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BARIUM GREASE

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This invention relates to the preparation of lubricating greases.

The principal object is to produce greases suitable for such commercial uses as the lubrication of automobile wheel bearings and the like, where it is desirable to employ greases that possess relatively high melting points and also the ability to resist emulsification with water.

In the past, greases from sodium soaps have been employed where high melting points were desired, and calcium soap greases were employed where it was important that the grease have water-resistant characteristics. However the calcium soap grease was unsatisfactory if high melting point was required and the sodium soap grease was unsatisfactory where there was danger of emulsification with water. This is particularly true in wheel bearing lubrication for automobiles where water may gain access to the bearings. So far as we have been able to learn, no commercial calcium soap grease has been used heretofore which exhibits a high melting point unless the melting point was artificially obtained by the inclusion of a comparatively high proportion of inert filler and no sodium soap grease has been used, which definitely resisted emulsification with water. Hence, no commercial grease has been used heretofore which had the characteristics of both sodium and calcium greases.

In our work we have discovered that barium soap greases possess both of the desired characteristics; i. e. high melting point and high resistance to emulsification when in contact with water, being substantially non-emulsifiable. These greases, in common with other greases, are prepared by saponifying a suitable fat or mixture of fat and fatty acids with the selected alkali (barium hydroxide in this case) and reducing the resultant soap with a suitable mineral lubricating oil to obtain the desired consistency in the grease. The most satisfactory of these greases have been prepared from basic barium soap, with or without a quantity of normal barium soap. Where normal soap has been included useful proportions thereof have varied from a very small percentage such as 2% or 3% to 30% or 40% of the total soap content. For example a high grade grease having a melting point of about 400° F. has been prepared where only about 3% of the soap was normal soap. However where the normal soap is allowed to run substantially in excess of about the 30% or 40% limit the resultant grease becomes less desirable for the reason that a softer

consistency is developed for comparative soap content and a definite lowering of melting point is encountered. Where a soap combining basic and normal soaps is to be used, it may be obtained either by mixing a basic soap and a normal soap, or by preparing the soap in such manner that the desired proportions of basic and normal soap are obtained as a result of the method of preparation; for example by employing an excess of the alkali barium hydroxide and subsequently adding suitable amounts of fatty acids or fats; or by the saponification of the fats in one operation with just the proper amount of the barium hydroxide to yield the desired mixture of basic and normal soaps. In compounding the grease, the total soap content may be made to vary according to the consistency and/or melting point desired, and in practice the limits probably will be about 10% of soap on the low side and around 40% on the high side, this variation being much the same as in connection with the manufacture of other greases. However it will be found in any case that for a grease of a given soap content the melting point will be much higher than that for a calcium soap grease of like soap content. As in the case of other greases the greater soap content results in a higher melting point. It has also been found that greases made entirely from basic soap are desirable and have melting points which are satisfactorily high. It has also been found that greases can be made from barium soaps consisting largely or entirely of normal barium soap. Such greases, however, possess a softer consistency and a lower melting point than greases consisting of comparative amounts of basic soap or the preferred mixtures of basic and normal soaps. But these normal soap greases do have a melting point distinctly higher than typical calcium soap greases of similar soap content. Moreover they are characterized by a transparent appearance and a melting point closer resembling typical aluminum soap greases of similar soap content. Also they possess the feature of being substantially non-emulsifiable with water and are therefore useful for some purposes.

The present application is concerned chiefly with greases made from basic barium soap or mixtures of basic and normal barium soaps. An important feature of these greases is that the water content is not so critical as in the case of calcium and sodium soap greases. Thus, in the case of sodium soap greases when they come in contact with water in material quantities the greases may

emulsify and, hence, lose much of their lubricating efficacy. Sodium soap greases under certain conditions of storage or exposure may absorb a small amount of water which is just sufficient to hydrate the soap and cause the hydrated soap to settle out from solution in the mineral oil. In the case of calcium soap greases a certain amount of water is necessary to cause the soap to remain in solution in the oil. If this water is removed there is a tendency of the dehydrated soap to settle out of solution from the mineral oil. However, with the barium soap greases such water as will affect the sodium and calcium soap greases has no corresponding effect and no soap separation results. The water content of these barium greases may run as high as ordinarily required for calcium soap greases (i. e., 1 to 3%), or these greases may be heated to remove most or all of the water as in the case of sodium soap greases. The chief effect which water has upon the barium soap greases is upon the melting point, for increase in water content within certain limits tends to lower the Ubbelohde melting point. For this reason when greases of high melting point are desired it is preferable to maintain the water content under 0.5% for example 0.1% or 0.2%, or to eliminate the water entirely.

