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METHOD FOR PREPARING LITHIUM BASE GREASES INVOLVING QUENCHING

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This invention relates to an improved process for the manufacture of greases containing lithium soaps of hydroxy fatty acids.

Lithium soap greases are conventionally prepared by methods which involve shock cooling a solution of lithium soap and oleaginous liquid from a temperature above the solution temperature of the soap through the transition temperature range wherein the grease structure is established, in order to obtain greases of satisfactory smoothness. Such methods involve pan cooling in very thin layers, or they require special equipment for obtaining extremely rapid mixing and uniform heat transfer in a large bulk of grease, and are therefore expensive and inconvenient for use in plant manufacture. Attempts to prepare these greases by the usual method of cooling down in the kettle at rates below about 25° F. per minute, have resulted only in grainy and unsatisfactory products and poor yields.

We have now found that lithium base greases may be very successfully prepared by a method which comprises cooling a solution of a lithium soap of a hydroxy fatty acid and an oleaginous liquid at a relatively low rate together with slow quenching through the transition temperature range. More specifically, we have found that greases thickened with lithium soaps of hydroxy fatty acids are very successfully prepared by cooling the grease mixture at a rate below about 25° F. per minute in about the 400–350° F. range while quenching with additional lubricating oil at a rate below about 0.05 gallon per minute of lubricating oil per pound of original grease mixture. This discovery is directly opposite to what has been supposed heretofore concerning the requirements of a successful quench procedure for the preparation of lithium hydroxy fatty acid soap greases. In previous attempts to prepare these greases by quench methods, the object has been to obtain the highest possible quench rates, in order to obtain the high cooling rates which were regarded as necessary on the basis of the experience with other cooling methods.

In accordance with this invention, a concentrate of a lithium soap of a hydroxy fatty acid in a suitable oleaginous liquid, obtained either by mixing together a preformed soap and oleaginous liquid or by saponification in situ, is heated to a temperature above the solution temperature of the soap to form a molten homogeneous mass and is then cooled through the transition temperature range at an average rate below about 25° F. per minute, and preferably below about 15° F. per minute, while quenching with additional oleaginous liquid at a rate from about 0.001 to about 0.05 gallon per minute of quench oil per pound of concentrate. The quenching is begun before the grease mixture has cooled substantially below the solution temperature of the soap, and preferably while the mixture is at a temperature above the solution temperature of the soap, and is carried out during the cooling to at least about 25° F. below the solution temperature of the soap. In the production of lithium 12-hydroxy-stearate greases, the quenching is begun

while the grease concentrate is at a temperature of about 385–420° F., preferably at about 390–405° F., and continued until the diluted concentrate is at a temperature of about 360° F. or lower. Very advantageously, the quenching may be carried out continuously during the cooling down to about 300° F. or lower, employing from about 10 percent to about 70 percent of the total oleaginous liquid in the finished grease. However, below about 350° F. the cooling rate and the quenching rate are not critical.

The quench oil is at a temperature substantially lower than that of the grease mixture, so as to obtain a continuous limited shock cooling effect during the cooling of the bulk of the grease mixture at a relatively low rate. The temperature of the quench oil is preferably not over about 150° F., and most suitably in about the 25–125° F. range. It is usually desirable to employ additional cooling, which is most conveniently obtained by carrying out the grease preparation in a jacketed kettle and passing a cooling liquid through the kettle jacket during the cooling process.

The quench oil may be any oleaginous liquid which is suitable for use in lubricating greases. It may be an oil of the same type as that employed in the grease concentrate, or it may be a different oil, such as an oil of either higher or lower viscosity. An oil of light or medium viscosity, such as an oil having a Saybolt Universal viscosity at 100° F. of about 100–600 seconds is particularly suitable for this purpose.

Suitable oleaginous liquids which may be employed for forming the grease concentrate and for quenching include 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 conventional mineral lubricating oils. Examples of these compounds are the aliphatic dicarboxylic acid di-esters, 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 Saybolt Universal viscosities in the range from about 100 to 2000 seconds 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.

