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RHEOPECTIC GREASE COMPOSITION

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Our invention relates to the production of a novel lubricant composition which has the property of fluidity as produced in the unworked state but which sets up to grease consistency on mechanical working. The product of the invention is specially adapted for use as a lubricant in capillary systems for lubricating remote parts of a mechanical system from a central point of lubricant supply.

The lubricant compositions of the invention comprise an oleaginous base thickened with a lithium hydroxy stearate. Although the use of lithium hydroxy stearates as grease thickeners is now quite conventional, the compositions of the invention differ markedly from conventional grease products in structure and in properties.

Conventional lithium hydroxy stearate greases are made by forming the lithium soap of a hydroxy stearic acid or glyceride thereof in oil. The oil mixture is usually heated to 230–250° F. to drive off water, and the temperature then is elevated to within the range of about 325° to 425° F. where finishing oil is graded into the mixture. The resulting grease mixture is gradually cooled and is usually homogenized before packaging. The product has a smooth gel-like grease structure with a consistency, measured in terms of ASTM penetration, which is primarily dependent upon soap content. A typical lithium grease has a soap content in the range of 5 to 15 percent by weight. Lithium hydroxy stearate greases exhibit excellent mechanical stability, often showing little or no penetration loss after mechanical working. They undergo minor viscosity changes under working conditions, i. e., viscosity reduction typical of conventional oil base lubricants. They do not show significant "work-up" properties, that is they do not "set up" or increase in consistency in use.

The grease compositions of our invention are unique in being fluid as produced but in having the property of setting up to grease consistency when exposed to high shear rates such as are encountered in dispensing systems or in gear cases. As produced, the grease is a rheopectic lubricant composition which essentially comprises an oleaginous base thickened with about 1 to 3½ percent by weight of a lithium soap of a hydroxy stearic acid. The soap is characterized in structure by an average particle size of less than 0.7 micron in length and a length to width ratio of about 10–50 to 1. Usually, the bulk of the soap particles lie in the range of about 0.4 to 0.5 micron length.

The novel compositions appear to have a characteristic structure comprising multi-particle agglomerates of soap dispersed in oil. This structure and the characteristic small size soap particles may be advantageously produced by subjecting the composition to a particular thermal sequence in preparation. Accordingly, our invention also provides a process for producing a "work-up" grease composition which comprises forming a lithium hydroxy stearate soap in oil, heating the resulting mixture to a temperature above the melting point of the soap and adjusting the soap concentration in oil

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to about 5 to 15 percent by weight. The resulting composition is chilled to about 100° to 150° F. and is homogenized. The homogenization step is important in dispersing the soap uniformly and in obtaining smooth texture but does not appear to affect particle size. A gel-like phase results from the rapid cooling from the melt state and homogenizing, which upon heating to a temperature of 150° to 250° F. can be diluted with oil to a soap concentration of about 1 to 3½ weight percent to obtain a smooth fluid or semi-fluid composition. Thus, the new product is a fluid "partially homogenized" (or dispensing rheopectic) grease which essentially comprises a homogenized grease comprising an oleaginous base thickened with about 5 to 15 weight percent of a lithium hydroxy stearate soap having a particle size of about 0.1 to 0.7 micron which has been cut-back to a soap content of about 1 to 3½ percent by weight on the oil.

In producing the lubricant compositions of the invention, a lithium hydroxy stearate soap is employed as the thickening agent. Any convenient source of hydroxy stearic acid may be used, but the use of 12-hydroxy stearic acid is advantageous. Hydrogenated ricinoleic acid or hydrogenated castor oil also can be employed. The soap can be readily prepared in a fired grease kettle or pressure jacketed reactor by melting the acid in sufficient oil to provide a reaction medium and adding lithium in the form of a base such as lithium hydroxide monohydrate. Although, so far as we have been able to determine, any oleaginous medium of suitable physical and chemical properties for compounding with a lithium hydroxy stearate can be employed, the use of a lubricating oil distillate fraction from a low pour point crude oil of highly branched paraffinic or naphthenic composition appears to have definite advantages. For example, a neutral oil derived from a Winkler (Texas) crude oil which characteristically is a low pour point, medium sulfur, isoparaffinic crude has been found particularly suitable. A lubricating oil distillate fraction having a viscosity in the range of about 55 to 2000 SSU at 100° F. is desired, and a distillate having a viscosity of the order of 300 SSU at 100° F. is preferred.

