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2,813,077

PREVENTION OF FOAMING IN LUBRICANTS

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The present invention relates to the prevention of foaming in lubricants and particularly in mineral oil lubricating oil compositions and related compositions which contain detergent additives, or other materials, which tend to promote foaming and frothing upon agitation.

This application is a continuation-in-part of copending application Serial No. 240,032, filed August 2, 1951, now abandoned.

As is well known in the prior art, excessive foaming or frothing of lubricating oils and the like interferes seriously, under some conditions, with their proper functioning. Hydraulic oils and those which serve dual purposes of hydraulic fluids and lubricants, as well as ordinary lubricants, frequently tend to foam excessively under conditions of severe mechanical shear and turbulence. This is particularly true of oil compositions which contain detergent agents such as soaps, sulfonates, certain aliphatic esters, and the like.

During recent years it has been found desirable to incorporate in lubricating oils, hydraulic oils, and the like appreciable portions of metallo-organic detergents such as the metal salts of phenols, phenol sulfides, sulfonates, alcoholates, alkali and alkaline earth metal soaps of high molecular weight fatty acids, metal salts of esters of phosphorous and thiophosphorous acids, long chain aliphatic amines and amides, etc. These detergents have the disadvantage of building up considerable froth and foam in the liquid lubricant upon agitation. Such metallo-organic detergents include mixtures of calcium alkyl phenate and calcium cetyl phosphate, the reaction product of phosphorus pentasulfide and the barium salt of tert. octyl phenyl sulfide, oil concentrate blends of the reaction product of phosphorus pentasulfide and barium tert. octyl phenol sulfide with calcium sulfonate, oil concentrate blends of barium tert. octyl phenol sulfide with calcium sulfonate, etc. The prior art, as represented by the U. S. Patent No. 2,430,858 and U. S. Patent No. 2,570,719, recognized this foaming tendency of the conventional detergents and proposed the use of certain oxygenated organic compounds and specific types of silicones to inhibit foaming. Other materials have been used to some degree, but the prevention of foaming in lubricants appears to be a specific problem, the solution of which cannot be predicted on any general principles at this time.

According to the present invention it has been found that the additives themselves which are to be incorporated in the lubricating oils, hydraulic oils, fuel oils and the like, for detergent or analogous purposes, may be rendered substantially non-foaming by treatment with dihydro dihalo silanes of a specific type. Thus dichloro silane, H_2SiCl_2 which is a gas at ordinary temperatures, but is not appreciably soluble in mineral oils or in the usual detergent additives for mineral oils, may be dissolved in a chemically inert solvent which is miscible with the additive detergent or related material. Thereafter the inert solvent may be removed by blowing with nitrogen or other inert gas leaving the dihydro dichloro silane incorporated

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in the additive. Other dihalo silanes, especially dibromo silane, H_2SiBr_2 may be used in place of the dichloro silane but the latter is preferred for reasons of economy.

The proportions of dihydro dihalo silane to be incorporated in the additive may vary somewhat, but are preferably between the limits of 0.001 and 1% by weight, based on the treated additive. Specifically preferred proportions are from about 0.1 to 0.5% by weight of dihalo silane, based on the additive or from about 0.005 to about 0.025% by weight based on a lubricating oil containing substantial proportions of the detergent, or other foam promoting type additive.

The method of the present invention is particularly effective in reducing the foam-promoting tendencies of metal sulfonates, metal alkyl phenol sulfides, phosphosulfurized metal alkyl phenol sulfides and mixtures thereof. As previously noted, these particular compounds are well known to the art as detergent additives for lubricating oils, particularly mineral lubricating oils. They are generally employed in the form of alkaline earth metal salts, though the sulfonates are frequently employed in the form of alkali metal salts. The metal sulfonates and their preparation are described in detail in U. S. Patent No. 2,467,176; the metal alkyl phenol sulfides and their preparation are described in detail in U. S. Patent No. 2,362,289; and the phosphosulfurized metal alkyl phenol sulfides and their preparation are described in detail in U. S. Patent No. 2,451,345. Specific examples of these detergent additives include:

