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LUBRICATING GREASES CONTAINING ETHYLENE-PROPYLENE COPOLYMER OR HALOGENATED ETHYLENE-PROPYLENE COPOLYMER

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ABSTRACT OF THE DISCLOSURE

Rubbery copolymers, of 30 to 80 wt. percent ethylene and 70 to 20 wt. percent propylene, having a viscosity average molecular weight of about 20,000 to 1,200,000 and which can be halogenated to 0.5 to 15 wt. percent halogen, impart stringiness and adhesiveness to lubricating greases thickened with calcium soap of C_{12} to C_{30} fatty acid or a mixture of calcium salts of C_1 to C_{10} fatty acid with calcium soap of C_{12} to C_{30} fatty acid.

This invention relates to calcium lubricating greases containing ethylene-propylene copolymer, or halogenated ethylene-propylene copolymer, which copolymers impart to the grease stringiness and adhesiveness to wet and dry surfaces.

Calcium soap and calcium soap-salt greases are widely used as chassis greases for automobiles and for bearing lubrication. These greases are usually dispensed from a pump and grease gun, under high pressure, and through narrow orifices into fittings and bearings. In many applications, particularly chassis lubrication, the grease needs a certain narrow degree of stringiness that is enough so as to insure good lubrication and yet not too much so as to fail to cleanly break when the grease gun is removed from the fitting or lubrication point. The stringiness property is of value in insuring that the rotating bearing continuously picks up grease. Otherwise with a nonstringy grease, the bearing might eventually form a channel in the grease and then suffer from lack of lubrication due to failure of grease to flow into contact with the bearing. Similar failure can occur with spring shackles, or other moving parts. In addition, these chassis greases need to have good adhesiveness to wet and dry metal surfaces. In general, calcium soap or soap-salt greases are deficient in these stringiness and adhesiveness properties. As a result, in the past, natural rubber and high molecular weight (e.g. 60,000 molecular weight Staudinger) polyisobutylene, have been used as stringiness and adhesiveness additives for these calcium greases. However, the natural rubber ages during use and loses its stringiness and adhesiveness properties, while polyisobutylene undergoes excessive shear breakdown when applied by the aforesaid normal grease dispensing equipment. In the latter case, a larger amount of polyisobutylene is normally used to allow for the loss of stringiness and adhesiveness properties in the dispensing system. It has now been found: that rubbery ethylene-propylene copolymers will impart adhesiveness and stringiness to calcium greases in the desired amounts, that they do not seriously degrade upon aging, and they are much more stable to mechanical shearing than polyisobutylene with the result that no excess additive is required to compensate for loss of stringiness due to mechanical shearing upon passage through the dispensing equipment. Furthermore, due to the shear stability of these ethylene-propylene copolymers, a more consistent product is injected into the bearings as compared with prior art polyisobutylene greases where the final degree of stringiness depended to a large extent upon the dispensing equipment. It has been further found that these ethylene propylene copolymers can be halogenated to impart extreme pressure properties while at the same time, the copolymers retain their effectiveness as stringiness additives.

The copolymers of the invention will be rubbery polymers, i.e. elastomers, having a viscosity average molecular weight estimated on the basis of viscosity measurement at 135° C. of solutions of .5 gram of copolymer in 100 ml. of decalin, in the range of about 20,000 to 1,200,000 e.g. 50,000 to 800,000. These copolymers will usually contain about 30 to 80 wt. percent ethylene monomer, and 70 to 20 wt. percent propylene monomer.

Ethylene-propylene copolymers are produced by methods well known in the art using Ziegler-type catalysts. The Ziegler-type catalyst used generally consists of a transition metal halide such as titanium tetrachloride, vanadium tetrachloride or vanadium oxytrichloride, and an aluminum alkyl compound such as aluminum triethyl or aluminum diethyl chloride and the like. The catalyst, where used, may vary in concentration from about .1 to about 5% by weight based on the reactants.