After the lithium soap has been formed by heating the fat and the base in oil, heating is continued to dehydrate the reaction mixture. Heating is continued until the soap is entirely melted which requires a temperature in the range of about 385° to 425° F. At this temperature, the grease mixture may be graded to the desired soap content, about 5 to 7 weight percent, by adding finishing oil. High intermediate soap concentrations can be employed, say up to about 15 percent. Additives of the type that are often added to grease composition to improve oxidation stability, anti-rust and E. P. properties may be conveniently added at this stage. The grease composition is now chilled to a temperature in the range of about 100 to 150° F. Yield is improved by cooling as rapidly as possible to below about 150° F. The cooling operation can be readily and advantageously effected on a cooling roll. The resulting solid is scraped off as flakes which may be charged directly to a homogenizer or colloid mill.

The homogenized grease is cut-back by reheating to a temperature in the range of about 150 to 250° F., advantageously above 200° F., and grading in additional oil. The same oil used as the base for producing the homogenized grease or a different oil, e. g., a typical dewaxed and solvent extracted Mid-Continent oil may be used. In the grading step, the soap concentration is diluted to the order of about 1 to 3½ weight percent on the oil. The resulting composition is fluid and apparently has a structure which is heterogeneous in the sense that the soap particles are not uniformly dispersed

throughout the oil medium but are believed to be present in the form of multi-particle agglomerates of relatively high soap content distributed in an oil phase of relatively dilute soap concentration. The result is to provide considerable potential gelling power which may account for the unique "work-up" feature of the new compositions when they are subjected to mechanical working. The mechanism of the gelling effect is not clearly understood, but the particle size of the soap thickener, in addition to the capacity of lithium hydroxy stearate in selected concentration in oil to give a multi-particle agglomerated structure, is believed to be an essential determinant. Thus, we have been unable to produce a grease with "work-up" properties by initially blending to the soap concentration of the invention. Lithium hydroxy stearate greases made by heating the grease mixture to the melting point of the soap or to a temperature sufficient to produce a smooth jelly-like consistency upon cooling are characterized by a gel structure comprising fibrous soap particles averaging about 1 micron or considerably larger in length. The soap particles of the compositions of the invention have typically half the length of soap particles in ordinary lithium greases, averaging about 0.4 to 0.5 micron in length. When the grease is made satisfactorily, the length to width ratio of the particles approximates about 10 to 50/1. The size and shape of the particles can be determined in comparison with other grease compositions by photographing smears of grease at high magnification with the aid of the electron microscope.

By way of example in manufacture according to the best mode known to us, approximately one-third of the total oil to be used in the batch is charged to a steam heated grease kettle. The use of a low pour point lubricating oil stock such as a Winkler lube stock is recommended. By way of illustration, an SAE-10 Winkler distillate having an API gravity of 22.5°, a flash point of 38° F., and a viscosity at 100° F. of 234 SSU is substantially wax free and has a pour point of -10° F. Its hydrocarbon composition, determined by correlation of density, refractive index and surface tension measurements, corresponds to 59 percent paraffins, 16 percent aromatics and 25 percent isoparaffins and naphthenes (with the major proportion isoparaffinic) and has 25 percent of its carbon content in the form of aromatic or naphthenic rings. An anti-oxidant (neutralized reaction product of P_2S_5 and polybutenes) and 12-hydroxy stearic acid are added, and the temperature is raised to 180°-200° F. Lithium hydroxide monohydrate and sufficient water to provide a slurry of the base are then added. After the reaction between the 12-hydroxy stearic acid and lithium hydroxide has taken place and the base thickens, the temperature is gradually increased to about 250° F. to dry the base. The balance of the oil is added, and the batch temperature is increased to about 400-425° F. The resulting homogeneous solution of melted soap in oil is discharged from the heated kettle to a pan beneath a cooling roll. The molten grease is picked up and is shock-chilled or gelled on a cooling roll. The grease may be cooled in this way in a matter of a few seconds from the order of 400° F. to less than 150° F. at the rate of 1000 to 1200 lbs. per hour, for example, with a roll turning at about 20 R. P. M. The resulting gel is homogenized by charging to a Cornell homogenizer.

To obtain the "work-up" grease of the invention, in a specific example, 21.25 pounds of the above grease base were charged to a steam heated grease kettle. Heat was applied while stirring the grease in the kettle, and at 150° F. the addition of a Winkler SAE-20 lube stock was started very slowly. The batch temperature was allowed to increase to 240° F. The batch was held at 240° F. while adding the oil. A total of 16 pounds of the oil was added, nearly all with the grease at 240° F.

The batch was finished at a reading of 315 units on the Brabender machine using the standard paddle.

The finished product showed a marked tendency to "work-up" or get harder in consistency when subjected to mechanical working or shearing. It is particularly suited for use as the lubricant in driver operated devices for the lubrication of ball-joint suspension points on automobile chassis such as the "Multi-Luber" manufactured by Lincoln Engineering Company. The "Multi-Luber" consists of a lubrication reservoir, a dispensing pump, individual nylon capillary tubes to each of the ball-joints, and dashboard controls. The device requires a lubricant which will flow readily from the reservoir to the pump but which, after application via the 1/8" O. D. capillary tubes, will not drip from the lubrication points. The use of this type of device eliminates the need for grease-gun chassis lubrications in service stations. The lubricant compositions of the invention satisfy these contradictory requirements since they are semi-fluid as made, and hence flow readily from reservoir to pump but are gelled to grease consistency by the resulting shearing action when pumped through the capillary tubes.

