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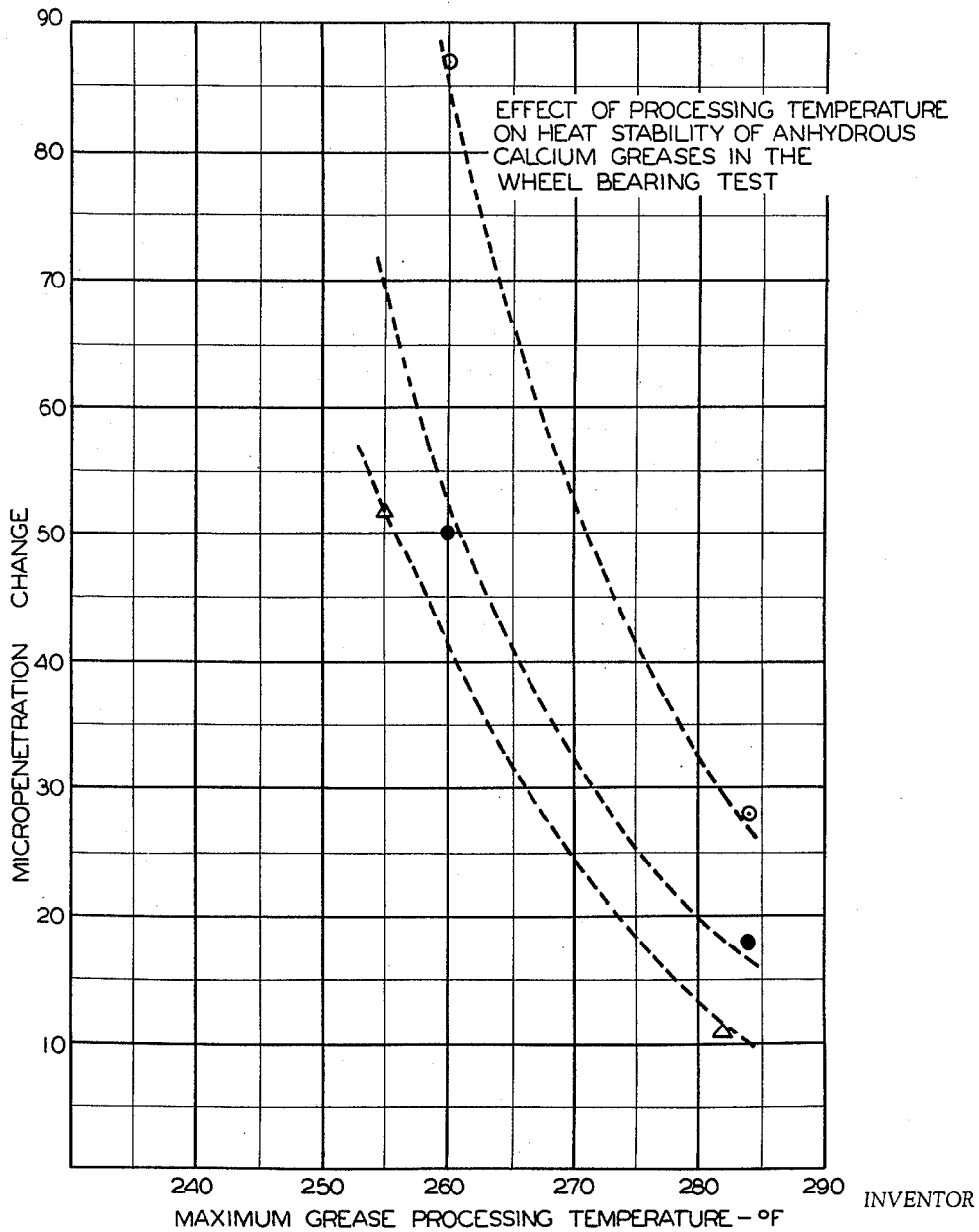
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2,915,467

METHOD OF PREPARING AN ANHYDROUS CALCIUM GREASE

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WHEEL BEARING TEST
60 MPH — 250°F — 6 HOURS



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2,915,467

METHOD OF PREPARING AN ANHYDROUS CALCIUM GREASE

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4 Claims. (Cl. 252—39)

This invention relates to greases useful for multipurpose applications including high temperature service and in particular relates to anhydrous calcium greases characterized by stability towards gelling up or hardening, a characteristic of anhydrous calcium greases in high temperature service.

