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LUBRICATING GREASE AND PROCESS OF MANUFACTURE

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The present invention relates to an improved lubricating grease and a process for its manufacture. The invention is particularly concerned with improvements in the process of preparing greases, and in a combination of ingredients used in such processes, resulting in products having better lubrication life, improved oxidation resistance and lower volatility.

It has previously been suggested that the high temperature performance of lubricating greases subjected to severe operating conditions, particularly where long life and sustained operation at elevated temperatures are required, may be improved by adding to the soap thickener various constituents of relatively low molecular weight. According to some authorities, these materials, namely the low molecular weight salts and the conventional metal soaps of long chain fatty acids, combine to form a complex which has the property of thickening lubricating oils to grease consistency and also imparting a high degree of mechanical and thermal stability. Thus, it has been suggested that combinations of conventional sodium, calcium and other metal soaps with salts of the same or related metals, such as the acetates, nitrates, acrylates, furoates, and the like, may be used for this purpose.

According to the present invention, still further improvements may be made in greases of the combined salt-soap complex type by the method of compounding and by selection of the lubricating oil constituents and by suitable choice and control of the conditions under which the soap and salt are added thereto.

Most commercial lubricating greases are prepared from mineral base lubricating oils thickened with soap, salt-soap mixtures, and the like, as is well-known in the art. In grease manufacture, it has been almost universal practice in the past to use mineral oil distillates of the lubricating oil range having a fairly large so-called aromatic or naphthenic content. Such oils have a comparatively low viscosity index. The reason for this preference is that the naphthenic or aromatic oils, that is, low A. P. I. gravity oils such as Gulf Coast oils and other asphaltic crudes and containing a substantial percent of non-paraffinic ingredients, are much better solvents and dispersants for soaps than are the paraffinic oils. Grease prepared from these give less trouble with

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soap separation than the paraffinic oils. It is simpler to make highly stable soap suspensions with these non-paraffinic, low viscosity index oils. For purposes of the present invention, it is preferred to use lubricating oils of viscosity index 0 to 60, viscosity at 100° F. of 250 to 1500 S. S. U., preferably at least 300 or higher, and flash points of 280° to 480° F., preferably 340° to 440° F.

On the other hand, it is well-known in the lubricating industry that the paraffinic type oils, obtained either from paraffinic crudes directly or by solvent extraction of mixed or asphaltic base crudes, have markedly superior viscosity indexes. For this reason, the highly paraffinic oils would be preferable if they could be compounded satisfactorily into greases. Another disadvantage of the conventional naphthenic or aromatic type oils is that they are relatively volatile for a given viscosity. Non-paraffinic oils of a given viscosity usually have a lower flash point than paraffinic oils of similar viscosity. The non-viscous naphthenic oils tend to flash at or even below grease cooking temperatures. Also, for high temperature lubrication, it has been considered necessary in the past to use oils of relatively very high viscosity in order to avoid undue volatility. At the same time, it has been necessary to use large quantities of soap to obtain a given grease consistency because of the higher soap solvency of the oil.

Since the paraffinic oils, on the other hand, have a very much lower volatility for the same viscosity, it would appear desirable to substitute them. However, as indicated above, they have not been used extensively in grease manufacture because of the difficulty of obtaining satisfactory soap dispersion and grease texture.

The paraffinic oils are superior to the naphthenic crude products in their resistance to oxidation. While naphthenic oils can be stabilized quite effectively by the proper use of oxidation inhibitors, they are still subject to greater oxidative deterioration than the paraffinic oils. Even the latter can, of course be improved by the use of good inhibitors.

According to the present invention, lubricating greases of the salt-soap thickened type may be prepared with especially desirable properties for high temperature performance by first forming a soap-salt concentrate in a relatively viscous

aromatic type oil. As noted above, such an oil should preferably have a viscosity of 250 to 1500 S. S. U. at 100° F., the higher ranges being preferred. Thereafter, a substantial quantity of a substantially paraffinic oil is blended into the soap-salt concentrate at continued grease cooking temperatures, e. g. 280° to 450° F., preferably 300° to 350° F., and a stable grease of good high temperature properties, suitable for long life lubrication, is thus prepared.

It is possible to use oils having a moderately good viscosity index, even for this first fraction. Oils derived from certain Panhandle or Mid-Continent crudes, or those obtained from semi-paraffinic stocks, or only partially refined by reduced solvent treatment, etc., may be employed.

