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[54] **LUBRICATING GREASE COMPOSITION**

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[58] **Field of Search**. 252/28, 37.2, 40.7, 42.1, 49.6, 252/54, 58, 389, 396, 388; 117/132 CF

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[57] **ABSTRACT**

A highly corrosion resistant lubricating grease cmposition comprising a lubricating oil thickened with a gelling agent wherein the lubricating oil is prepared by intimately admixing a synthetic halogen containing polymeric lubricating oil and a fluorocarbon resin, freezing the mixture and thawing the frozen product.

14 Claims, No Drawings

LUBRICATING GREASE COMPOSITION

BACKGROUND OF INVENTION

The present invention relates to a synthetic lubricating grease composition.

The employment of greases as lubricants in special applications where design simplicity, less need for maintenance and decreased realing requirements preclude the use of oils is well known. Recently, however, there has been an increasing demand for greases which are capable of application in high temperature environments, i.e., aircraft, military equipment, rocketry, etc. The greases based on petroleum oil compositions are entirely unsuitable in these areas because of their relatively low heat resistances.

As a result many grease compositions based on synthetic oils have been suggested for use in high temperature environments. For example, it has been suggested to employ certain polyesters as bases for high temperature greases. Thus, di(2-ethylhexyl) sebacate and other polyester oils have been employed to formulate such greases. These polyester based greases are only effective, however, at temperatures up to about 300°–350°F.

The so-called silicone greases have been suggested for use at higher temperatures. Although the silicones resist temperatures up to as high as 450°F., their lubricity is relatively poor for gears, actuators and other sliding devices. Attempts to overcome this disadvantage by blending the silicones with polyesters have met with only limited success.

It has also been suggested to employ thickened alkyl biphenyl and polyphenyl ester oils as greases; however, they have only a limited range of uses.

Most recently it has been proposed to formulate high temperature greases from poly- and per-halogenated polymer oils. Greases based upon these oils have an extremely high resistance to elevated temperatures and evidence excellent lubricity properties. A serious disadvantage associated with these greases, however, is that it is extremely difficult to avoid corrosion of the metal parts which come in contact with the grease in the presence of moisture. Metals which are corroded in the presence of these greases include steels, copper and aluminum. The halogenated greases are particularly disadvantageous when employed in systems constructed of aluminum. Such greases commonly detonate when in contact with aluminum at high temperatures under conditions of shear.

Heretofore it has been suggested to improve the corrosion properties of the poly-halogenated greases by in-corporating various anti-corrosion agents therein. For example, such anti-corrosion agents as amine salts, metal sulfonate and naphthenates, esters, sodium nitrite, and non-ionic surfactants have been employed to avoid water and salt spray corrosion.

The use of these anti-corrosion agents has more or less met with failure, however, due in part to a prior lack of understanding as to the reasons for the great susceptibility of metals to corrosion in the presence of polyhalogenated oils. Indeed, it has recently been found that these oils actually promote or catalyze the corrosion of metals in the presence of moisture. The dilemma facing the prior art in solving the problem has reached such proportions that efforts to avoid corrosion have taken the form of attempts to completely exclude moisture from the environments wherein these greases are utilized. As will be apparent to those skilled in the art, systems contemplating the complete avoidance of moisture would entail the use of very elaborate and expensive controls. Indeed, it would defeat the very advantages associated with the use of greases, namely, design simplicity, decreased sealing requirements, maintenance reductions, etc.

An additional disadvantage associated with the use of anti-corrosion agents in these types of greases is that these materials very often tend to inhibit or deleteriously affect the lubricating action of the greases. Indeed, in some instances, these agents actually promote the decomposition of the polyhalogenated polymers making up the greases.

Finally, the use of anti-corrosion agents increases the expense involved in formulating high-temperature greases.

It is an object of the present invention to provide lubricating grease compositions based on polyhalogenated polymeric oils which avoid and substantially completely inhibit the corrosion of metals with which it comes in contact in the presence of moisture.

It is a further object of the invention to provide a lubricating grease composition based on polyhalogenated polymeric oils which is anti-corrosive in the absence of added anti-corrosion agents.

It is still a further object of the invention to provide a lubricating grease composition based on polyhalogenated polymeric oils which is anti-corrosive without the necessity for excluding the presence of moisture from systems wherein they are employed.

SUMMARY OF THE INVENTION

These and other objects of the invention are realized by the provision of a new lubricating grease composition containing a polyhalogenated polymeric oil prepared according to the hereinafter-described process.