For example, the grease of the above example was liquid as produced and too soft to test for penetration by the standard ASTM procedure (217-52T using 1/4 size cone). After delivery through the tubes of the "Multi-Luber," the grease had a penetration of 390. By comparison, a relatively soft lithium hydroxy stearate grease of conventional manufacture (about 0-grade), having a soap content of 4 percent, has a penetration (unworked) of 386 and a penetration of 399 after 750 strokes in the ASTM grease worker which approximates the working the grease would undergo in delivery through the tubes of the "Multi-Luber." Thus, the conventional grease loses consistency, or softens rather than setting up to a firmer consistency. Also, when 9 pounds of the above grease were graded with 14 pounds of the Winkler oil while holding the temperature below 100° F., the product did not "work-up" when subjected to mechanical shearing. Although more oil can be added at the low grading temperature for a given consistency, the grease tends to be aerated and softens excessively upon heating.

The new compositions also have special value for lubricating gear boxes, particularly where non-drip characteristics are required, and for use in locations of difficult accessibility.

We claim:

1. A lubricant composition which is fluid as produced in the unworked state and which sets up to grease consistency on mechanical working which essentially comprises a mineral oil base containing about 1 to 3 1/2 percent by weight of a lithium hydroxy stearate and which is characterized by a soap particle size of about 0.1 to 0.7 micron in length and a multi-particle soap agglomerate-in-oil structure in the unworked state, said soap particle size and soap particle-oil structure formed by chilling such a composition from the melted soap state to about 100° to 150° F., homogenizing, reheating the homogenized composition to 150° to 250° F. and diluting to such a soap content.

2. The composition of claim 1 in which the average soap particle size is about 0.4 to 0.5 micron in length.

3. The composition of claim 1 in which the mineral oil base is a lubricating oil distillate derived from a low pour point crude oil and has a viscosity in the range of about 55 to about 2000 SSU at 100° F.

4. The composition of claim 3 in which the soap is a lithium soap of 12-hydroxy stearic acid.

5. A partially homogenized lubricant composition which is fluid in the unworked state and which sets up to grease consistency on mechanical working which essentially comprises a homogeneous grease comprising a mineral oil base thickened with about 5 to 15 weight percent of a lithium hydroxy stearate having an average

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particle size in the range of about 0.1 to 0.7 micron in length which has been cooled from the melted state, homogenized, reheated and cut-back to about 1 to 3½ weight percent soap content.

6. The composition of claim 5 in which the average soap particle size is of the order of about 0.4 to 0.5 micron in length.

7. The composition of claim 5 in which the mineral oil base is a lubricating oil distillate derived from a low pour point crude oil and has a viscosity in the range of about 55 to about 2000 SSU at 100° F.

8. The composition of claim 7 in which the soap is a lithium soap of 12-hydroxy stearic acid.

9. A process for producing a lubricant composition which is fluid in the unworked state and which sets up to grease consistency on mechanical working which comprises forming a lithium hydroxy stearate soap in mineral oil, heating the resulting mixture to above the melting point of the soap and adjusting the soap concentration to about 5 to 15 weight percent on oil, chilling the mixture to about 100 to 150° F., homogenizing the resulting grease, reheating to 150° to 250° F., and diluting the homogenized grease with oil to provide a soap concentration of about 1 to 3½ weight percent on oil.

10. The process of claim 9 in which the homogenized grease is reheated to about 200° to 250° F. for dilution with oil.

11. The process of claim 9 in which the oil is a lubricating oil fraction derived from a low pour point crude oil and which has a viscosity in the range of 55 to about 2000 SSU at 100° F.

12. The process of claim 9 in which the soap is a lithium soap of 12 hydroxy stearic acid.

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13. The process of claim 9 in which the intermediate soap concentration is about 5 to 7 weight percent on the oil.

14. A fluid lubricant composition characterized by capacity to set up to typical grease consistency on mechanical working which essentially comprises a mineral oil base and a lithium hydroxy stearate soap wherein the soap has an average particle size in the range of about 0.1 to 0.7 micron length and is dispersed in the base in the form of multi-particle agglomerates and is present in a cut-back concentration of about 1 to 3½% by weight and which has been formed by cooling a mixture of said mineral oil base and soap from the melted state to form a grease, homogenizing said grease, and thereafter reheating the homogenized grease and cutting it back with additional oil to the aforesaid soap concentration.

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