The ethylene-propylene copolymers usable in the invention may contain a third unsaturated monomer such as, for example, a bicyclic, alicyclic or aliphatic nonconjugated diolefin containing from about 6 to about 15 carbon atoms. The amount of third monomer present in the copolymer will generally be in the range of from about 0.5 to 20 mole percent, preferably from about 1 to about 7 mole percent. Nonlimiting examples of suitable monomers include cyclopentadiene, methylene norbornene, hexadiene, dicyclopentadiene, 5-vinyl-2-norbornene, 2-methylnorbornene, 2,4-dimethyl-2,7-octadiene, 3-methallyl cyclopentene, and 3-(2-methyl-1-propene) cyclopentene and the like.

The ethylene-propylene copolymer can be halogenated so as to contain 0.5 to 15.0, preferably 2 to 10 wt. percent halogen, with a halogenating agent such as chlorine, bromine, iodine, fluorine, dichlorodimethylhydantoin, N-bromo-succinimide, and the like. Chlorine is preferred.

Methods of preparing ethylene-propylene copolymers and their halogenation are known in the art, e.g. see U.S. Patent 3,026,795.

The calcium greases of the invention are formed by thickening lubricating oil with 5.0 to 40.0 wt. percent, e.g. 10 to 25 wt. percent, of calcium soap, or calcium soap-salt. These greases will contain 0.2 to 5.0 wt. percent, e.g. .4 to 2.0 wt. percent, of the copolymer. All of said preceding wt. percent being based on the total weight of the grease composition. The soap and soap-salt thickeners are formed by the neutralization of appropriate fatty acids with calcium base, e.g. lime. These fatty acids fall in three general classes; namely, high molecular weight fatty acid, intermediate molecular weight fatty acid, and low molecular weight fatty acid.

The high molecular weight fatty acids include naturally occurring or synthetic, substituted and unsubstituted, saturated and unsaturated, mixed or unmixed, fatty acids having about 12 to 30, e.g. 16 to 22, carbon atoms per molecule. Examples of such acids include stearic, hydroxy stearic, such as 12-hydroxy stearic, di-hydroxy stearic, poly-hydroxy stearic and other saturated hydroxy fatty acids, arachidic, oleic, ricinoleic, hydrogenated fish oil, tallow acids, etc.

Intermediate molecular weight fatty acids include those aliphatic, saturated or unsaturated, unsubstituted, monocarboxylic acids containing 7 to 10 carbon atoms per molecule, e.g. capric, caprylic, nonanoic acids, etc.

Low molecular weight fatty acids include saturated and unsaturated, substituted and unsubstituted, aliphatic carboxylic acids having about 1 to 6 carbon atoms. These acids include fatty acids such as formic, acetic, propionic, etc. Acetic acid or its anhydride is preferred.

The calcium soap greases are simply greases thickened with calcium soaps of the aforesaid high molecular weight fatty acids. The soap-salt greases will include greases wherein a mixture of 1 to 20 moles of the intermediate and/or low molecular weight fatty acid is coneutralized in lubricating oil with a molar proportion of the aforesaid high molecular weight fatty acid by using lime as the coneutralizing agent. The grease is then usually dehydrated by heating to 220° to 500° F. until the water of reaction is removed. Alternatively, the preformed calcium soap and calcium salts can be added to the lubricating oil, preferably followed by heating. These soap-salt greases are well known in the art, along with various modifications and processes for their formation, for example, see U.S. Patents 2,846,342, 2,867,619, 2,909,485, 3,033,787, etc.

The ethylene-propylene copolymer can be directly added to the calcium grease and dispersed by slight heating; or preferably it can be made up as a concentrate in lubricating oil, which concentrate in turn may be added to the grease. In the case of the halogenated copolymer, it is preferably first dissolved in an inert volatile solvent such as heptane, which is mixed with oil, and then the volatile solvent is evaporated by heating to form an oil dispersion of the halogenated copolymer, which in turn is added to the grease.

These greases will generally also contain one or more various other additives, (e.g. 0.1 to 10.0 wt. percent), including oxidation inhibitors such as phenyl-alpha-naphthylamine; corrosion inhibitors, such as sorbitan monooleate and sodium nitrite; dyes; other grease thickeners and the like.

