United States Patent Office 3,173,869 Patented Mar. 16, 1965

3,173,869

GREASE COMPOSITION

William B. Watson, Park Forest, and Lewis D. Loring, Jr., Dolton, Ill., assignors, by mesne assignments, to Sinclair Research Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Aug. 4, 1960, Ser. No. 47,380
3 Claims. (Cl. 252—39)

This invention relates to a grease composition. More particularly, the invention is concerned with grease compositions containing a major amount of a selected oil product.

The petroleum industry has encountered numerous difficulties when attempting to produce fatty soap greases which utilize lube distillate fractions from mixed base oils such as Mid-Continent crude oils as the major component. These lube distillates contain unstable molecules which oxidize readily and degrade the grease which includes them. Solvent refined Mid-Continent lube oils produce greases which may be inhibited to have satisfactory oxidation stability, but these lube oils have relatively poor yield, i.e., high soap content for a given penetration. Also, the grease compositions formed from these oils have a rough, grainy texture and thus the greases are undesirable both from the functional and physical standpoint. Sulfuric acid-treated Mid-Continent lube oils when used in grease compositions yield a somewhat satisfactory grease, but acid treating is an expensive and time-consuming process and also, unfortunately, yields sludge as a by-product which is difficult to remove. Further, the acid fumes create an air-pollution problem when utilized in large amounts in refinery operations.

The composition of the present invention overcomes the above-mentioned problems and is an advantageous grease which is relatively simple to produce in good yields, has good texture and appearance and is not unduly prone to oxidize. Thus, from a Mid-Continent or mixed petroleum crude oil we are able to produce greases exhibiting the advantageous characteristics of products made with naphthenic oils but yet our grease has better viscosity properties than products obtained from the low viscosity index naphthenic oils.

The grease of this invention includes a major amount of a base petroleum oil which is a phase-separated raffinate fraction from an extract obtained in solvent refining of Mid-Continent lube distillates or a comparable fraction from solvent refining a raw lube distillate and extract blend; and a minor amount of a grease-forming soap selected from the group consisting of the alkali metal soaps and alkaline earth metal soaps or mixtures thereof. The saponifiable materials employed in the production of the soaps are generally higher fatty acids containing from about 10 to 32, preferably 12 to 20, carbon atoms or the glycerides or other esters thereof. The fatty soap material is present in an amount sufficient to thicken the oil to grease consistency. Generally, the amount of soap present in the final grease composition will be about 5 to 35 percent by weight, preferably about 10 to 25 percent. The base oil of this invention is normally present in the final composition in amounts of from about 65 to 95 percent by weight, but blends of this oil and small amounts of other lubricating oils can be employed.

The base oil of the grease composition of the present invention is a select portion of an extract oil. Advantageously, the extract oil source is obtained in the production of a lubricating oil having a viscosity index of at least 85, to obtain a raffinate where the raffinate includes about 20 to 70 volume percent of the original extract. Thus, the base oil of the present invention is obtained by the separation of a select portion of an extract oil in a manner whereby a raffinate oil including

about 20 to 70 volume percent of the extract is obtained. This can be accomplished by several methods. For example, where the extract oil being treated consists essentially of a blend of an extract oil and a paraffin distillate, the select portion desired can be separated by solvent extracting the blend with a solvent which is selective for aromatics to obtain a raffinate yield of about 20 to 90 volume percent based on the blend, the optimum yield of extraction of the blend depending primarily upon the quantity of extract present. A second general procedure for obtaining the select portion of extract oil involves phase separation. In this procedure the extract is treated as a solution in a solvent selective for aromatics, either alone or with various amounts of paraffin distillate, for example up to about 0.75 part of distillate per part of extract and preferably from about zero to 0.25 part of distillate per part of extract. To separate the desired raffinate fraction the solvent extract solution is subjected to conditions such that the solvency power of the solvent for a portion of the solubilized oil is reduced and a phase separation occurs. This can be effected by the introduction of a non-solvent, or by lowering the temperature of the solution sufficiently to effect a phase separation, or by a combination of injection of a non-solvent and the lowering of temperature.

