United States Patent Office 2,972,579 Patented Feb. 21, 1961

2,972,579

OIL COMPOSITIONS HAVING REDUCED FOAMING TENDENCIES

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No Drawing. Filed Aug. 6, 1957, Ser. No. 676,508

2 Claims. (Cl. 252—33.4)

This invention relates to foam inhibition of oil compositions. Particularly, it relates to the inhibition of foaming by mineral oil compositions containing additives which normally tend to promote foaming. More particularly, the invention relates to a combination of silicone polymer and an organic polar material, which combination more effectively inhibits foaming of additive containing oil compositions than either component of the combination alone.

The excessive foaming of various oil compositions, such as lubricating oils, hydraulic oils and the like may cause operating difficulties in machinery as well as in the processing of the oils themselves. Oil additive materials, which are desirable because they prevent sludging, deposition of gum and the like, are frequently strong foam promoters and the modern tendency to use such materials in increasing quantities gives rise to increasing difficulties with foaming. It had been proposed to use a silicone polymer to inhibit foaming of such compositions. However, generally, the silicones either will not suppress foaming or, if they initially do suppress foaming, they lose their effectiveness upon standing. It has now been found that the effectiveness of silicone polymers as antifoamants in certain oil blends can be materially increased and enhanced by use of hydrocarbon compounds having a single polar group at the end of the molecule. The use of these latter materials, in conjunction with the silicones, increases the initial effectiveness of the silicone and also gives increased foam stability, that is, there is no material lessening of the foam inhibition upon standing. This combination is much more effective than either the silicone or the polar material alone. It has further been found that the effectiveness of these materials can be even further increased by heating the oil composition containing the silicone and the polar material.

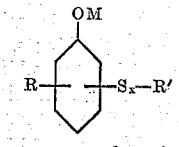
In general, the heavier the hydrocarbon oil and the greater its content of additive, the greater will be its tendency to foam and the more difficult to inhibit its foaming. Additives such as the oil-soluble sulfonates; the salts of alkylated aromatic compounds such as: alkyl phenols, alkyl phenol sulfides, and the phosphorus sulfide treated derivatives of such materials; and the like, frequently tend to promote foaming in conventional mineral base hydrocarbon oils.

According to the present invention, additives of the above types and various mixtures of such additives are treated, preferably in oil solution, with 0.001 to 1.000, e.g. 0.01 to 0.20. weight percent of a silicone and about 0.03 to 15.0, e.g. 0.5 to 15, weight percent of a polar material, said weight percentages being based on the weight of dry additive. This treatment may be carried out by simply mixing the silicone and polar material into the detergent concentrate. Where the polar material is normally solid at room temperature, then the mixture of silicone, polar material and detergent concentrate may be heated sufficiently to melt the polar material so as to obtain a homogeneous mixture after agitation.

The method of the present invention is particularly effective in reducing the foam-promoting tendencies of metal sulfonates, metal alkyl phenol sulfides, and mixtures thereof. These particular compounds are well known to the art as detergent additives for lubricating oils, particularly mineral lubricating oils, and are generally employed in the form of alkaline earth metal salts (the sulfonates are frequently also employed in the form of alkali metal salts).

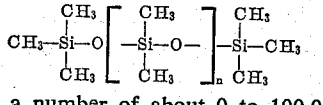
These metal sulfonates are oil-soluble salts of high molecular weight sulfonic acids which are generally produced by the treatment of petroleum oils of the lubricating oil range with fuming sulfuric acid. The sulfonic acids which are employed in the production of lubricating oil additives have molecular weights of about 350 to 650, frequently of about 400 to 550. These petroleum sulfonates have been described in numerous patents as, for example, U.S. 2,467,176. The sulfonates can also be derived from relatively pure sulfonic acids having from about 10 to 33 carbon atoms per molecule. For example, sulfonated products of alkylated aromatics such as benzene, toluene, xylene, etc., alkylated with olefins or olefin polymers of the type of polypropylene, polyisobutylene, etc. can be used. Specific examples of such sulfonates include: calcium petroleum sulfonate, barium petroleum sulfonate, sodium petroleum sulfonate, calcium C_8 alkyl benzene sulfonate, barium C_9 alkyl benzene sulfonate, sodium C_{16} alkyl benzene sulfonate, etc.

