

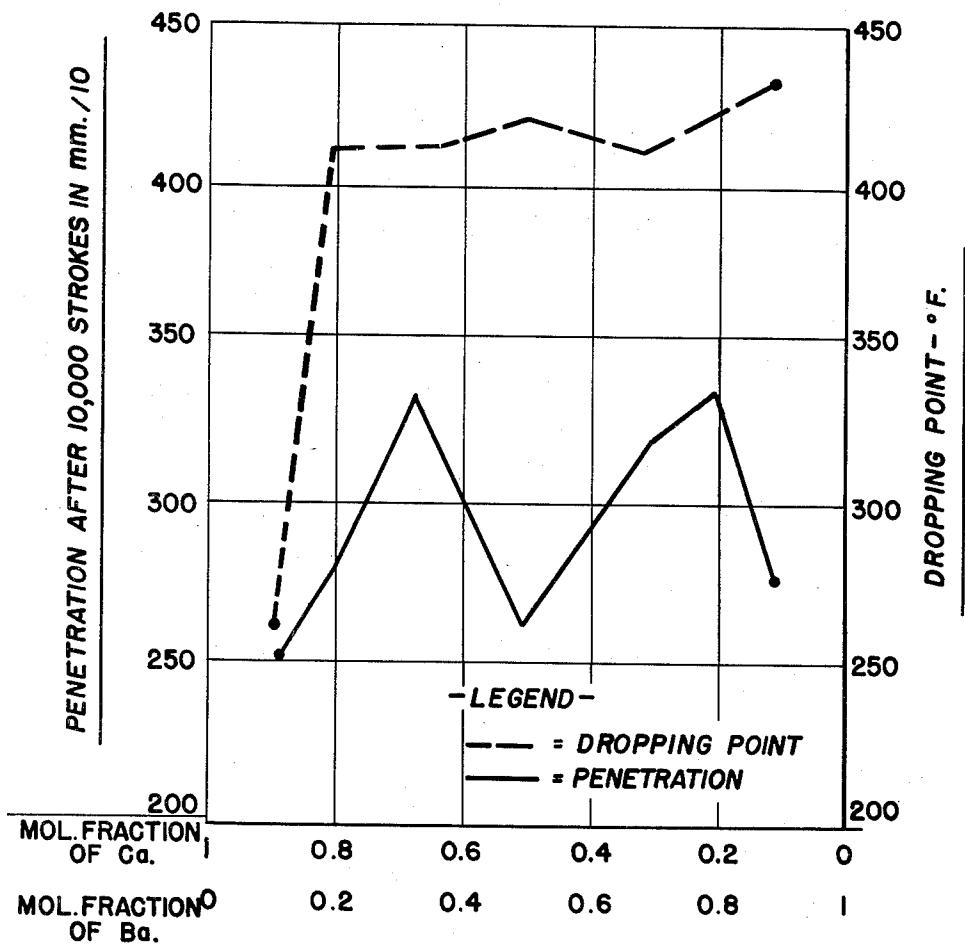
May 17, 1955

E. O. FORSTER

2,708,659

METHOD FOR THE PREPARATION OF MIXED BASE GREASES

Filed July 28, 1952



Eric O. Forster Inventor  
By Edwin M. Thomas Attorney

# United States Patent Office

2,708,659  
Patented May 17, 1955

1

2,708,659

## METHOD FOR THE PREPARATION OF MIXED BASE GREASES

Eric O. Forster, Hillside, N. J., assignor to Esso Research  
and Engineering Company, a corporation of Delaware

Application July 28, 1952, Serial No. 301,194

7 Claims. (Cl. 252—39)

This invention relates to lubricating grease compositions. Particularly the invention relates to lubricating grease compositions having outstanding structural stability and high temperature performance. More particularly, the invention relates to a lubricating grease composition having excellent all-purpose utility which comprises a lubricating oil thickened to a grease consistency with a complex of a calcium soap and a soap selected from the class consisting of barium, strontium and magnesium which is prepared by a sequence of specific processing steps.

The preparation of calcium base greases is old in the art and is well described by the patent literature. Such greases are excellent in structure, water resistance and appearance. However, the high temperature properties of calcium greases are very poor. This is due to the necessity of incorporating water with the calcium soaps during the manufacture of calcium soap greases. At temperatures above about 200° F. the water of formulation is driven off and the grease structure breaks down.