The introduction of paraffinic oil into a preformed grease is not merely a matter of blending. While some types of mineral lubricating oils may be worked into soap concentrates successfully when cold, the highly paraffinic oils, which are particularly desirable because of their high viscosity indexes and decreased volatility, do not combine with the concentrates to form stable greases. They are subject to soap separation, particularly when subjected to heating and cooling as in high temp. service. They also tend to separate soap from oil in storage at ordinary temperatures. According to the present invention, however, if the paraffinic oils are added very gradually, and at the cooking temperatures which are usually available in standard steam heated grease kettles and worked mechanically while being stirred into the preformed thick grease or soap-salt concentrate, greases of good structure stability may be prepared. For this purpose, paraffinic oils of 90 to 120 viscosity index, with viscosities of about 200 to 500 S. S. U. at 100° F., and with flash points of 300° to 500° F., preferably 440° to 480° F., are preferred.

Another feature of the present invention is the discovery that the dispersion of the soap-salt thickener, which largely determines the structural stability of the grease, may be greatly improved by drastic mechanical homogenization, e. g., in a drastic homogenizer of the Manton-Gaulin type. Alternatively, the grease may be milled in a paint mill, or the like, with quite satisfactory results.

The invention will be more fully understood by reference to the examples below. In general, however, about 2 to 20 parts by weight of suitable fatty acids of the C_{12} to C_{24} range, preferably saturated or substantially so, are first combined at ambient temperatures with about 20 to 50 parts by weight of the aromatic or naphthenic (or mixed base) type mineral oil of relatively high viscosity. About 1 to 15 parts by weight of the other soap-salt constituent, e. g., a low molecular weight carboxylic acid or an aldehyde capable of undergoing the Cannizzaro reaction to form such an acid, is added to this mixture along with a sufficient quantity of a metal base to saponify the fatty acids and to combine with the acid or to undergo the Cannizzaro reaction with the aldehyde where an acid-forming aldehyde, such as furfural, benzaldehyde, formaldehyde, or the like, is used.

The mixture of ingredients described above is heated to soap-cooking temperature, normally between about 300° and 350° F. until the reactions are substantially complete and the water resulting therefrom has been substantially or completely evaporated. Oil refinery equipment is often heated with steam at available pressure and temperature, usually around 125 p. s. i. g. and 340° F. Where the Cannizzaro reaction is taking place, e. g., where an aldehyde such as furfural or thiophene is being used, alcohols resulting therefrom should be substantially removed. In some cases, minor proportions of such alcohols may be permitted to remain in the grease, as is now known in the art.

The foregoing process results in a soap or soap-salt concentrate in relatively viscous aromatic or other non-paraffinic type oil which has relatively good solvent properties for the soap constituent. Without substantially lowering the temperature, 25 to 50 parts by weight of a relatively lower viscosity paraffinic oil (of higher A. P. I. gravity, higher flash point, and higher viscosity index, relative to its viscosity) are blended in gradually, heat being applied to keep up the temperature and stirring being continued throughout the blending. This process produces a good product which may be further improved in texture and mechanical stability by extensive homogenization or mechanical milling, as suggested above.

Example I

A composition of the following ingredients was prepared in the general manner described above.

Ingredients	Percent Weight
Fatty acids about C_{18} average ("Hydrofol Acids 53")	15.00
Napthenic type mineral oil 1200 S. U. S. Vis./100° F., Flash 440° F. (Conventionally refined Coastal oil)	34.50
Furfural	10.00
Sodium hydroxide	5.00
Highly refined paraffinic type oil of 150 S. U. S. Vis./100° F., Flash 440° F	34.50
Phenyl alpha naphthylamine (antioxidant)	1.00