An extract generally containing at least about 25 volume percent of the material treated should be used. Thus, in general a blend consisting essentially of an extract and a paraffin distillate wherein the extract makes up at least 25 volume percent of the blend, and can comprise as much as 100 volume percent, is used as the starting material. Where it is desired to produce the oil by solvent extraction it is preferred to employ a blend containing about 25 to 60 volume percent of extract and more particularly 30 to 60 volume percent. Optimum results are achieved with the phase separation procedure when the material approaches or is 100% extract. One of the significant reasons for this diversity of optimum extract concentrations can be attributed to how the oil extract is to be integrated with existing facilities. Thus, where a supply of extract free of the solvent with which it is obtained is available, it usually is most desirable to blend the extract with a suitable distillate and solvent extract the resulting blend. On the other hand, it may be more advantageous to process the extract immediately upon its production in order to avoid the necessity for providing storage facilities. In this event, it may be desirable to treat the solvent-extract solution as such and the described phase separation procedure is tailored for this alternative. While the paraffin distillate could be added to this solvent-extract solution, it can be seen that such procedures involves an additional step; thus 100 percent of the extract is optimum.

More specifically, where a solvent extraction of a blend containing the extract is to be carried out, about 50 to 600 volume percent of solvent at a temperature of about 90 to 150° F. when using phenol can be employed while a temperature of about 90 to 200° F. can be used with furfural. Whatever solvent is employed for the extraction to obtain the desired raffinate, conditions are adjusted so that about 20 to 70 volume percent of the raffinate produced originates in the extract portion of the blend so that a suitable oil in an adequate yield is obtained. This result is achieved generally simply by extracting the defined blend to a raffinate yield of about 50 to 90 volume percent based on blend. The optimum yield for any blend will depend upon its composition taking into consideration quality of product and the economics of the process. Examples of optimum yield ranges are as follows: for a blend containing about 45 to 60 percent of the extract, the optimum raffinate yield is about 50 to 70 percent; for blends containing 25 to

40 percent of the extract, a raffinate yield of about 75 to 90 percent appears to be best.

The phase separation method procedure can be accomplished by two general procedures or by a combination of the two procedures. For example, the solvent extract solution as obtained in normal refinery practice can be cooled from its tower bottom temperature, that is from about 180° F. to a temperature within the range from about 100 to 125° F. to produce a two phase separation; the upper phase is a raffinate and comprises about 20 to 70 volume percent based on the volume of extract charged and preferably about 25 to 60 volume percent and the lower phase is a solution of the solvent and the remaining portion of the extract. The lower phase is withdrawn and the solvent recovered, for example, by distillation or flashing. The upper phase is withdrawn from the settler, which can be of the batch or continuous type, and distilled as by vacuum distillation to remove any solvent present.

The second general procedure for effecting phase separation involves changing the solvent's ability to hold the extract oil in solution by the introduction of a suitable material which is soluable in solvent at conditions met but not a solvent for the extract oil. The preferred material for this procedure is water though, of course, other non-solvents can be used. By "non-solvent" is meant a material which, at the conditions of operation, does not solubilize extract oil yet is soluable in phenol and similar solvents employed to extract lubricating oils in the production of high viscosity index lube oils. In accordance with the second general procedure a quantity of water is injected into the solvent-extract solution to separate out a raffinate oil in a yield based on the volume of the extract charged of about 20 to 70 percent and preferably about 25 to 60 percent. As the effect of a non-solvent on the solvent present in the extract solution varies with temperature, it will be apparent that the optimum quantity of non-solvent to be employed will be dependent upon the temperature. It is preferred to employ about 5 to 25 volume percent of water in conjunction with moderately low temperatures in order to minimize subsequent separatory problems though the phase separation can be effected merely by water injection alone at higher temperatures by using larger quantities of water. Temperatures of about 105 to 135° F. in conjunction with 5 to 25 percent water produce satisfactory results.

Extract oils as employed in the present invention result upon the solvent extraction of lubricating oil fractions such as neutral oils, especially solvent extraction designed to improve viscosity index. Since Mid-Continent oils are involved in the extract results upon solvent extracting to produce a raffinate oil with a viscosity index of at least 85 and preferably at least 90. The Mid-Continent or mixed base crudes providing the lubricating oil are typically composed of about 0–30% aromatics, about 15–45% naphthenes and about 40 to 85% paraffins. The extract is derived by treating a lubricating oil base stock with a solvent selective for aromatic constituents, for example phenol, furfural, nitrobenzene or liquid sulfur dioxide or similar solvents. Phenol is preferred and generally about 100 to 1000 volume percent based on the lubricating oil treated is used and the extraction is carried out at a temperature of about 155 to 210° F. at atmospheric or elevated pressures. Employing furfural a temperature range such as 150 to 250° F. is used while a lower temperature, i.e., under 150° F. is used with sulfur dioxide. Normally, solvent is then recovered from the extract. For purposes of the phase separation step of the present invention, the solvent removal step is omitted and the extract as a solution in its solvent is used as such.