Anhydrous calcium greases employed in high temperature service, as exemplified by the ASTM wheel bearing test at 60 m.p.h. and 250° F., generally develop a structure which is described by those skilled in the art as "gelling up"; the change in the grease is highly undesirable because the grease can no longer feed properly to the parts to be lubricated. The gelling up resulting in high temperature service appears to be a structural change in the calcium grease fiber from the normal microscopic mixture of gel particles in a matrix of soap in oil solution. These gel particles consist of a continuous network of soap fibers in oil, and possess rigidity and elasticity as to true gels. Since the interaction between adjacent gel particles is not as great as between adjacent fibers in the same gel particle, the microscopic grease behaves as a plastic or paste. The "gelling up" that occurs in high temperature service is due to a continuous soap fiber network formed throughout the entire grease mass. This network is formed at the high temperatures when the crystals of soap, being very mobile, grow adjacent microscopic gel particles together, forming a macroscopic or rigid gel.

I have now discovered that anhydrous calcium greases can be produced which are not subject to gelling up in high temperature service. Particularly, I have discovered that a defined heat treatment of an anhydrous calcium grease can result in a grease characterized by immobility and inactivity of adjacent soap crystals, so that when such greases are employed in high temperature service, the soap crystals will not grow together to form a rigid gel. While the chemical or physical changes occurring in the grease as a result of the defined heat treatment are not completely understood, the resulting greases are stabilized for high temperature service.

The advantages resulting from the present invention are obtained by subjecting anhydrous calcium grease to a post-dehydration heat treatment at a temperature which is higher than the dehydration temperature. Dehydration normally is accomplished at a temperature of about 35° to 65° F. below the dropping point of the grease, i.e. at temperatures of about 230° to 260° F. The post-dehydration heat treatment is accomplished by heating the grease at an elevated temperature with an external source of heat to stabilize the inherent structure and consistency of the grease. The temperatures which can be employed range from about the maximum dehydration temperature to just below the dropping point temperature of the grease treated. These temperatures normally range from about 260° to 300° F. or higher. For greases produced in accordance with the procedures outlined in the application of McCormick et al. Serial No. 442,198, filed July 8,

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1954, now U.S. Patent No. 2,831,811, a satisfactory temperature range is 260° to 295° F. While the temperatures within these ranges are effective to result in greases with the described stability, it is preferable to employ temperatures which approach but do not coincide with the actual dropping point of the grease. It is important that temperatures equivalent to the dropping point of the grease are avoided even at localized points because soap separation occurs. It has been found that the use of the higher temperatures within the range described results in stabilization in a very rapid time, for example one hour or so. A particularly satisfactory temperature range for the greases prepared by the procedure of the above-identified McCormick et al. application is from about 275° to below 295° F. and especially 280° to 285° F. A preferred range for anhydrous calcium greases in general is about 5° to 20° F. below the dropping point of the grease.

The period of treatment to be employed is dependent upon the temperature used. At temperatures barely removed from the dehydration temperature, stability results after hundreds of hours. At temperatures of 5° to 20° F. below the dropping point of the grease, stability of structure results in short periods, i.e. from about 15 minutes to 3 hours or more and usually in about 1 hour. In addition to the necessity of employing the defined temperature to impart stability to the grease, I have found it necessary to heat treat after dehydration. In general, the water content of the grease should not exceed 0.3 weight percent. The term "anhydrous" as used in this specification is intended to indicate a water content of about 0.0 to 0.3 weight percent. Any significant amount of water present in a grease at elevated temperatures would cause the grease to become excessively grainy. Grainy texture greases are undesirable for a number of reasons including bleeding or oil separation and the fact that small lumps in a grease will plug lubricator systems.

