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NONFOAMING COMPOSITIONS

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The present invention relates to spumiferous compositions of matter containing foam depressing agents, and more particularly the invention is concerned with lubricating oils, compounded lubricants, fluid greases, and other related compositions such as hydraulic oils, shock absorber oils and the like, incorporating a small amount of anti-foaming agent.

This application is a continuation-in-part of application Serial No. 516,547, filed December 31, 1943, by the present applicants, now Patent No. 2,435,206, dated February 3, 1948.

The formation of foam is distinctly disadvantageous under many circumstances, as, for example, in engine oils for internal combustion engines, particularly the heavy duty type of oils. It is customary to add to lubricating oils various additives which modify the physical properties to the lubricant, such as viscosity, viscosity index, and the like, or which improve chemical properties, by increasing resistance to oxidation, corrosion of bearings, and the like. Among the additives commonly employed are certain esters, such as fumarates, polyfumarates, and the like, and also various other esters including the partial esters of polyhydric alcohols, for example, pentaerythritol monooleate, sorbitan monooleate, and various related compositions. Some of these materials, particularly the fumarates and to some extent numerous other esters, tend to contribute to the foaming of the lubricant under certain conditions.

Many internal combustion engines employ both pressure and splash system of lubrication, whereas other motors use only one of the systems. In either case the formation of foam on top of the oil during the operation of the motor leads to serious consequences due to lack of lubrication. This is particularly so in lubricating systems employing the so-called "dry sump" operation where the oil returning from the engine parts is picked up by a scavenging pump and returned to the lubricant reservoir. Since the scavenging pump normally has a capacity of several times the volume of the oil returning from the engine, a large amount of air is pumped along with the lubricant and as a result foam tends to build up in the oil reservoir to a point where some oil may be lost through the breather pipe or to a point where the pressure pump delivers foam instead of oil to the various moving parts of the engine, with a resultant lack of proper lubrication. In the case of gear lubricants, such as those designed for the lubrication of automobile rear ends and transmissions when such lubricants

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show a marked tendency to form foam during use, the foam entraps the lubricant to such an extent that the oil level will fall below the gear train.

Hydraulic oils and shock absorber oils likewise need protection against foaming. High pressure hydraulic systems are composed of three essential elements, an oil reservoir, a high pressure accumulator and a hydraulic cylinder. During normal operation oil is pumped from the oil reservoir to the high pressure accumulator where it is held under pressure usually by means of compressed air. The oil is then released as needed directly to the hydraulic cylinder. In the reverse operation of the hydraulic cylinder, oil is released directly into the oil reservoir. Due to the sudden release in pressure, the air which was either dissolved in or forced into the oil at the high pressure existing in the accumulator, escapes from the oil, creating a froth or foam on the surface of the oil. In those cases where this foam is of a persistent character such as to eventually interfere with the proper operation of the machine, it is necessary at certain intervals to replace the froth or foam with new oil. Troublesome foaming also occurs in the hydraulic and shock absorber equipment of airplanes when such aircraft operate at high altitudes due to the fact that the greatly reduced air pressure at higher altitudes permits the air dissolved in the oil at ground level to be released. It is therefore apparent that the presence of an anti-foaming agent in hydraulic media would serve a useful purpose.

The principal object of the present invention is to provide lubricating compositions and pressure transfer media which will not froth or foam during use. This and other objects will be apparent to those skilled in the art upon reading the following description.

It has now been found that certain highly fluorinated organic compounds, that is organic compounds of the aliphatic type in which the major proportion of the hydrogen has been replaced with fluorine, will, when present in small amounts materially depress foaming in compositions of matter such as lubricating oil (both compounded and uncompounded), turbine oils, industrial lubricants, process oils, engine oils, hydraulic fluids, shock absorber oils, cutting oils, saturating compositions, asphaltic oils, gear lubricants and various other related compositions, as well as oil concentrates containing from 0.5 to 50% of additives. The fluorinated hydrocarbons may be added to the oleaginous compositions at any stages of their manufacture or may be incorporated with

one or more of the additives prior to the addition of the additive or mixture of additives to the oily material, as for instance the fluorinated hydrocarbon may be included with the esters which tend to promote foaming, such as those referred to above, e. g. the fumarates, polyfumarates, etc. Specific examples are given hereinbelow. The fluorinated compounds may also contain other halogens, oxygen, nitrogen, phosphorus, sulfur, or metal salts of acid radicals in the molecule.

