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WATER- AND CORROSION-RESISTANT LUBRICATING GREASES GELLED WITH INORGANIC COLLOIDS

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This invention relates to improved grease compositions. More particularly, it is concerned with greases gelled with inorganic colloids and improved with respect to water resistance and corrosion protection by the presence of certain haloepoxides.

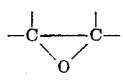
Lubricating greases contain a lubricating oil base and a gelling agent. The gelling agent is usually a soap of a fatty acid or a hydroxy fatty acid. Soaps are subject to phase changes as the temperature increases, so that soap-gelled lubricating greases soften at elevated temperature and finally become liquid.

Inorganic colloids have already been used as gelling agents in lubricating greases. Lubricating greases containing such gelling agents are able to retain their consistency over a far wider temperature range.

Lubricating greases containing an inorganic gelling agent generaly have, however, a poor resistance to disintegration by the action of water. In order to improve such lubricating greases in this respect surface-active agents, such as long chain amines, amides, ammonium salts and salts of higher fatty acids, have already been incorporated therein.

It has now been found that aliphatic compounds containing a halogen atom and an epoxy-oxygen atom (e. g. haloepoxyalkanes), are effective to improve the water resistance of lubricating greases containing an inorganic gelling agent. The said aliphatic compounds have the additional advantage of improving the corrosion properties of lubricating greases at the same time; this is particularly the case when the greases are applied to highly sensitive steel surfaces.

The expression "epoxy-oxygen atom" means an oxygen atom which is present in a radical of the following formula:



Accordingly, the present invention provides a lubricating grease comprising a hydrocarbon lubricating oil base, thickened to a lubricating grease consistency by means of a normally hydrophilic inorganic gelling agent, and a minor proportion of an aliphatic compound containing a halogen atom and an epoxy-oxygen atom. The preferred class comprises those compounds containing 3–10 carbon atoms per molecule, of which the chloroepoxyalkanes have the most satisfactory effect.

Examples of suitable halo-epoxy aliphatic compounds are:

1,2-epoxy-3-chloropropane (epichlorohydrin)
2,3-epoxy-4-chlorobutane
1,2-epoxy-3-isopropyl-3-iodopropane
1,2-epoxy-4-chlorobutane
1,2-epoxy-5-chloropentane
1,2-epoxy-3-methyl-3-chloropropane
1,2-epoxy-3,3-dimethyl-3-chloropropane
1,2-epoxy-2-methyl-3-bromopropane
2,3-epoxy-4-methyl-1-chlorohexane
1,2-epoxy-4-methyl-5-bromopentane

These compounds are added to the lubricating greases in minor proportions. The proportion used depends, among other things, on the desired improvement of water resistance and the amount of hydrophilic inorganic gelling agent present in the grease. Generally the proportion of the aliphatic compound lies between 0.01 and 3% by weight, based on the whole lubricating grease. In many cases a proportion of from 0.05 to 0.5% by weight (0.25%–25% by weight of the gelling agent), and particularly of approximately 0.1% by weight, imparts satisfactory properties to the lubricating greases.

Although the said compounds improve the corrosion properties of the lubricating greases, a further improvement of these properties is generally obtained by adding a further anti-corrosion agent. The preferred anti-corrosion agents for this purpose are the aliphatic polycarboxylic acids containing one or more alkyl or alkenyl groups with at least 3 carbon atoms, and the corresponding thio acids, as well as the amides, anhydrides and esters of these acids. Examples of suitable acids are the malonic, succinic, glutaric, adipic, pimelic, sebacic, azelaic, tartaric, citric, maleic and citraconic acids which are substituted by alkyl or alkenyl groups of the type mentioned above, particularly those containing 10 to 18 carbon atoms. Examples of suitable amides and esters are the mono-amides of alkyl-substituted succinic acids, the mono-oleyl esters of alkenyl-substituted succinic acids and the mono-octyl esters of alkyl-substituted sebacic acids. Dimerized unsaturated fatty acids also are suitable corrosion inhibitors for use in these compositions.

When additional anti-corrosion additives are used these are employed in minor proportions, suitably in proportions of from 0.01 to 3% by weight, and particularly from 0.05 to 1% by weight, based on the whole lubricating grease.