The metal alkyl phenol sulfides and polymers thereof used as oil additives and their preparation are also well known to the art and have been described in numerous patents, as for example, U.S. 2,451,345 and U.S. 2,362,289. These materials have the general formula:



wherein M represents a metal such as aluminum, cobalt, chromium, magnesium, sodium, lead, tin, etc., or the alkaline earth metals as calcium, barium, strontium, etc. (in the case of polyvalent metals, the other valences of the metal may be joined to other inorganic or organic groups or to another alkyl phenol sulfide group), R is generally an alkyl group of 5 to 20, e.g. 8 to 10 carbon atoms, R' is an aryl, alkyl, aralkyl, alkyl-aryl radical, etc., or another alkyl phenol sulfide group, while x is a number about 1 to 5. Specific examples of these materials include barium tertiary octyl phenol sulfide, calcium tertiary octyl phenol sulfide, barium-calcium tertiary octyl phenol sulfide, barium tertiary amyl phenol sulfide, calcium tertiary amyl phenol sulfide, barium nonyl phenol sulfide, etc. Mixtures of metal sulfonates with metal alkyl phenol sulfides in proportions of about 5 to 95% by weight, preferably about 10 to 50% by weight, of the metal sulfonate, are frequently employed in lubricating oil compositions.

Silicones which may be used are the dimethyl silicones of the general formula:



wherein n is a number of about 0 to 100,000, e.g. 100 to 900. These silicone polymers will generally have viscosities of 0.65 to 60,000 cs., e.g. 100 to 12,500 cs. at 25° C. depending upon the molecular weight. A preferred silicone oil is Dow Corning Fluid 200, which has a viscosity at 25° C. of about 1,000 cs. and is a dimethyl polysiloxane. Other silicones having longer alkyl groups or aryl groups attached to the silicon atoms do not

have the same effectiveness as the dimethyl silicones in the compositions of the invention.

The polar materials which may be used include those C_6 to C_{40}, e.g., C_{16} to C_{30} aliphatic hydrocarbons, saturated or unsaturated, straight chain or branched chain which at the end of the molecule are substituted with a single polar group such as —OH, —CHO, —COOH, —NH_2, and —SH groups. Those materials having 16 to 40 carbon atoms in the chain are particularly preferred as they are more effective than the shorter chain materials. Specific examples of these materials include alcohols such as: hexadecanol-1, octadecyl alcohol, docosanol-1, hexacosanol-1, 1-methyl eicosanol-1, triacontanol-1; aldehydes such as heptadecanol, etc.; acids such as palmitic, stearic, oleic, linoleic, etc.; and mercaptans such as nonadecanethiol-1, hexadecane-thiol-1, triacontane-thiol-1, etc. One group of shorter chain alcohols which may be used are the Oxo alcohols, which are isomeric mixtures of highly branched chain primary alcohols. These alcohols are prepared from olefins, such as polymers and copolymers of C_3 and C_4 monoolefins, which are reacted with carbon monoxide and hydrogen, in the presence of a cobalt-containing catalyst such as a cobalt carbonyl catalyst, at temperatures of about 300 to 400° F., and pressures of about 1000 to 3000 p.s.i. to form aldehydes. The resulting aldehyde product is then hydrogenated to form the alcohol which is recovered from the hydrogenation product.