The highly fluorinated compounds contemplated within the scope of the present invention are known, methods for their production having been described by both Bochemuller and Simons. See "Organische Fluorverbindungen" by Bockemuller, Berlin, Verlag Chemie, 1936, and article by J. H. Simons and L. P. Block, "Journal American Chemical Society," volume 61, page 2962 (1939). The detailed preparation of these fluorinated hydrocarbons is set forth more fully in an article entitled "Preparation of Fluorocarbons by Catalytic Fluorination of Hydrocarbons" by George H. Cady et al., "Industrial and Engineering Chemistry," March, 1947, pages 290 and 291. A series of articles immediately following in the same publication described various alternative procedures and techniques. The specific process for forming these compounds is no part of the present invention. For the purpose of the present invention it is preferred to use those highly fluorinated compounds which have boiling points about 85° C. at atmospheric pressure and viscosity between 30 and 2,000 S. U. S. at 210° F. This range includes those highly fluorinated compounds having from 5-50 carbon atoms to the molecule, such as heptafluoropentane ($C_5H_5F_7$), octafluoropentane ($C_5H_3F_8$), dodecafluoropentane (C_5F_{12}), and similar derivatives of such hydrocarbons as pentadecane and eicosane. These fluorinated hydrocarbons will contain from about 60 to about 80% fluorine, from about 20 to about 37% carbon and from zero to about 3% hydrogen. It is preferred to use fluorinated compounds in which substantially all of the hydrogen has been replaced by fluorine.

In the practice of the present invention for suppressing foam in compositions such as lubricants, hydraulic media and the like, the fluoro-organic compound is added to such compositions in an amount from .0001-10% by weight. The fluoro-organic compounds are substantially insoluble in such fluids and although having a greater specific gravity than many common fluids, it is believed that the fluorine compounds possess the characteristics of concentrating at the interface between the liquid phase and the gaseous foam phase, thereby breaking or destroying any foam bubbles present or as formed.

Many methods might be devised for showing the inherent characteristics of an oleaginous material to form foam and such methods could, with equal facility be employed to compare the foam-depressing properties of various anti-foaming agents. One particularly informative method is to agitate the material by partially immersing in it a mechanical mixer rotating at the rate of about 1,000 R. P. M. for 10 minutes, the material being held at a temperature of 100° F. The percentage volume change of the material due to dispersion of air into it is then taken as a measure of the foaming tendency of the material. Compounds possessing potent defoaming action hold the percentage increase in volume to less than 10% and the preferred defoamers re-

strict the percentage volume change to 6% or less.

Another acceptable method of indicating the foaming characteristics of a material or to compare the action of defoamers is by bubbling air through a dispersing device into the material maintained at a uniform temperature, at a fixed rate of air flow and for a fixed time interval. In this test the volume of foam formed can be used directly for comparing the foaming characteristics of the material under test. Further helpful information can at times be obtained by running this test at different fixed temperatures.

The following examples are given merely for the purpose of illustrating the principles of the present invention.

EXAMPLE 1

(a) As a starting material, a light lubricating oil distillate from solvent extracted Panhandle crude oil was subjected to standard foaming tests described below.

(b) To the oil of (a) above there was added 1% by weight of the fumaric acid ester of a commercial grade of lauryl alcohol known as "Lorol B." This alcohol is in reality a mixture of saturated alcohols having from about 10 to about 14 carbon atoms, alcohols of the middle of this range (lauryl) predominating. This also was tested.

(c) To the oil and ester composition (b) above was added 0.1% by weight of a highly fluorinated-aliphatic hydrocarbon containing about 24.25% carbon, 0.05% hydrogen, and 73.59% fluorine. This material was likewise subjected to the foaming test and, as indicated in data below, was much improved by the small quantity of fluorinated hydrocarbon used. Foaming was suppressed to a very satisfactory degree.

EXAMPLE 2

(a) A sample of high grade aviation lubricating oil of about 80 S. U. S. viscosity, naphthenic base, was tested.

(b) The aviation oil in (a) was modified by adding thereto 1% by weight of pentaerythritol monooleate and subjected to the standard tests. Considerable foaming resulted.

(c) The aviation oil containing pentaerythritol monooleate, described in (b) above, was modified by the addition of 0.1% by weight of the highly fluorinated material described in Example 1 (c). The foam inhibition was not quite as complete as in the case of the fumarate ester (Example 1 (c)) but was quite satisfactory.

The foam test procedure employed is set forth in detail in C. R. C. Handbook 1946, page 441, published by the Coordinating Research Council 30 Rockefeller Plaza, New York. Briefly, the procedure is as follows:

A standard 1,000 ml. graduated cylinder, fitted with a two-hole rubber stopper, has introduced through the stopper an air supply tube extending nearly to the bottom of the cylinder and terminating in a 1-inch spherical gas diffusing stone. One hole in the stopper is left open as a vent. A controlled-temperature bath is provided for the graduate.

