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STABILIZATION OF SILICONE FLUIDS WITH AN IRON COMPOUND AND A POLYCARBOXYLIC ACID

Fritz A. Buehler, Erlton, N.J., assignor to Mobil Oil Corporation, a corporation of New York

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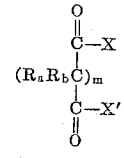
This invention relates to stable fluid compositions and more particularly to silicone fluid compositions capable of withstanding high temperatures.

Silicone fluids have achieved wide acceptance as lubricants and hydraulic fluids which function effectively under conditions requiring high-temperature stability. At elevated temperatures, for example in the range of about 350° to about 450° F., mineral oils or synthetic lubricants become unduly viscous or even deteriorate during extended use. Silicone fluids have been found to be a satisfactory substitute. More recently, however, with the advent of engines and other machinery operating at relatively higher temperatures than before even these silicones have shown evidence of failure. At temperatures of about 600° F. and above, silicone fluids tend to gel or solidify in so short a time that the useful life of lubricants prepared from these fluids has been undesirably decreased.

Hitherto, it has been attempted to improve the service life of silicone-based lubricants and hydraulic fluids by admixing therewith certain additives which prevent or at least delay gel formation. Of these additives, iron compounds, such as iron oxide, iron octoate, and iron salts of other carboxylic acids, as described in U.S. Patent No. 2,445,567, have been used with some success. Unfortunately, with the ever-increasing demand for functional lubricants and fluids to operate for long periods of time at such extreme temperatures, it has been found that the stabilization obtained from the use of these iron compounds alone is not always sufficient and further improvement in the stability of silicone fluids would be highly desirable.

The major object of the present invention is to provide silicone fluids having extended service life at high temperatures. A further object is to provide silicone fluids containing iron compounds having improved high temperature stability. These and other objects will become apparent from the following description.

It has now been discovered that the high temperature stability of silicone fluids may be improved by adding thereto a minor amount of an iron compound and an aliphatic polycarboxylic acid compound. The polycarboxylic acid compounds which may be employed in this invention have the formula



wherein R_a and R_b each may be hydrogen, hydroxy, carboxy, sulfhydryl, thio, amino, and alkyl, and they may be the same or different, X and X′ are either each hydroxy or together a single oxygen atom shared by the two carboxy-carbon atoms, and m is from 0 to 8.

The polycarboxylic acid compounds of this invention thus include the anhydride form, as well as the acid, and they may have three or more carboxyl groups. These acids or anhydrides may also contain an inner double bond, i.e. when m is 2 or greater.

The silicone fluids which are used in the practice of this invention are polysiloxanes having as its repeating unit the formula

$$R_nSiO_{4-n/2}$$

wherein n is in the range of from about 1.1 to about 2.9 and R is an alkyl or aryl radical, which terms cover cycloalkyl, alkaryl, and aralkyl. R also includes substituted radicals containing halogen, oxygen and nitrogen atoms attached thereto, such as halogenated hydrocarbon groups, ether groups, carboxylate groups, ester groups, and cyanoalkyl groups. In general, R contains from 1 to about 20 carbon atoms. Included in the above definition are methyl, propyl, pentyl, hexyl, decyl, and the like as examples of alkyl groups; cyclohexyl, cyclopentyl and the like as examples of cycloalkyl groups; and phenyl, naphthyl, benzyl, tolyl, xylyl and the like as examples of the various aromatic groups. Also included are mixed groups in which R may be both alkyl and aryl in the same molecule. Of special interest in this invention are polysiloxane fluids wherein the R group contains (1) alkyl radicals, (2) mixed alkyl and aryl radicals wherein the mol ratio of alkyl to aryl is in the range of 1 to about 15 or (3) mixed alkyl, aryl, and haloaryl radicals wherein the mol ratio of alkyl to the total aryl and haloaryl is from 1 to about 15, and the said haloaryl radicals contain from 1 to 5 halogen atoms each. Instead of the above groups being mixed in the same molecule, polysiloxanes containing one or more of the R groups of (1), (2) and (3) above in physical mixture are also within the scope of this invention.

The molecular weight of these silicone fluids vary depending upon the method of preparation and the reactants used in their preparation. Broadly, these fluids may possess molecular weights from about 200, and more frequently from about 500, to about 10,000.

