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MODIFIED ACIDIC COPOLYMER-FATTY ACID SOAP GREASES

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The present invention relates to greases in which the gelation agent is a mixture of alkaline earth metal salts of acidic copolymers and fatty acids and, more particularly, to greases containing at least one acidic copolymer, at least one fatty acid having at least 16 carbon atoms, at least one aliphatic, monocarboxylic acid having less than six carbon atoms and an amount of at least one alkaline earth metal slightly in excess of that required to convert all of the aforementioned acidic constituents to salts or soaps of said alkaline earth metals.

In the co-pending application for United States Letters Patent Serial No. 215,859 filed March 15, 1951, filed in the name of John J. Giammaria, it has been disclosed that lubricating greases can be compounded from mineral oil of lubricating grade and a novel class of gelling agents comprising metal salts of acidic copolymers formed by reacting long-chain, aliphatic compounds containing a terminal vinyl group, $-CH=CH_2$, with an alpha, beta-unsaturated, polycarboxylic acid or anhydride in the presence of an organic peroxide catalyst.

It has been further disclosed in the aforesaid co-pending application that the vinyl compounds which can be used to form the acidic copolymers with the alpha, beta-unsaturated polycarboxylic acids are aliphatic alpha olefins, allyl esters of aliphatic acids, allyl ethers of aliphatic alcohols, vinyl esters of aliphatic acids and vinyl ethers of aliphatic alcohols. It has also been disclosed in the aforesaid co-pending application that the alpha olefins, $R—CH=CH_2$; and allyl esters,

$$RCOOCH_2CH=CH_2$$

in both of which R is an alkyl radical having at least 10 and up to 30 carbon atoms, preferably 10 to 22 carbon atoms and especially a mixture averaging 18 carbon atoms, are especially suitable for the preparation of the copolymers per se, the metal salts of which are the novel gelling agents. Illustrative of the alpha olefins are 1-dodecene, 1-hexadecene, 1-octadecene and higher alpha olefins and mixtures thereof such as are obtained by thermal cracking of petroleum wax or waxy petroleum stocks or fractions. Illustrative of the allyl esters are allyl laurate, allyl myristate, allyl palmitate, allyl stearate, mixed allyl esters such as are obtained by esterifying allyl alcohol with hydrogenated fish fatty acids which contain aliphatic, monocarboxylic acids having 10 to 22 carbon atoms and, in general, allyl esters obtained by esterifying allyl alcohol with an aliphatic, monocarboxylic acid having 10 to 22 carbon atoms.

As disclosed in the aforesaid co-pending application, the allyl ethers can be either the allyl ethers of monohydric or polyhydric alcohols although the ethers of monohydric alcohols of ten or more carbon atoms are preferred. Thus, for example, allyl lauryl ether, allyl hexadecyl ether, methallyl octadecyl ether and the like can be used.

Of the alpha, beta-unsaturated, aliphatic polycarboxylic acids, the dicarboxylic acids are preferred. Illustrative of the preferred dicarboxylic acids are maleic, fumaric, itaconic, glutaconic, mesaconic, and citraconic, and the tri-carboxylic aconitic acid. While maleic acid in the form of its anhydride is preferred at this time, it will be recognized by those skilled in the art that the anhydrides of the acids or acid halides as well as the acids themselves having less than 10 carbon atoms per se can be used although it is generally preferred to use the anhydrides in the preparation of the acidic copolymers.

Suitable catalysts for the copolymerization of an aliphatic compound having a terminal vinyl group,

$$—CH=CH_2$$

and an alpha, beta-unsaturated, aliphatic, polycarboxylic acid, especially a dicarboxylic acid, are the organic peroxides such as benzoyl peroxide, di-tertiary-butyl peroxide and lauroyl peroxide and hydroperoxides, such as cumene hydroperoxide.

The copolymerization of the aliphatic compound having a terminal vinyl group with an alpha, beta-unsaturated, aliphatic, polycarboxylic acid or anhydride is accomplished by heating substantially equi-molar quantities of the reactants at temperatures within the range of about 75° C. to about 150° C. in the presence of about 0.1 to about 5.0 per cent of peroxide catalyst. The copolymerization can be carried out in the presence or absence of a solvent such as toluene, xylene, dioxane, highly acid-refined mineral oil such as white oil and the like.

