecyl ester of 9,10-tetradecenoic acid, hexyl ester of 6,7-octadecenoic acid, methyl ester of 6,7-octadecenoic acid, amyl ester of 9,10-octadecenoic acid, methyl ester of 11,12-octadecenoic acid, dodecyl ester of 13,14-docosenoic acid, methyl ester of 15,16-tetracosenoic acid, amyl ester of 9,10,12,13-octadecenoic acid and undecyl ester of 9,10,11,12,13,14-octadecatrienoic acid.

The reaction between the polyhalomethane and the unsaturated acid or ester is effected in the presence of a free radical-forming compound as a catalyst. For this purpose benzoyl peroxide, diacetyl peroxide, alkyl acyl peroxides, hydroperoxides and ditertiary butyl peroxides may be mentioned as specific examples. Of these, benzoyl peroxide is particularly preferred.

The reaction conditions required for the preparation of our novel compounds are essentially those described in the article by M. S. Kharasch et al. (Science, vol. 102 (1945), p. 128) relating to the addition of carbon tetrachloride and chloroform to olefins. Thus, the reaction is readily effected by adding to the unsaturated acid, or ester, an excess of the polyhalomethane and a small amount, about 0.02 mol of the peroxide catalyst, and heating the reaction mixture. Preferred reaction temperatures are those obtained by heating at the reflux temperatures of the reaction mixtures, although broadly, temperatures falling within the range varying between about 30° C. and about 100° C. are entirely satisfactory.

We have found that the reaction conditions vary somewhat depending on the particular polyhalomethane reactant employed, since these compounds vary noticeably in reactivity. Thus, we have found that bromotrichloromethane reacts most readily. Accordingly, with this compound as the polyhalomethane, the reaction times are relatively short, i. e. from about 5–10 minutes to about one hour. Also, although ordinarily the amount of peroxide catalyst used may vary from about 0.001 mol to about 0.5 mol per mol of unsaturated acid or ester with bromotrichloromethane the amount required is in the lower end of this range. In fact, we have found that bromotrichloromethane will react without a peroxide catalyst under the influence of ultraviolet light.

On the other hand, with carbon tetrachloride, and particularly with chloroform, the required reaction times are greatly increased, ranging broadly from several hours to upwards of 100 hours. Also, the amount of organic peroxide catalyst required is in the higher end of the aforesaid range, i. e. from about 0.01 mol to about 0.5 mol per mol of acid, or ester, reactant.

The proportions of reactants employed in preparing the reaction products of the invention may be varied considerably. However, it is preferable to employ an excess of the polyhalomethane reactant. We have found that the use of at least about 4 mols of polyhalomethane to 1 mol of the unsaturated acid in the reaction is particularly advantageous, since when this ratio of reactants is used, polymerization of the acid reactant is largely minimized with a corresponding increase in the yield of the monomeric adduct, the general formula of which is given hereinabove. Even when this ratio of reactants is employed, however, the reaction products obtained usually contain minor amounts of relatively high molecular weight compounds formed either by polymerization of the acid reactant, or by interaction of the organic peroxide with one or both of the reactant materials. This is indicated by the fact that product yields greater than that accounted for by the chlorine content of the products are obtained where the polyhalomethane reactant is chloroform and particularly where the relatively larger amounts of the organic peroxides within the above ranges, are used. However, the reaction products may be readily separated by fractionation, such as by means of a molecular still, if the pure materials are desired. In any case, the reaction products are comprised predominantly of the polyhalogenated acids or esters and are effective extreme pressure ingredients. Accordingly, when the products are to be utilized for this purpose no purification treatment is necessary.

As indicated by the generic formula given hereinbefore, salts of the aforesaid polyhalogenated acids are also contemplated in the invention. These salts may be prepared by reaction of the acid with a metal oxide, or hydroxide, or with a non-metallic base, such as ammonium hydroxide, or by metathesis with a suitable metal salt, such as a chloride, acetate, nitrate, etc. Metal salts can also be prepared by reacting the sodium salt of the acid with an alcohol solution of a salt of the desired metal. Among the metals contemplated for this purpose are: copper, aluminum, magnesium, calcium strontium, barium, zinc, cadmium, tin, lead, vanadium, chromium, manganese, iron, cobalt and nickel. Of these metals zinc, tin and lead are particularly preferred.