- Barium tert. octyl phenol sulfide
- Calcium tert. octyl phenol sulfide
- Barium-calcium tert. octyl phenol sulfide
- Barium tert. amyl phenol sulfide
- Calcium tert. amyl phenol sulfide
- Barium-calcium tert. amyl phenol sulfide
- Barium nonyl phenol sulfide
- Calcium nonyl phenol sulfide
- P_2S_5 treated barium tert. octyl phenol sulfide
- P_2S_5 treated calcium tert. amyl phenol sulfide
- P_2S_5 treated barium-calcium nonyl phenol sulfide
- 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

Mixtures of such metal sulfonates with alkyl phenol sulfides and/or phosphosulfurized metal alkyl phenol sulfides in proportions of 5 to 95% by wt., preferably about 10 to 50% by wt., of the metal sulfonate, are employed frequently in lubricating oil compositions.

Since it was known in the prior art that silicone and siloxane polymers, such as dimethyl silicone are active anti-foamants, it might be supposed that all compounds of this general type would be effective to reduce the foaming tendencies of oils containing foam promoting materials. This is not true, however, and it has been found that treatment of the additive with dimethyldichloro silane, the usual starting material for the preparation of dimethyl silicones which are highly effective per se, has no utility in the present process. Thus, a typical lubricating oil containing 5% by weight of a detergent additive that is normally a strong foam promoter was very satisfactorily inhibited against foaming by incorporating 0.01% of H_2SiCl_2 in the additive before placing the additive in the lubricating oil. This percentage was based upon the weight of the total finished oil composition. By contrast, a similar proportion of $(\text{CH}_3)_2\text{SiCl}_2$ placed in the same oil under the same conditions showed no foam reduction whatever.

The same experiments were repeated with different types of foam promoting detergent additives and in each case the dichloro silane was a highly effective foam inhibitor.

In each case the foam inhibitor is incorporated by mixing it with an organic solvent, ether being preferred, or chloroform, although other solvents such as carbon tetrachloride and analogous organic materials may be used. Upon evaporation of the solvent the silane is left finely dispersed if not actually dissolved in the foam promoting additive or in the vehicle which contains it. The data of the above tests are tabulated as follows: In the table "FT" and "FS," respectively, indicate foaming tendency and foam stability under the standard test conditions.

Detergent A was an additive concentrate consisting essentially of (1) about 62.5% by wt. of a mineral oil (lubricating viscosity) solution containing as the active ingredient about 40% by wt. of phosphosulfurized barium tert. octyl phenol sulfide and (2) about 37.5% by wt. of a mineral oil (lubricating viscosity) solution containing as the active ingredient about 30% by wt. of calcium petroleum sulfonate. The phosphosulfurized barium tert. octyl phenol sulfide was prepared by adding about four parts by weight of P_2S_5 to about 100 parts by weight of an oil solution containing about 40% by wt. of barium tert. octyl phenol sulfide at about 100° C. over a period of about 0.5 hour, soaking the reaction mixture for about two hours at about 150° C., blowing the reaction mixture at about 150° C. with N_2 for two hours, filtering, cooling the reaction mixture to about 60° C. and air blowing the reaction mixture for about eight hours. Detergent additive B was an additive concentrate consisting essentially of (1) about 62.5% by wt. of a mineral oil (lubricating viscosity) solution containing as the active ingredient about 40% by wt. of barium tert. octyl phenol sulfide and (2) about 37.5% by wt. of a mineral oil (lubricating viscosity) solution containing as the active ingredient about 30% by wt. of calcium petroleum sulfonate.

Table I

[Milliliters of foam—measured by ASTM Foam Test D892-46T.]