The other major component which may be present in the material treated to yield the desired oil is a paraffin distillate preferably having a viscosity of about 35 to 75 SUS at 210° F. obtained from a Mid-Continent crude oil. Raw paraffin distillate is intended to designate distillate fractions, for example, any distillate lubricating oil, or other overhead or side stream from a vacuum or other type of a reduced crude, which need not have been chemically or physically treated as by acids, alkalies, earth contacted, solvent extracted or subjected to other similar treatment normally associated with commercial lubricant maufacturing. In addition to or in lieu of such distillates, other materials such as deresined bright stock or deasphalted and deresined residuals can be present. The distillate and extract can be blended merely by pouring together ambient temperatures.

The processing step applied to the raffinate oil recovered in the select separation step can include dewaxing and earth contacting if necessary to meet specifications or if desired. These two processes are known in the art generally. Typical conditions for a dewaxing step, for example benzene-toulene-methylethyl ketone dewaxing, include employing about 100 to 600 volume percent solvent per volume of oil treated at temperatures of about 0 to −20° F. It is possible to dewax the extract or extract-containing blends prior to the select separation step; but in such instance, greater quantities of oil need be handled since all of the oil is thus dewaxed rather than just the separated portion and additional dewaxing may be required to meet specifications and thus dewaxing as a first step frequently is uneconomic. The dewaxed material can be contacted with clay such as fuller's earth or bauxite or the like in an amount of about 2 to 15 pounds of clay per barrel of oil and at a temperature of about 200 to 400° F. to improve color and odor stability, if desired. Typical polishing or clean-up clay contacting can also be employed at the choice of the operator.

The base oil of this invention is thickened to grease consistency with the conventional type soaps of the alkali metals such as sodium, lithium or potassium and the alkaline earth metals such as barium, strontium and calcium. The saponifiable component employed in the production of these soaps may be a higher fatty acid containing from about 10 to 32 carbon atoms, or the glyceride or other esters thereof, such as myristic acid, palmitic acid, stearic acid, behenic acid, oleic acid and the like and includes fatty materials such as tallow, lard, hydrogenated castor oil, hydrogenated fish oil and various other fats and fatty acids. Also, soap of soap-forming hydroxy fatty acids can be employed.

The production of greases thickened with lithium soaps of hydroxy fatty acids is regarded as a particularly important application of the invention because of the increasing commercial importance of such greases and the large amount of difficulty which has been experienced in their manufacture. 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 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 hydroxy fatty acid contains about 16 to about 20 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. These soap type thickeners are generally present in amounts of from about 5 to 35 percent, preferably in amounts of from 10 to 25 percent of the final grease composition.

Materials normally incorporated in greases to impart

special characteristics can be added to the composition of the present invention. These include anti-oxidants, extreme-pressure agents, corrosion inhibitors, anti-wear agents, etc. The amount of the additives added to grease compositions usually ranges from about .01 percent to 10 percent by weight of final grease composition and in general can be employed in any amounts desired so long as the grease of the present invention is not deleteriously affected.

The grease of the present invention may be prepared by using the normal type of grease-making equipment. One of the most important advantages in terms of cost of the grease is that it can be made conveniently in a steam jacketed kettel at a moderate dehydration temperature in the order of about 300 or 320 to 350° F. In one process of manufacture, an appropriate amount such as one-half or one-third of the base oil and the fatty acid component such as a tallow fatty acid or hydrogenated castor oil are mixed and then charged to the kettle and the temperature is raised to about 180° F. so as to melt the fatty component. A base such as lithium hydroxide monohydrate or hydrated lime is slurried in another portion of the base oil and then charged to the kettle. During the neutralization of the fatty component and dehydration of the grease, the temperature is raised to about 230–330° F. The remainder of the base oil is then added and, if desired, an adjustment of water content is made to provide the required degree of hydration, if any, necessary for stabilizing the composition. Also, if desired, additives may be added to the composition at temperatures of from about 180 to 300° F. Prior to packaging the grease may be processed through a colloidal mill or homogenizer at a temperature of from about 130–180° F. Thus, the grease composition of this invention is formed which has a smooth buttery texture and shows superior lubricating properties such as stability and the like. The formation of the thickening soap in-situ, i.e. in all or a portion of the base oil, is preferred but the soap could be preformed and then compounded with the base oil to give the grease.