As to glycerine content this may be varied much as in other greases according as it is desired to vary the appearance and transparency. The glycerine content may be controlled as usual by substituting fatty acids for portions of the fats.

In the light of the above the invention may be broadly stated as residing in barium greases having comparatively high melting point characteristics similar to those afforded by sodium soap greases and being substantially non-emulsifiable with water after the fashion of calcium soap greases. The invention resides further in such greases which have been prepared from soaps containing both basic barium soap and normal barium soap, the normal soap being in the smaller proportion. Also the invention includes a barium soap grease prepared from a basic barium soap. The invention also includes such barium soap greases wherein the water content is maintained sufficiently small to insure comparatively high melting points. The invention also includes such barium soap greases wherein the water and glycerine contents are varied to produce greases of different melting points and appearance. The invention also includes barium soap greases made largely or entirely from normal barium soap, such greases being non-emulsifiable in water.

By the term "greases" we mean those prepared from soaps and mineral oils of the nature of lubricating oils. Thus the composition of this invention is a petroleum grease prepared with barium soap. In common with sodium and calcium soap greases, the amount of soap should be limited because if too much soap is used the grease-like characteristics will be lost. It is preferable therefore to use minor quantities of soap and major quantities of oil, these terms being used merely to imply that the quantity of soap is limited in such manner that the grease-like character is not destroyed.

In carrying out the invention a suitable basic barium soap is first prepared with or without a content of normal barium soap. The specific proportions may be varied to produce different greases as will be more completely described hereinafter. When normal soap is to be included with the basic soap its percentage may range

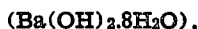
anywhere from about 1% up to about 30% or 40% of the total soap. Excellent greases have been made from basic barium soap containing respectively about 3%, 10%, and 20% of normal soap, the fatty agents from which the soaps were prepared being varied more or less to yield the various soaps. Such a combined soap may be obtained by mixing previously prepared basic and normal soaps. Again such a combined soap may be prepared in one mass by controlling the method of saponification of the fatty agent so that a normal barium soap will be formed along with the basic barium soap. In fact this method of preparing the combined soap is the preferred method. Thus one procedure may consist in saponifying an appropriate fat mixture in the presence of sufficient alkali ($\text{Ba}(\text{OH})_2$) to produce first basic soap of the type $\text{BaO} \cdot \text{Ba}(\text{OH})\text{R}$. There is added subsequently, at an appropriate stage during the operation of incorporating mineral oil, a fat or fatty acid, either in just sufficient amount to form soap all of the type $\text{Ba}(\text{OH})\text{R}$, or in greater amount to yield a soap which is a mixture of $\text{Ba}(\text{OH})\text{R}$ and BaR_2 , the latter being increased by increasing the fat or fatty acid added. (The reaction of course can be made to proceed to the point where all of the soap would be of the type BaR_2 , but this type has been found not to be so desirable.) Also, the fat mixture may be saponified with just enough $\text{Ba}(\text{OH})_2$ to yield a basic soap of the type $\text{Ba}(\text{OH})\text{R}$, after which the soap may be compounded with oil; or the soap may be converted, if desired, to a mixture of basic and normal soaps by the addition of fat or fatty acids before the compounding operation with mineral oil is completed. Also, the fat mixture may be saponified with just enough $\text{Ba}(\text{OH})_2$ to yield a soap containing basic and normal soap in the desired proportions.

A suitable method of preparation comprises treating an appropriate fat or fatty mixture, such as a p. m. e. tallow, with a solution of barium hydroxide either at atmospheric or at elevated pressures, the barium hydroxide being used in sufficient quantity or in excess of the quantity required to saponify the stocks and form a basic soap. (For details see hereinafter.) The batch is heated in a steam kettle or the like at temperatures ranging as high as about 230° F. for a time sufficient to complete the saponification. After the saponification is completed an appropriate amount of mineral oil is added to reduce the soap content of the mass to about 35% to 40%, at which time the grease is in a workable condition, and, hence, readily permits the incorporation of the proper amount of fat or fatty acids for the purpose of adjusting the composition of the soaps to yield a soap which is a mixture of basic and normal soaps. During this saponification stage the basic barium soaps will be formed, and during the subsequent addition of the fats or fatty acids a proportion of normal barium soap will be formed.

It has been found preferable to include with the saponification charge a sufficient proportion of a suitable mineral oil to maintain the resultant soap in a plastic, workable condition. The mineral oil should have adequate solvent properties for the barium soaps. An example of such an oil is an asphaltic base or naphthenic base lubricating oil such as the commonly known Western oils. For the purpose of the examples here given a Western asphalt base lubricating oil having a Saybolt universal viscosity of 200 at 100° F. and a color of 3 N. P. A. was used. Also

other oils of proper solvent properties may be used.