Suitable metals for the preparation of the novel class of gelling agents, i. e., the metal salts of the acidic copolymer of an aliphatic compound having a terminal vinyl group and an unsaturated, aliphatic, polycarboxylic acid are the metals of groups I, II and III of the periodic system. Lithium, calcium, barium and aluminum salts of the acidic copolymers are preferred.

It was further disclosed in the aforesaid co-pending application that the aforesaid metal salts of the acidic copolymers can be used alone as gelation agents or in combination with other gelation agents such as soaps of conventional fatty or hydroxy fatty acids, carbon black, silica flour and the like.

Thus, for example, it has been disclosed in the aforesaid co-pending application that greases having a very smooth texture can be prepared by converting a mixture of an acidic polymer and a fatty acid to metal salts in an oleaginous vehicle. Mixtures containing about 10 per cent to about 90 per cent of fatty acid, and about 90 per cent to about 10 per cent (by weight) of oil-free acidic copolymers can be used to produce the salts which are the novel mixed gelation agents. However, it is preferred to use about equal parts by weight of an acidic copolymer having a molecular weight of about 1000 to about 2000 and a straight-chain, saturated, fatty acid. The fatty acids suitable for this purpose are the individual fatty acid or mixtures of fatty acids or hydroxy fatty acids or mixtures of one or more fatty acids and one or more hydroxy fatty acids having 10 to 22 carbon atoms in the molecule such as capric, lauric, stearic, hydroxystearic acid and hydrogenated fish oil fatty acids. The acidic copolymer and fatty acid are reacted with a single metal compound or a plurality of compounds of a plurality of metals of groups I to IV of the periodic system. Furthermore, the mineral oil vehicle can be replaced wholly or in part by synthetic oils of the polyester, polyether and silicone types. Thus, for example, the mineral oil vehicle can be replaced wholly or in part by an oleaginous vehicle, for example, an ester type synthetic oil such as 2-ethylhexyl sebacate, or by a polyether synthetic oil such as polyalkylene glycol or by a silicone such as methyl polysiloxane, or by a polymer oil obtained by polymerization of an olefin such as ethylene.

Illustrative of greases having mixed gelation agents comprising the salts of acidic copolymers and fatty acids having 10 to 22 carbon atoms per molecule disclosed in the aforesaid co-pending application is that of a grease prepared from a mixture of 50 parts by weight oil-free acidic coplymer, 50 parts by weight stearic acid, 20 parts by weight calcium hydroxide, 15 parts by weight water, and 500 parts by weight of a solvent refined naphthenic oil having a viscosity of 513.5 S. U. S. at 100° F. This grease had an A. S. T. M. penetration @ 77° F. of 290 (unworked) and 300 (worked); an A. S. T. M. dropping point of 237° F. and a water resistance (Spec. A. N.—g—5A) of 0.15 per cent. It is manifest to those skilled in the art that this is a satisfactory grease except for its low dropping point. The present invention provides a means for raising the dropping point of this grease and other greases having the novel mixed acidic-polymer salts—fatty acid salts gelation agents.

It has been found that stable greases containing the

novel mixed gelation agents and having high dropping points can be obtained by incorporating in the oil blend about 1 to 2% of a low molecular weight fatty acid having less than six carbon atoms and an amount of calcium and/or barium compound capable of neutralizing said low molecular weight fatty acid. Preferably, the calcium and/or barium compound is the hydroxide. Thus, a high dropping point, smooth textured, stable calcium or barium grease can be prepared from a blend containing about 9 to about 11% by weight of an acidic copolymer of the class described hereinbefore, about 6 to about 8% by weight of a high molecular weight fatty acid and about 1 to about 2% by weight of a low molecular weight fatty acid having less than six carbon atoms in the molecule.

In the aforementioned co-pending patent application it was shown that a grease prepared from the calcium salt of an acidic copolymer of the class described had a dropping point in the range of 400° to 500° F. It was also shown therein that, when a mixture of such a copolymer and a high molecular weight fatty acid such as stearic acid was used to prepare a grease containing the calcium salt or salts of the aforesaid copolymer and fatty acid as the gelation agent, the grease was smoother in texture than the grease in which the calcium salt of the acidic copolymer was the sole gelation agent but had a low dropping point in the range of 220° to 270° F.