The following examples, while serving to illustrate the present invention are not to be taken as limiting.

Example I

A raw Mid-Continent lube distillate hereafter called Feedstock A, having an API gravity of 29.4° API gravity, 100 SUS viscosity at 100° F. and 80° F. pour point is solvent refined with phenol in a conventional counter-current extraction tower. The operating conditions and tests on the products are listed below.

Extraction conditions:	
Feedstock A feed rate ____b./d__	6,536
Phenol feed rate ____b./d__	11,076
Phenol to oil ratio ____	1.7 to 1.0
Water to top of tower ____b./d__	442
Top tower temperature ____° F__	190
Bottom tower temperature ____° F__	180
Yield of waxy raffinate (Raff. B) vol. percent	62.6
Yield of extract (Extract C) ____vol. percent	37.4

Tests on Products	Raffinate B	Extract C
Gravity, °API	32.6	20.5
Viscosity, SUS/100° F	157.6	----
Viscosity, SUS/210° F	44.1	42.0
Pour, ° F	95	----

Extract C is then retreated on the extraction tower in blend with Feedstock A. Operating conditions and tests on the products are shown below.

Extraction conditions:	
Feedstock A feed rate ____b./d__	4,558
Extract C feed rate ____b./d__	2,256
Phenol feed rate ____b./d__	4,992
Phenol to oil ratio ____	0.73 to 1.0
Water to top of tower ____b./d__	450
Water to bottom of tower ____b./d__	65
Top tower temperature ____° F__	130
Bottom tower temperature ____° F__	131
Yield of waxy raffinate (Raff. D) vol. percent	84.9
Yield of extract (Extract E) ____do__	15.1

Tests on Products	Raffinate D	Extract E
Gravity, °API	29.5	9.4
Viscosity, SUS/110° F	102.2	----
Viscosity, SUS/210° F	39.3	49.0
Pour, ° F	80	40

Raffinate D is then dewaxed on a conventional continuous solvent dewaxing unit using a 50/50 blend of methyl ethyl ketone and toluene as the solvent. Solvent dilution is 157 volume percent based on oil feed and cold solvent wash 181 volume percent. The filter temperature is —7° F. The yield of dewaxed oil (Lube Oil F) is 86.5 volume percent and tests 27.3° API gravity, 125.2 SUS/100° F. viscosity, 40.4 SUS/210° F. viscosity, 59 viscosity index, and 10° F. pour point. Lube Oil F is fractionated on a vacuum still to yield 65 volume percent of an overhead product (Lube Oil G) testing 28.1° API gravity, 101 SUS/100° F. viscosity, 38.7 SUS/210° F. viscosity, 60 viscosity index, and 15° F. pour point. One third of Lube Oil G oil and the tallow fatty acids are charged to a conventional open kettle and the temperature raised to about 180° F. to melt the fatty acids. Hydrated lime is slurried in one third of Lube Oil G and then charged to the kettle. The temperature is then raised to 230° F. and the fatty acids neutralized. Upon completion of the reaction the remainder of Lube Oil G is added to the kettle. The grease has the following composition:

	Weight percent
Tallow fatty acids	15.0
Hydrated lime	2.3
Lube Oil G	82.7

Example II

A raw Mid-Continent lube distillate (Feedstock H) testing 23.4° API gravity, 325 SUS/130° F. viscosity, 71.6 SUS/210° F. viscosity, and 115° F. pour point is contacted with phenol on a conventional, counter-current extraction tower. Operating conditions follow:

Feedstock H feed rate ____b./d__	4,680
Phenol feed rate ____b./d__	10,296
Phenol to oil ratio ____	4.6 to 1.0
Water to top of tower ____b./d__	303
Top tower temperature ____° F__	205
Bottom tower temperature ____° F__	200

The extract phase (oil plus phenol) from the bottom of the tower is passed through a cooler and cooled to 125° F. The cooled extract stream is allowed to settle into two phases. The top phase from this separator is steam stripped to remove phenol. The resultant waxy oil (Raffinate J) represents 23.8 volume percent yield from Feedstock H. Raffinate J tests 24.3° API gravity and 115° F. pour point.