In the above example, a mixture by weight of 100 parts of tallow, 14 parts of cottonseed oil and 20 parts of asphaltic base lubricating oil was saponified with 140 parts of barium hydroxide.



After the saponification operation and the addition of 300 parts more of the mineral oil, 25 parts of tallow fatty acids were incorporated to yield approximately 205 parts of soap consisting of a mixture of approximately 164 parts of basic soap of the type $\text{Ba}(\text{OH})\text{R}$ and 41 parts of normal soap of the type BaR_2 . After obtaining the desired mixture of soaps, 470 parts of asphaltic base lubricating oil were added to bring the grease to the desired consistency. During the addition of this lubricating oil, the mixture of mineral oil, water, glycerine, basic and normal barium soap was gradually raised in temperature and finally heated to a temperature around 300°F . to 320°F . As the temperature limit given was approached the grease in the kettle changed markedly in appearance, and a heavy, somewhat doughy mixture resulted which formed in large lumps or balls as a contrast to the considerably softer mixture from which it resulted. For convenience this stage is called the first gelation stage. Further heating around these temperature limits caused the grease to undergo a second change which will be referred to as the second gelation stage, and in this stage the grease was found to be much heavier than in the first stage and considerably more granular. There is a third gelation stage which will occur if the heating is continued, and in this third stage the heavy granular mass of the second stage will become a smooth, viscous, transparent liquid of a reddish and much darker color. The appearance and texture of the grease must be noted closely in order that the proper body is developed in the grease without the products being allowed to darken excessively in color. It is preferred, for these reasons, to heat the grease only until the beginning of the third gelation stage is reached.

The grease, having just reached the third gelation stage, was further treated in each of three ways for the production of greases of different textures and appearance. To produce a smooth, clear dark-colored grease, the batch was cooled, preferably with cold circulating water in the kettle jacket, until the temperature was reduced to 260°F . to 270°F . and a small quantity of water (0.2% to 3.0%) added in order to disintegrate the gel and hydrate the grease. Treatment with steam could also be utilized instead of the addition of water to hydrate the grease. The grease was then maintained at a temperature of 270°F . to 280°F . to develop the proper body, and then drawn into pans and cooled. The product was subsequently worked or milled or treated in a homogenizing device to bring it to a smooth non-fibrous commercial consistency. Such a grease had a soap content of around 20% and a Ubbelohde melting point above 300°F . The Ubbelohde melting point may be defined as the temperature at which the material drops from the orifice of a receptacle surrounding the bulb of a thermometer and containing the material examined. A description of the method is given in various references on oils, fats and waxes, such as Holde's "Examination of hydrocarbon oils and of saponifiable fats and waxes."

For the production of a second type of grease, a

smooth, opaque and somewhat lighter colored product, the batch was cooled as before but to a temperature of about 210°F . and a small quantity of water (0.2% to 3.0%) added, as before. The grease was then heated to 270°F . to 280°F . to develop the proper body, drawn into pans and cooled. This product was subsequently worked or homogenized to bring it to a smooth non-fibrous commercial consistency. Such a grease had a soap content of around 20% and a Ubbelohde melting point above 300°F .

For a third type of grease of somewhat fibrous character, the grease mixture at the beginning of the third gelation stage was cooled to a temperature of about 210°F . and a small amount of water around 1% was added. The grease was then cooled to 170°F . before reheating was started. The reheating operation was then carried slowly up to 270°F . as in the case of the other grease. The product was drawn, cooled and worked as in the case of the other types of grease thus yielding a somewhat fibrous grease such as is frequently used for lubrication of ball-bearings and the like.

In preparing the above greases the water content was maintained around 0.5% or 0.3% in order to obtain the glossy texture and improved melting point which such a small amount of water affords. This water content, as previously pointed out may vary considerably since it is not critical as in the cases of sodium and calcium soap grease, it being desired only to keep the water content low enough to insure suitably high melting points and pleasing appearance. For this purpose the water content is varied below 0.5% according to the melting point required in the product. Thus 0.3% water yields a melting point over 300 in one grease containing 20% to 30% of soap, and a trace of water in another grease yields melting points as high as 400°F . Thus, these greases possess the desired high melting point characteristic which is usually above 300°F . and also possess the desired quality of being highly resistant to emulsification with water.