It will be noted that both greases had a smooth texture and were stable. Consequently, the use of a low molecular weight fatty acid having less than six carbon atoms in the molecule in the presence of a calcium or barium compound capable of neutralizing said low molecular weight acid, i. e., the hydroxide, the carbonate, etc., to raise the dropping point of a smooth textured, stable grease is not to be confused with the use of a calcium salt of a monocarboxylic, aliphatic acid having not more than six carbon atoms nor with the use of barium salt of a mineral acid or of a low molecular weight organic acid to stabilize the structure of the normal calcium or barium soap grease as described in U. S. Patents Nos. 2,197,263 and 2,417,433 respectively. That is to say, stabilizing the structure of an unstable grease is not necessarily related to raising the dropping point of an already stable grease.

The dropping point of a smooth textured stable grease prepared from a mixture of an acidic copolymer of the class described hereinbefore and a high molecular weight (10–22 carbon atoms) fatty acid is increased from that of about 220° to about 270° F. to about 300° to about 500° F. by incorporating a relatively small amount, say 1% to 2%, of a low molecular weight (less than six carbon atoms) fatty acid and a neutralizing amount of calcium or barium in the grease mixture.

For economic reasons it is advantageous to substitute for the acidic polymer a substantial amount of fatty acid but the grease so obtained, while satisfactory in every respect, has a limited use because of the relatively low dropping point. By incorporating the low molecular weight fatty acid in the grease, the economic advantages of the smooth textured, stable grease are retained but the dropping point is raised and thus the field of use expanded to its full scope.

As a general procedure, varying proportions of acidic copolymer and high molecular weight fatty acid are blended in a suitable oil base, such as a solvent-refined naphthenic oil, by heating the oil and copolymer-fatty acid mixture to about 150° F. The low molecular weight fatty acid, sufficient of the calcium and/or barium compond to neutralize the three acidic components and a small amount of water are added and the mixture stirred and heated to about 300° to about 400° F. for a period of time sufficient to permit the saponification and dehydration to take place, say about 2 to about 6 hours, and the grease cooled either statically or with agitation.

Accordingly, the grease of the present invention is a high dropping point grease, i. e., about 300° to about 500° F., having as gelation agents a salt of an acidic copolymer of the class described hereinbefore and in co-pending application Serial No. 215,859, and a metal of group II of the periodic system, preferably calcium and barium, a salt of one of the aforesaid metals, preferably calcium and barium, and a saturated, aliphatic, monocarboxylic acid containing 12 to 22 carbon atoms. Preferably these fatty acids are those containing 18 carbon atoms such as a mixture of acids found in fractions of hydrogenated fish oil acids, which have an average of 18 carbon atoms. Small amounts of unsaturated acids can be used but preferably the amount of unsaturated, high molecular weight, fatty acids is limited to 5% or less. The third component is the dropping point increasing material which is a salt of one of the aforesaid metals and an aliphatic, monocarboxylic acid having less than six carbon atoms such as formic acid, acetic acid, butyric acid and valeric acid of which acetic is preferred.

In neutralizing a mixture of the three acidic components, complex mixtures of mixed or cross-linked soaps are probably formed rather than the pure soaps of each acidic component.

The proportions of the three acidic components used in preparing the novel high dropping point greases may be varied within fairly wide limits depending upon the types of acidic components, type of oil vehicle, the consistency required, etc. Concentration ranges can vary as follows: about 5 to about 12 weight per cent acidic copolymer; about 5 to about 12 weight per cent high molecular weight fatty acid (12 to 22 carbon atoms) and about 0.5 to about 3 weight per cent low molecular weight fatty acid (less than six carbon atoms).

The total concentration of these three components can vary from about 10 to about 25 weight per cent although, generally, about 15 to about 20 weight per cent is required. For example, when a solvent-refined, naphthenic oil of about 500 S. U. S. @ 100° F. is employed as the base oil, satisfactory greases are prepared from a mixture comprising about 9 to about 11 weight per cent acidic copolymer, about 6 to about 8 weight per cent of high molecular weight fatty acid and about 1 to about 2 weight per cent low molecular weight fatty acid, i. e., about 16 to about 21 total weight per cent.

The following grease compositions are illustrative of the high dropping point greases of the present invention.