Polysiloxanes of the type used in the present invention are well known to the art. Their preparation and purpose are disclosed in "Introduction to the Chemistry of the Silicones," E. G. Rochow, Second Edition (1951) John Wiley & Sons, New York, and "Organo Silicon as Compounds," C. Eaborne (1960), Academic Trust, New York.

These polysiloxane fluids (also termed silicone fluids for the purpose of this invention) contain, as a first additive stabilizer, an iron compound, such as iron oxide, and preferably the iron salts of organic acids. The organic acids used to prepare the iron compound stabilizers are carboxylic acids which may be saturated or unsaturated; aliphatic, cycloaliphatic or aromatic acids. Included in this category are acetic, propionic, butyric, 2-ethylhexanoic (octoic), benzoic, toluic, cyclohexanoic, and other iron salts disclosed in U.S. Patent No. 2,445,567. Of primary interest in this invention is iron octoate.

The second additive which provides the increased stabilization of the polysiloxane fluids as described above are polycarboxylic acids having the formula

$$HOOC(CR_aR_b)_mCOOH$$

wherein R_a and R_b each may be hydrogen, hydroxy, carboxy, sulfhydryl, thio, amino and alkyl, and mixtures thereof, and m is 0 to 8; and the anhydrides thereof. The preferred acids are the dicarboxylic acids, i.e. in which neither R_a nor R_b is a carboxy group, and which include oxalic, malonic, succinic, glutaric, adipic, pimelic, sebacic and azelaic. The acid may also be unsaturated, such as maleic anhydride. Other classes of acids include the hydroxy-substituted acids and tricarboxylic acids, such as malic, tartaric, and citric. Other substituents on the inner carbon atoms are sulfhydryl or thio radicals, amino radicals, as in cystine, and alkyl groups. The total number of carbon atoms contained in the polycarboxylic acids of this invention are in the range of from 2 to 20, and preferably from 2 to 10.

The amounts of the two stabilizers to be added to the silicone fluids of this invention are in minor proportion. The concentration of iron compound is in the range of about 0.001% to about 10% by weight. These iron compounds are so effective that as little as about 0.001% to

about 0.75% furnish significant results in extending the service life of these fluids. With regard to the polycarboxylic acid component, amounts ranging from about 0.05% to about 10% and preferably about 0.25% to about 5% by weight of the total composition are employed. While relatively ineffective by themselves to provide high temperature stabilization, when used in the presence of the iron compounds these acids so unexpectedly enhance the high temperature resistance of the silicone fluids as to evidence a synergistic response.

The following examples are intended to illustrate the instant invention without introducing limitations thereto.

EVALUATION OF SILICONE COMPOSITIONS

The high temperature stability of the silicone compositions of this invention is measured by subjecting the fluid composition to 600° F. temperature in the presence of air and by determining the time at which the composition "gels" or commences to turn solid. The test procedure is as follows:

A sample of the silicone fluid composition is added to a Pyrex beaker and is placed in an oven held at 600° F. under forced air circulation. The fluidity of the compositions is checked visually at regular intervals until the sample shows no gravity flow. The time elapsed from the beginning of the test to this point is denoted as the "gel time" of the sample.

The compositions in these examples may be prepared by any simple mixing means using any desired sequence of addition.

Example I

The silicone fluid used in this example is a methyl phenyl polysiloxane having a methyl to phenol mol ratio of 8.1, a molecular weight of about 3000 and a kinematic viscosity at 210° F. of 20 centistokes. To three portions of the silicone fluid were added varying quantities of oxalic acid, iron octoate and the two in a combined composition. The high temperature gel test was applied to the uninhibited silicon fluid and to the three compositions. The results are tabulated below in Table 1.

TABLE 1

Additive	Weight percent	Gel Time, Hrs.
1 None		15
2 Oxalic acid	1.0	15
3 Iron octoate	0.20	550
4 Oxalic acid	0.5	1,100
Iron octoate	0.20	

Example II

The silicone fluid of Example I was combined with 0.2% by weight of iron octoate (or about 0.017% by weight of iron). To samples of the resulting composition were added varying amounts of polycarboxylic acids as employed in the instant invention. The high temperature stability test was applied to these compositions with the following resuls tabulated in Table II. In this table, columns headed "R_a, R_b" and "*m*" refer to the above-mentioned formula.

