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## 3,096,363 FLUORINATED ESTERS OF POLYCARBOXYLIC ACIDS

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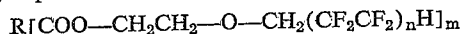
This invention relates to novel esters of polycarboxylic acids and particularly to novel 2-(1H,1H, $\omega$ H-perfluoroalkoxy)ethanol esters of saturated polycarboxylic acids.

The rapid development of industrial technology and the advancement in the design of jet engine aircraft have created a demand for stable lubricants and fluids for power and heat transmission which are capable of withstanding high temperatures. It is desired that such fluids be stable at temperatures of at least 400° F. or higher, even as high as 600° F.; and form no sludge on continued use. It is further desired that such fluids have good oxidative stability and low volatility.

Conventional fluids, such as the esterlubes and the petroleum oils, do not have satisfactory thermal and oxidative properties at temperatures above 300° F., while silicone oils gel at elevated temperatures. It is now generally recognized that dibasic acid esters of fluoro-alcohols as a class have better oxidative and thermal stability, as well as lower flammability, than the conventional esterlubes and petroleum oils. However, in general, they are too volatile for practical use in any but closed systems.

It is an object of this invention to provide new esters of polycarboxylic acids which have a novel combination of advantageous beneficial properties, particularly having superior viscosity characteristics and surprisingly low volatility characteristics. Another object is to provide new esters of such character which are stable and which are useful as high temperature lubricants and as fluids for the transmission of heat and power. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accord with this invention which comprises the normally liquid esters of the formula



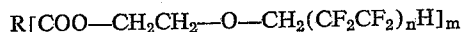
wherein R represents a saturated hydrocarbon radical of 2 to 20 carbon atoms having only one carboxy group attached to any one carbon atom,  $m$  is an integer of 2 to 4, and  $n$  is an integer of 1 to 5. By "normally liquid" is meant that the esters have a pour point of less than 100° F.

It has been found that the esters of this invention have a novel combination of advantageous beneficial properties. They have improved viscosity-temperature characteristics over those possessed by prior polyfluoroalkyl esters of the corresponding acids. Particularly they have an extremely low volatility, materially lower than would be expected from their molecular weight. In addition, they have excellent oxidative and thermal stability and are substantially noncorrosive to metals. Due to such combination of properties, they are especially useful as high temperature lubricants and as fluids for the transmission of heat and power. Particularly because of their low volatility, they have the advantage over the prior

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polyfluoroalkyl esters of the corresponding acids of being useful as lubricants and as fluids for the transmission of heat and power in open systems where evaporation is a problem, as well as in closed systems.

The novel esters of this invention are the neutral esters derived from saturated polycarboxylic acids and 2-(1H,1H, $\omega$ H-perfluoroalkoxy)ethanols, which esters have the formula



wherein R represents a saturated hydrocarbon radical of 2 to 20 carbon atoms having only one carboxy group attached to any one carbon atom,  $m$  is an integer of 2 to 4, and  $n$  is an integer of 1 to 5. Such esters include the individual esters of a single polyfluoroalkoxyethanol and a single polycarboxylic acid, the mixed esters of a mixture of polyfluoroalkoxyethanols and a single polycarboxylic acid wherein two or more of the alcoholic group of the ester are different in the value of  $n$ , and mixtures of two or more of such esters.

The 2-(1H,1H, $\omega$ H-perfluoroalkoxy)ethanols have the formula  $HO-CH_2CH_2-O-CH_2(CF_2CF_2)_nH$  wherein  $n$  is an integer of 1 to 5, preferably 2 to 4. Representative polyfluoroalkoxyethanols are 2-(1H,1H,3H-tetrafluoropropoxy)ethanol, 2-(1H,1H,5H-octafluoropentoxy)ethanol, 2-(1H,1H,7H-dodecafluoroheptoxy)ethanol, 2-(1H,1H,9H-hexadecafluorononyloxy)ethanol and 2-(1H,1H,11H-eicosafluoroundecyloxy)ethanol.