It has now been found, and forms the object of this invention, that a calcium base grease having all the advantages of water resistance and characteristic structural stability of the calcium greases and having, in addition, excellent high temperature properties may be prepared by combining with the calcium soap of the prior art varying amounts of a soap of a metal selected from the group consisting of magnesium, barium and strontium. It is to be especially noted that there are certain steps in the manufacture of the grease compositions of invention which must be carried out in order for the resulting product to have the desired properties. These are, briefly, the dispersal of the calcium soap portion of the thickening agent prior to the dispersal of the other soap, and heating the mixture of soaps and oil to a temperature in excess of 350° F. during the preparation. These steps will be explained in more detail below.

The lubricating oil which is utilized as a dispersant for the soaps in preparing the greases of the invention may be selected from a wide variety of lubricating oils. A mineral lubricating oil preferably of naphthenic origin may be chosen as the grease base. It should have a viscosity within a range of from about 40 SUS at 100° F. to about 4000 SUS at 100° F. As in the preparation of most grease compositions, the mineral oil chosen should be that lubricating oil which would be used to furnish proper lubrication if a liquid oil could be used. It is preferred to use a mineral oil having a viscosity of from about 300 to 1500 SUS at 100° F. to formulate the greases of this invention.

Although a mineral lubricating oil, such as a conventionally refined distillate, is preferred for the preparation of the improved greases of invention, a synthetic oil may also be utilized as the dispersing agent. Although a synthetic lubricant of the ester type, for example, the esters of dibasic acids and long chain alcohols, is a preferred type, other well known synthetic lubricants may be used. Complex esters made from dibasic acids, glycols, and alcohols may be used as may the polymerized glycol

2

esters, glycol ethers, polymerized olefins, alkylated aromatics, polymerized silicones, formals, mercaptals, and the like. The only prerequisite is that the dispersant chosen be one that will furnish the desired lubrication when utilized as a grease composition.

The acid used to form the soaps that are used in formulating the greases of invention may be any of the high molecular weight fatty acids commonly used in grease making. Such fatty acids as the hydrogenated fish oil acids, stearic acid, oleic acid, hydroxy acids, tallow, any of the generally known fatty acid glycerides or mixtures of these in any proportions may be used. The acids prepared by the "Oxo" process having from 10 to 30 carbon atoms may also be used. Of the high molecular weight fatty acids the preferred embodiment contemplates the use of the hydrogenated fish oil acids.

As was stated above, the thickening agent used in formulating these new and improved greases is a mixture of calcium soap and a soap of a metal selected from the group consisting of barium, strontium and magnesium. The calcium soap must be present in amounts ranging from about 2.5% to about 15.0% by weight, based on the weight of the finished composition. The amount of the soap of the other metal used is such that the molar ratio of the calcium soap to the second metal soap is between 8:1 to 1:8 with a mol ratio within the range of 2:1 to 1:2 being especially preferred. The amount of the combined soaps present will depend somewhat upon the desired final consistency of the product. Ordinary usage would call for a grease composition according to the instant invention containing from about 5% to 30.0% by weight of combined soap, with a range of from 10.0% to 20.0% of soap being especially preferred.

In addition to the two critical limitations outlined above, that is, use of a combination of calcium soap with limited amounts of a barium, strontium, or magnesium soap of a high molecular weight substantially saturated fatty acid as the thickener, there are two other process limitations which must be met in preparing the grease compositions of this invention. It is an essential feature in the preparation of these grease formulations that the calcium soap be dispersed in the lubricating oil base before the other metal soap is added and dispersed. The exact reason for this phenomenon is not known, but it is believed that the calcium soap increases the solubility and hence improves the degree of dispersion of the other metal soap in the oil and thus increases the yield as well as the structural stability of the finished product.

The second critical feature in the method of formulation is that the total mixture of oil and soap must be heated to a temperature above about 350° F. after dehydration. It is believed that a phase transition of the soap mixture occurs at or above 350° F. producing a new arrangement of the soap molecules that is stable both at low and elevated temperatures, i. e. it does not reverse to the original phase upon cooling. Only those greases that are so treated show the heat stability characteristics that are desired, together with the well known excellent lubricating properties of the heat unstable straight calcium greases.

In order more clearly to illustrate the instant invention, the following examples are given.

### EXAMPLE I

In accordance with the concepts of the instant invention but without heating above 350° F. the following grease composition was prepared by the procedure given below:

#### Formulation

17.00% hydrogenated fish oil acids (Sap. No. 195)  
0.88% calcium hydroxide  
5.63% barium hydroxide octahydrate  
76.49% mineral oil distillate (70 SUS/210° F.)