A mineral lubricating oil is generally used as the hydrocarbon lubricating oil base. The mineral lubricating oils used may be of any origin and their properties may vary within wide limits. The viscosity generally lies within a range of 1° to 50° E. at 50° C. and the viscosity index between 0 and 80, but oils with a viscosity and a viscosity index outside these limits may also be used. While hydrocarbon oils are preferred as the grease base, other non-ester oleaginous fluids such as silicones and halocarbons (e. g. dimethyl silicone or hexachlorobutadiene) may be utilized.

Suitable gelling agents are the known normally hydrophilic inorganic gelling agents. Colloidal inorganic oxides, hydroxides, sulfides, sulfates, silicates and carbonates, such as silica, alumina, magnesia, calcium oxide, copper sulfide, calcium sulfate and mixtures thereof, par-

ticularly mixtures of silica with magnesia, as well as synthetic zeolites, and natural clays, such as hectorite and bentonite, may be used. The gelling agent is used in a proportion sufficient to thicken the lubricating oil base to the desired lubricating grease consistency. The proportion of the gelling agent generally lies between 2 and 20% by weight based on the whole lubricating grease.

If desired, minor proportions, e. g. 0.01 to 5% by weight, based on the whole lubricating grease, of other additives may be incorporated in the lubricating greases in order to improve specific properties. As such may be mentioned, for example, anti-oxidants, especially phenolic anti-oxidants, such as alkyl phenols, e. g. 2,6-di-tert.-butyl-4-methyl phenol, and amines, such as phenyl-α-naphthylamine, extreme pressure agents such as sulfur, lead naphthenate and sulfurized and/or chlorinated fats or fatty oils and tackiness agents, such as rubber and poly-isobutylene.

The lubricating greases may be prepared by any one of the known methods. For instance, a volatile silicon compound, such as silicon tetrachloride, may be burnt in the vapor phase, thus forming a colloidal silica which may be dispersed in the lubricating oil base in any desired way, e. g. by milling. It is also possible to start from a hydrogel and expel the water therefrom by means of a low-boiling organic liquid, such as methyl or ethyl alcohol or acetone, after which the gel is heated to above the critical temperature of the liquid and the latter is evaporated. The resultant so-called aeorgel is then dispersed in the lubricating oil base. It is also possible to expel the water present in a hydrogel by a water- and oil-miscible liquid, and then again expel the liquid by means of the lubricating oil base. In most cases, more than one organic liquid is used. The water is first expelled, for example, by means of alcohol or acetone, this liquid being expelled by means of the lubricating oil base. The additives desired in the lubricating grease can be incorporated in the lubricating grease mixture at any stage of these processes, provided of course, that such a stage is not chosen that the additives are washed away or destroyed during the further course of the process.

The following example illustrates the benefits of this invention.

Three lubricating greases were prepared having the following compositions:

A. 91% by weight of mineral oil
   9% by weight of silica
B. 90.9% by weight of mineral oil
   9% by weight of silica
   0.1% by weight of epichlorohydrin
C. 90.8% by weight of mineral oil
   9% by weight of silica
   0.1% by weight of epichlorohydrin
   0.1% by weight of octadecenyl succinic acid

The mineral oil was a lubricating oil with a viscosity of 19° Engler at 50° C. obtained by distillation and extraction of a Venezuelan crude oil.

The silica was a colloidal silica obtained by burning in air hydrogen saturated with silicon tetrachloride.

In order to prepare the lubricating greases, the oil was gradually poured on to the silica, while constantly stirring. In preparing the lubricating greases B and C, the epichlorohydrin and the anti-corrosion agent were previously dissolved in the oil. The mixture thus obtained was twice passed through a roll mill.

The penetration, water resistance and corrosion properties of the lubricating greases were determined.

The penetration was determined according to the A. S. T. M. Method D217–48 (so-called "worked penetration").

