United States Patent Office 2,754,268
Patented July 10, 1956

2,754,268

LUBRICATING GREASE CONTAINING A METAL SALT OF ALGIN

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No Drawing. Application July 15, 1953, Serial No. 368,222

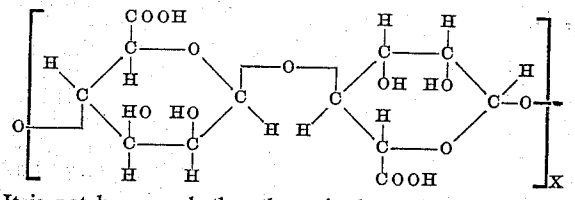
18 Claims. (Cl. 252—41)

The present invention relates to improved lubricating greases. More specifically, the invention is concerned with lubricating greases having high dropping points and high structural stability to mechanical working over long periods of time at relatively low thickener concentrations. In its broadest aspect, the invention pertains to greases thickened with a soap-type grease thickener which contains a substantial proportion of a metal soap of algin, preferably in the form of a complex with the metal salt of a low molecular weight carboxylic acid.

Prior to the present invention, greases having desirably high dropping points and high mechanical stability to working have been prepared by using the alkali or alkaline earth metal soaps of combinations of high and low molecular weight carboxylic acids. It is also known that these greases require soap contents of at least 10% to exhibit the desired structural stability and freedom from oil separation. As the soap thickeners are diluted with lubricating oil, i. e. as the soap concentration of the grease decreases, the dropping point is materially lowered and semi-fluid products of poor structural stability result.

It has now been found that greases having excellent high dropping points and highly desirable structure and stability characteristics at much reduced soap requirements may be obtained by incorporating into the grease thickener at least a substantial proportion of a metal soap, particularly an alkali metal soap, of alginic acid. Preferably, the alginic acid soap forms all or part of the high molecular weight fatty acid soap constituent of a thickener of the high molecular weight-low molecular weight complex soap type discussed above.

Alginic acid, more commonly called algin, is a seaweed colloid usually extracted by alkalis from brown algae (Phaeophyta) especially from members of the kelp order (Laminariales). The alginic acids are generally regarded as being hydrophilic colloidal polymers of anhydro-β-D-mannuronic acid units having the structural formula which is generally accepted to be:



It is not known whether the units have the pyranose or furanose structure, but the former is indicated in view of the excellent stability of alginic acid with respect to hydrolysis and the large negative rotation of the acid.

Natural algin in kelp is probably a combination of calcium alginate and aliphatic acid; it is insoluble in water and easily converted to a water solution of the sodium salt. In commercial preparation procedures the kelp is easily digested with sodium carbonate or hydroxide, the resulting viscous liquor is separated from the residue, and alginic acid is precipitated by the addition of strong mineral acids. Since alginic acid is rather heat unstable whereas its salts or soaps are quite stable, it is generally marketed as sodium alginate. Various methods of producing algins are known to the art. Representative procedures are discussed in "Colloid Chemistry" Reinhold, New York, 1946, volume VI, pages 629–734. A preferred procedure is disclosed in U. S. Patent 2,036,922 to Clark et al. In general, polymers of anhydro-mannuronic acid and the stereo isomers thereof are suitable in the practice of the present invention.

Some of the advantages of the invention may be realized by using metal soaps, particularly alkali metal soaps of an alginic acid as the sole or essentially sole thickener. Soap concentrations of about 2–15% should be used in this case. However, in accordance with the preferred embodiment of this invention, the alginic acid soap is present in the grease in the form of a complex with a salt, preferably an alkali metal salt of a low molecular weight carboxylic acid. In many cases, it may be desirable to incorporate into the complex a soap of a high molecular weight fatty acid other than alginic acid. Thickeners of this type may contain about 10–75 wt. percent, preferably about 25–50 wt. percent, of algin soap. The low molecular weight acid salts and total high molecular weight acid soaps may be present in equi-molecular proportions. However, the low molecular weight acid may be present in smaller or larger proportions, mol ratios of 1:1 to 3:1 of low to total high molecular weight acids being preferred.

The total complex thickener content may vary within the wide range of about 2–40 wt. percent of the finished grease. It is however a particular advantage of the present invention that excellent greases having high dropping points and high structural stability to mechanical working may be obtained by using substantially less than 10 wt. percent and even as little as 2.5 wt. percent of an alginic acid soap containing-thickener. Complex soap concentrations of about 5–10 wt. percent are, therefore, preferred for most purposes.

The low molecular weight acids to be combined with the alginic acid to form the complex soap thickener of the invention may be any aliphatic carboxylic acid having 1–5 carbon atoms per molecule, such as formic, acetic, propionic, butyric, valeric, furoic, acrylic acids, etc. The preferred low molecular weight acids are formic and acetic acids. High molecular weight fatty acids which may be used together with alginic acid and the low molecular weight acids here specified include saturated or unsaturated fatty acids having 10–30 carbon atoms per molecule, such as hydrogenated fish oil acids, stearic acid, oleic acid, behenic acids, etc., saturated acids having 18–22 carbon atoms per molecule being preferred.

