United States Patent Office 2,929,785 Patented Mar. 22, 1960

2,929,785

GREASE COMPOSITIONS CONTAINING SALTS OF CARBOXYLIC COPOLYMERS

Arnold J. Morway, Rahway, Jeffrey H. Bartlett and Anthony H. Gleason, Westfield, and Samuel B. Lippincott, Springfield, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Application August 6, 1954
Serial No. 448,364

2 Claims. (Cl. 252—41)

This invention relates to grease compositions and more particularly relates to lubricating grease compositions which contain a thickener comprising a metal salt of a carboxylic copolymer and more particularly a metal salt of a copolymer of an α, β-unsaturated carboxylic compound with an aliphatic unsaturated compound copolymerizable therewith. The invention also relates to the metal salts themselves and to a method of preparing grease compositions containing them.

Lubricating greases normally consist of lubricating oils thickened by alkali and alkaline earth metal soaps or other thickeners to a solid or semi-solid consistency. The soaps may be prepared by the neutralization of high molecular weight fatty acids or by the saponification of fats which is usually carried out in a portion of the oil to be thickened.

The present invention pertains to highly valuable stable lubricating greases in which the high molecular weight fatty acids are replaced or at least supplemented by a new grease making material. It has now been found that such greases may be prepared by incorporating into lubricating oils a grease thickener comprising a metal salt of a carboxylic copolymer and more particularly a metal salt of a copolymer of an α, β-unsaturated carboxylic compound with an aliphatic unsaturated organic compound copolymerizable therewith. The aliphatic unsaturated compounds include alkyl or aralkyl α olefins, conjugated diolefins, vinyl esters and isopropenyl esters. The copolymer salt thickeners of this invention generally have a molecular weight in the range of about 200 to 20,000, preferably about 300 to 8,000, and are employed in grease compositions in the proportions of about 2 to 35% by weight, based on the total composition.

THE α, β-UNSATURATED CARBOXYLIC COMPOUNDS—GROUP I

The α, β-unsaturated carboxylic compounds of this invention include the monocarboxylic acids which contain about 3 to 10 and preferably 3 to 6 carbon atoms. Among these acids may be mentioned acrylic and methacrylic.

THE POLYMERIZABLE ALIPHATIC UNSATURATED COMPOUNDS—GROUP II

The α olefins which are suitable for copolymerization in this invention include those which may be readily prepared by cracking petroleum hydrocarbons, although some polymeric olefins may also be employed. In general, the preferred type of olefins are those with straight or branched chains and which respond readily to polymerization. Especially preferred are olefins of the formulae:

$$RCH=CH_2$$

and

$$R_2C=CH_2$$

where R is selected from alkyl or aralkyl radicals containing about 2 to 30 carbon atoms per molecule. As examples of these α olefins may be mentioned butenes, amylenes, octenes, decenes, dodecenes, cetenes, octadecenes, etc.

The conjugated diolefins of this invention are those preferably containing from about 4 to 10 carbon atoms such as butadiene, isoprene, piperylene, dimethyl butadiene, cyclopentadiene, etc.

The vinyl esters and isopropenyl esters are preferably those derived from monocarboxylic acids containing about 2 to 25 carbon atoms. Examples of these acids include acetic, propionic, butyric, stearic, palmitic, lauric, behenic, etc.

Copolymerization

The copolymers of this invention are prepared by well-known copolymerization methods which involve forming a mixture of a compound selected from group I and a compound copolymerizable therewith from group II, which groups are described above, and heating the mixture preferably in the temperature range of about 60 to 140° C. for a period of time preferably in the range of about 1 to 24 hours in the presence of a polymerization catalyst such as benzoyl peroxide, cumene hydroperoxide, 2,2-bis (t-butyl peroxy) butane, t-butyl hydroperoxide, lauroyl peroxide, potassium persulfate, etc. Usually 0.2 to 5% of catalyst by weight based on total monomers, and preferably 0.5 to 2% by weight will be employed.

In the copolymerization reaction generally about one mole of a compound selected from group I will be reacted with about 0.2 to 20.0 moles, preferably one mole, of a compound selected from group II.

It will be further understood that the products of the copolymerization reaction are generally mixtures of copolymers having a range of molecular weights as is true generally in this type of reaction.