The water resistance of the lubricating greases was tested in the so-called "glass strip test." In this test a layer of grease 100 millimeters long, 10 millimeters wide and 1 millimeter thick is laid on a glass strip 160 millimeters long and 15 millimeters wide. The glass strip is placed in a narrow, high beaker filled with 100 cubic centimeters of distilled water. A part of the layer of grease should extend above the water so that the degree of change of the grease may be better assessed. The strip is allowed to stand in the water for 48 hours at 20° C. After this period it is determined how far the water has become turbid and the grease has emulsified or decomposed.

In order to test the corrosion properties the lubricating greases were applied in a thin layer on steel plates. A quantity of 2 grams of the grease to be tested was placed on the plates and then uniformly distributed over the whole plate by rubbing in at moderate pressure with a pad (twisted rag) which had been previously soaked in the same grease. The plates were then placed in a glass cupboard for four weeks at 40° C., in an atmosphere with a relative humidity of 100%, in such a way as to be protected from water condensing on the glass walls and running or trickling down. After this period the corrosion of the plates is assessed.

The results of the tests are summarized in the following table:

Lubricating grease	Penetration	Resistance to water	Corrosion of the plates
A	205	poor [a]	weak to medium weak.
B	207	good [b]	very weak.
C	210	good [b]	traces.

[a] The grease decomposed completely.
[b] The grease did not decompose at all; it only showed a very slight tendency to emulsify; the water was still clear.

The unexpected improvement in water resistance of the compositions, caused by the addition of such small quantities of low molecular weight materials (e. g. epichlorohydrin) indicates the possibility that reaction may have occurred between the additive and the gel surface, or that the gel may have catalyzed the polymerization of the additive to form poly(alkylene oxide) coatings having hydrophobic haloalkyl (chloromethyl) substituents. The remaining possibility comprises simple adsorption of the additive on the gel surfaces.

We claim as our invention:

1. A grease composition consisting essentially of a hydrocarbon lubricating oil, a grease-forming proportion of an inorganic hydrophilic colloidal gelling agent of the group consisting of inorganic oxides, hydroxides, sulfides, sulfates, silicates and carbonates, and from about 0.01% to about 3% by weight of an aliphatic compound having 3–10 carbon atoms per molecule and containing a halogen atom and an epoxy-oxygen atom, the amount of said compound being sufficient to improve the water resistant characteristic of the grease.

2. A grease composition consisting essentially of a mineral lubricating oil, a grease-forming proportion of an inorganic hydrophilic colloidal amorphous silica gelling agent, and from about 0.01% to about 3% by weight of a monohaloepoxyalkane having 3–10 carbon atoms per molecule, the amount of said alkane being sufficient to improve the water resistant characteristic of the grease.

3. A grease composition consisting essentially of a mineral lubricating oil, a grease-forming proportion of an inorganic hydrophilic colloidal clay gelling agent and from about 0.05% to about 1% by weight of a monochloroepoxyalkane having 3–10 carbon atoms per molecule, the amount of said alkane being sufficient to improve the water resistant characteristic of the grease.

4. A grease composition consisting essentially of a mineral lubricating oil, a grease-forming proportion of an inorganic hydrophilic colloidal amorphous silica gelling agent, 0.05% to about 1% by weight of a monochloroepoxyalkane having 3–10 carbon atoms per molecule, the amount of said alkane being sufficient to improve the water resistant characteristic of the grease.

5. A grease composition consisting essentially of a mineral lubricating oil, a grease-forming proportion of an inorganic hydrophilic colloidal silica gelling agent and from about 0.05% to about 1% by weight of a monochloroepoxyalkane having 3–10 carbon atoms per molecule, the amount of said alkane being sufficient to improve the water resistant characteristic of the grease.

6. A grease composition consisting essentially of a mineral lubricating oil, a grease-forming proportion of an inorganic hydrophilic colloidal silica gel and from about 0.05% to about 1% by weight of epichlorohydrin.

7. A grease composition consisting essentially of a major proportion of a mineral lubricating oil and a grease-forming proportion of an inorganic hydrophilic colloidal gelling agent of the group consisting of inorganic oxides, hydroxides, sulfides, sulfates, silicates and carbonates, rendered water-resistant by the addition of 0.01–3% by weight of a haloepoxyalkane having 3–10 carbon atoms per molecule.

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