I have found that a lubricating oil which remarkably resists the corrosion of metals with which it comes in contact in the presence of moisture is produced by:

1. intimately admixing a halogenated polymeric oil with a fluorocarbon resin
2. freezing the resulting mixture to a solid state, and
3. thawing the frozen mixture to produce the anti-corrosive lubricating oil composition.

DETAILED DESCRIPTION OF THE INVENTION

The invention is predicated on the discovery that a new and highly anti-corrosive synthetic grease may be formulated from a halogenated polymeric oil prepared from ingredients which are themselves relatively highly corrosive to metals in the presence of moisture by the afore-described method involving intimate admixture, freezing and thawing.

I am unaware of the mechanism by which this method imparts anti-corrosive properties to the oil composition. Nor am I aware of the physical or chemical changes which take place in the ingredients of the oil composition to render the latter anti-corrosive. It has been found, however, that the oil and fluorocarbon resin admixture must be subjected to only one freeze and thaw cycle. If the thawed composition is again frozen and thawed, whatever corrosion resistant properties were imparted to the composition by the first cycle

of freezing and thawing are lost. Care should be taken therefore to avoid refreezing the composition after thawing.

It is critical to the practice of the invention that the steps of the above method be carried out in the exact order set forth. The composition produced by merely admixing the oil and resin ingredients without freezing is not anti-corrosive. Moreover, merely freezing the various ingredients without having first intimately admixed them produces no change in the anti-corrosive characteristics thereof. Furthermore, the oil and resin must be intimately admixed prior to freezing. Freezing and thawing the ingredients separately and then admixing them does not render the mixture anti-corrosive.

Any of the well-known synthetic halogen containing polymeric oils may be utilized in the practice of the invention. These oils are well known in the art and generally, although not necessarily, comprise fluorinated synthetic polymers having a degree of polymerization sufficient to impart a relatively high viscosity to the resulting liquid. Although the oils most commonly employed comprise fluorinated polymers, it is to be understood that the invention is applicable to any synthetic polymeric oil containing fluorine, chlorine, bromine, iodine or mixtures thereof. Typical among these are the poly-halogenated vinyl halides, poly-halogenatedethylenes, poly-halogenated silicones, poly-halogenated ethers, etc. Exemplary of these oils are trifluorovinyl chloride polymers, chlorotrifluoroethylene polymers, trifluoroproplymethylpolysilicones, perfluoroalkylpolyethers, etc. It is to be understood that the foregoing examples of suitable oils are not limitative of the scope of the invention. Any synthetic halogenated lubricating oil composition may be rendered substantially non-corrosive to metals in the presence of moisture according to the present invention. Obviously, the selection of a particular oil will depend upon the application intended or the system in which it is to be employed.

The above-described synthetic halogenated oils are well known and may be prepared according to methods similarly well known in the prior art. For example, the chlorotrifluoroethylene polymeric oils may be prepared by separating into fractions of oils, greases and waxes the products of the polymerization of chlorotrifluoroethylene and then pyrolyzing the products to produce a halocarbon oil of low boiling range having a relatively high viscosity and a molecular weight lower than the original polymeric product. The oil, grease and wax fractions may be pyrolyzed singly or in combination. The halogenated polyvinyl, silicone, polyether, etc., oils may also be prepared according to methods well known in the prior art.

I have found that the invention is applicable only to the employment of a fluorocarbon resin. As previously stated, the reasons for the unique susceptibility of only this type of material for aiding in the improvement of the anticorrosive nature of the aforedescribed oils are at present unknown. Suffice it to state that numerous different types of materials have been tested and found unsuitable.

The fluorocarbon resin is most preferably reduced to a finely divided state and suspended in a liquid, e.g., a silicone oil, compatible with the halogenated oil with which it is to be mixed to form a grease-like product. The preferred fluorocarbon resin is polytetrafluoroethylene. A product manufactured under the name Dixon 164 by the Dixon Corporation, Bristol, Rhode Island has been found to be particularly useful.

The highly anti-corrosive properties are imparted to the oil composition by ultimately admixing from about 3.0 percent to about 5.0 percent, preferably about 4.0 percent, by weight, of the fluorocarbon grease with the oil, freezing the admixture to a solid state, and thawing the frozen mixture. It is to be understood, however, that the addition of any amount of the fluorocarbon resin in accordance with the practice of the invention will result in imparting at least a degree of anti-corrosiveness to the oil.