Grease manufacture

The grease compositions of this invention are generally prepared by conventional grease-making procedures. The copolymer salts of this invention are employed in grease compositions in the proportion of about 2 to 35% by weight, based on the total composition. It will be understood that the copolymer thickeners of this invention may be employed in conjunction with other conventional thickeners such as soaps and soap-salt complexes of high molecular weight carboxylic acids with low molecular weight carboxylic acids. The preferred greases of this invention are those produced by employing alkali metal hydroxides, carbonates, etc. as the neutralization or saponification material.

In accordance then with this invention, a mineral lubricating oil base is initially mixed in grease-making proportions with the copolymer, the basic reacting compound of the metal and any conventional grease-making ingredients, preferably in aqueous solution. The amount of the metal reacting compound which is used should be sufficient to form at least one COOM (where M=a metal) group in each saponified copolymeric molecule in addition to substantially neutralizing any conventional low and high molecular weight carboxylic acids present. Greater amounts of the metal reacting compound may be employed, if desired, up to an amount which would react with substantially all of the carboxylic groups present in the original copolymeric molecule. The mixture is then heated to about 250° to 320° F. until dehydration is essentially complete and the temperature is then

raised to about 400° to 600° F. The composition is maintained at this temperature until the desired conversion has been obtained, which is usually the case after about 0.5 to 5 hours. The reaction mixture is thereafter quenched or allowed to cool and then may be diluted with further amounts of lubricating oil to obtain the desired grease consistency.

Soaps or soap-salt complexes of conventional grease-making materials may also be employed in the manufacture of the greases of this invention. Thus, for example, high molecular weight acids such as hydrogenated fish oil acids, C_{12} to C_{22} naturally occurring acids of animal or vegetable origin, stearic acid, hydroxystearic acids such as 12-hydroxy stearic, dihydroxy stearic, polyhydroxy stearic, and arachidic acid, tallow acids, etc., may be mixed with the lubricating oil and the copolymers of this invention prior to the neutralization, dehydration and cooking steps described above. The soaps of these conventional high molecular weight acids may be used in amounts ranging from about 2 to 30 wt. percent and preferably about 5 to 15 wt. percent based on the finished product. Also, salts of low molecular weight acids such as those carboxylic acids having 1 to 5 carbon atoms per molecule such as formic, acetic, furoic, acrylic and similar acids may be likewise used in proportions of about 1 to 10 wt. percent and preferably about 2 to 6 wt. percent, based on the finished product. However, it will be understood that at least about 20 wt. percent of the thickener in the grease should be the novel copolymer salt of this invention. Preferably the copolymer salt thickener of this invention comprises about 30 to 50 wt. percent of the total grease thickener or about 2 to 25 wt. percent of the finished grease. The remainder of the grease thickener is preferably made up of a suitable soap-salt complex of the type described above. The proportion of thickener derived from the copolymer to soaps and salts derived from other acids may be about 1:4 to 4:1 and preferably is about 1:1 on a weight basis. Other conventional thickeners, anti-oxidants, corrosion inhibitors, tackiness agents, load-carrying compounds, viscosity index improvers, oiliness agents, and the like may be added prior, during or after the grease-making process described above as will be apparent to those skilled in the art.

The base oil employed in forming the mixture prior to the grease-making process should be a non-saponifiable oil, preferably a mineral lubricating oil. However, after the grease has been formed and cooled, synthetic lubricating oils having a viscosity of at least 30 SSU at 100° F. such as esters of monobasic acids (e.g. ester of C_8 Oxo alcohol with C_8 Oxo acid, ester of C_{13} Oxo alcohol with octanoic acid, etc.), esters of dibasic acids (e.g. di-2-ethyl hexyl sebacate, dinonyl adipate, etc.), esters of glycols (e.g. C_{13} Oxo acid diester of tetraethylene glycol, etc.), complex esters (e.g. the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, complex ester formed by reacting one mole of tetraethylene glycol with two moles of sebacic acid and two moles of 2-ethyl hexanol, complex ester formed by reacting together one mole of azelaic acid, one mole of tetraethylene glycol, one mole of C_8 Oxo alcohol, and one mole of C_8 Oxo acid), esters of phosphoric acid (e.g. the ester formed by contacting three moles of the mono methyl ether of ethylene glycol with one mole of phosphorus oxychloride, etc.), halocarbon oils (e.g. the polymer of chlorotrifluoroethylene containing twelve recurring units of chlorotrifluorethylene), alkyl silicates (e.g. methyl polysiloxanes, ethyl polysiloxanes, methyl-phenyl polysiloxanes, ethyl-phenyl polysiloxanes, etc.), sulfite esters (e.g. ester formed by reacting one mole of sulfur oxychloride with two moles of the methyl ether of ethylene glycol, etc.), carbonates (e.g. the carbonate formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol), mercaptals (e.g. the mercaptal formed by reacting 2-ethyl hexyl mercaptan with formaldehyde), formals (e.g. the formal formed by reacting C_{13} Oxo alcohol with formaldehyde), polyglycol type synthetic oils (e.g . the compound formed by condensing butyl alcohol with fourteen units of propylene oxide, etc.), or mixtures of any of the above in any proportions, may be added alone or in addition to the mineral lubricating oil to bring the grease to the desired consistency. The oil base preferably comprises about 55 to about 95% of the total weight of the finished grease.