EXAMPLE I

An acidic copolymer was prepared by copolymerizing maleic anhydride with the allyl ester of distilled, hydrogenated, fish oil acids (available as Hydrofol Acids 150) containing about 77.6% stearic acid, about 17.7% palmitic acid, about 0.5% myristic acid, about 1% arachidic acid and about 3.2 oleic acid. Benzoyl peroxide was used as the catalyst and the copolymerization carried out in the manner described in co-pending application Serial No. 215,859, and hereinbefore. About fifty parts of the resulting oil-free, acidic copolymer, (having a neutralization number of 208), about 50 parts of stearic acid, about 150 parts of acid-refined, naphthenic oil having a viscosity of 232 S. U. S. @ 100° F. about 350 parts of solvent-refined, naphthenic oil having a viscosity of 513.5 S. U. S. @ 100° F. were heated to 160° F. in a suitable grease kettle. Ten parts of acetic acid, 24 parts of calcium hydroxide ($Ca(OH)_2$) (4.4 parts excess over theoretical amount required to neutralize acids. Represents about 0.5% free CaO in final grease) and 10 parts of water were added and the mixture was heated. The gel which quickly formed became softer at 185° F. and fairly fluid at 300° F. The mass began to thicken at 330° F. and finally formed a heavy gel at 400° F. After heating for about 0.5 hour, the source of external heat was removed and the grease was stirred while cooling. Sufficient oil was stirred into the grease at room temperature to give a total content of the three components, i. e., salt or salts of acidic copolymer, high molecular weight fatty acid and low molecular weight fatty acid, of 19 weight per cent.

EXAMPLE II

A mixture of about 50 parts by weight of oil-free, acidic copolymer similar to that used in Example I, having a neutralization number of 216, about 50 parts by weight of stearic acid, and about 500 parts by weight of a solvent-refined, naphthenic oil having a viscosity of 513.5 S. U. S. @ 100° F. was heated to 155° F. in a suitable grease kettle. About 7.5 parts by weight of acetic acid, about 20 parts by weight of $Ca(OH)_2$ (1.8 parts excess over the theoretical amount required to neutralize acids. Represents about 0.2% free CaO in final

grease), and about 10 parts by weight of water were added and the mixture heated. A soft gel was formed at 175° F. which became more fluid at 230° F. The mass again thickened at about 300° F. and gelled at 315° F. The gel became heavy and grainy at 350° F. and changed to a tough, smooth gel at 360° F. The temperature was finally raised to 375° F. at which temperature the grease was softer and smoother. The mixture was cooled statically to 175° F. About 2 parts by weight of $Ca(OH)_2$ (represents an additional amount of about .2% CaO in final grease or a total of about 0.4% free CaO) were then added and the grease was stirred while cooling to ambient temperature. The total salt content was 19 weight per cent.

EXAMPLE III

A mixture of about 50 parts by weight of the oil-free copolymer used in Example I, about 50 parts by weight of stearic acid and about 500 parts by weight of naphthenic oil was heated to about 160° F. in a suitable grease kettle. About 5 parts by weight of acetic acid, about 18 parts by weight of $Ca(OH)_2$ (with the two parts added later providing about 3.5 parts excess over the theoretical amount required to neutralize acids) and about 10 parts by weight of water were added and the mixture was heated to about 360° F. during a period of about three hours to form a smooth grease. It was cooled statically to about 200° F. About 2 parts of $Ca(OH)_2$ were then added and the grease stirred while cooling to ambient temperature. The total salt content of the grease was about 18 weight per cent and the free CaO content was about 0.4%.

EXAMPLE IV

In the manner described in Example I, an acidic copolymer of an allyl ester of Hydrofol Acids 51 and maleic anhydride was prepared. Hydrofol Acids 51 contain about 8.5% myristic acid, about 35.2% palmitic acid, about 28.2% stearic acid, about 15% arachidic acid, about 8.8% behenic acid, about 1.1% palmitoleic acid, about 1% oleic acid, about 1.2% gadoleic acid and about 1% erucic acid. A mixture of about 50 parts by weight of this acidic, oil-free copolymer having a neutralization number of 228, about 35 parts by weight of "Hydrofol Acids 150" and about 450 parts by weight of a solvent-refined, naphthenic oil was heated to about 160° F. in a grease kettle. About 7 parts by weight of acetic acid, about 17 parts by weight of $Ca(OH)_2$, (0.6 part excess) and about 10 parts by weight of water were added and the mixture was heated to about 380° F. during a period of about 4 hours. About 2 parts by weight of $Ca(OH)_2$ were added and the grease cooled with stirring to ambient temperature. The total salt content of the grease was about 18 weight per cent and the free CaO content was about 0.35%.