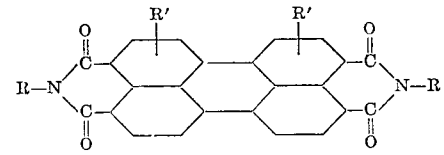
TABLE II

Polycarboxylic Additive	Weight Percent	m	R_a, R_b	Gel Time, Hours
None	0			550
Succinic Acid	1.5	2	H_4	800
	1.0	2	H_4	1,045
Maleic Anhydride	0.5	2	H_2	1,400
Malic Acid	1.0	2	H_3, OH	1,300
Glutaric Acid	1.0	3	H_6	990
Citric Acid	1.0	3	H_4, OH, COOH	1,155
Adipic Acid	0.5	4	H_8	1,100

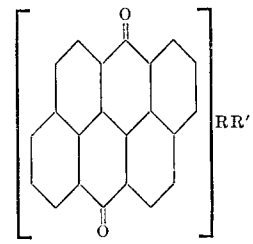
It will be noted from the results of the gel test in the above examples that the polycarboxylic acids, when used in combination with iron containing stabilizers, are surprisingly effective in improving the high temperature stability of silicone fluids. Alone, however, these acids appear to have no effect on stability whatever.

The stabilized silicone compositions of this invention may be employed as lubricants, whether alone or in admixture with petroleum oils or synthetic oils, and as hydraulic fluids in many industrial applications. The silicone fluid compositions of this invention may also contain other known additives including detergents, rust inhibitors, viscosity improving agents, and extreme pressure agents.

These fluids may also be thickened into lubricating greases by the addition of known pigment thickeners. Chief among these are the perylimids which have the structure



wherein R and R′ may be hydrogen, alkyl, aryl, alkaryl, and halogen derivatives thereof, and may be alike or different. Another suitable thickener are the anthanthrones:



wherein R and R′ are the same or different, being halogen, alkyl, aryl, alkoxy, and halogen derivatives thereof. Also suitable are azoles, naphthalic imidazoles. Milori blues (ferrocyanides), indanthrene blue pigment or vat dye, polyaryl ureas, ammeline and hydrophobic clays. One or several of these thickeners may be used together and they may represent about 5% to 75% by weight, and preferably about 15% to 30%, of the total composition. The remainder of the grease composition is the silicone and sulfur-containing substance of this invention.

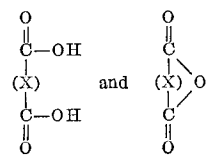
The present invention has been described and illustrated by reference to certain specific examples without intending to limit the invention in any way thereto; and modifications may be employed without departing from the scope of this invention thereby, except as indicated in the following claims.

I claim:

1. A high temperature stabilized fluid composition comprising a major proportion of a polysiloxane fluid having the unit formula:

$$R_nSiO_{4-n/2}$$

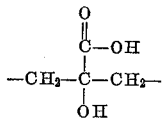
wherein *n* has a value from about 1.1 to about 2.9 and R represents an organyl radical selected from the group consisting of alkyl, cycloalkyl, aralkyl, aryl, and alkaryl, and a minor proportion sufficient to stabilize said fluid of (1) an iron compound selected from the group consisting of iron oxide and iron salts of carboxylic acids and (2) a polycarboxylic acid compound having a formula selected from the group consisting of



and the group (X) is selected from the group consisting of $-(CH_2)_m-$ wherein m is from 0 to 8;

$$-CH(OH)-CH_2-;\ -CH=CH-$$

and



2. The fluid composition of claim 1 wherein the said dicarboxylic acid is selected from the group consisting of oxalic, succinic, glutaric and adipic.

3. The fluid composition of claim 1 wherein the polycarboxylic acid is citric acid.

4. The fluid composition of claim 1 wherein the said acid is malic acid.

5. The fluid composition of claim 1 wherein the said acid is maleic anhydride.

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DANIEL E. WYMAN, *Primary Examiner.*

W. H. CANNON, *Assistant Examiner.*