Blend	75° F.		200° F.		75° F. (After 200° F.)	
	FT	FS	FT	FS	FT	FS
SAE 30 Oil+5% Detergent A.....	470	425	110	0	485	430
SAE 30 Oil+5% Detergent A+ 0.01% H_2SiCl_2 ¹	20	0	45	0	30	0
SAE 30 Oil+5% Detergent A+ 0.01% Me_2SiCl_2 ¹	580	520	100	0	495	465
SAE 30 Oil+5% Detergent B.....	470	410	230	0	465	400
SAE 30 Oil+5% Detergent B+ 0.05% H_2SiCl_2 ²	10	0	150	0	20	0
SAE 30 Oil+5% Detergent B.....	500	350	280	0	485	325
SAE 30 Oil+5% Detergent B+ 0.05% H_2SiCl_2 ²	10	0	240	0	10	0

¹ Ether solution of silicon compound mixed with additive followed by N_2 blowing on steam bath.

² $CHCl_3$ solution of silicon compound mixed with additive followed by N_2 blowing on steam bath.

As indicated above it appears to be quite impossible to predict the potency of foam inhibitors. The present invention has resulted in the discovery of a method of treating additive containing lubricants which is quite distinct from the usual procedures of adding silicone polymers to the compounded oil.

It will be understood that the invention comprehends not only the process but also the oil compositions having foaming tendencies and containing the new type additive with or without conventional modifiers such as anti-

oxidants, thickeners, viscosity index improvers, pour point depressants, metal deactivators, corrosion inhibitors. These modifiers and like additives may be used in lubricating oils, hydraulic fluids, and hydrocarbon fuels in the usual proportions. In general, the invention is applicable to hydrocarbon oils and non-hydrocarbon oils, being especially applicable to hydrocarbon oils of viscosity ranging from that of kerosene up to the heavy, viscous lubricants of 1000 or more S. S. U. viscosity at 210° F.

What is claimed is:

1. The process for reducing the foaming tendency of hydrocarbon oil compositions containing a detergent additive comprising a mineral oil solution of calcium petroleum sulfonate and a sulfide taken from the group consisting of barium tertiary octyl phenol sulfide and phosphosulfurized barium tertiary octyl phenol sulfide, which comprises mixing said additive with a solution of about 0.001-1 wt. percent, based on the additive, of dihydro dichloro silane in an organic solvent, removing the solvent to leave a residue, and incorporating said residue into said hydrocarbon oil.

2. The process of claim 1 wherein the hydrocarbon oil has a viscosity between that of kerosene and 1000 S. S. U. viscosity at 210° F.

3. The process of claim 1 wherein the organic solvent is selected from the group consisting of ether, chloroform, and carbon tetrachloride.

4. The process of claim 2 wherein the amount of dihydro dichloro silane mixed with the additive is about 0.1-0.5 wt. percent, based on the additive.

5. The process for reducing the foaming tendency of hydrocarbon oil compositions containing a detergent additive consisting essentially of (1) about 62.5 wt. percent of a lubricating oil solution containing about 40 wt. percent phosphosulfurized barium tertiary octyl phenol sulfide and (2) about 37.5 wt. percent of a lubricating oil solution containing about 30 wt. percent calcium petroleum sulfonate, which comprises mixing said additive with a solution of about 0.001-1 wt. percent, based on the additive, of dihydro dichloro silane in an organic solvent, evaporating the organic solvent therefrom by blowing with an inert gas to leave a residue, and incorporating said residue into said hydrocarbon oil.

6. The process for reducing the foaming tendency of hydrocarbon oil compositions containing a detergent additive consisting essentially of (1) about 62.5 wt. percent of a lubricating oil solution containing about 40 wt. percent barium tertiary octyl phenol sulfide and (2) about 37.5 wt. percent of a lubricating oil solution of about 30 wt. percent calcium petroleum sulfonate, which comprises mixing said additive with a solution of about 0.001-1 wt. percent, based on the additive, of dihydro dichloro silane in an organic solvent, evaporating the organic solvent therefrom by blowing with an inert gas to leave a residue, and incorporating said residue into said hydrocarbon oil.

7. The lubricating oil composition produced according to the process of claim 1.

8. The lubricating oil composition produced according to the process of claim 5.

9. The lubricating oil composition produced according to the process of claim 6.

References Cited in the file of this patent

UNITED STATES PATENTS

2,426,121	Rust	Aug. 19, 1947
2,435,124	Bollinger	Jan. 27, 1948
2,761,845	Rogers	Sept. 4, 1956