Further details as to the procedures which may be utilized in synthesizing the compounds contemplated herein may be obtained from the following illustrative examples describing the preparation of typical reaction products:

EXAMPLE I

Undecylenic acid—CCl_4 product

Two hundred and seventy-six grams (1.5 mols) of undecylenic acid and 924 grams (6 mols) of carbon tetrachloride were refluxed (about 75–80 C.) for eight hours with 6 grams (.025 mol), of benzoyl peroxide. The solution was washed with dilute NaOH, then dilute HCl followed by water washes. Topping to 159° C. at 8 mm. yielded 408 grams of a product having the following analysis:

Found	Theory For $C_{11}H_{19}Cl_4COOH$
Percent Chlorine—35.7 Neutralization Number—167.8	Percent Chlorine—42 Neutralization Number—165.5

EXAMPLE II

Preparation of the lead salt of the carbon tetrachloride—undecylenic acid product

One hundred and thirty-five grams of the undecylenic acid —CCl_4 product previously described were mixed with 76 grams of

$Pb(CH_3COO)_2.3H_2O$

Heat was applied with stirring until the temperature reached 140° C. Then the condenser was set downward for distillation and the acetic acid and water distilled out in a stream of nitrogen. The reaction product was flushed clear of water and acetic acid by blowing with nitrogen for one hour. One hundred and sixty-seven grams of a dark orange, very viscous liquid were obtained. The theoretical yield is 176 grams. The product analyzed 24.3% lead and 24.09% chlorine. Theoretical values for these constituents are 24% lead and 32.6% chlorine, respectively. (NOTE.—The theoretical values are based on a pure undecylenic acid —CCl_4 product.) However, the undecylenic acid product (Example I) was not purified and was found by actual analysis to contain 35.7% chlorine and had an N. N. of 167.8. On the basis of this acid, the following comparative values are given:

Expected Values (on the basis of the unpurified undecylenic acid —CCl_4 product)	Found
Percent Cl=28.8% Percent Pb=25.1% Yield=167 grams	24.09% Chlorine 24.3% Lead 167 grams

EXAMPLE III

Amyl ester of undecylenic acid—CCl_4 product

Ninety-five grams of an undecylenic acid-carbon tetrachloride product having 34.4% chlorine and N. N. of 196.5 was mixed with 44 grams of isoamyl alcohol, 110 cc. of toluene and 1 gram of para-toluenesulfonic acid. The solution was refluxed for five hours at 120° C. with the separation of 5 cc. of water in a side arm water trap. The solution was water washed and topped to 150° C. at 2–3 mm., yielding 106 grams (about 87% yield) of a product which had the following analysis:

Found	Expected for $C_{11}H_{19}Cl_4COOC_5H_{11}$ (on the basis of unpurified undecylenic acid)
Percent Chlorine=28.4% Neutralization Number=1	Percent Chlorine=28.0% Neutralization Number=Nil

EXAMPLE IV

Undecylenic acid—chloroform product

Three hundred and sixty-eight grams (2 mols) of undecylenic acid and 1500 cc. of chloroform were heated at gentle reflux (60–64° C.) for 72 hours with the addition of 2 grams of benzoyl peroxide every hour during the day except the last hour of the day when 5 gms. of benzoyl peroxide were added before heating and stirring overnight. A total of 63 gms. (.26 mol) of peroxide was added. The solution was topped to 161° C. at 2 mm. which removed the excess chloroform, benzoic acid formed by decomposition of the benzoyl peroxide, and a small amount of unreacted undecylenic acid. After cooling, the dark oily product was filtered by suction to remove a few crystals of benzoic acid which had fallen back on the surface. Five hundred and fifty-four grams (91% yield) of a product that had a specific gravity of 1.145 at 27° C. was obtained. Undecylenic acid at the same temperature had a gravity of 0.030. The analysis of the product was as follows:

Found	Theory for $C_{11}H_{20}Cl_3COOH$
Percent Chlorine=29.7 Neutralization Number=172.3 Bromine Addition Value=0.5	Percent Chlorine=35.1 Neutralization Number=184 Bromine Addition Value=Nil

EXAMPLE V

Oleic acid—CCl_4 product

Two hundred-eighty-three and five-tenths (283.5) gms. (approx. 1 mol) of oleic acid were mixed with 1413 gms. (approx. 9.1 mols) of carbon tetrachloride. Five grams of benzoyl peroxide were added and the contents of the flask were heated to reflux. Reaction was continued for 98 hours with the addition of 2 grams every hour of the day except for the last hour of the day when 5 grams of benzoyl peroxide were added before heating and stirring overnight. A total of 95 grams (.39 mol) of benzoyl peroxide were added. The pot temperature during reflux was 80° C. most of the time. Excess carbon tetrachloride and some benzoic acid were removed by distillation to a pot temperature of 150° C. under 9 mm. pressure. The residue was then extracted nine times with 500 cc. portions of a 50% alcohol solution in water to remove the remainder of the benzoic acid. Topping of the product to 150° C. at 2 mm. pressure gave 405 grams (93.2% yield) of a dark red viscous oil which had a specific gravity at 26° C. of 1.151 compared with a gravity of 0.8862 for oleic acid. The analysis of the product was as follows:

Found	Theory for $C_{18}H_{33}Cl_4COOH$
Percent Chlorine=30.3 Bromine Addition Value=1.9 Neutralization Number=116.8	Percent Chlorine=32.6 Bromine Addition Value=Nil Neutralization Number=128.4

EXAMPLE VI

Oleic acid—chloroform product

Two hundred and eighty-two grams (1 mol) of oleic acid and 1000 grams (8.3+ mols) of chloroform were mixed and heated to reflux at 67–72° C. with the addition of 2 grams of benzoyl peroxide. The reaction was run for 195 hours with the addition of 2 grams of benzoyl peroxide every hour during the day, except that 5 grams were added the last hour of the day before heating and stirring overnight. A total of 174 grams (.72 mol) of benzoyl peroxide was added. Most of the excess chloroform was removed under reduced pressure and the product extracted 26 times with 300 cc. portions of 50/50 alcohol/water solution to remove benzoic acid formed from the benzoyl peroxide. The product was taken up in a high boiling hydrocarbon solvent and topped to 170° C. pot temperature at 2 mm. pressure to remove solvent and benzoic acid. The product was 373 grams (93% yield) of a red oil having a specific gravity of 1.016. The analysis was as follows:

Found	Theory for $C_{18}H_{34}Cl_2COOH$
Percent Chlorine=14.85 Bromine Addition Value=9.0 Neutralization Number=115.7	Percent Chlorine=26.5 Bromine Addition Value=Nil Neutralization Number=140

EXAMPLE VII

Oleic acid-linoleic acid mixture—CCl_4 product

Two hundred and eighty-one grams of a mixture which is comprised of approximately 40 parts of oleic acid and 60 parts of linoleic acid were mixed with 400 grams of carbon tetrachloride and 2 grams of benzoyl peroxide and then heated to reflux at 78–79° C. Reaction was continued for 102 hours with the stepwise addition of 2 grams of benzoyl peroxide every hour of the day except the last hour of the day when 5 grams of benzoyl peroxide were added before heating and stirring overnight. A total of 86 grams (.35 mol) of benzoyl peroxide was added. The unreacted CCl_4 was topped off under reduced pressure. The residue was extracted with a 50/50 alcohol-water solution, taken up in 300 cc. of a high boiling hydrocarbon solvent and topped to 160° C. pot temperature at 2 mm. pressure to remove the solvent and benzoic acid. Four hundred and nine grams of a dark red oil with a specific gravity of 1.064 at 32° C. were obtained. The analysis was as follows:

Percent chlorine=18.04
Bromine addition value=12.2
Neutralization number=114.5

This product is probably a polymer with about one CCl_3 group per dimerized fatty acid.