EXAMPLE V

A mixture of about 50 parts by weight of the oil-free copolymer used in Example IV, about 35 parts by weight of "Hydrofol Acids 150" and about 450 parts by weight of solvent-refined, naphthenic oil was heated to about 170° F. in a grease kettle. About 10 parts by weight of water, about 10.3 parts by weight of butyric acid and about 17 parts by weight of $Ca(OH)_2$ (0.6 part excess) were added and the resultant mixture was heated to 360° F. during a period of about four hours. About 2 parts by weight of $Ca(OH)_2$ were added and, after stirring about 10 minutes at about 360° F., the grease was cooled with stirring to ambient temperature. At room temperature the grease was very soft and grainy. However, it was converted into a smooth texture and stiffer consistency by milling. The total salt content was about 19 weight per cent. The free CaO content of the grease was about 0.35%.

EXAMPLE VI

An acidic copolymer was prepared by polymerizing maleic anhydride with 1-octadecene using benzoyl peroxide as the catalyst. A mixture of about 36 parts by weight of this acidic copolymer having a neutralization number of 187, about 25 parts by weight of "Hydrofol Acids 150" and about 330 parts by weight of solvent-refined, naphthenic oil was heated to about 165° F. in a grease kettle. About 5 parts by weight of acetic acid, about 12 parts by weight of $Ca(OH)_2$ (1.3 parts excess) and about 10 parts by weight of water were added and

the mixture was heated to about 400° F. during a period of about five hours. About one part $Ca(OH)_2$ was added and the grease was cooled to ambient temperature whilst it was stirred. The total salt content was about 19 weight per cent, while the free CaO content was about 0.43%.

To illustrate the effect of the addition of an aliphatic, monocarboxylic acid having less than six carbon atoms upon the dropping point of these greases, a grease was prepared without the low molecular weight aliphatic monocarboxylic acid in the manner described in Example VII.

EXAMPLE VII

A mixture of about 50 parts by weight of oil-free copolymer similar to that used in Example I (N. N.=216), about 50 parts by weight of stearic acid and about 500 parts by weight of solvent-refined, naphthenic oil was heated to about 160° F. in a grease kettle. About eighteen parts by weight of $Ca(OH)_2$ (4.4 parts excess) and about 10 parts by weight of water were added and the mixture was heated to about 350° F. during a period of about six hours. The grease was then cooled whilst stirring. The total salt content was about 18 weight per cent. The excess $Ca(OH)_2$ would represent about 0.54% free CaO in final grease.

The dropping points of the greases prepared as described in Examples I through VII are given in table I.

Table I

Grease of:	Dropping point, °F.[4]
Example I[1]	490
Example II[1]	384
Example III[1]	325
Example IV[1]	440
Example V[2]	445
Example VI[1]	430
Example VII[3]	230

[1] Formulation includes acetic acid.
[2] Formulation includes butyric acid.
[3] No low molecular weight, aliphatic, monocarboxylic acid.
[4] A. S. T. M. Designation D–566.

Those skilled in the art will recognize readily that the grease in which no low molecular weight, aliphatic monocarboxylic acid was used had a dropping point about 160° F. lower than a comparable composition containing a low molecular weight, aliphatic, monocarboxylic acid. Thus, the grease of Example VII in the formulation of which no low molecular weight acid was used had a dropping point of only 230° F., whereas the greases in the formulation of which acetic or butyric acid was used had dropping points ranging from 325° F. to 490° F. In addition to having high dropping points, the greases containing an aliphatic, monocarboxylic acid having less than six carbon atoms retain the good mechanical stability, the smooth texture, and the absence of a bleeding tendency displayed by the unmodified greases. The modified greases are equivalent to the greases in which the acidic copolymer is the only gelation agent in every respect save resistance to oxidation. However, this characteristic can be improved by incorporating an antioxidant, for example phenothiazine, in the grease.

A test for determining the resistance of greases to oxidation is that having the A. S. T. M. Designation: D–942 "Tentative Method of Test for Oxidation Stability of Lubricating Greases by the Oxygen Bomb Method." In order to increase the severity of the test, tests were conducted at 250° F. instead of the standard temperature of 210° F. These data are shown in table II.

