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2,870,090

METHOD OF GREASE MANUFACTURE COMPRISING SHEARING

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This invention relates to an improved method of grease manufacture. More particularly it relates to an improved method for the preparation of greases thickened with lithium soaps of hydroxy fatty acids.

In accordance with this invention, lubricating greases are prepared by a method which comprises cooling the grease mixture from a temperature near the melting point of the soap to a suitably low temperature and then subjecting the cooled mixture to a limited amount of shearing by passing it through a shear valve with a pressure drop across the valve of about 15–200 p. s. i. The amount of shearing employed is represented by an amount of work expended upon the grease below about 1000 foot pounds per pounds of finished grease, and preferably from about 50 to about 500 pounds per pound of finished grease.

We have found that this limited amount of shearing in the manner described produces a different effect upon the grease properties than are obtained by other shearing methods which have been employed heretofore. In particular, it produces the desired improvements in grease texture with only a small change in worked penetration, differently from other mild shearing methods such as stirring, which are ineffective to produce a good grease texture in certain greases, such as lithium hydroxy fatty acid greases, which are difficult to prepare in satisfactorily smooth form, and also differently from the conventional milling operations, which produce a large amount of hardening on the basis of both worked and unworked penetration. Such hardening results in lowered soap content for a given grade, and is undesirable where superior stability and other lubricating characteristics are required.

The shearing operation is carried out at a temperature below the phase transition temperature range of the grease mixture, that is, below the range wherein any substantial thermal effect is obtained upon cooling. The suitable temperature range is represented by a substantially flat portion of the temperature differential curve. In the case of greases having a single phase transition upon cooling, the flattening out of the temperature differential curve generally occurs gradually over a wide temperature range, and the suitable temperature range for the shearing operation is therefore much below the temperature range wherein the major thermal effect occurs. For example, in the case of lithium hydroxy fatty acid soap greases, which have a range of major thermal effect at about 400–350° F. upon cooling, the suitable range for the shearing is below about 200° F. In the case of greases which have more than one phase transition upon cooling, the shearing operation is carried out after the grease mixture has been cooled through the lowest phase transition temperature range, which is below about 185° F. in the case of sodium base greases.

The method of this invention may be employed advantageously in grease manufacture generally, as for example in the manufacture of greases thickened with soaps of sodium, potassium, lithium, calcium, barium, strontium, aluminum or lead, or mixtures of such soaps. The saponifiable material employed in the production of these soaps

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may be a higher fatty acid containing from about 10 to 32 carbon atoms per molecule, or the glyceride or other ester thereof, such as myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid, tallow, hydrogenated fish fatty oils, etc.

A particularly important application of this invention is found in the production of greases thickened with lithium soaps of hydroxy fatty acids, wherein it affords a means of obtaining both the desired grease texture and the higher soap contents in the softer grade greases which are necessary to meet the requirements for certain types of service, such as AAR Specification M-917-53 for a No. 0 grade journal roller bearing grease. Lithium hydroxy fatty acid soap greases are conventionally prepared by shock cooling the grease mixture, and then subjecting the cooled grease to a severe milling operation, usually by passing it through a colloid mill containing a rotor and stator at about 0.003 inch clearance, in order to obtain a satisfactory grease texture. This milling operation results in a large amount of hardening of the grease on the basis of both worked and unworked penetration, in contrast to the result obtained with the present method, wherein No. 0 grade greases of about 2 percent higher soap content are obtained. The effect obtained with the present method is also unexpectedly different from that obtained by shearing the grease mixture at elevated temperatures, which also causes a large amount of hardening on the basis of the worked penetration and generally produces greases having a very wide spread between worked and unworked penetrations.

Suitable soap-forming hydroxy fatty acid materials which may be employed in the production of the lithium hydroxy fatty acid soap greases are essentially saturated hydroxy fatty acids containing 12 or more carbon atoms and one or more hydroxyl radicals separated from the carboxyl group by at least one carbon atom, the glycerides of such acids and the lower alkyl esters of such acids. Preferably, the acid contains about 16 to 22 carbon atoms. Such materials may be obtained from naturally occurring glycerides, by hydroxylation of fatty acids, by hydrogenation of ricinoleic acid or castor oil, or otherwise by processes such as the catalytic oxidation of hydrocarbon oils and waxes which have been extracted and fractionated to the desired molecular range. Particularly suitable materials of this character are hydrogenated castor oil, 12-hydroxystearic acid and the methyl ester of 12-hydroxystearic acid.

The oleaginous liquid employed in the greases may be any suitable oils of lubricating characteristics, including the conventional mineral lubricating oils, the synthetic lubricating oils prepared by cracking and polymerizing products of the Fischer-Tropsch process and the like, as well as other synthetic oleaginous compounds such as polyesters, polyethers, etc., within the lubricating oil viscosity range. Such synthetic oleaginous compounds, including mixtures thereof, may be substituted in whole or in part for the conventional mineral lubricating oils. Examples of these compounds are the aliphatic dicarboxylic acid diesters such as di-2-ethyl hexyl sebacate, di(secondary amyl) sebacate, di-2-ethyl hexyl azelate, di-iso octyl adipate, etc. Suitable mineral oils are those having viscosities in the range from about 100 to 2000 seconds Saybolt Universal at 100° F., and may be either naphthenic or paraffinic in type or blends of the two. When the saponification is carried out in the presence of a portion of the oil included in the grease, an oil which is not hydrolyzed under the saponification conditions is preferably employed for this purpose, most suitably a mineral oil fraction.