Branched chain "Oxo" acids, prepared by the "Oxo" synthesis, are also useful as a component of the high molecular weight acids. In general, these acids may be prepared by any one of several well-known processes, such as by the catalytic reaction of an olefin with carbon monoxide and hydrogen at temperatures in the order of 300° to 400° F., and at pressures above about 1000 p. s. i., using cobalt carbonyl or other suitable catalyst. The resulting branched chain aldehydes or alcohols may then be oxidized or otherwise converted to the "Oxo" acids. In general, "Oxo" acids should be employed along with other high molecular weight acids in concentrations below about 50% by weight based on the total non-alginic high molecular weight acid constituent.

Metal bases suitable for the formation of complex soaps in accordance with the invention include the hydroxides and carbonates of alkali, alkaline earth and certain other metals, for example, lithium, sodium, potassium, calcium, barium, and aluminum. However, alkali metal bases, particularly the hydroxides of sodium and

lithium, which form complex soaps of satisfactory water insolubility and temperature characteristics, are preferred.

Regarding lubricating oil bases suitable for the greases of the invention, all types of mineral lubricating oils as well as synthetic oils including diesters, complex esters, formals and hydrocarbon polymers having lubricating oil characteristics may be used.

Greases in accordance with the invention may be prepared by preforming the alginic acid soap or soap complex with other acids and incorporating the same in the lubricating oil by mechanical mixing. The preformed soap or soap complex may be prepared by neutralizing the alginic acid or mixtures thereof with the other acids to be used by means of substantially stoichiometric amounts of the desired metal base preferably in aqueous solution, recovering the complex soap formed and compounding the same with the lubricating oil at grease-making conditions.

However, the preferred method of the invention involves formation of the soap or soap complex in situ in the lubricating oil in the course of the grease-making process. For this purpose the alginic acid and other high molecular weight fatty acids, if any, may be charged to a reaction zone and heated together with a portion of the lubricating oil to about 130°–170° F. Thereafter the low molecular weight acid may be added and the mixture neutralized, preferably with a slight stoichiometric excess of an aqueous solution of the metal base of about 30–50% concentration. Sufficient metal base should be used to give the grease a free alkalinity of about 0.1–1% as NaOH.

The mixture may then be dehydrated at temperatures of about 250°–350° F. When dehydration is substantially complete, further lubricating oil may be added and heating continued to about 450°–550° F. Thereafter, the grease may be cooled. When temperatures below 300° F. are reached other conventional additives, such as antioxidants, particularly amino compounds, extreme pressure agents containing sulfur, halogen and/or phosphorus, etc., may be added in any conventional manner.

The invention will be further illustrated by the following specific examples.

EXAMPLE I

Ingredients

	Weight percent
Alginic acid [1]	10.00
Hydrofol Acids 54 [2]	10.00
Acetic acid (glacial)	4.00
Sodium hydroxide	6.50
Phenyl alpha-naphthylamine	1.00
Blend of naphthenic-type mineral oil distillates having a viscosity of 50 S. S. U. at 210° F.	68.50

[1] Commercial alginic acid which was a free-flowing fibrous powder.

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

Preparation

The alginic acid, Hydrofol acid and about ½ of the mineral oil were charged to a grease kettle and warmed to 150°–160° F. At this temperature the acetic acid was charged followed immediately by a 40% aqueous solution of sodium hydroxide. Heating was continued and at 300° F., when the soap mass in the kettle was fairly dry, the balance of the mineral oil was added. The mixture was further heated to about 500° F. At this temperature heating was discontinued and the mass cooled to 250° F., at which temperature the phenyl alpha-naphthylamine was added. The grease was further cooled to 200° F., and homogenized by passage through a Gaulin homogenizer. Gaulin homogenization of the grease at higher rates of shear result in an excellent, smooth, uniform product.

Properties

Percent free alkalinity as NaOH	0.72.
Penetrations, 77° F. mm./10:	
Unworked	102.
Worked, 60 strokes	114.
Worked, 100,000 strokes (270 1/16" hole worker plate)	Too hard—did not run.
Dropping point, °F.	500+.
Water washing test, percent loss	None.
Norma Hoffmann oxidation test, hours to 5 p. s. i. drop in O_2 pressure	210.

EXAMPLE II

The grease of Example I was diluted with 100% additional mineral oil by mixing together at 80° F. and then Gaulin homogenizing. The mineral oil employed was a solvent extracted paraffinic-type oil, having low volatility, high viscosity index, and good oxidation resistance with a viscosity of 45 S. S. U. at 210° F. It is not possible to employ this type of mineral oil exclusively as a grease base due to the poor solubility or colloidal dispersibility of the soap in this less polar mineral oil.