The treatment of the foam-producing detergent additives with silicone and the polar material, in accordance with this invention, is preferably carried out with the additives in the form of additive concentrates. Generally, these additive concentrates will contain about 10 to 70%, e.g., 25 to 50% by weight of the dry additive. The remainder of the concentrate will be predominantly a diluent oil such as a mineral lubricating oil, in which the detergent additives are soluble. In certain instances, the additive concentrate may contain minor proportions of other additives such as antioxidants, viscosity index improvers, and the like. After the addition of the silicone and the polar material to the additive concentrate, the mixture may then be heated to temperatures of about 100 to 500° F., e.g., 150 to 300° F., for about 10 minutes to 5 days, e.g., 1 to 24 hours. Although not essential, it has been found that the heating generally gives better results. If a lower temperature is used, then a longer time of heating is desirable. For example, it has been found that treatment at 300° F. for about ¼ hour is about equivalent to treating at 140° F. for about 48 hours.

The invention is further illustrated by the following examples which include preferred embodiments of the invention.

EXAMPLE 1

A series of tests were conducted using a base oil composition of 9.0 weight percent, based on the weight of the total composition, of a detergent additive concentrate in 91 weight percent of mineral lubricating oil (SAE 50 grade). The additive concentrate consisted of: (1) about 65% by weight of a mineral oil (lubricating viscosity) solution containing as the active ingredient about 35% by weight of a barium nonyl phenol sulfide having a sulfur to barium ratio (weight basis) of about 0.37 and (2) about 35% by weight of a mineral oil (lubricating viscosity) solution containing as the active ingredient about 35% by weight of calcium synthetic sulfonate made from sulfonation of alkylated benzene. This calcium sulfonate had a molecular weight ranging from 780 to 1120 and an average molecular weight of about 912. The above base composition was treated without heating with silicone alone and the polar material alone and then various combinations of the silicone oil plus the polar material. These various compositions were tested for foam tendency (cc. of foam after 5 minutes aeration) and foam stability (cc. of foam volume after 10 minutes' settling), according to the A.S.T.M. foam test, D–892–46T. The results of these tests are summarized in the following table wherein "FT" stands for foaming tendency and "FS" for foam stability and all weight percents are based on the weight of the dry additive.

Table I

Amount of Stabilizer (Based on Weight of Dry Additive)	Initial, FT/FS	2 Weeks' Storage, FT/FS
None	600/550	610/580
5.70% 1-octadecanol [1]	480/330	
11.40% 1-octadecanol	250/30	280/20
0.029% dimethyl silicone oil [2]	590/390	640/560
0.058% dimethyl silicone oil	440/280	580/560
5.70% 1-octadecanol and 0.029% dimethyl silicone oil	40/0	50/0

[1] Sold under the trade name "Lorol 28."
[2] Dow Corning 200 Fluid, 350 cs. (25° C.) grade.

As seen from the above data, using either the 1-octadecanol or silicone alone had little effect upon decreasing the foaming of the composition. However, when both the alcohol and silicone were used together the foaming tendency and foam stability were markedly improved.

EXAMPLE 2

A series of tests were run similar to that of Example 1, except that various other polar materials in varying percentages were added to the detergent-containing base oil, and a different grade of dimethyl silicone was used. In each case, after the addition of the polar material, the oil composition was then heated to 300° F. for 10 minutes, then cooled and tested. Results of these tests are summarized in the following table where the weight percentages are based on the weight of the dry detergent additive.

Table II

Run	Percent Polar Material Added to Base Oil [1]	Percent Silicone [2] Added to Base Oil	Foam Level	
			Initial, FT/FS	Stored (14 Days), FT/FS
	None	0.085	360/50	560/480
1	3.2% 1-Octadecanol (Lorol 28)	0.085	30/0	50/0
2	6.4% 1-Octadecanol (Lorol 28)	0.085	40/0	50/0
3	12.8% 1-Octadecanol (Lorol 28)	0.085	60/20	60/20
4	12.8% C_{13} Oxo Alcohol	0.085	240/10	320/10
5	12.8% C_{13} Oxo Alcohol	0.085	220/10	350/20
6	6.4% C_{10} Oxo Acid	0.085	180/0	280/5
7	6.4% C_9 Oxo Aldehyde	0.085	190/10	250/0
8	6.4% C_{12} Lorol Mercaptan	0.085	120/5	390/30

[1] Base oil was the same as used in Example 1, i.e., containing the 9 weight percent of detergent concentrate.
[2] Dow Corning Fluid 200, 1000 cs. (25° C).