Table II

MODIFIED A. S. T. M. BOMB TEST FOR OXIDATION STABILITY OF LUBRICATING GREASES

Grease from Example	Hours required for Pressure Drop of 10 lbs. at 250° F.
1	4
1+0.25% phenothiazine	211

Barium can be substituted for calcium in the aforedescribed novel greases as the following illustrative but not limiting examples demonstrate.

EXAMPLE VIII

A mixture of about 50 parts by weight of the oil-free, acidic copolymer used in Example I, about 35 parts by weight of "Hydrofol Acids 150," about 150 parts by weight of an acid-refined, naphthenic oil having a viscosity of 232 S. U. S. @ 100° F. and 250 parts of a solvent-refined, naphthenic oil having a viscosity of 513.5 S. U. S. @ 100° F. was heated in a grease kettle to about 160° F. About 50 parts by weight of $Ba(OH)_2.8H_2O$ (1.5 parts excess) were added and the mixture was heated to about 415° F. during a period of about 3.5 hours. The source of external heat was removed and the mass was stirred while cooling it to ambient temperature. The total salt content was about 21 weight per cent. The excess barium hydroxide represents about 0.15% BaO in the final grease. The grease had a dropping point of 315° F.

EXAMPLE IX

A mixture of about 50 parts by weight of the oil-free, acidic copolymer used in the formulation of the grease described in Example I, about 35 parts by weight of "Hydrofol Acids 150," about 150 parts by weight of acid-refined, naphthenic oil having a viscosity of 232 S. U. S. @ 100° F. and about 300 parts by weight of solvent-refined, naphthenic oil having a viscosity of 513.5 S. U. S. @ 100° F. was heated to about 160° F. in a grease kettle. About 7 parts by weight of acetic acid and about 70 parts by weight of $Ba(OH)_2.8H_2O$ (3.1 parts excess: represents about 0.25% free BaO in final grease) were added and the mixture was heated to about 400° F. during a period of about 3.5 hours. The source of external heat was removed and the mass stirred while cooling to ambient temperature. The total salt content of the grease was about 21 weight per cent. The dropping point of this grease was 470°+ F. as compared with 315° F. for the grease of the same formulation, save for the absence of acetic acid, described in Example VIII.

Thus, it is manifest that the addition of an aliphatic monocarboxylic acid having less than six carbon atoms and the stoichiometric equivalent of a group II metal compound capable of reacting with said monocarboxylic acid, for example the hydroxides and carbonates, raises the dropping point of greases containing the novel mixed gelling agents, to wit: salts of a metal of group II of the periodic system and at least one acidic copolymer of the class described hereinbefore and a high molecular weight, saturated, aliphatic, monocarboxylic acid having 12 to 22 and preferably 18 carbon atoms whilst the greases having raised dropping points retain the stability, smooth texture and absence of a tendency to bleed possessed by the greases having low dropping points.

The exact sequence of operations whereby the novel greases of the present invention are prepared, at this time, does not seem to be too important. That is to say, the novel greases can be prepared by charging the required amount of acidic copolymer, the required amount of aliphatic, monocarboxylic acid having 10 to 22 carbon atoms and the required amount of aliphatic, monocarboxylic acid having less than 6 carbon atoms together with an amount of basic calcium or barium compound at least sufficient to neutralize all of the acidic components, a small amount of water and the oleaginous vehicle to a stable container such as a grease kettle. The mixture is heated to about 300° to 400° F. until a smooth grease is formed. The mixture is then cooled statically or with agitation to ambient temperature.

Alternatively, the required amount of acidic copolymer, the required amount of aliphatic, monocarboxylic acid having 10 to 22 carbon atoms and an amount of basic calcium or barium compound to neutralize the aforesaid acidic components together with the required amount of oleaginous vehicle and a small amount of water are charged to a stable container, for example, a grease kettle. The mixture is heated to about 330° to 400° F. until a smooth grease is formed. The mixture is then cooled to at least 200° F. and an aqueous solution of calcium or barium salt of an aliphatic, monocarboxylic acid having less than 6 carbon atoms is added. The mixture is then heated again to about 300° to 400° F. until the major portion of the water is driven off and then cooled to ambient temperature with or without agitation.