Particularly satisfactory greases which can be employed are those obtained by the methods described in the copending application of McCormick et al. above-identified. In the process described in that application, anhydrous calcium greases are prepared by methods whereby foaming is eliminated, smooth greases in high yields are produced and the entire grease-making procedure is effected in about 6 hours rather than the usual 12 or more hours. The greases produced by the process in the McCormick et al. application are preferred for use in the present invention; however, anhydrous calcium greases prepared by other methods can be heat treated in accordance with my invention. For example, greases prepared by adding a soap to a suitable lubricating oil and thickening the lubricating oil to a grease consistency followed by a step designed to dehydrate the grease may be employed. In general, any anhydrous calcium grease formed with any of the normally employed fatty components, i.e. hydroxy fatty acids, glycerides and their esters, can be used in this invention. Preferred saponifiable materials are those in which the hydroxyl group is at least 12 carbon atoms removed from the carboxyl group, for example 12 hydroxy stearic acid and hydro-generated castor oil.

The oils which can be employed to produce greases useful in accordance with the teachings of this invention include mineral and synthetic oils. Particularly satisfactory oils are mineral lubricating oils having a viscosity within the range of about 50 SUS at 100° F. to about 2000 SUS at 210° F. Such oils can be highly refined and solvent-treated, if desired, by known methods. Among the synthetic lubricants which can be employed are polymerized olefins, alkylated aromatics, silicone polymers, polyalkylene glycols and their partial or com-

plete ethers and esters. A particularly satisfactory synthetic di-ester base grease employs di-(2-ethyl hexyl adipate) as the base.

The post-dehydration temperature heat treatment of the present invention has as a primary objective the stabilization of the inherent structure and consistency of the grease. There are, however, other desirable properties imparted to the greases as a result of this novel invention. For example, I have discovered that the water stability, mechanical stability and low temperature viscosity of the anhydrous calcium greases are often enhanced by my treatment. In addition, I have determined that no other property of the grease is deleteriously affected by the heat treatment.

My invention will be further described in connection with the attached graph of change of micropenetration vs. maximum processing temperature and the following specific example:

EXAMPLE I

An anhydrous calcium soap grease was formed by adding a mixture of a stoichiometric quantity of hydrated lime contained in one part oil to a mixture containing two parts of oil and one part of solid 12-hydroxy stearic acid at room temperature. The oil employed was a blend having a viscosity of 82 SUS at 100° F. of 80 volume percent solvent-treated Mid-Continent neutral oil and 20 volume percent of a conventionally refined naphthenic base petroleum Coastal stock. The temperature was slowly raised and thickening was observed at about 130° F. Saponification was completed while gradually raising the temperature to about 190° F. During saponification free water was rejected from the mass and was observed at the surface and edge of the reaction mass in the kettle; the rejected free water changed in appearance from cloudy to clear, showing essentially complete reaction of the lime and acid. The visible non-emulsified water was removed by evaporation

by raising the temperature slowly to about 225° F. An additional five parts of the oil blend (based on the weight of fatty acid employed) was incorporated while raising the temperature to 240° F. Dehydration, which had begun during the addition of five parts of oil and which was accompanied by gradual smooth gel formation, was completed by raising the temperature to about 250° to about 255° F. and holding the temperature for about one hour. The grease was then permitted to cool while finishing oil and a conventional oxidation inhibitor (diphenylamine) were added. The grease was then milled in a conventional colloid mill. The homogeneous grease, which had a dropping point of 296° F., was then heated at a temperature of 282° F. for one hour.

While the greases prepared in accordance with the foregoing example can be subjected to our heat treatment as such, it is preferred, for economic reasons, to treat the dehydrated grease at the elevated temperature prior to the incorporation of finishing oil or additives.

For example, upon dehydrating the grease of Example I at a temperature of about 255° F., I prefer to raise the temperature to about 280° F. and maintain this temperature for about one hour after which the heat source is cut off and the grease is permitted to cool while adding finishing oil and such additives as desired. Upon addition of finishing oil the grease is usually homogenized by processing through a colloid mill before packaging as indicated in Example I.

Three greases were prepared and were then subjected to various heat treatments for the same length of time in order to demonstrate the improvement in grease structure and properties resulting from the present invention. The dehydration period and temperature, and the stabilization temperature and length of treatment in addition to the grease compositions and the data obtained relating to the ASTM penetrations, mechanical stability, work stability, water stability, and stability of low temperature viscosity are tabulated below.