The "Hydrofol acids" (substantially saturated) and the naphthenic type mineral oil were charged to a steam heated grease kettle and mixed without heating. A 33⅓% aqueous solution of sodium hydroxide was added and the acids neutralized. The furfural was then added and by a Cannizzaro reaction it was reacted with the excess sodium hydroxide used, over and above that required for the neutralization of the "Hydrofol acids." Heating was then initiated, and the mass was dehydrated and substantially de-alcoholized. The resulting soap-salt complex was thus dispersed in the high viscosity naphthenic type mineral oil to form a thick grease or soap concentrate. The concentrate was heated to 320°–340° F. (highest temperature obtainable with usually available steam pressures). After cooking for approximately one hour, the low viscosity paraffinic type oil was slowly added to the hot soap dispersion, cooking and stirring being continued. When this oil was completely added, the phenyl alpha naphthylamine was added to inhibit oxidation. Thereafter, the grease was cooled to about 110° F. while agitating, by releasing the steam and running cold water through the kettle jacket. Then the grease product was semi-fluid; it could be poured slowly at room temperature. Homogenizing the grease by passing through a paint mill or Manton-Gaulin type homogenizer thickened it very substantially to a solid smooth grease structure. This product showed no flow

whatsoever at room temperature. It showed the following inspections:

Penetrations mm./10 (77° F.):
- Unworked ---------- 285
- Worked 60 strokes ---------- 321
- Worked 60,000 strokes ---------- 356

Dropping point, °F---------- 500+

Example II

Ingredients	Percent Weight
"Hydrofol Acids 53"	15.00
Close cut Coastal type mineral oil 300 S. U. S. Vis./100° F., 350° F. Flash point	30.00
Furfural	10.00
Sodium hydroxide	5.00
Paraffinic type mineral oil of 250 S. S. U. Vis./100° F., 460° F. Flash point	39.00
Phenyl alpha naphthylamine	1.00

Prepared in similar manner to Example I.

Penetrations mm./10:
- Unworked ---------- 214
- Worked 60 strokes---242
- Worked 60,000 strokes 352

Dropping point, °F.-------500+

Norma Hoffman bomb 700 hours—no drop in oxidation. oxygen pressure.

Lubrication life---------1300
10,000 R. P. M. spindle test at 300° F. hours.

Example III

Ingredients	Percent Weight
Oleic acid	7.5
"Hydrofol Acids 53"	7.5
Naphthenic mineral oil, 1200 S. U. S. vis. at 100° F., as in Example I	34.5
Furfural	10.0
Sodium hydroxide	5.0
Paraffinic oil of 150 S. U. S. vis. at 100° F., as in Example I	34.5
Phenyl alpha naphthylamine	1.0

Prepared in similar manner to Example I.

Since the temperature of 330° F. was the maximum obtainable in this particular steam kettle, the grease was then transferred to a fire heated kettle and heated to 400° F. The grease drawn at 330° F. was semi-fluid and further homogenization did not materially thicken it. The grease cooked to 400° F. was substantially harder.

Grease from steam kettle after homogenization:
- Penetration mm./10---------- 332
- Dropping point °F---------- 500+

Grease heated to 400° F.: Penetration mm./10 ---------- 210

Example IV

Ingredients	Percent Weight
"Hydrofol Acids 53"	20.00
Acetic acid (glacial)	4.00
NaOH	6.34
Phenyl alpha naphthylamine	1.00
Highly paraffinic base stock of about 250 S. U. S. vis. at 100° F	34.33
Close cut aromatic type mineral oil, 300 S. U. S. vis. at 100° F	34.33

The "Hydrofol acids" and the aromatic mineral oil were charged to a steam heated grease kettle and heated to 150° F. The acetic acid was then added and both acids were co-neutralized with the sodium hydroxide (40% aqueous solution).

The soaps thus formed were next dispersed in the aromatic mieral oil by heating and stirring and the product dehydrated at 330° F. The paraffinic oil base was then slowly worked into the soap dispersion while the temperature was maintained at 330° F. and stirring was continued. Thereafter, the phenyl alpha naphthylamine was added and the grease was allowed to cool with no further working.

Appearance—Slightly rough—smooths out on homogenization

Penetration unworked---------- 131

Penetration worked 60 strokes---------- 147

Comparison of greases (volatility and spindle life)

	Percent Volatility [1]	10,000 R. P. M. Spindle Test at 300° F. Hours
Example II	24.0	[2] 1300
Similar grease of same viscosity mineral oil but containing all aromatic type oil. (Average of 3 greases)	35.0	[3] 400–600

[1] Percent loss from packed bearing held 500 hours in an oven at 300° F.

[2] The grease in this high speed spindle bearing was found to be rather heavy, probably from evaporation of the more volatile oil constituents, but no oil was found condensed in the quill. Lubrication was continuously satisfactory.

[3] This grease residue was dry and powdery and a large amount of oil was found condensed in the quill. Lubrication had failed.