As those skilled in the art know, a portion of the oleaginous vehicle can be charged to the grease kettle, the grease formed and sufficient of the oleaginous vehicle then added to bring the consistency of the grease to the right degree.

Other agents can be incorporated in the basic formulations described hereinbefore. Thus, extreme pressure agents, tackiness agents, inorganic fillers and the like, all well known to those skilled in the art, can be added to the aforedescribed formulations. Inorganic thickening agents such as carbon black and silica flour can be used in combination with the novel gelling agents to reduce the required concentration of the latter to produce a grease of required consistency.

While the illustrative but not limiting examples provided hereinbefore have been typical of formulations of satisfactory greases wherein naphthenic oils were used, those skilled in the art will understand that lubricating fractions of mineral oil from any crude source can be used to replace the naphthenic oils of the illustrative greases wholly or in part.

I claim:

1. A modified grease comprising a major proportion of a lubricating oleaginous vehicle, a minor proportion of a mixed gelling agent and an amount of an aliphatic monocarboxylic acid having less than six carbon atoms and a molar equivalent of a metal of group II of the periodic system sufficient to provide a grease having a dropping point of at least 300° F., said gelling agent comprising a mixture of salts of a metal of group II of the periodic system and (1) an acidic copolymer of an alpha,beta-unsaturated polycarboxylic acid and an aliphatic compound having a terminal vinyl group, said acidic copolymer having a molecular weight of about 1000 to about 2000, and (2) a saturated aliphatic monocarboxylic acid having 10 to 22 carbon atoms.

2. A grease comprising a mineral lubricating oil fraction, an amount sufficient to gel said oil fraction to a grease of an aliphatic monocarboxylic acid having 10 to 22 carbon atoms, an acidic copolymer having a molecular weight of about 1000 to about 2000 of an aliphatic compound having a terminal vinyl group and an alpha,beta-unsaturated polycarboxylic acid, at least the stoichiometric equivalent of said acid and said acidic copolymer of a metal of group II of the periodic system, and an amount sufficient to raise the dropping point of the said grease of an aliphatic, monocarboxylic acid having less than six carbon atoms and at least a stoichiometric equivalent of a metal of group II of the periodic system.

3. A grease comprising a mineral lubricating oil fraction, an amount sufficient to gel said mineral oil fraction to a grease of a mixture of (1) a saturated, aliphatic, monocarboxylic acid having 10 to 22 carbon atoms, (2) an acidic copolymer having a molecular weight of about 1000 to about 2000 of an aliphatic compound having a terminal vinyl group and an alpha,beta-unsaturated aliphatic polycarboxylic acid having not more than 10 carbon atoms, and (3) at least a stoichiometric equivalent of said aliphatic acid and said acidic copolymer of a metal of group II of the periodic system, and an amount, sufficient to raise the dropping point of the aforesaid grease, of (1) a saturated aliphatic monocarboxylic acid having less than six carbon atoms, and (2) at least the stoichiometric equivalent of said acid having less than six carbon atoms of a metal selected from the group consisting of calcium and barium.

4. A grease comprising about 5 to about 12 weight per cent of an acidic copolymer of an alpha,beta-unsaturated polycarboxylic acid and an aliphatic compound having a terminal vinyl group, said acidic copolymer having a molecular weight of about 1000 to about 2000, about 5 to about 12 weight per cent of a saturated aliphatic monocarboxylic acid having 12 to 22 carbon atoms, at least the stoichiometric equivalent of the foregoing of a metal of group II of the periodic system, about 0.5 to about 3 weight per cent of a saturated aliphatic monocarboxylic acid having less than six carbon atoms, and at least the stoichiometric equivalent of said aliphatic monocarboxylic acid having less than six carbon atoms of a metal selected from the group consisting of calcium and barium, and the balance, to make 100 weight per cent, an oleaginous vehicle.

5. A grease comprising about 5 to about 12 weight per cent of an acidic copolymer of an alpha,beta-unsaturated polycarboxylic acid and an aliphatic compound having a terminal vinyl group, said acidic copolymer having a mo-

lecular weight of about 1000 to about 2000, about 5 to about 12 weight per cent of a saturated aliphatic monocarboxylic acid having 12 to 22 carbon atoms, at least the stoichiometric equivalent of the foregoing of a metal of group II of the periodic system, about 0.5 to about 3 weight per cent of a saturated aliphatic monocarboxylic acid having less than six carbon atoms, and at least the stoichiometric equivalent of said aliphatic monocarboxylic acid having less than six carbon atoms of a metal selected from the group consisting of calcium and barium and the balance, to make 100 weight per cent, mineral lubricating oil fraction.