Table I

	Grease A		Grease B		Grease C	
Dehydration Period:						
Temp., ° F.	255	255	260	260	260	260
Time, Hours.	1	1	1	1	1	1
Post-dehydration, Heat Treatment Period:						
Temp., ° F.	255	282	260	284	260	284
Time, Hours.	1	1	1	1	1	1
Grease Comp., Wt. Percent:						
Calcium 12-Hydroxy Stearate	8.00	8.00	8.00	8.00	6.80	6.50
Mineral Oil	91.40	91.41	90.90	90.92	92.10	92.42
Moisture	0.00	0.00	0.00	0.00	0.00	0.00
Free Alkali as CaO	0.10	0.09	0.10	0.08	0.10	0.08
Diphenylamine	0.50	0.50				
Phenyl alpha naphthylamine			1.00	1.00	1.00	1.00
Mineral Oil—Solvent refined Mid-Continent Neutral Oil:						
Vis. at 100° F., SUS	81.5		439.5			
Vis. at 210° F., SUS	37.6		59.2			
Viscosity Index	89		92			
ASTM Penetrations:						
Unworked	300	284	277	270	321	306
Worked 60 strokes	293	287	278	260	318	294
Worked 100,000 strokes	330	317	319	281	347	312
ASTM Dropping Pt., ° F.	301	301	298	300	298	301
Wheel Bearing Test:						
60 m.p.h., 250° F.	Glazed	No chg.	Glazed	No chg.	Glazed	No chg.
Leakage, Grams	6.6	4.0	3.4	1.7	12.0	5.4
Micropenetration before	131	112	116	107	156	137
Micropenetration after	40	64	30	61	35	76
Micropenetration repack	79	101	66	89	69	109
MIL-G-10924 Spec. Tests:						
Work stability	+52	+33				
Water Stability	+60	+31				
Head Bleed, Percent Sep. Oil	2.9	2.5				
ANG-10 Bleed, Percent Sep. Oil			2.52	2.04	5.40	5.90
	(-65° F.)		(0° F.)			
Apparent Viscosity:						
Poises at 25, 1/secs. Shear R.	11,800	10,600	2,450	2,400	1,700	1,700
Poises at 100, 1/secs. Shear R.	5,150	5,000	1,200	1,050	940	830
Poises at 500, 1/secs. Shear R.	2,150	1,900	570	500	500	400

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As may be seen from the data appearing in Table I, greases which were subjected to a stabilization period at a temperature insufficiently removed from the dehydration temperature evidenced a change of structure upon being used for high temperature service. Thus referring to the data under wheel bearing tests, microscopic study of the grease structure showed that in each case where a low temperature heat stabilization period was employed the structure of the grease appeared to be glazed, whereas the same grease which had been subjected to a stabilization period in accordance with my invention showed no change in its structure. Penetrations obtained on the greases in Table I before and after the 250° F. 60 m.p.h. wheel bearing test show severe hardening in the case of the non-heat treated greases compared to minor change in consistency of the heat treated grease. These data are shown graphically in the attached graph. Similarly, it can be seen from the data relating to military specification tests and the apparent viscosity tests that in all cases of greases subjected to my heat treatment they either retained their characteristics or were improved.

I claim:

1. In the preparation of an anhydrous calcium soap grease wherein the soap is formed from hydroxy fatty components and the grease dehydrated at a temperature not exceeding about 260° F. to a water content at least as low as 0.3 weight percent, the step of heating the dehydrated grease at a temperature which is higher than

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the dehydration temperature and is about 5° to 20° F. below the dropping point of the grease for a period of about 15 minutes to 3 hours and sufficient to stabilize the essential structure of the grease.

2. The preparation of claim 1 wherein the soap is calcium 12-hydroxy stearate.

3. In the preparation of an anhydrous calcium soap grease wherein the soap is formed from hydroxy fatty components and the grease is dehydrated at a temperature not exceeding 260° F. to a water content at least as low as 0.3 weight percent, the step of heating the dehydrated grease at a temperature of about 280° to 285° F. for about one hour.

4. In the preparation of an anhydrous calcium 12-hydroxy stearate grease wherein the grease is dehydrated at a temperature not exceeding about 260° F. to a water content at least as low as 0.3 weight percent, the step of heating the dehydrated grease at a temperature of about 280° to 285° F. for about one hour.

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