Such polyfluoroalkoxyethanols of the present invention are the 1:1 adducts of the corresponding fluorotelomer alcohols and ethylene oxide. The fluorotelomer alcohols and their preparation are described by R.M. Joyce in U.S. Patent 2,559,628. The fluorotelomer alcohols which are useful for preparing the polyfluoroalkoxyethanols of this invention have the formula  $H(CF_2CF_2)_nCH_2OH$  wherein  $n$  is an integer of 1 to 5, preferably 2 to 4, and mixtures of two or more thereof which are obtained by the process disclosed by Joyce. Representative fluorotelomer alcohols are:

- 1H,1H,3H-tetrafluoropropyl alcohol (C<sub>3</sub>)
- 1H,1H,5H-octafluoropentyl alcohol (C<sub>5</sub>)
- 1H,1H,7H-dodecafluoroheptyl alcohol (C<sub>7</sub>)
- 1H,1H,9H-hexadecafluorononyl alcohol (C<sub>9</sub>)
- 1H,1H,11H-eicosafluoroundecyl alcohol (C<sub>11</sub>)

The polyfluoroalkoxyethanols employed in this invention are readily prepared by reacting the fluorotelomer alcohol or a mixture of two or more thereof with ethylene oxide at elevated temperatures in the presence of an alkali metal hydride or an alkali metal hydroxide catalyst. The method of preparing the polyfluoroalkoxyethanols is illustrated by the following Example 1.

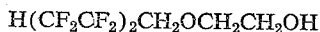
### EXAMPLE 1

A solution of 15 grams of sodium hydride catalyst in 1020 grams of 1H,1H,7H-dodecafluoroheptyl alcohol was treated with ethylene oxide in 140° C. to 150° C. until 148 grams had been absorbed. The product  $H(CF_2CF_2)_3CH_2OCH_2CH_2OH$ , was washed and distilled at 80° C.-90° C. at 0.2 mm. of mercury. Product analysis calculated as C<sub>9</sub>H<sub>8</sub>O<sub>2</sub>F<sub>12</sub>, carbon 28.7; hydrogen 2.1; found carbon 28.3, 28.3 and hydrogen 2.2, 2.3.

By following the details of Example 1 using 59.2 g. of

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50.6% sodium hydroxide, 2100 g. of 1H,1H,5H-octafluoropentyl alcohol (C<sub>5</sub>), absorbing 399 g. of ethylene oxide, yield of 1484 g. of the product,



was obtained, boiling at 99° C.-101.5 C. at 13-15 mm. of mercury.

All the fluorine-containing telomer alcohols heretofore mentioned can be reacted with ethylene oxide by following this procedure to form the corresponding 1:1 adducts.

The polycarboxylic acids of this invention may be represented by the formula R(COOH)<sub>m</sub> wherein R is a saturated hydrocarbon radical of 2 to 20 carbon atoms, having only one carboxy group attached to any one carbon atom, and *m* represents an integer of 2 to 4, preferably 2 to 3. The saturated hydrocarbon radicals represented by R may be acyclic (open chain) or alicyclic (containing a carbocyclic ring), including alkyl substituted carbocyclic hydrocarbons. Preferably, R will contain from 3 to 8 carbon atoms and, in the case of the alicyclic hydrocarbon radicals, 6 to 8 carbon atoms. Representative saturated polycarboxylic acids which can be used to prepare the esters of this invention are:

Succinic acid  
2-methyl succinic acid  
Glutaric acid  
Adipic acid  
3-methyl glutaric acid  
3,3-dimethyl glutaric acid  
2,2-dimethyl glutaric acid  
Pinic acid  
Pimelic acid  
Nor-camphoric acid  
3-methyl-2-ethyl glutaric acid  
Suberic acid  
1,4-dicarboxy cyclohexanoic acid  
Sebacic acid  
Camphoric acid  
2,2,5,5-tetramethyl adipic acid  
2,5-dicyclohexyl adipic acid  
Tricarballic acid  
3-methyl tricarballic acid  
1,2,5-pentanetricarboxylic acid  
Camphoronic acid, and  
1,2,3,4-butanetetracarboxylic acid

The esters are prepared from the polyfluoroalkoxyethanol and the polycarboxylic acid according to conventional techniques. For example, the polycarboxylic acid or a functional derivative thereof, preferably the anhydride, may be heated in a hydrocarbon or halohydrocarbon solvent. An acid catalyst may be used. Normally, a strong acid catalyst is preferred, such as sulfuric acid, hydrochloric acid, *p*-toluene sulfonic acid, perfluorobutyric acid, or mixtures of strong acids. The water is removed as the solvent refluxes. The solvent and excess alcohol may be removed by vacuum distillation, the residue cooled, washed with dilute alkali to remove any remaining acid present and the product purified by vacuum distillation.