6. A grease comprising about 5 to about 12 weight per cent of an acidic copolymer of an alpha,beta-unsaturated polycarboxylic acid and an aliphatic compound having a terminal vinyl group, said acidic copolymer having a molecular weight of about 1000 to about 2000, about 5 to about 12 weight per cent of a saturated aliphatic monocarboxylic acid having 12 to 22 carbon atoms, at least the stoichiometric equivalent of the foregoing of a metal selected from the group of calcium and barium, about 0.5 to about 3 weight per cent of a saturated aliphatic monocarboxylic acid having less than six carbon atoms, at least the stoichiometric equivalent of said monocarboxylic acid having less than six carbon atoms of a metal selected from the group consisting of calcium and barium, and the balance, to make 100 weight per cent, mineral lubricating oil fraction.

7. A grease comprising about 36 to about 50 parts by weight of an acidic copolymer of an alpha,beta-unsaturated polycarboxylic acid and an aliphatic compound having a terminal vinyl group, said acidic copolymer having a molecular weight of about 1000 to about 2000 and having a neutralization equivalent of about 150 to about 250, about 25 to about 35 parts by weight of a saturated aliphatic monocarboxylic acid having 10 to 22 carbon atoms, about 5 to about 11 parts by weight of a saturated aliphatic monocarboxylic acid having less than six carbon atoms, about 7 to about 13 parts by weight calcium sufficient to at least neutralize the three acidic components, and the balance, to make about 400 to about 600 parts, mineral lubricating oil fraction.

8. A grease comprising about 50 parts by weight of an acidic copolymer of maleic anhydride and the allyl ester of a mixture of saturated aliphatic monocarboxylic acids having an average of about 18 carbon atoms, about 50 parts by weight stearic acid, about 7.5 to about 10 parts by weight acetic acid, calcium in amount sufficient to at least neutralize the three acidic components, and the balance, to make about 600 to about 700 parts, mineral lubricating oil fraction.

9. A grease comprising about 50 parts by weight of an acidic copolymer of maleic anhydride and the allyl ester of a mixture of aliphatic monocarboxylic acids having an average of about 18 carbon atoms, about 35 parts by weight of a mixture of saturated aliphatic monocarboxylic acids having an average of 18 carbon atoms, about

7 parts by weight of acetic acid, calcium in amount sufficient to at least neutralize the three acidic components, and the balance, to make about 500 to about 600 parts by weight, mineral lubricating oil fraction.

10. A grease comprising about 50 parts by weight of an acidic copolymer of an alipha,beta-unsaturated polycarboxylic acid and an aliphatic compound having a terminal vinyl group, said acidic copolymer having a molecular weight of about 1000 to about 2000, about 35 parts by weight of a mixture of saturated aliphatic monocarboxylic acids having an average of 18 carbon atoms, about 10.3 parts by weight of butyric acid, calcium in amount at least sufficient to neutralize the three acidic components, and the balance, to make about 500 to about 600 parts by weight, mineral lubricating oil fraction.

11. A grease comprising about 50 parts by weight of an acidic copolymer of an alpha,beta-unsaturated polycarboxylic acid and an aliphatic compound having a terminal vinyl group, said acidic copolymer having a molecular weight of about 1000 to about 2000, about 35 parts by weight of a mixture of saturated aliphatic monocarboxylic acids having an average of about 18 carbon atoms, about 7 parts by weight of acetic acid, barium in amount sufficient to at least neutralize the three acidic components, and the balance, to make about 500 to about 600 parts, mineral lubricating oil fraction.

12. A grease comprising about 36 parts by weight of an acidic copolymer of maleic anhydride and 1-octadecene, about 25 parts by weight of a mixture of saturated aliphatic monocarboxylic acids having an average of 18 carbon atoms, about 5 parts by weight of acetic acid, calcium in amount sufficient to at least neutralize the three acidic components and the balance to make about 400 to about 500 parts by weight mineral lubricating oil fraction.

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