Suitable soap forming hydroxy fatty acid materials which may be employed in the production of the lithium hydroxy fatty acid greases are essentially saturated hydroxy fatty acids containing twelve or more carbon atoms and one or more hydroxyl groups 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 about 22 carbon atoms. Such materials may be obtained from naturally occurring glycerides, by hydroxylization 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 greases may contain various additives of the usual type such as corrosion inhibitors, oxidation inhibitors, extreme pressure agents, antiwear agents, and so forth. Preferably, they contain an oxidation inhibitor, which

may suitably be an oxidation inhibitor of the amine type, such as diphenylamine, phenyl alpha naphthylamine or tetramethyl diamino diphenyl methane. Compounds of this type 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 following examples describe in detail the manufacture of lithium 12-hydroxystearate greases by the method of this invention.

EXAMPLE I

A series of lithium 12-hydroxystearate greases was prepared employing as the base oil a mineral lubricating oil having an SUS viscosity at 100° F. of about 475, comprising an approximate 1:1 blend by weight of a refined wax distillate oil having a viscosity index of about 96 and an SUS viscosity of about 182 at 100° F., and a refined paraffinic residual oil having a viscosity index of about 80 and an SUS viscosity of about 103 at 210° F., obtained by furfural refining, clay and acid treating and solvent dewaxing a Manvel residual oil.

The fatty acid material employed was the methyl ester of 12-hydroxystearic acid, sold commercially under the trade name of Paricin-1. It had an acid value of 3, a saponification number of 175, an iodine number of 8, and a hydroxyl number of 171.

The greases were prepared in 200 and 300 pound laboratory batches, employing a 300 pound capacity Dowtherm heated kettle. The grease mixture was obtained by saponifying the fatty acid material with lithium hydroxide in the form of an approximately 10% aqueous solution in the presence of about one third of the lubricating oil employed in the grease. The saponification was carried out at a temperature of about 160–220° F. for about one hour, and the mass dehydrated by heating for an additional hour at about 270–300° F. Following the dehydration, additional oil was added and the mixture heated to about 395–405° F. until the soap appeared to be completely melted. Stirring of the kettle contents was carried out continuously during the preparation of the grease mixture and the subsequent cooling process.

Grease mixtures obtained as described above were cooled down in the kettle to about 200–250° F. by circulating cold Dowtherm through the kettle jacket and by quenching with additional lubricating oil comprising from about one seventh to about one third of the total lubricating oil contained in the grease, the temperature of the quench oil being in about the 75–130° F. range. Good greases were obtained when the grease mixture was cooled at a rate below about 25° F. per minute in about the 400–350° F. range with quenching at rates below about 0.05 gallon of quench oil per minute per pound of original grease mixture, employing as the quench oil the blend described above as well as the distillate oil and the heavier residual oil components of the blend. By quenching at still lower rates, very substantially improved yields were obtained, optimum yields being obtained by quenching at rates below about 0.02 gallon of quench oil per minute per pound of original grease mixture, and cooling at rates of about 3–15° F. per minute in about the 400–350° F. range. At cooling rates below about 3° F. per minute in this range the yield began to deteriorate, and fell off more rapidly at rates below about 2° F. per minute. When the quenching was carried out at rates above about 0.05 gallon of quench oil per minute per pound of original grease mixture, very grainy and unsatisfactory greases were obtained at cooling rates within this preferred range as well as at high cooling rates. With quench rates above about 0.1 gallon of quench oil per minute per pound of concentrate the yields became extremely poor, only fluid products being obtained in some cases with soap contents of 8 percent or more.

Table I below shows representative data obtained upon these greases prepared by the method of this invention and also upon these greases prepared with higher cooling and quench rates. The quenching in these preparations was carried out at uniform rates during the cooling until the temperature of the grease was below about 250° F., employing as the quench oil a portion of the distillate oil component of the oil blend contained in the finished grease. The estimated soap content for a 280 penetration grease shown in the table was obtained by allowing one percent of soap for twenty points difference in penetration.