Alternately, the product need not be distilled from the reaction vessel, but can be purified by conventional techniques. For example, impurities may be removed by solvent extraction, washing, adsorption on solid substrates, and the like. The product thus obtained is a clear, colorless or light yellow oil.

Mixtures of two or more of the polyfluoroalkoxyethanols can be reacted with a polycarboxylic acid or with a mixture of two or more of the polycarboxylic acids to provide mixed esters and mixtures of esters of this invention. Also, a single polyfluoroalkoxyethanol may be reacted with a mixture of two or more polycarboxylic acids to provide mixtures of esters of this invention. Such mixed esters and mixtures of esters, as well as mixtures

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obtained by mixing two or more individual esters, also have the advantageous beneficial properties of the individual esters and are included within the scope of this invention.

In order to more clearly illustrate this invention, preferred modes of carrying it into effect and the advantageous results to be obtained thereby, the following examples are given in which the parts are by weight, except where specifically indicated otherwise.

#### EXAMPLE 2

A mixture of 45.5 g. (0.25 mole) of camphoric anhydride, 188 g. (0.50 mole) of 2-(1H,1H,7H-dodecafluoroheptoxy)ethanol, 100 ml. of toluene as reaction solvent and 1 ml. of concentrated sulfuric acid as catalyst was refluxed with continuous removal of water until no more water was formed. A total of 5 ml. of water was recovered. The mixture was cooled, treated with 0.1 N aqueous KOH while stirring and the layers separated. The crude ester was washed with water, treated with 5 g. of activated alumina and 3 g. of activated charcoal, and the toluene and excess alcohol were removed by stripping under vacuum. A final stripping action was carried out at a pressure of 0.4 mm. of mercury while the temperature was increased to 140° C.-150 C. When all evolution of vapors had ceased, the hot ester was filtered under suction through a medium-porosity sintered glass funnel giving 155 g. (72% of theory) of bis-[2-(1H,1H,7H-dodecafluoroheptoxy)ethyl]camphorate, a nearly colorless oil, having a refractive index *n*<sub>25</sub><sup>D</sup> of 1.3818, 1.3819 and a density *D*<sub>4</sub><sup>25</sup> of 1.5419. Analysis of the product as C<sub>28</sub>H<sub>26</sub>O<sub>6</sub>F<sub>12</sub>, calculated carbon 36.7; hydrogen 3.06; fluorine 49.8; found carbon 36.6, 37.0; hydrogen 3.1, 2.9; fluorine 50.3, 50.5.

All the esters of this invention may be prepared by following this procedure.

#### EXAMPLE 3

When the details of Example 1 were repeated using a mixture of 91 g. (0.5 mole) of camphoric anhydride, 304 g. (1.1 moles) of 2-(1H,1H,5H-octafluoropentoxy)ethanol and 200 ml. of toluene as reaction solvent, 292 g. (75.4% of theory) of bis-[2-(1H,1H,5H-octafluoropentoxy)ethyl]camphorate, a clear amber oil, were obtained by vacuum stripping at 150° C. and 0.4 mm. mercury. The oil had a refractive index *n*<sub>25</sub><sup>D</sup> of 1.3961, 1.3961 and a density *D*<sub>4</sub><sup>25</sup> of 1.4513.

#### EXAMPLE 4

When the details of Example 1 were repeated using a mixture of 30 g. (0.1875 mole) of 3,3-dimethylglutaric acid, 115 g. (0.417 mole) of 2-(1H,1H,5H-octafluoropentoxy)ethanol and 75 ml. of toluene as reaction solvent, 114 g. (94.5% of theory) of bis-[2-(1H,1H,5H-octafluoropentoxy)ethyl]3,3-dimethylglutarate, a colorless oil, were obtained by vacuum stripping at 150° C. and less than 0.5 mm. mercury. The refractive index of the product was *n*<sub>25</sub><sup>D</sup> 1.3803, 1.3804 and its density *D*<sub>4</sub><sup>25</sup> was 1.4636.