## 3

## Procedure

The total charge of the fish oil acids and one third of the mineral oil were mixed and heated until a homogeneous solution was obtained. An oil slurry of calcium hydroxide was added and the temperature was allowed to rise to 210° F. When the reaction and the subsequent evolution of water vapor had stopped, dry barium hydroxide octahydrate was added to the mixture and the temperature allowed to reach 240-250° F. After complete dehydration the soap mixture was cut back with the remaining mineral oil while the temperature was brought up to about 300° F. When all the oil was added, the mixture was removed from the heating medium and allowed to cool without stirring.

The inspection data on this grease composition are set out in Table I.

## EXAMPLE II

By the procedure set out in detail in Example I above, a second grease composition was prepared employing strontium rather than barium hydroxide. This grease had the following formulation:

17.00% hydrogenated fish oil acid (Sap. No. 195)  
0.88% calcium hydroxide  
4.73% strontium hydroxide octahydrate  
77.39% mineral oil distillate (70 SUS/210° F.)

The inspection data on this grease are set out in Table I.

## EXAMPLE III

A third grease composition, prepared by the procedure of Example I but employing magnesium rather than barium hydroxide had the following formulation:

17.00% hydrogenated fish oil acid (Sap. No. 195)  
0.88% calcium hydroxide  
4.15% magnesium hydroxide  
77.97% mineral oil distillate (70 SUS/210° F.)

The inspection data of this grease are set out in Table I.

## EXAMPLE IV

This grease, prepared as described in Example I had the following formulation:

17.00% hydrogenated fish oil acid (Sap. No. 195)  
1.77% calcium hydroxide  
84.23% mineral oil distillate (70 SUS/210° F.)

In the preparation of this grease composition, there was, of course, no addition of the second metal hydroxide and dehydration temperatures were attained after the adding of the balance of the mineral oil. The data is reported in Table I.

## EXAMPLES V AND VI

To demonstrate the importance of heating to temperatures above 350° F., in Examples V and VI the greases described in Examples I and II were heated to 380-420° F. and then were cooled. Inspection data on the resulting greases are given in Table I.

## 4

An examination of the data of Table I above will point out the outstanding characteristics of the grease compositions and the importance of the heating process claimed in this invention. It will be noted that whereas the straight calcium base grease had a dropping point of 177° F., the greases of Examples I and II were in excess of 290° F., almost double that of Example IV. Upon heating the same greases to 380-420° F., as described in Examples V and VI, the dropping points increased to almost 400° F., or better. After being subjected to a temperature of 250° F. for 400 hours, the calcium base grease of Example IV lost 180 points (mm./10) in penetration, that is to say it almost doubled in hardness, indicating the lack of stability of the grease composition. The grease samples of Examples I and II, however, retained their grease structure with a slight increase only in the case of the calcium-barium grease.

## EXAMPLES VII-XIV

In order to evaluate the effect of the mol ratio of the calcium soap to the second metal soap of the formulation of inventions, a study of the calcium-barium soap system was made which extended over the whole range from pure calcium soap to pure barium soap. These grease samples were prepared using hydrogenated fish oil acids having a saponification number of 195-197 and the same mineral oil used in Examples I-VI.

The total charge of acids was added to one third of the mineral oil and the mixture was heated until a homogeneous solution was obtained. An oil slurry of calcium hydroxide was then added and the temperature allowed to rise to 210° F. After the reaction had subsided and the evolution of water vapor had ceased, dry barium hydroxide octahydrate was added to the solution and the mixture allowed to reach 240-250° F. After complete dehydration of the mixture the balance of the mineral oil was added and the temperature was increased to above 350° F., usually to between about 380 and 420° F. The mixture was then allowed to cool without stirring.

In all, eight grease samples were prepared by the procedure outlined above, two each of mol ratios of calcium soap to barium soap of 8:1, 2:1, 1:1 and 1:8. In each case the total soap content was 17 weight percent. One of the samples at each mol ratio was adjusted so as to be an acid grease, that is a slight excess over stoichiometric amounts of the fatty acid was added, and one at each mol ratio was prepared on the alkaline side, that is a slightly less than stoichiometric amount of acid was used. The grease samples, after preparation, were all subjected to the action of a Morehouse mill and were tested by ASTM procedures for dropping points and penetrations. The data obtained are set out in Table II below.