Table I

Grease No.	1	2	3	4	5
Soap Content, Percent:					
Before quench	15.9	13.0	13.0	9.3	13.0
After quench	11.0	10.0	10.1	6.0	10.2
Estimated for 280 worked pene.	13.6	9.9	10.1	7.3	7.7
Conditions of Quench:					
Amt. of quench oil (percent of total oil)	33.3	25	25	36	14
Rate of quenching—					
gal./min.	28	14	7	2.1	1.3
gal./min./lb. conc.	0.138	0.099	0.049	0.0103	0.0075
gal./min./lb. grease	0.093	0.070	0.035	0.0071	0.0065
Cooling Rate, °F./min.:					
400-350° F. range	7.5	44	9.3	13.3	2.5
350-200° F. range	(400-250° F.)	3.5	2.6	5.0	----------
Tests on Milled Product:					
Penetration—					
Unworked	311	268	262	283	208
Worked	331	278	280	306	230
Appearance	grainy	grainy	smooth	smooth	smooth

EXAMPLE II

A second series of lithium 12-hydroxystearate greases was prepared by the method of this invention, employing as the base oil a blend of refined distillate oils having an SUS viscosity at 100° F. of about 475 and consisting of 15% by weight of a paraffinic oil having an SUS viscosity of about 90 at 210° F., 35% by weight of a naphthenic oil having an SUS viscosity of about 90 at 210° F., and 50% by weight of a paraffinic oil having an SUS viscosity of about 185 at 100° F.

The fatty acid material employed was a commercial 12-hydroxystearic acid having a neutralization number of about 180 and a saponification number of about 187.

The preparation of these greases was carried out very successfully in both laboratory batches and in plant manufacture employing oil heated and cooled 12,000 pound capacity kettles. The grease mixture was prepared as described in Example I, and cooled at rates below about 25° F. per minute, while quenching at rates below about 0.05 gallon per minute of additional lubricating oil per pound of original grease mixture.

Table II below shows representative results obtained in plant manufacture under the preferred conditions, employing cooling rates below about 15° F. per minute and quenching rates below about 0.02 gallon per minute of

quench oil per pound of grease mixture. The quenching was carried out continuously at uniform rates in these preparations until the grease had cooled to below about 250° F., employing an oil of the same type as that employed in the preparations of Table I.

Table II

Grease No.	6	7	8	9
Soap Content, Percent:				
Before quench	15.5	15.5	14.4	15.5
After quench	6.8	6.0	6.2	6.2
Estimated for 280 worked pene	6.6	6.4	5.9	5.6
Conditions of Quench:				
Amt. of quench oil (percent of total oil)	48	42	60	43
Rate of quenching—				
gal./min.	73	46	37	28
gal./min./lb. conc.	0.0106	0.0085	0.0066	0.0035
gal./min./lb. grease	0.0058	0.0042	0.0029	0.0021
Cooling Rate, °F./min.:				
400-350° F. range	11.8	8.8	4.7	5.2
350-200° F. range				
Tests on Milled Product:				
Penetration—				
Unworked	294	295	308	283
Worked	277	288	275	269
Appearance	smooth	smooth	smooth	smooth

In addition to the above examples, other grease preparations have been carried out very successfully by the method of the invention starting with grease mixtures containing about 5 to about 20 percent by weight of lithium hydroxy fatty acid soap in lubricating oils of various types and employing lubricating oils of various types for quenching, including both naphthenic and paraffinic oils of viscosities ranging from about 200 to 1600 SUS at 100° F. By quenching grease mixtures of relatively low soap contents, N.L.G.I. No. 1 grade greases were obtained with less than 4 percent by weight of lithium 12-hydroxystearate and No. 0 grade greases were obtained with less than 3 percent by weight of lithium 12-hydroxystearate.

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.

We claim:

1. The method of preparing lubricating greases which comprises heating a mixture of a lithium soap of a hydroxy fatty acid and an oleaginous liquid in a grease-forming proportion to a temperature above the solution temperature of the soap so as to form a molten homogeneous mass in a grease kettle, and then cooling the said mixture in a maintained agitated body in the grease kettle from a temperature near the solution temperature of the soap to at least 25° F. below the solution temperature of the soap at an average rate of at least about 2° F. but below about 25° F. per minute by quenching with an additional oleaginous liquid at a rate of about 0.001–0.05 gallon of oleaginous liquid per minute per pound of the said mixture and by any additional cooling employed which is obtained substantially entirely by means of cooling surfaces in contact with the said agitated body of mixture in the grease kettle.