Ingredients

	Weight percent
Alginic acid grease base of Example I	50.00
Additional mineral oil	50.00
or	
Alginic acid	5.00
Hydrofol Acid 54	5.00
Acetic acid	2.00
NaOH	3.25
Naphthenic-type original oil	34.25
Paraffinic-type additional oil	50.00
Phenyl alpha-naphthylamine	0.50

Properties

Appearance of grease	Excellent, smooth, homogeneous.
Dropping point, °F.	480.
Penetrations, 77° F. mm./10:	
Unworked	233.
Worked, 60 strokes	275.
Worked, 17,000 strokes (270 1/16" hole worker plate)	280.
Water washing test, percent loss	10.
Norma Hoffmann oxidation test, hours to 5 p. s. i. drop in O_2 pressure	145.

The invention is not limited to the specific figures of the foregoing examples. The relative proportions of the grease constituents may be varied within the limits indicated above to obtain greases of different consistency and varying characteristics.

What is claimed is:

1. A lubricating grease comprising a major proportion of a lubricating oil and a minor grease-making proportion of a carboxylic acid metal salt complex grease thickener containing at least 10 wt. percent of a metal salt of alginic acid, said metal being selected from the group consisting of alkali metals, alkaline earth metals and aluminum.

2. The grease of claim 1 in which said complex thickener comprises a carboxylic acid metal salt complex of a metal salt of alginic acid and a metal salt of a low molecular weight carboxylic acid.

3. The grease of claim 2 in which said complex thickener comprises a high molecular weight fatty acid soap in addition to said metal salt of alginic acid and said metal salt of a low molecular weight carboxylic acid.

4. A lubricating grease comprising a major proportion of a lubricating oil and a minor grease-making proportion of a carboxylic acid metal salt complex grease thickener containing about 10–75 wt. percent of a metal salt of

alginic acid, said metal being selected from the group consisting of alkali metals, alkaline earth metals and aluminum.

5. A grease as claimed in claim 4 which contains about 2–40 wt. percent of said thickener.

6. A lubricating grease comprising a major proportion of a lubricating oil and about 2–40 wt. percent of a carboxylic acid metal salt complex grease thickener containing at least 10 wt. percent of a metal salt of alginic acid and a metal salt of a low molecular weight carboxylic acid, said metal being selected from the group consisting of alkali metals, alkaline earth metals and aluminum.

7. A grease as claimed in claim 6 in which said complex thickener contains high molecular weight fatty acid soap in addition to said metal salt of alginic acid and said metal salt of a low molecular weight carboxylic acid.

8. A grease as claimed in claim 6 in which said metal is an alkali metal.

9. A grease as claimed in claim 6 in which said low molecular weight acid has 1–5 carbon atoms.

10. A grease as claimed in claim 7 in which said high molecular weight fatty acid has 10–30 carbon atoms.

11. A lubricating grease comprising about 60–98 wt. percent lubricating oil and about 2–40 wt. percent of a carboxylic acid salt complex grease thickener containing about 10–75 wt. percent, based on thickener, of an alkali metal salt of alginic acid, the remainder of said thickener comprising an alkali metal soap of a high molecular weight fatty acid having 18–22 carbon atoms and an alkali metal salt of a low molecular weight carboxylic acid having 1–5 carbon atoms, the mol ratio of low molecular weight acid salt to high molecular weight fatty soap plus alginic acid salt being 1–3.

12. A grease as claimed in claim 11 which contains about 5–10 wt. percent of said thickener, the latter containing about 25–50 wt. percent of said alginic acid salt.

13. A grease as claimed in claim 11 in which said high molecular weight fatty acid soap is the sodium soap of hydrogenated fish oil acids and said low molecular weight carboxylic acid salt is sodium acetate.

14. The method of preparing lubricating greases which comprises heating a lubricating oil containing a minor thickening proportion of alginic acid to about 130°–170° F., adding a minor proportion of a low molecular weight carboxylic acid, neutralizing the mixture with sufficient alkali metal hydroxide to give the mixture a free alkalinity of about 0.1–1% calculated as NaOH, dehydrating the mixture at temperatures of about 250°–350° F., further heating the mixture to about 450°–550° F., and cooling the mixture.

15. The method of claim 14 in which said lubricating oil is a naphthentic oil and said cooled mixture is diluated with a paraffinic lubricating oil.

16. The method of claim 14 in which said lubricating oil contains additionally a thickening proportion of a high molecular weight fatty acid having 18–22 carbon atoms.

17. The method of claim 14 in which said hydroxide is sodium hydroxide.

18. A lubricating grease comprising about 90–95 wt. percent of mineral lubricating oil, about 1 wt. percent of an oxidation inhibitor and about 4–9 wt. percent of a complex carboxylic acid salt grease thickener consisting of about 40–42 wt. percent of the sodium salt of alginic acid, about 40–42 wt. percent of the sodium soap of hydrogenated fish oil acids and about 16–20 wt. percent of sodium acetate.

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