EXAMPLE VIII

Preparation of the undecylenic acid-bromotrichloromethane product

One hundred and eight-four grams (1 mol) of undecylenic acid and 1000 grams (5+ mols) of bromotrichloromethane were mixed and 2 grams of benzoyl peroxide were added. At 80° C. an exothermic reaction took place and the temperature rose quickly to 104° C. An ice bath was applied to control the vigorous reflux and the temperature went down to 70° C. Heat was again applied and at 85° C. an exothermic reaction again took place but to a lesser extent. An additional 2 grams of benzoyl peroxide (total .013 mol) were added and the reaction mass was held between 88° C. and 92° C. for an hour.

The excess bromotrichloromethane and any unreacted undecylenic acid were distilled, and benzoic acid from the catalyst was sublimed, by topping to a maximum pot temperature of 170° C. at 2 mm. mercury pressure. The residue weighed 369 grams which represented a yield of 96.5% based on a monomeric addition product. The analysis was as follows:

Found	Theory for $C_{11}H_{19}BrCl_3COOH$
Neutralization Number=147½ Bromine Addition Value=1.0 Percent Chlorine=24.7 Percent Bromine=22.0	Neutralization Number=146½ Bromine Addition Value=0.0 Percent Chlorine=27.84 Percent Bromine=20.9

Under the conditions outlined in the foregoing examples the various unsaturated acids and esters mentioned earlier in this specification may be reacted with carbon tetrachloride, chloroform or bromotrichloromethane to produce novel polyhalogenated products of the type contemplated herein.

It is to be understood that the foregoing examples are given by way of illustration only and that the invention is not to be limited to the particular reactants, procedures or reaction conditions described therein.

To demonstrate the effectiveness of the materials contemplated by this invention as extreme

pressure lubricant ingredients, we have prepared and tested various compositions comprised of the several reaction products described above and a hydrocarbon lubricant oil as the carrying agent. More specifically, we have prepared various lubricant blends from a mineral lubricating oil fraction having a Saybolt Universal viscosity of 64 to 67 seconds at 210° F., to which a minor proportion of the product obtained by the reaction of the polyhalomethanes with the unsaturated acids have been added. These blends were subjected to the Almen pin test (described by Wolf And Mougey, Proc. A. P. I., 1932, pp. 118–130); the S. A. E. test (described in S. A. E. Journal 39, 23–24, 1936) and the Timken test. These three tests are commonly accepted in the art as standards for determining the extreme pressure characteristics of a lubricant.

In the table given below we show the results obtained from the above tests using the oil without the addition agent and samples of the same oil blended with the compounds of the invention.

TABLE

Product Added	Conc. In Oil, Percent	Almen Test (Lbs. Failed)	S. A. E. Test (Lbs. Failed)	Timken Test (Lbs. Failed)
None		4,000	Less than 20.	Less than 10.
Undecylenic Acid—CCl_4	10	30,000	520	55.
Undecylenic Acid—CCl_4	5	30,000	350	65.
Undecylenic Acid—CCl_4	1	6,000	280	
Undecylenic Acid—$HCCl_3$	5	9,000	360	
Oleic Acid—CCl_4	10	6,000	324	
Oleic Acid—$HCCl_3$	10	5,000	80	
Amyl ester, Undecylenic—CCl_4	10	7,000	80	
Amyl Ester, Undecylenic—CCl_4	5	5,000	66	45.
Undecylenic Acid—$BrCCl_3$	10	30,000	462+	

From the foregoing table it will be seen that the product compounds of this invention are highly efficient extreme pressure lubricant bases. The amount of these product materials which may be added to a hydrocarbon lubricant oil, or other suitable carrying agent, to form an extreme pressure lubricant composition may be varied from about 0.5% to about 20% by weight.