#### EXAMPLE 5

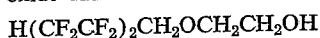
When the details of Example 1 were repeated using a mixture of 44.1 g. (0.25 mole) of tricarballic acid, 241 g. (0.874 mole) of 2-(1H,1H,5H-octafluoropentoxy)ethanol, 100 ml. of toluene as reaction solvent and 20 drops of concentrated sulfuric acid as catalyst, 228 g. (91.2% of theory) of tris-[2-(1H,1H,5H-octafluoropentoxy)ethyl]tricarballic acid, a colorless oil, were obtained by vacuum stripping at 130° C. and 0.35-0.45 mm. mercury. The refractive index was *n*<sub>D</sub><sup>25</sup> 1.3773, 1.3775 and the density was *D*<sub>4</sub><sup>25</sup> 1.5720.

The physical properties of the esters of this invention are listed in Table I, in comparison with those of the corresponding esters of unmodified fluorotelomer alcohols.

Table I

Ester	Molecular Weight	Viscosity, cs.		Viscosity Index (ASTM D 567)	ASTM Slope (100-210° F.)	Volatility at 400° F., percent in 2 hrs.
		210° F.	100° F.			
Camphorate of:						
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	628	6.50	80.1	-28	0.888	>100
H(VF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	716	8.94	109.4	42	0.809	13
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH	828	8.20	113.8	1	0.858	65
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	916	10.49	149.6	34	0.809	9
3,3-Dimethylglutarate of:						
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	788	3.86	28.05	-46	0.892	>100
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	676	4.71	33.86	34	0.829	49
Tricarballiate of:						
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	818	6.64	76.3	-23	0.867	27
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	950	9.28	114.1	46	0.802	8

The superior viscosity-temperature characteristics of the esters of this invention are demonstrated by the lower ASTM slopes as compared with the corresponding esters of the fluorotelomer alcohols. Furthermore, the lower volatility of the esters of this invention is quite unexpected in comparison with that of the corresponding esters of the fluorotelomer alcohols. Although it is to be expected that the volatility would decrease as the molecular weight of the ester is increased, the magnitude of the decrease is far greater than could be expected. The additional molecular weight provided by the ethylene oxide unit is only 44 for each polyfluoroalkyl chain. This is very considerably less than that provided by the additional —CF<sub>2</sub>CF<sub>2</sub>— units required to produce the same reduction in volatility, each —CF<sub>2</sub>CF<sub>2</sub>— unit increasing the molecular weight of each polyfluoroalkyl chain by 100. As seen in the case of the camphorates, for example, the volatility of the ester of H(CF<sub>2</sub>CF<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>OH is greater than 100% and the addition of a —CF<sub>2</sub>CF<sub>2</sub>— unit, as in the ester of H(CF<sub>2</sub>CF<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>OH, reduces the volatility to 65%. On the other hand, the addition of the ethylene oxide unit as in



reduces the volatility to 13%.

The volatility of the esters was determined in flat bottomed machined aluminum test cups, 3/16" deep and 1 3/8" inside diameter with 1/16" thick walls and bottoms, by the following procedure: The aluminum test cups were weighed to 0.1 mg., about 2-3 grams of the oil sample were placed therein, and the cups reweighed to 0.1 mg. The cups containing the samples were placed on a hot plate, the temperature of which was maintained at 400° F. ± 5° F. At the end of the two-hour test period, the samples were removed, the cups allowed to cool and then reweighed to 0.1 mg. The sample weight loss was determined and is reported as percent evaporation.

The oxidative stability and simultaneous corrosive effect of the esters on metals were determined by the test method described by E. E. Sommers and B. M. Sturgis in U.S. Patent 2,840,593. The results are given in the following Table II.