2. The method of claim 1 wherein the said soap is lithium 12-hydroxystearate.

3. The method of claim 1 wherein the said mixture is cooled at an average rate of about 2–15° F. per minute.

4. The method of claim 1 wherein the quenching is at a rate of about 0.001–0.02 gallon of said oleaginous liquid per minute per pound of said mixture.

5. The method of claim 1 wherein the said mixture is quenched from a temperature above the solution temperature of the soap.

6. The method of preparing a lubricating grease which comprises heating a mixture of lithium 12-hydroxystearate and an oleaginous liquid in a grease-forming proportion to a temperature of about 390–420° F., so as to form a molten homogeneous mass in a grease kettle, and then

cooling the said liquid in a maintained agitated body from a temperature of about 385° F. to below about 350° F. at an average rate of at least about 2° F. but below about 25° F. per minute by quenching with additional oleaginous liquid at a rate of about 0.001–0.05 gallon of oleaginous liquid per minute per pound of the said mixture, and by any additional cooling employed which is obtained substantially entirely by means of cooling surfaces in contact with the said agitated body of mixture in the grease kettle.

7. The method of claim 6 wherein the said mixture is cooled at an average rate of about 2–15° F. per minute.

8. The method of claim 6 wherein the quenching is at a rate of about 0.001–0.02 gallon of said oleaginous liquid per minute per pound of said mixture.

9. The method of claim 6 wherein the said oleaginous liquid is a mineral lubricating oil.

10. The method of preparing a lubricating grease which comprises heating a mixture of lithium 12-hydroxystearate and an oleaginous liquid in a grease-forming proportion to a temperature of about 390–405° F. so as to form a molten homogeneous mass in a grease kettle, and then cooling the said liquid in a maintained agitated body from a temperature of about 390° F. to below about 350° F. at an average rate of about 2–15° F. per minute by quenching with additional oleaginous liquid at a rate of about 0.001–0.02 gallon of oleaginous liquid per minute per pound of the said liquid and by maintaining the said agitated body of mixture in the grease kettle in contact with cooling surfaces as substantially the only additional cooling means employed.

11. The method of claim 10 wherein the quenching is continued until the mixture has been cooled to below 300° F. employing about 10–70 percent of the total oleaginous liquid in the finished grease for the quenching.

12. The method of claim 10 wherein the said oleaginous liquid is a mineral lubricating oil.

13. The method of preparing a lubricating grease which comprises heating a mixture of lithium 12-hydroxystearate and a mineral lubricating oil having an SUS viscosity of 400–1200 at 100° F. in a grease-forming proportion to a temperature of about 390–405° F. so as to form a molten homogeneous mass in a grease kettle, and then cooling the said mixture in a maintained agitated body from a temperature of about 390° F. to below about 350° F. at an average rate of about 2–15° F. per minute by quenching with mineral lubricating oil having an SUS viscosity of about 100–600 at 100° F. at a rate of about 0.001–0.02 gallon of said lubricating oil per minute per pound of said mixture, and by maintaining the said agitated body of mixture in the grease kettle in contact with cooling surfaces as substantially the only additional cooling means employed.

14. The method of claim 13 wherein the quenching is continued until the grease mixture has cooled to below 300° F., employing about 25–70 percent of the total

mineral lubricating oil in the finished grease for the quenching.

15. The method of claim 13 wherein the said mineral lubricating oil employed for quenching is at a temperature of about 25–125° F.

16. The method of claim 13 wherein the said mixture before quenching contains about 5–20 percent by weight of lithium 12-hydroxystearate.

17. The method of preparing a lubricating grease which comprises heating a mixture of a lithium soap of a hydroxy fatty acid and an oleaginous liquid in a grease-forming proportion to a temperature above the solution temperature of the soap so as to form a molten homogeneous mass and then cooling the said mixture in a jacketed grease kettle with continuous stirring from a temperature near the solution temperature of the soap to at least about 25° F. below the solution temperature of the soap at an average rate of about 2–25° F. per minute by quenching with additional oleaginous liquid at a rate of about 0.001–0.05 gallon of oleaginous liquid per minute per pound of the said mixture, and by passing a cooling liquid through the kettle jacket as substantially the only additional cooling means employed.

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