The greases may also contain various additives of the usual types such as corrosion inhibitors, oxidation inhibitors, anti-wear agents, extreme pressure agents and so

forth. The additive may be added either before or during the cooling down process. They are preferably added while the temperature of the grease is between about 300° F. and about 180° F.

The grease mixture may be obtained in any suitable manner, such as by merely mixing together a preformed soap and oleaginous liquid in grease-forming proportions with heating, or by saponifying in situ in a portion of the oleaginous liquid component of the grease, followed by dehydration at a higher temperature and blending in of the remainder of the oleaginous liquid component during the cooling.

In carrying out the preparation of greases thickened by lithium soaps of hydroxy fatty acids, the so-called high temperature process is preferably employed, wherein the mixture of soap and oleaginous liquid is heated at a temperature above the melting point of the soap for a sufficient period to obtain a molten homogeneous mixture. The cooling process is preferably carried out at a relatively low rate such as below about 15° F. per minute, very advantageously by means of the recycle cooling process of R. F. Nelson, R. C. Givens and H. J. Pitman described in their application Serial No. 365,076, filed January 30, 1953, now U. S. 2,830,023, or by the combined quench and recycle cooling method of R. C. Givens and H. J. Pitman described in their application Serial No. 494,441, filed March 15, 1955.

The following example is given for the purpose of further disclosing the invention:

EXAMPLE 1

A series of greases comprising mineral lubricating oils thickened with about 3-12 percent by weight of lithium 12-hydroxystearate was prepared by the method of this invention. The greases were prepared in about 300 pound batches in a jacketed Dowtherm heated and cooled laboratory kettle connected to a recycle system for recycling the kettle contents through an external cooler as described in application Serial No. 365,076 mentioned above. The greases were finished by passing the grease mixture at a temperature below 200° F. through a shear valve with a pressure drop in the range of about 10-200 p. s. i.

A representative grease of this series comprised 6 percent lithium 12-hydroxystearate in a lubricating oil which was a blend in about a 1:1 ratio by weight of a refined wax distillate oil having an SU viscosity at 100° F. of 179 seconds and a refined residual motor oil stock from a Manvel crude, having an SU viscosity of 106 seconds at 210° F. The blend had an SU viscosity at 100° F. of 485 seconds, a flash point of 450° F. and a pour point of +5° F.

The method of preparation in detail was as follows: The grease mixture was obtained by saponifying a hydroxy fatty acid material with lithium hydroxide in the form of an approximately 10 percent aqueous solution in the presence of about one half of the residual motor oil stock in the finished grease. The fatty acid material was a commercial material consisting essentially of the methyl ester of 12-hydroxystearic acid, having a saponification number of 178, a neutralization number of 4.6 and a hydroxyl number of 176. The saponification was carried out at a temperature of about 180-220° F. for about one hour, and the mixture dehydrated by heating to 300-310° F. Following the dehydration, the remainder of the oil was added and the mixture heated to about 395-405° F. so as to completely melt the soap. The stirring of the kettle contents was carried out continuously during the preparation of the grease mixture and the subsequent cooling process. Recycling of the grease through the external cooler was carried out during the cooling from about 400° F. to about 200° F. at a rate

of about 28 gallons per minute. The cooling rate of the grease in the range from about 400° F. to about 300° F. was about 8½° F. per minute.

Portions of the cooled grease mixture at about 175° F. were withdrawn from the kettle through a shear valve adjusted to give a 65 or 90 pounds pressure drop. Another portion of the grease was taken off and milled in the conventional manner by passing it through a Premier colloid mill adjusted to a 0.003 inch clearance. The following table shows a comparison of the effect of the different finishing methods upon the worked and unworked penetrations of the grease.

Table I

Finishing Method	ASTM Penetration, 77° F.	
	Unworked	Worked
None	400+	379
Colloid Mill	288	315
Shear Valve, pressure drop:		
65 p. s. i.	370	366
90 p. s. i.	356	357

The above greases, prepared by shearing at both 65 and 90 p. s. i. pressure drop, very satisfactorily met AAR Specification M-917-53 for a No. O grade journal roller bearing grease. The following table shows the properties of the grease finished by shearing with a 90 p. s. i. pressure drop across the valve (designated A) as compared with the specification requirements.

Table II

	A	AAR Specification limits
Penetration, ASTM:		
Unworked	356	
Worked, 60 strokes, 77° F.	354	340-370.
Worked, 100,000 strokes, 77° F.	345	390 max.
Worked, 77° F., pene. at 0° F.	249	200 min.
Dropping point, ° F.	391	325 min.
Oxidation Stability, p. s. i. drop 100 hr.	5 ck 7	10 max.