What is claimed is:

1. The process of making a stable high temperature lubricating grease which comprises combining 2 to 20 parts by weight of fatty acid of the C_{12} to C_{24} range with 20 to 50 parts of an aromatic type mineral base lubricating oil of relatively high viscosity, adding 1 to 15 parts of organic material having a molecular weight below about 160 selected from the group consisting of carboxylic acids and aldehydes undergoing the Cannizzaro reaction and a sufficient amount of a metal base selected from the group consisting of alkali metal and alkaline earth metal bases to form a soap-salt complex with said fatty acid and said organic material, heating the aforesaid ingredients with stirring to a soap-cooking temperature for a period of time to substantially complete said soap-salt reaction, and thereafter gradually adding and blending in 25 to 50 parts of a relatively low viscosity and low volatility mineral lubricating oil of paraffinic type while applying heat, the amount of said paraffinic-type oil being not substantially smaller than that of said aromatic-type oil and substantially maintaining a cooking temperature between about 280° F. and 450° F. to form a grease of relatively high viscosity index and relatively low volatility.

2. The process of preparing a stable lubricating grease of relatively high viscosity index and relatively low viscosity, which comprises combining about 2 to 20 parts by weight of substantially saturated fatty acid of the C_{12} to C_{24} range with about 20 to 50 parts of a relatively viscous aromatic mineral base lubricating oil at substantially ambient temperatures, adding an excess of an alkali metal base saponifying agent, adding 1 to 15 parts of an organic aldehyde of molecular weight below about 160 capable of undergoing the Cannizzaro reaction with said base, beating and stirring to a grease cooking temperature of about 300° to 350° F. for a period of time to substantially convert said fatty acid and said aldehyde into a soap and salt mixture concentrate in said oil, thereafter substantially maintaining said cooking temperature between about 300° and 350°

F. and gradually stirring in about 25 to 50 parts of substantially paraffinic type lubricating oil of viscosity substantially lower than said aromatic type oil, cooling the grease and subjecting it to drastic mechanical working to homogenize it.

3. Process according to claim 1 wherein said organic material is furfural.

4. Process according to claim 1 wherein said fatty acid is substantially saturated.

5. Process according to claim 2 wherein said alkali metal base is NaOH.

6. Process according to claim 2 wherein said aldehyde is furfural.

7. Process according to claim 1 wherein said organic material is a carboxylic acid of 2 to 7 carbon atoms.

8. Process according to claim 1 wherein said organic material is an aliphatic carboxylic acid of 2 to 4 carbon atoms.

9. A structurally stable lubricating grease composition consisting essentially of about 20 to 50 parts by weight of a relatively viscous non-paraffinic type mineral lubricating oil of relatively low viscosity index, 25 to 50 parts of a relatively less viscous paraffinic type mineral lubricating oil, the amount of paraffinic-type oil being not substantially smaller than that of said non-paraffinic oil, said oils being thickened to a grease consistency with a combination of about 2 to 22 parts of a metal selected from the group consisting of alkali and alkaline earth metals and metal soap of fatty acid of the C_{12} to C_{24} range and about 2 to 20 parts of the salt of the same metal and carboxylic acid of less than 8 carbon atoms and molecular weight below about 160, said grease being stabilized structurally by sustained cooking of the blend of non-paraffinic oil and soap at a temperature between 280 and 450° F., while said paraffinic oil is gradually blended therein.

10. Composition according to claim 9 wherein said metal salt is sodium.

11. Composition according to claim 9 wherein said carboxylic acid comprises a furoic acid.

12. Composition according to claim 9 characterized by an extremely fine dispersion of salt-soap thickener as obtained by severe mechanical homogenization of the cold final blend.

13. Process according to claim 1 wherein said grease is cooled and thereafter mechanically milled to give it a solid consistency.

14. A solid milled structurally stable lubricating grease of the salt-soap complex type, comprising substantial proportions of relatively paraffinic high viscosity index mineral oil of low viscosity and not substantially more than equal proportions of relatively non-paraffinic low viscosity index mineral oil of relatively high viscosity and a grease forming proportion of sodium soap of substantially saturated fatty acids of the C_{12} to C_{24} range combined with sodium salt of carboxylic acid of molecular weight below 160, said grease being stabilized structurally by sustained cooking of the blend of non-paraffinic oil and soap at a temperature between 280 and 450° F., while said paraffinic oil is gradually blended therein.

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