Table II  
OXIDATIVE STABILITY  
[500° F.—24 hour test]

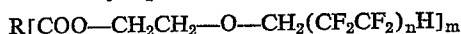
Ester	Cu Catalyst wt. loss, mg./cm. <sup>2</sup>	Sludge	Final Total Acid No., mg. KOH/g.	Viscosity Change, Percent		Evap. loss, g./ml.
				210° F.	100° C.	
Camphorate of:						
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	0.6	none	1.8	-4.2	-8.2	0.10
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	0.8	none	2.5	-2.0	-6.0	0.09
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OH	0.4	none	1.4	-4.7	-12	0.14
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	1.2	none	3.4	+7.4	+3.2	0.14
3,3-Dimethylglutarate of:						
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	0.3	none	1.4	-1.9	-0.8	0.05
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	0.6	none	5.8	-2.2	-4.4	0.16
Tricarballiate of:						
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OH	0.3	cloudy	1.3	-----	+2.4	0.03
H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>2</sub> OH	0.5	trace	3.6	-10	-20	0.23

It will be understood that the preceding examples have been given for illustrative purposes solely and that this invention is not limited to the specific embodiments described therein. On the other hand, it will be readily understood by those skilled in the art that, subject to the limitations set forth in the general description, other esters, mixed esters, and mixtures of esters of this invention can be prepared, without departing from the spirit or scope of this invention.

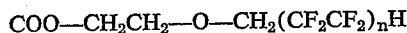
It will be apparent from the preceding description that the novel esters of this invention possess a novel, valuable combination of beneficial properties, such as surprisingly low volatility, superior viscosity-temperature characteristics, and excellent oxidative stability. These combinations of properties render such esters effective for the purpose of fulfilling the demand for stable, non-volatile, high temperature lubricants and fluids for transmission of heat and power in open as well as closed systems. Accordingly, it will be apparent that this invention constitutes a valuable advance in and contribution to the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A normally liquid ester of the formula

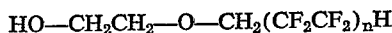


wherein R represents a saturated hydrocarbon radical of 2 to 20 carbon atoms, in which ester only one



group is attached to any one carbon atom of R, *m* is an integer of 2 to 4 and *n* is an integer of 1 to 5.

2. A normally liquid camphoric acid diester of an alcohol of the formula



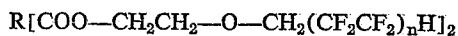
wherein *n* is an integer of 2 to 4.

3. Bis - [2-(1H,1H,7H - dodecafluoroheptoxy)ethyl]-camphorate.

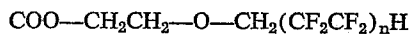
4. Bis - [2 - (1H,1H,5H-octafluoropentoxy)ethyl]-camphorate.

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5. A normally liquid ester of the formula

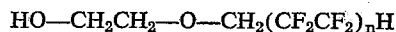


wherein R represents a saturated acyclic hydrocarbon radical of 3 to 5 carbon atoms, in which ester only one



group is attached to any one carbon atom of R, and  $n$  is an integer of 2 to 4.

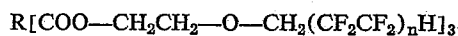
6. A normally liquid 3,3-dimethylglutaric acid diester of an alcohol of the formula



wherein  $n$  is an integer of 2 to 4.

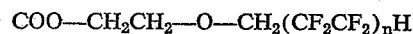
7. Bis - [2 - (1H,1H,5H-octafluoropentoxy)ethyl]-3,3-dimethylglutarate.

8. A normally liquid ester of the formula



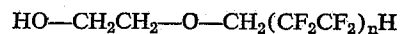
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wherein R represents a saturated acyclic hydrocarbon radical of 3 to 5 carbon atoms, in which ester only one



group is attached to any one carbon atom of R, and  $n$  is an integer of 2 to 4.

9. A normally liquid tricarballic acid triester of an alcohol of the formula



10 wherein  $n$  is an integer of 2 to 4.

10. Tris - [2-(1H,1H,5H-octafluoropentoxy)ethyl]-tricarballic acid triester.

#### References Cited in the file of this patent

- 15 Baer: "Fluoro Alcohols," Ind. and Eng. Chem., 51, 829-30 (1949).  
 Faurote et al.: Ind. and Eng. Chem., 49, 189-191 (1957).  
 20 Lovelace et al.: Aliphatic Fluorine Compounds (New York, 1958), pages 162 and 230.