As shown by the above table, the shear valve finishing method produced a lithium 12-hydroxystearate grease having a worked penetration within the range required by the AAR specification for a No. O grade grease, and also having the required high dropping point and other properties. Lithium 12-hydroxystearate greases of the same soap content which were prepared by methods involving milling in the usual manner were too hard on the basis of the worked penetration to meet this specification. Lithium 12-hydroxystearate greases of lower soap contents prepared by the usual methods having worked penetrations within the required range were deficient in other properties required for this purpose, particularly in resistance to leakage from the bearings in service.

The following table shows the results obtained by the shear valve finishing method upon a different lithium 12-hydroxystearate grease, containing 4.1 percent of lithium 12-hydroxystearate in a different lubricating oil. This grease was prepared in substantially the manner described above except that the grease mixture was quenched during the recycle cooling from about 400° F. to about 350° F., employing about 6.5 percent of the total oil contained in the grease for the quenching, and finished by passing the grease mixture at a temperature below 200° F. through a shear valve with different pressure drops across the valve.

Table III

Pressure Drop, p. s. i.	ASTM Penetration, 77° F.	
	Unworked	Worked
15.....	Too soft	392
40.....	340	345
92.....	334	339
165.....	333	336
174.....	335	334

The amount of work expended upon the greases in passing them through the shear valve at pressures from 15 to 174 p. s. i. was from about 38 to about 445 foot pounds per pound of grease. This compares, for example, with about 17,000 foot pounds of work expended upon the grease in milling it in the conventional manner in a Premier colloid mill at a 0.003 inch clearance.

All of the above greases were of excellent texture and appearance, being fully equivalent in this respect to the greases obtained by milling in the conventional manner. In addition, as shown by the tables, the greases had relatively high soap contents on the basis of their worked penetrations and high working stability, as shown by the very narrow spread between worked and unworked penetrations.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of grease manufacture which comprises cooling a mixture of lithium hydroxy fatty acid soap and oleaginous liquid in grease-forming proportions to a temperature below its phase transition temperature range and then subjecting the said grease mixture to a limited amount of shearing, represented by an amount of work below about 1000 foot pounds per pound of finished grease, by passing the said cooled grease mixture through a shear valve with a pressure drop of about 15-200 p. s. i. across said valve, with substantially no additional working of the grease during the finishing process.

2. The method of claim 1 wherein the amount of work performed upon the grease is from about 50 to about 500 foot pounds per pound of finished grease.

3. The method of grease manufacture which comprises providing a molten homogeneous mixture of a lithium hydroxy fatty acid soap and an oleaginous liquid in grease forming proportion at an elevated temperature above the solution temperature of the soap, maintaining a body of relatively large volume of the said mixture with agitation while reducing the temperature thereof until a grease consistency is obtained by continuously withdrawing a stream of relatively small volume from said body of mixture, passing the said stream through an external cooler and returning it to the maintained body of mixture, and

then subjecting the said mixture at a temperature below its lowest phase transition temperature range to a limited amount of shearing, represented by an amount of work below about 1,000 foot pounds per pound of finished grease by passing the said mixture through a shear valve with a pressure drop of about 15-200 p. s. i. across said valve, with substantially no additional working of the grease during the finishing process.

4. The method of preparing a lubricating grease which comprises cooling a molten homogeneous mixture of a lithium hydroxy fatty acid soap and an oleaginous liquid in grease forming proportions from a temperature above about 385° F. to a temperature below about 300° F. at a rate below about 15° F. per minute, further cooling the said grease mixture to a temperature below about 200° F., and then subjecting the said cooled grease mixture to a limited amount of shearing, represented by an amount of work below about 1000 foot pounds per pound of finished grease, by passing the said mixture through a shear valve with a pressure drop of about 15-200 p. s. i. across said valve, with substantially no additional working of the grease during the finishing process.

5. The method of claim 5 wherein the said cooling in the range from about 385° F. to about 300° F. is carried out by maintaining a body of relatively large volume of the said mixture with agitation while continuously withdrawing a stream of relatively small volume from said body of mixture, passing the said stream through an external cooler, and finally returning said stream to the maintained body of mixture.

6. The method of preparing a lithium 12-hydroxystearate grease which comprises providing a molten homogeneous mixture of lithium 12-hydroxystearate and an oleaginous liquid in grease forming proportions at a temperature above about 390° F., maintaining a body of relatively large volume of the said mixture with agitation while reducing the temperature thereof at a rate below about 15° F. per minute until a grease consistency is obtained by continuously withdrawing a recycle stream of relatively small volume from said body of mixture, passing the said stream through an external cooler, and finally returning the said stream to the maintained body of mixture, and then subjecting the said grease mixture at a temperature below about 200° F. to a limited amount of shearing, represented by an amount of work below about 500 foot pounds per pound of finishing grease, by passing the said mixture through a shear valve with a pressure drop of about 15-200 p. s. i. across said valve, with substantially no additional working of the grease during the finishing process.

References Cited in the file of this patent

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