As seen from Table II, the combination of the silicone and polar materials improved both the initial and stored foaming tendency and foam stability. The best improvement, however, was achieved by use of the longer chain octadecanol as compared to the shorter chain polar material. Runs 4 and 5 were duplicate runs to show the reproducibility of the results of the foaming tests.

EXAMPLE III

To further illustrate the invention, another series of tests were made similar to the manner of Example I, using stearic acid as the polar material, with and without heating. The results of these tests are summarized in Table III where all of said weight percents are based on the weight of dry additive.

Table III

Run	Percent Stearic Acid Added to Base Oil [1]	Percent Silicone [2] Added to Base Oil	Heated [3]	Foam Level (cc.)	
				Initial, FT/FS	7 days' Storage, FT/FS
1	0	0	No	640/600	670/630
2	0	0	Yes	580/520	530/480
3	0	0.085	No	490/410	540/470
4	0	0.170	No	450/350	500/440
5	0	0.085	Yes	320/230	430/320
6	0	0.170	Yes	230/110	240/120
7	11.5	0	No	600/520	690/630
8	23.0	0	No	580/510	690/650
9	11.5	0	Yes	450/350	520/440
10	23.0	0	Yes	490/390	500/430
11	11.5	0.085	No	70/0	230/50
12	11.5	0.085	Yes	0/0	0/0

[1] Base oil similar to that of Example I but of a different batch. The base oil consisted of 91 weight percent mineral oil and 9.0 weight percent of additive concentrate of barium nonyl phenol sulfide and calcium synthetic sulfonate.
[2] Dimethyl silicone—DC-200 fluid, 1000 cs. (25° C.) Grade.
[3] Heated for 15 minutes at 300° F., then cooled and tested for FT/FS

As seen from Table III, heating the base oil had only a slight effect on decreasing the foaming (see runs 1 and 2). The use of the silicone alone, with and without heating, resulted in a slightly further improvement (see runs 3 to 6). The use of the acid alone, both with and without heating, again showed only a slight improvement (runs 7 to 10). However, when both the acid and silicone (run 11) were added to the base oil a very pronounced reduction in the foaming level was obtained, and when this mixture was then heated (run 12), the foaming was completely eliminated.

In summary, the invention relates to the foam inhibition of oils containing additive materials by adding to said oils a mixture of a dimethyl silicon oil and a polar material of the general formula: RX, where R is an aliphatic hydrocarbon radical (e.g. an alkyl radical), and X is a radical such as —OH, —CHO, —COOH, —NH_2, and —SH, and which may or may not be followed by heating.

What is claimed is:

1. An improved mineral oil composition having a decreased foaming tendency consisting essentially of a major proportion of mineral oil and a minor amount of an oil-soluble detergent additive selected from the group consisting of metal sulfonates, metal alkyl phenol sulfides and mixtures thereof, about 0.001 to 1.000 gram of a dimethyl silicone polymer per 100 grams of dry additive and about 0.03 to 15 grams per 100 grams of dry additive of 1-octadecanol, said dimethyl silicone polymer having a viscosity at 25° C. in the range of 100 to 12,500 cs.

2. The mineral oil composition of claim 1 wherein the amount of silicone polymer used is about 0.01 to 0.20 gram per 100 grams of dry additive and the amount of 1-octadecanol used is about 0.5 to 15.0 grams per 100 grams of dry additive.

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