The invention will be further understood by reference to the following specific description and examples, which include preferred embodiments of the invention:

Part A.—The ethylene-propylene copolymer used in the following examples was a commercial rubbery polymer having a Mooney viscosity at 212° F. of about 40 and consisting of about 43 wt. percent ethylene and about 57 wt. percent propylene, in a random sequence in the polymer chain, prepared using Ziegler type catalysts and having a viscosity average molecular weight of about 250,000.

Part B.—The chlorinated ethylene-propylene polymer used in the following examples was prepared as follows: 200 g. of the copolymer of Part A was cut into small pieces and dissolved in 3800 ml. of benzene in a 5 liter 4-necked flask by stirring overnight. Then chlorine was passed over the surface solution, while vigorously stirring and slightly warming, at a rate of about 0.1 g./min. until 80 grams of chlorine was added. At the end of the chlorine treatment, the flask contents were heat soaked for 30 minutes at 69° F., and the unreacted chlorine in the reaction flask removed by treatment with aqueous sodium bisulfite and by blowing with nitrogen gas. During chlorination, the flask was protected from light.

The resulting chlorinated reaction product was washed with water until the off water gave only a faint test for chloride ion with silver nitrate. The polymer was precipitated from the benzene by adding isopropyl alcohol, after which the polymer was redissolved in heptane and precipitated again. The resulting precipitated polymer was dried at 80° C., first in an oven under about 25 mm. Hg pressure, and then finally dried at below 1 mm. Hg pressure. The resulting final product was a rubbery polymer which contained 6.7 wt. percent chlorine, having an inherent viscosity in decaline (.5 gm. of chlorinated polymer in 100 ml. decalin) at 135° C. of 2.51 (roughly about 140,000 viscosity average mol. wt.) and an Wijs Iodine No. of 38.7.

EXAMPLE 1

8 wt. percent of the ethylene-propylene rubber of Part A was dissolved in 92.0 wt. percent of a mineral lubricating oil having a viscosity of 55 SUS at 100° F., by heating to 250° F. and stirring until a complete clear solution occurred. 1 wt. percent of this solution was then mixed with 99.0 wt. percent of a calcium soap-salt grease having the following formulation by weight:

	Percent
Tallow fatty acids of 56 Wijs Iodine No. and 190 mg. KOH/gm. Sap. No.	10.0
Glacial acetic acid	19.0
Hydrated lime	11.9
Phenyl α-naphthylamine	1.0
Naphthenic type mineral lubricating oil having a viscosity at 210° F. of 55 SUS	54.1
50/50 dispersion of sodium nitrite in mineral lubricating oil	4.0

The calcium soap-salt grease (about 9.4 to 1 mol. ratio of low to high mol. wt. acid) was prepared by mixing the lime and mineral oil to form a slurry, warming the slurry and adding the tallow fatty acids. Acetic acid was then added and the mixture was heated, while agitating, to a temperature of about 320° F. until dehydrated. The grease was then cooled to 200° F. and the phenyl α-naphthylamine was added. The grease was next homogenized in a Morehouse mill and then finally cooled to room temperature.

EXAMPLE 2

8 parts by weight of the chlorinated ethylene-propylene rubber of Part B was dispersed in 92.0 parts by weight of heptane. This heptane dispersion was then mixed with 92 parts by weight of a mineral lubricating oil having a viscosity of 55 SUS at 210° F. The resulting mixture was next heated to evaporate the heptane thereby leaving a clear dispersion of the chlorinated ethylene-propylene rubber in the mineral oil.

1 wt. percent of the above oil dispersion was then added to 99.0 wt. percent of a simple calcium soap thickened lubricating grease (a cup grease) and mixed by passage through a Morehouse mill. This grease was made by neutralizing 10 wt. percent animal fat in 87.55 wt. percent mineral lubricating oil having a viscosity of 50 SUS at 210° F. with 1.4% hydrated lime, dehydrating at about 310° F., then cooling to about 210° F. where 1.0 wt. percent water and 0.05 wt. percent phenyl-beta-naphthylamine was added before cooling to room temperature.