TABLE I  
Effect of composition and manufacturing conditions on  
mixed calcium base greases

Example No.	I	II	III	IV	V	VI
Type	Ca-Ba	Ca-Sr	Ca-Mg	Ca	Ca-Ba	Ca-Sr
Mol Ratio	1/1.5	1/1.5	1/1.5		1/1.5	1/1.5
Soap Content, wt. percent	17	17	17	17	17	17
Top Manufacturing Temperature, ° F.	300	300	300	300	420	420
Dropping Point (° F.)	332	298	298	177	410	398
Water Solubility (30 min./210° F.)	None	None	None	None	None	None
Micro-Penetration: (mm./10 @ 77° F.):						
Worked (10 strokes, 60 mesh screen)	58	46	245	280	95	98
Initial						
Worked after 400 hrs. @ 250° F.	43	85	92	100	(*)	(*)

\*Not determined.

TABLE II

*Effect of mol ratio and acidity on the penetration and dropping point of calcium-barium greases*

Example Number	Mol Ratio Calcium- Barium	Acid Grease		
		Dropping Point (° F.)	Penetra- tion* (mm./10 at 77° F.)	ASTM Neut. Number (Percent Oleic)
VII	8:1	269	255	0.37
VIII		410	337	0.03
IX		420	265	0.06
X		434	278	0.06
Alkaline Grease				
XL	1:8	308	272	0.73
XII		384	336	0.37
XIII		401	218	0.62
XIV		420	336	0.58

\*After 10,000 strokes in grease worker using fine hole plate.

Inspection of the data in Table II indicates that any amount of barium soap added to a calcium soap in the course of grease manufacture will improve the high temperature qualities and structure stability of the final product. Although small amounts of barium soap will cause substantial improvements, the most marked appear when the mol ratio of calcium to barium is smaller than 8:1, i. e. 4:1 or 2:1, etc. Thus, following the ultimate uses contemplated, the grease composition can be varied in such a manner as to meet a large variety of specification requirements.

The fact that changes from acidic to alkaline reacting grease compositions do not affect to any appreciable extent the finished product adds to the desirability of this composition and eases the control of manufacturing procedures.

The data of Table II above are shown graphically in the accompanying drawing. In the drawing, the dotted line represents the dropping points and the solid line depicts the penetrations of the greases of Examples VII through X. It is clearly seen from this drawing that the soap combination of the grease of invention imparts desirable properties of high temperature stability and overall structural stability.

What is claimed is:

1. A process for the preparation of lubricating grease

compositions having outstanding water resistance and high temperature properties which comprises the steps of dispersing in the presence of water from about 2.5% to about 15.0% by weight, based on the weight of the final grease composition, of a calcium soap of a high molecular weight fatty acid in a lubricating oil, subsequently dispersing a second soap selected from the group consisting of barium, strontium and magnesium soaps of high molecular weight substantially saturated fatty acids in said mixture in amounts such that the mol ratio of said calcium soap to said second soap is from 8:1 to 1:8, and heating the resulting mixture up to a temperature of about 250° F. to dehydrate said resulting mixture, subsequently heating to a temperature between about 350° to 420° F. and cooling the resulting composition.

2. A process according to claim 1 wherein from 5% to 30% by weight of total soap is utilized.

3. A process according to claim 1 wherein said mol ratio of calcium soap to said second soap is from 2:1 to 1:2.

4. A process according to claim 1 wherein said second soap is barium and wherein said mol ratio of said calcium soap to said barium soap is 2:1 to 1:2.

5. A process according to claim 1 wherein said second soap is strontium.

6. A process according to claim 1 wherein said second soap is magnesium.

7. A process for the preparation of lubricating grease compositions having outstanding water resistance and high temperature properties which comprises the steps of dispersing in the presence of water from about 2.5% to about 15.0% by weight, based on the weight of the final grease composition, of a calcium soap of a high molecular weight fatty acid in a lubricating oil, subsequently dispersing a second soap selected from the group consisting of barium, strontium, and magnesium soaps of high molecular weight substantially saturated fatty acids in said mixture in amounts such that the mol ratio of said calcium soap to said second soap is from 8:1 to 1:8, heating the mixture up to a temperature of about 250° F. to dehydrate said mixture, subsequently heating to a temperature within a range of about 380° to 420° F., and cooling the resulting composition.

#### References Cited in the file of this patent

#### UNITED STATES PATENTS

2,070,781	Brunstrum et al. -----	Feb. 16, 1937
2,389,523	Leyda -----	Nov. 20, 1945
2,409,950	Meyer -----	Oct. 22, 1946
2,417,429	McLennan -----	Mar. 18, 1947