Although it is generally preferred in the grease making procedure of this invention to form the metal salts of the carboxylic copolymers in situ, it will be understood that, if desired, they may be initially prepared in a separate step and then subsequently added to the mixture of the grease ingredients prior to the step of heating the ingredient mixture to an elevated temperature to promote formation of the complex grease. These salts of the carboxylic copolymers may be simply prepared by adding the desired amount of the basic reacting compound of the metal to the copolymer and mixing the two ingredients together, at an elevated temperature, generally in the range of about 100° to 500° F. The time required for completion of the reaction will depend upon the temperature employed as well as the nature and the molecular weight of the copolymer. More specifically the neutralization of the low molecular weight copolymers will require only a few minutes whereas the saponification of the higher molecular weight copolymers may require a period of time in the range of about 0.5 to 10 hours. The amount of the metal compound employed will be the same as that set forth previously in this specification in the procedure for preparing the salts in situ. When the salts of the carboxylic copolymers are formed in a separate step, the reaction is preferably carried out in an aqueous or alcohol medium, which medium is subsequently removed by simple distillation after the reaction is completed.

A preferred thickener is that formed from the copolymer of a conjugated diolefin with an α,β-unsaturated acid such as the copolymer of butadiene with acrylic acid. In general, it is desirable to utilize conjugated diolefinic hydrocarbons of relatively low molecular weight having from 4 to 10 carbon atoms. Among these diolefins are: butadiene, isoprene, piperylene, dimethyl butadiene, cyclopentadiene, etc. The α,β-unsaturated acids and their derivatives which are suitable for copolymerization with the conjugated diolefins are those of low molecular weight such as: acrylic acid and methacrylic acid.

EXAMPLE 1

Preparation of butadiene—acrylic acid copolymer

Approximately 380 g. of butadiene of 98% purity and 20 g. of freshly distilled glacial acrylic acid were added to 900 ml. of heptane containing 25 ml. of cumene hydroperoxide of 50% purity and 1.5 g. of diisopropyl xanthogen disulfide. The mixture was heated in a stainless steel bomb for about 24 hours at about 110° C. The copolymer which had a molecular weight in range of 4,000–5,000 was obtained as an oil containing 7 wt. percent of combined acrylic acid. The conversion, based on monomers, was 42% and was preferably kept below 70% in order to avoid any gel formation. The unconverted butadiene was removed from the copolymer by simple distillation. If desired, it would have been possible to have removed the unreacted acrylic acid by azeotropic distillation in the presence of higher boiling hydrocarbons such as naphthas. The copolymer prepared above was then used in the preparation of the following lubricating grease.

FORMULATION

Ingredients	Percent Weight
Copolymer formed by reaction of Butadiene and Acrylic Acid	10.00
Hydrofol Acid 54 [1]	10.00
Acetic Acid (Glacial)	4.00
Sodium Hydroxide	6.50
Phenyl alpha naphthylamine	1.00
Lubricating Oil II [2]	68.50

[1] Hydrogenated fish oil acids corresponding to commercial stearic acid in degree of saturation.

[2] Blend of naphthenic type mineral oils having a viscosity of about 55 S.S.U. at 210° F. and a viscosity index of about 63.

PREPARATION

The copolymer, hydrofol acids and one-third of lubricating oil II were charged to a grease kettle and warmed to about 150° F. The glacial acetic acid was then added followed immediately by the addition of a 40% aqueous solution of the sodium hydroxide. Heating was continued to about 300° F. to drive off the water. The balance of lubricating oil II was then added and the composition was heated to about 485° F., at which point the grease was solid. Heating was then discontinued and the composition was cooled to about 275° F. and the phenyl α naphthylamine was added and cooling was continued to 200° F., after which the grease was homogenized in a Gaulin homogenizer.