Any conventional apparatus may be employed for admixing the oil and grease; it being necessary only that an intimate admixture of the two ingredients be obtained. If desired, conventional emulsifying agents may be added to the ingredients to facilitate mixing.

The intimate admixture is then frozen to the solid state. This may be accomplished according to any well known freezing method. The most convenient and practical method is to place the mixture in a suitable container which is resistant to low temperatures and immerse the container in a cyrogenic fluid such as liquid nitrogen, argon, neon, oxygen, etc. It is to be understood, however, that any system capable of producing temperatures sufficiently low to freeze the oil-resin admixture may be employed to achieve freezing. It is necessary only that the mixture be frozen to a substantially completely solid state.

Following freezing, the mixture is thawed and formulated into the grease composition. Prior to preparing the grease, however, the pH of the mixture should be adjusted to a minimum value of about 5.1.

The lubricating greases of the invention may be prepared by thickening the above-described anti-corrosive oil with any suitable gelling agent.

Finely divided silica is the preferred gelling or thickening agent. It is to be understood, however, that any conventional thickening agent may be employed.

Exemplary of the gelling agents suitable for use in formulating the greases of the invention are the fatty acid soaps of lithium, calcium, sodium, aluminum, barium, etc. Suitable fatty acids include oleic, palmitic, stearic and carboxylic acids derived from tallow, hydrogenated fish oil, castor oil, wool grease, rosin, etc. Additional gelling agents which may be utilized are the finely divided bentonite and hectorite clays which have been surface modified with organic materials such as quaternary ammonium compounds and carbon black.

The greases of the invention may be prepared according to any of the well known methods for formulating grease compositions. In addition, any of the well known additives conventionally employed in grease compositions may be included.

The amount of gelling agent employed is not critical and will depend upon the intended use of the grease. When employing the preferred gelling agent, i.e., finely divided silica it has been found that the presence of 5 wt. percent of silica in the oil yields a grease having an NLGI (National Lubrication Grease Institute) value, at room temperature, of approximately 0. The presence of 10 wt. percent silica yields an approximate NLGI value of 1. By increasing the amount of silica in increments of 5 wt. percent, the NLGI value is increased by approximately 1 with each addition.

Thus, it will be apparent that a grease having any desired consistency may be prepared by varying the amount of gelling agent over a wide range. Generally, amounts of gelling agent above 25 wt. percent, dependent upon the nature of the gelling agent, yield solidifed products having limited utility as greases.

Any mixing apparatus may be employed to admix the oil and gelling agent. It is only necessary to achieve an intimate and homogenous admixture between the oil and gelling agent in order to provide a suitable grease composition.

The invention will be further illustrated by reference to the following non-limiting specific examples wherein all parts are by weight:

EXAMPLE 1

229 g of a polychlorotrifluoroethylene oil having a pour point of −50°C., a viscosity at 100°F. of 34, and initial boiling point of 500°F. and a cloud point of 18°F. were added along with 9.16 g of a polytetrafluoroethylene resin suspension (Dixon 164 - Dixon Corporation, Bristol, Rhode Island) to a commercial household type "blender". The mixture was agitated at a blender speed of 19,000 RPM until the components were completely and intimately admixed. The admixture was then poured into a container and covered with a securely fitting cap. The container was completely immersed in liquid nitrogen contained in a DeWar vessel for 1½ hours until frozen solid.

The container was removed from the liquid nitrogen and allowed to thaw undisturbed at room temperature. After thawing, the contents of the container were poured into a homogenizer and homogenized. The homogenized mixture was returned to the blender and 0.24 g of linear aural sulfate detergent and 1.2 g of polyisobutylene wetting agent added thereto. The contents were blended for several minutes to ensure complete mixing of the ingredients. The mixture was found to have an average pH of 6.7

A sufficient amount of fumed silica (Cabosil ST-1, Cabot Co., Boston, Mass.) was added to one pint of the above oil in a stainless steel vessel to yield a product containing 10 wt. percent of silica. The mixture was thoroughly hand-stirred with a stainless-steel rod until the silica was completely and intimately admixed with the oil. The resultant grease was found to have an NLGI value of approximately 1.

The grease was employed to lubricate an operating valve in a hot water line (198°–200°F). The bronze valve was found to be non-corroded after extended use. In addition, the grease remained unaffected during operation of the valve.

EXAMPLE 2

40.2 g of a polytrifluorovinyl chloride oil having a pour point of −40°C., a viscosity of 100°F. of 35 and initial boiling point of 100°C. and 1.6 g. of a polytetrafluorethylene suspension (Dixon 164) were admixed and processed according to the procedure set forth in Example 1.