Lubricating oil concentrates are also contemplated herein, such concentrates containing substantially larger amounts of the extreme pressure ingredients than those just above mentioned. That is, relatively large amounts, upwards of about 20% weight, of the said materials may be incorporated in an oil fraction and the oil concentrates so obtained may thereafter be diluted with a suitable quantity of an oil prior to use to produce the desired operable ultimate concentration.

Although it is generally preferred to use the characterizing ingredients of the invention incorporated with ordinary petroleum type lubrication oils as the carrying agents therefor, it is not intended that the invention be limited to any particular carrying or blending medium, but the invention includes broadly extreme pressure lubricants containing these ingredients dissolved, dispersed or emulsified in any other suitable carrying medium, such for example as relatively non-viscous petroleum hydrocarbons, such as kerosene, as well as fatty vegetable or animal oils, alcohols, esters, ethers, etc.

It is to be understood that the characterizing ingredients of the invention may be used in the

carrying medium in combination with other oil addition agents, such, for example, as sulfur type E. P. additives, oiliness agents, antioxidants, pour point depressants, detergents, viscosity index improving agents, etc.

As stated hereinbefore, the novel compounds of the invention are useful chemical intermediates from which other valuable compounds may be prepared. Thus, the halogen in our compounds may be replaced by reaction with various metal salts or may be eliminated as hydrohalogen acid yielding an olefin. The tricholoromethane group can be converted to an ortho ester and to an acid. The acids, of course, will form metal or ammonium salts or soaps which are useful as grease components for greases subjected to extreme load conditions.

It is to be understood that while we have herein described compounds obtained with certain specific materials, and have illustrated exemplary methods of preparing such compounds, the invention is not limited to the specific compounds described or to the specific methods of preparation thereof but includes such variations in reactants and procedure as fairly come within the scope of the appended claims.

This application is a division of our copending application, Serial Number 34,827, filed June 23, 1948, now abandoned.

We claim:

1. As a new composition of matter, a compound of the general formula

$$[R—CHA—CHB—(CH_2)_mCOO—]_nR'$$

where R is selected from the group consisting of hydrogen, alkyl and alkenyl radicals, R' is selected from the group consisting of hydrogen, metal and basic ion, m is an integer from 4 to 13, n is an integer from 1 to 3, and where A and B are univalent radicals selected from the group consisting of —CCl_3, —Cl and —Br, one of them always being —CCl_3, but never both.

2. As a new composition of matter, a compound of the general formula

$$[A—CH_2—CHB—(CH_2)_mCOO—]_nR'$$

where R' is selected from the group consisting of hydrogen, metal and basic ion, m is an integer from 4 to 13, n is an integer from 1 to 3, and where A and B are univalent radicals selected from the group consisting of —CCl_3, —Cl and —Br, one of them always being —CCl_3, but never both.

3. As a new composition of matter, a compound of the general formula

$$[R—CHA—CHB—(CH_2)_mCOO—]_nR'$$

where R is alkyl, R' is selected from the group consisting of hydrogen, metal and basic ion, m is an integer from 4 to 13, n is an integer from 1 to 3 and where A and B are univalent radicals selected from the group consisting of —CCl_3, —Cl and —Br, one of them always being —CCl_3, but never both.

4. As a new composition of matter, the compound

$$Cl_3C—CH_2—CHCl—(CH_2)_8—COOH$$

5. As a new composition of matter, the compound

$$CCl_3—CH_2—CHBr(CH_2)_8—COOH$$

6. As a new composition of matter, the compound

$$[Cl_3C—CH_2CHCl—(CH_2)_8COO]_2Pb$$

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,262,813	Morway et al.	Nov. 18, 1941
2,319,183	Badertscher	May 11, 1943
2,425,426	Joyce	Aug. 12, 1947
2,449,547	Byrkit	Sept. 21, 1948
2,561,516	Ladd et al.	July 24, 1951
2,568,859	Ladd et al.	Sept. 25, 1951

OTHER REFERENCES

Kharasch et al.: J. Am. Chem. Soc., vol. 68, p. 1545 (1946).

Kharasch: Science, 102, p. 128 (1945).