Raffinate J is dewaxed in a batch process using a 50/50 blend of methyl ethyl ketone and toluene as the solvent. Dilution solvent is 500 volume percent based on oil feed and cold solvent wash 300 volume percent. Filter temperature is —5° F. Yield of dewaxed oil is 85.9 volume percent. The dewaxed raffinate is contacted with 3 weight percent fuller's earth at 450° F. in a conventional manner to yield Lube Oil K. Lube Oil K tested 22.6° API gravity, 1170 SUS/100° F. viscosity, 79.9 SUS/210° F. viscosity, 54 viscosity index, and 5° F. pour point.

A grease composition is made using a steam-heated open kettle into which one-half of the base oil and the hydrogenated castor oil are charged to the kettle and then heated to 180° F. The lithium hydroxide is slurried in 3 to 5 parts of hot water and then charged to the kettle. Following the completion of saponification, the temperature is raised to approximately 330° F. and held for about one hour to dehydrate the soap base. Heating is discontinued and then the remainder of the oil is added. Phenyl alpha naphthylamine is added at about 200° F. Prior to packaging the grease is processed through a colloid mill at 150° F.

This grease has the following composition:

	Weight percent
Hydrogenated castor oil	10.0
Lithium hydroxide monohydrate	1.5
Phenyl alpha naphthylamine [1]	0.5
Lube Oil K	88.0

[1] Oxidation inhibitor.

Example III

A raw Mid-Continent lube distillate (Feedstock L) testing 25.8° API gravity, 131.8 SUS/130° F. viscosity, 49.4 SUS/210° F. viscosity, and 90° F. pour point is solvent treated with phenol on a conventional, countercurrent extraction tower. Operating conditions are:

Feedstock L feed rate	b./d.	6,500
Phenol feed rate	b./d.	11,076
Phenol to oil ratio		1.7 to 1.0
Water to top of tower	b./d.	480
Top tower temperature	° F.	192
Bottom tower temperature	° F.	186

The extract phase (oil plus phenol) from the bottom of the tower is admixed with water and passed through a cooler to reduce the temperature to 110° F. The water is added at a 1095 b./d. rate to the extract phase. The resultant cooled mixture is allowed to separate into two phases. The top phase is withdrawn, steam stripped, dewaxed and clay contacted as in Example II. Yield of waxy oil is 26.2 volume percent based on Feedstock L. Yield on dewaxing is 90.0 volume percent. The finished product (Lube Oil M) tests 21.0° API gravity, 584 SUS/100° F. viscosity, 57.8 SUS/210° F. viscosity, viscosity index, and 5° F. pour point. This oil is used in making the grease composition shown below.

	Weight percent
Tallow fatty acids	10.5
Hydrated lime	1.5
Flake caustic	0.1
Phenyl alpha naphthylamine	0.5
Lube Oil K (see Example II)	34.8
Lube Oil M	52.6

The grease is prepared in the same manner as shown in Example I.

Thus, the composition of this invention provides satisfactory petroleum greases which may be produced from lube distillates of Mid-Continent crude oils so as to be superior in appearance and texture and also have a high yield and good viscosity characteristics. The grease composition of this invention is smooth and buttery in appearance and particularly well suited as a multi-purpose grease.

We claim:

1. A lubricating grease composition consisting essentially of a major amount of an oil of lubricating viscosity derived from a mixed base petroleum crude oil and a minor amount sufficient to thicken the oil to grease consistency of a soap selected from the group consisting of alkali metal and alkaline earth metal grease-forming soaps, said oil being a secondary raffinate oil separated from an extract oil and including about 20 to 70 volume percent of said extract oil, said extract oil being obtained in the extraction of a mixed base lubricating oil stock with a solvent selective for aromatics to produce a primary raffinate oil and said extract oil, and said oil of lubricating viscosity being further characterized by being less soluble in a solvent which is selective for aromatics than the unseparated portion of said extract.

2. The grease composition of claim 1 wherein the oil of lubricating viscosity is present in amounts of about 65 to 95 percent by weight of final composition and the soap material is present in amounts of about 5 to 35 percent by weight of final composition.

3. The grease composition of claim 2 wherein the soap is lithium 12-hydroxy stearate.

References Cited in the file of this patent

UNITED STATES PATENTS

2,831,811	McCormick et al.	Apr. 22, 1958
2,916,452	Givens et al.	Dec. 8, 1959