The tests are conducted in three sequential steps. In the first 191 ml. of oil are placed in the graduate and, with the oil at a temperature of about 75° F. air is introduced through the diffuser stone in the bottom of the graduate at the rate of 0.2 cubic feet per minute for five minutes after the first bubbles start to rise. Read-

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ings of the volume of foam are taken (A) immediately at the end of the aeration and (B) ten minutes later.

The second step in the sequence is conducted as above except that the oil is heated and maintained at a temperature of 200° F. The third step is conducted like the first, using the oil which has gone through the second step, cooled to a temperature of 75° F. A clean diffuser stone is employed in each step.

The results of the tests of all the examples given above, through the sequence described, with both A and B readings, are given in the following table.

Table 1

Sequence.....	Vol. foam in ml.					
	A			B		
	1	2	3	1	2	3
<i>Examples</i>						
1 (a) Light lub. oil.....	210	30	110	0	0	0
1 (b) Light lub. oil plus 1% lauryl fumarate.....	620	90	610	255	0	210
1 (c) Light lub. oil plus 1% lauryl fumarate and 0.1% foam suppressor.....	50	150	50	0	0	0
2 (a) Aviation oil.....	100	190	260	10	0	10
2 (b) Aviation oil plus 1% pentaerythritol monooleate.....	580	70	570	535	0	485
2 (c) Aviation oil plus 1% pentaerythritol mono-oleate and 0.1% of foam suppressor.....	370	250	280	110	0	30

It will be understood that although specific esters are mentioned in the above data, the foam suppressing effect of the highly fluorinated materials described above is quite general and appears to extend to all the esters commonly used in mineral oil base lubricants. In general, the highly fluorinated aliphatic hydrocarbons of 5 to 50 carbon atoms, containing 60 to 80% fluorine have utility in spumiferous oils or oils containing foam promoting esters. The patent mentioned above, No. 2,435,206, describes and claims the use of these fluorinated materials in oils containing metallo-organic additives which promote foaming, whereas the present case is directed to the use of these compounds in spumiferous oils containing ester type additives, and the like, including such varied compounds, as the phosphatides, e. g. lecithin, various esters of the unsaturated dibasic acids, e. g. fumaric and maleic acids, and polymers thereof, and in general the esters which have objectionable foaming properties to a notable degree.

In the preferred fluorinated compounds the hydrogen is very largely replaced. The compound described above in connection with Examples 1 and 2 showed a hydrogen content of only 0.05% and a fluorine content of 73.59%. As more fully described in the aforesaid copending application, of which this is a continuation-in-part, other suitable materials may have a carbon content of 26.30%, hydrogen 0.09% and fluorine 71.30%, or

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carbon 24.24%, hydrogen 0.12%, fluorine 67.03%, or carbon 24.66%, hydrogen 0.18% and fluorine 68.07%.

These fluorinated materials are preferably used in small quantities, of the order of 0.1 to 0.2%, based on the total composition, but much smaller or much larger quantities also may be used. The proportions may be as little as .0001 or as much as 10%. Usually the hydrogen content is very low, approaching 0%, but it may go as high as 3%.

We claim:

1. A composition of matter consisting essentially of a mineral lubricating oil containing organic ester additives which tend to cause excessive foaming of said oil upon heating and/or working, and .0001 to 10% by weight, based on the total composition, of a substantially oil-insoluble highly fluorinated aliphatic hydrocarbon having 5 to 50 carbon atoms, said fluorinated hydrocarbon being composed of 60 to 80% by weight of fluorine, 20 to 37% carbon and 0 to 3% hydrogen.

2. As a composition of matter, a mineral lubricating oil containing 0.1 to 10% of a fatty acid ester of fumaric acid, having 10 to 14 carbon atoms in the acid radical, and about 0.1 to 0.2% of a highly fluorinated aliphatic hydrocarbon containing about 24% carbon, 0 to 3% hydrogen, and 73 to 76% fluorine, said fluorinated hydrocarbon being substantially insoluble in said lubricating oil.

3. Composition according to claim 1 wherein said ester is a partial ester of a polyhydric alcohol.

4. Composition according to claim 1 wherein said ester is a fumaric acid ester of an aliphatic alcohol.

5. Composition according to claim 1 wherein said ester is pentaerythritol monooleate.

6. Composition according to claim 1 wherein said ester is present in proportions of 0.1 to 10%, based on the weight of the total composition.

7. A composition consisting essentially of 70 to 99.5% mineral oil, 0.1 to 10% of an organic ester which tends to promote foaming when said oil containing said ester is subjected to working, heating or aeration, and 0.01 to 1% of a substantially oil insoluble highly fluorinated hydrocarbon composed of 0 to 3% hydrogen, 60 to 80% fluorine and 20 to 37% carbon.

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