PROPERTIES

Percent free alkalinity as NaOH	1.61.
Appearance	Excellent smooth homogeneous hard grease.
Penetrations 77° F. mm./10— after Gaulin homogenization:	
Unworked	167.
Worked 60 strokes	180.
Worked 67,000 strokes	240.
Dropping point, ° F.	500.
Water washing test percent loss	None.
Norma - Hoffmann oxidation, hrs. to 5 p.s.i. drop in O_2 pressure	350.
Structure	Slightly rubbery.

EXAMPLE 2

FORMULATION (WT. PERCENT)

Ingredients	Percent Weight
Grease of Example 2	50.0
Lubricating Oil III [1]	50.0
or	
Copolymer (Butadiene-Acrylic Acid)	5.00
Hydrofol Acid 54	5.00
NaOH	3.25
Acetic Acid (Glacial)	2.00
Phenyl Alpha-Naphthylamine	0.50
Lubricating Oil II	34.25
Lubricating Oil III [1]	50.00

[1] A blend of a residual mineral oil and a high viscosity index solvent refined mineral oil. This oil blend had a viscosity of about 55 at 210° F. and a viscosity index of about 100.

PREPARATION

The grease of Example 1 was mixed with an equal amount of lubricating oil III by weight and the soft semi-fluid product was homogenized in a Gaulin homogenizer to ultimate hard consistency. The reduction of the soap content together with the addition of the less polar lubricating oil III resulted in the excellent smooth product with reduction or removal of most of the rubbery nature of the grease of Example 1.

PROPERTIES

Appearance	Excellent smooth homogeneous grease—very slight trace of cohesiveness, which may be regarded as advantageous.
Penetrations 77° F. mm./10:	
Unworked	205.
Worked 60 strokes	285.
Worked 67,000 strokes	325.
Dropping point, ° F.	440.
Water washing test, percent loss	None.
Norma - Hoffmann oxidation, hrs. to 5 p.s.i. drop in oxygen pressure	275.

What is claimed is:

1. A lubricating grease composition comprising a major proportion of a mineral lubricating oil; in the range of 2 to 35 wt. percent of an alkali metal salt of an acidic polymeric material; and in the range of 2 to 6 wt. percent of an alkali metal salt of a low molecular weight acid having in the range of 1 to 5 carbon atoms per molecule and about 2 to 30 wt. percent of an alkali metal soap of a C_{12} to C_{22} carboxylic acid, said soap and said alkali metal salts being heated to a temperature in the range of 400° to 600° F. for a time in the range of 0.5 to 5 hours and said acidic polymeric material consisting of a copolymer of one mole of a monocarboxylic alpha-beta unsaturated acid having in the range of 3 to 6 carbon atoms per molecule, within the range of 10 to 20 moles of a conjugated diolefin containing in the range of 4 to 10 carbon atoms per molecule; said copolymer being formed by heating the acid and diolefin to a temperature in the range of 60° to 140° C. for a time in the range of 1 to 24 hours in the presence of a polymerization catalyst.

2. A lubricating grease consisting essentially of a major proportion of a mineral lubricating oil, an antioxidant, in the range of 2 to 6 wt. percent of the sodium salt of acetic acid, about 2 to 30 wt. percent of a sodium soap of a C_{12} to C_{22} carboxylic acid and in the range of 2 to 35% by weight of the sodium salt of a copolymer of butadiene and acrylic acid having a molecular weight in the range of 4,000 to 5,000, and a molar ratio of butadiene to acrylic acid in the range of 10 to 20:1, said sodium salts and soap being heated to a temperature in the range of 400° to 600° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,047,398	Voss	July 14, 1936
2,359,038	Hopff et al.	Sept. 26, 1944
2,527,081	Ross et al.	Oct. 24, 1950
2,616,849	Giammaria	Nov. 4, 1952
2,619,477	Banes et al.	Nov. 25, 1952
2,698,297	Giammaria	Dec. 28, 1954
2,698,298	Giammaria	Dec. 28, 1954
2,698,299	Giammaria	Dec. 28, 1954
2,737,494	Frank	Mar. 6, 1956
2,771,459	Banes et al.	Nov. 20, 1956