Properties of the greases of Examples 1 and 2 are summarized in the following table:

TABLE

	Example 1	Example 2
Type Grease	Calcium Soap-Salt	Calcium Soap.
Type Stringiness Additive	.08% Ethylene-propylene	.08% Chlorinated Ethylene-propylene.
Appearance	Smooth, uniform, stringy grease.	Smooth, uniform, stringy grease.
Effect of Ultra-violet Light	None	None.
Adhesiveness to Metal:		
Dry	Excellent	Excellent.
Wet	do	Do.
Shear Stability	Good	
Spatter Test	No spatter	No spatter.

The effect of ultra-violet light in the foregoing table was determined by simply exposing the greases for 24 hours to bright sunshine and also under ultra-violet light in a fadometer cabinet. There was no noticeable change in the stringiness or adhesiveness of the greases.

The adhesiveness to wet metal was determined by dispensing the grease through a grease gun onto a steel plate having water flooding across the plate. The greases of the invention displaced the moving water and adhered to the wet steel.

The Spatter Test in the table was carried out by letting a 200 gm. weight fall from a height of one foot onto a 2.0 gram portion of the grease. A grease having the proper degree of stringiness will be sufficiently cohesive to itself so as to not spatter, whereas a grease with little cohesiveness or stringiness will spatter and fall apart under the shock of the impact, sometimes flying as far as 5 feet from the impact point.

Shear stability was determined by passing the grease sample through a high shear grease gun (a typical service station grease gun) and determining whether or not there was any loss in stringiness qualities by visual examination of the grease and also by subjecting the sheared grease to the aforedescribed Spatter Test and Adhesiveness Test.

As seen by the preceding table both the calcium soap-salt greases and the calcium soap grease, neither of which greases per se are stringy greases, were both converted into a smooth, uniform stringy grease by the addition of very small amounts of the chlorinated or unchlorinated ethylene-propylene copolymer. Greases similar to the types of Examples I and II but to which polyisobutylene was added as a stringiness agent, when dispensed through said high shear grease gun, substantially lost their anti-spatter properties due to shear breakdown of the polyisobutylene.

What is claimed is:

1. A normally solid lubricating grease comprising a major amount of lubricating oil, and a grease thickening amount of thickener selected from the group consisting of calcium soap of C_{12} to C_{30} fatty acid, and calcium soap-salt consisting essentially of calcium salt of 1 to 20 molar proportions of C_1 to C_{10} fatty acid per molar proportion of calcium soap of C_{12} to C_{30} fatty acid, and a stringiness and adhesiveness improving amount, less than 5 wt. percent, of a polymer selected from the group consisting of

rubbery copolymers of ethylene-propylene having a viscosity average molecular weight of about 20,000 to 1,200,000 and consisting essentially of about 30 to 80 wt. percent ethylene monomer and 70 to 20 wt. percent propylene monomer, and halogenated derivatives thereof containing 0.5 to 15 wt. percent halogen.

2. A grease according to claim **1**, wherein said lubricating oil is mineral oil, said thickener is calcium soap-salt, said C_1 to C_{10} fatty acid is acetic acid, the amount of said polymer is about 0.08 wt. percent based on the weight of the total grease, and said polymer consists of a major weight amount of propylene and a minor weight amount of ethylene, said polymer having a viscosity average molecular weight of about 50,000 to 800,000.

3. A grease according to claim **1**, wherein said lubricating oil is mineral oil, said thickener is calcium soap, and said polymer is a chlorinated derivative.

4. A normally solid lubricating grease consisting essentially of a major amount of mineral lubricating oil and a grease thickening amount of calcium soap-salt prepared by coneutralizing a mixture of about 1 to 20 molar proportions of acetic acid per molar proportion of a C_{16} to C_{22} fatty acid with lime in situ in at least a portion of said oil, followed by heating to dehydrate said grease, and a stringiness and adhesiveness improving amount, less than 2 wt. percent of an ethylene-propylene rubbery copolymer consisting essentially of about 30 to 80 wt. percent ethylene and about 70 to 20 wt. percent propylene, said copolymer having a viscosity average molecular weight in the range of about 50,000 to 800,000.

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