A sufficient amount of fumed silica (Cabosil ST-1) was added to one pint of the oil to produce a mixture containing 15 wt. percent of silica. The mixture was thoroughly admixed as in example 1 to provide a grease having an NLGI value of approximately 2.

The grease was applied to separate carbon steel and stainless-steel surfaces and subjected to an atmosphere of hydrogen sulfide for 100 hours. The metal surfaces remained non-corroded.

EXAMPLE 3

220 g of trifluoropropylmethylpolysilicone oil having a viscosity of 100°F. of 25 and an initial boiling point of 400°F. and 8.8 g of a polytetrafluoroethylene suspension (Dixon 164) were admixed and processed according to the procedure set forth in Example 1.

A sufficient amount of fumed silica (Cabosil ST-1) was added to one pint of the oil to produce a mixture containing 20 wt. percent of silica. The mixture was thoroughly admixed as in Example 1 to yield a very viscous grease having an NLGI value of approximately 3.

The grease was cut with 50 wt. percent of Freon and applied to the steel chain linkage of a sprocket type, chain-driven drying kiln with a brush. After evaporation of the freon, the kiln was operated continuously for three days. Despite exposure to high temperatures and excess moisture, the grease provided a high degree of lubricity while protecting the metal surfaces from corrosion.

EXAMPLE 4

105 g of a perfluoroalkylpolyether oil having a pour point of −55°C., a viscosity of 100°F. of 36 and an initial boiling point of 550°F. and having 4.2 g of a polytetrafluoroethylene suspension (Dixon 164) were admixed and processed as in Example 1.

A sufficient amount of fumed silica (Cabosil ST-1) was added to one pint of the oil to produce a mixture containing 25 wt. percent of silica. The mixture was thoroughly admixed as in Example 1 to yield a very viscous grease having an NLGI value of slightly less than 4.

In the foregoing examples, Dixon 164 is a 60 percent suspension of polytetrafluoroethylene in a silicone oil.

The greases of the present invention have a variety of applications, particularly in those areas wherein the metalic parts contacted by the oils are highly susceptible to corrosion. Exemplary of such systems are those reactive with conventionally employed petroleum hydrocarbon greases; systems for processing liquid oxygen, hydrogen and other highly reactive materials; flotation and damping equipment; valves and stopcocks; high pressure systems; heavy duty gear boxes, transmissions; pumping equipment; stationary and mobile hydraulic systems such as those utilized on ships and planes, etc.

The grease is particularly suited for use in aluminum component containing systems which normally cause the detonation of conventional lubricants under conditions of high shear. The greases of the present invention, on the other hand, are highly resistant to detonation in the presence of aluminum under shear. Accordingly, they find particular application in the aircraft industry wherein high temperature and corrosion resistant greases are constantly in demand for use with aluminum containing components and systems.

I claim:

1. A corrosion resistant lubricating grease composition comprising a lubricating oil thickened with a gelling agent wherein said oil is prepared by intimately admixing effective amounts of a synthetic halogen containing polymeric lubricating oil and a fluorocarbon

resin, freezing said mixture to a solid state and thawing said frozen mixture.

2. The composition of claim **1** wherein said halogen is selected from the group consisting of chlorine, fluorine, bromine, iodine and mixtures thereof.

3. The composition of claim **2** wherein said halogen is fluorine.

4. The composition of claim **2** wherein said oil is a polychlorotrifluoroethylene.

5. The composition of claim **2** wherein said oil is a polytrifluorovinyl chloride.

6. The composition of claim **2** wherein said oil is a trifluoropropylmethyl polysilicone.

7. The composition of claim **2** wherein said oil is a perfluoroalkylpolyether.

8. The composition of claim **1** wherein said fluorocarbon resin is polytetrafluoroethylene.

9. The composition of claim **8** wherein said polytetrafluoroethylene is in the form of a suspension thereof in a liquid silicone miscible with and inert with respect to said oil.

10. The composition of claim **1** wherein said gelling agent is a fatty acid metal soap.

11. The composition of claim **10** wherein said metal is selected from the group consisting of lithium, calcium, barium and aluminum.

12. The composition of claim **1** wherein said gelling agent is selected from the group consisting of organic agent surface modified, finely divided bentonite and hectorite clays.

13. The composition of claim **1** wherein said gelling agent is finely divided silica.

14. The composition of claim **1** wherein said grease contains up to about 25 wt. percent of gelling agent.

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