Considering the preparation of stable greases from the standpoint of their melting point the following are given as examples of greases prepared according to the procedures outlined above. A mixture of 2000 parts of prime tallow and 285 parts of cottonseed oil was saponified in the presence of 785 parts of the above described Western lubricating oil, with about 2800 parts of barium hydroxide. The excess barium hydroxide was then neutralized with approximately 450 parts of tallow fatty acids. Thereafter the resultant soap was reduced to appropriate consistency with additional quantities of the mineral lubricating oil. The grease of this example contained about 24% of basic barium soap and about 6% of normal barium soap or a total soap of about 30%, 0.3% of free fatty acid and a trace of water. The Ubbelohde melting point of this grease was 355°F .

In another instance about 800 parts of prime tallow together with 1500 parts of tallow fatty acids were saponified in the presence of 400 parts of lubricating oil with 3400 parts of barium hydroxide. After saponification and partial reduction with mineral oil, the excess barium hydroxide was neutralized with 500 parts of tallow fatty acids. The finished grease contained about 28% of basic barium soap and about 1% of normal barium soap (total soap about 29%) and only a trace of water. The normal soap was thus

about 3% of the total soap. The resultant grease had a Ubbelohde melting point of 405° F.

Again, a 100% basic barium soap was prepared from tallow in the presence of mineral oil with an excess of barium hydroxide and without the use of cottonseed oil, and then neutralized with fatty acids. A grease produced with 20% of this soap had a Ubbelohde melting point of about 345° F.

It is to be observed that in reducing soaps with lubricating oil after the soap mixture has been properly prepared, the total soap content with respect to the added oil should be sufficiently high to maintain a satisfactory melting point and at the same time should not exceed certain limits, much as in the case of other greases. Thus the soap ranges for average practice will run between approximately 12% and 35% of soap. For purposes of comparison it will be noted, as previously stated, that a barium soap grease containing a given percentage of soap will possess a higher melting point than a corresponding calcium soap grease, and it will be also noted that a barium soap grease containing about 20% of soap according to the method herein disclosed will have an average melting point higher than 300° F. so long as the water content is kept within the reasonable limits defined, whereas the corresponding calcium soap grease of similar soap content will have a melting point of about 200° F. or lower. Thus while calcium soap greases resist emulsification and miscibility with water, their low melting point renders them undesirable as compared with barium soap greases produced according to the present invention. While these barium soap greases will not in all cases have melting points as high or higher than corresponding sodium soap greases, yet such melting points nevertheless are amply high for all practical purposes, and are much higher than other non-emulsifying greases.

Since all of the limitations herein set out with respect to quantities, percentages and the like are broad and allow much latitude, these barium soap greases lend themselves readily to commercial production. Thus only ordinary practice is required as to glycerine content, and this is very easy to control. A reasonably large glycerine content is by no means prohibited and again desirable greases may be produced with relatively large proportions of fatty acids. Excess amounts of barium hydroxide may be readily employed and these thereafter neutralized with the fatty acids. In fact this step including the neutralization stage is one of the most desirable procedures for forming the desired basic and normal soaps since it results in suitable soap formation in a single operation and avoids the necessity of preparing separate batches of the two soaps. However, soaps containing the desired proportion of basic and normal barium soap can be prepared by saponification of the fats or fatty acid mixtures with the calculated amount of barium hydroxide in one saponification operation, as previously described. The proportions of the two soaps are not exacting and the respective percentages of basic and normal soaps may vary within considerable limits and without materially affecting melting points. Again water contents are not critical since neither too much nor too little water will cause the soap to drop out of the grease. Only the melting point and appearance will be affected, and the melting point may be readily controlled. Nor will contact of the barium grease with water

during use materially affect the grease due to its non-emulsifying characteristics.

Thus, much latitude in manufacture is permissible, the percentages of soap and glycerine in the grease being entirely within the range of usual grease practice, and the restrictions as to water being much less severe than is the case with other greases. While such limitations as are required are important, they are nevertheless wide and may be followed with great ease in commercial operations.

It is to be understood that the disclosures hereof are to be taken only as illustrative of the invention set forth and not as limiting. It is obvious that many variations within the scope of the appended claims will be apparent to those skilled in the art.

We claim:

1. A method for manufacturing barium grease comprising treating a saponifiable fatty material with an excess of barium hydroxide sufficient to produce a preponderant proportion of basic barium soap and at an elevated temperature for a time sufficient to effect saponification, adding mineral oil having good solvent properties for barium soap, adding a fatty acid to neutralize the excess barium hydroxide, heating to a temperature to effect formation of basic barium soap, cooling the grease to a temperature suited to the addition of moisture, hydrating the grease, raising the temperature to effect desired body in the grease, and cooling the product, the proportions of soap and oil being such that the grease contains a major quantity of mineral lubricating oil and a minor quantity of the soap.
2. A method according to claim 1, wherein the temperature during soap formation is elevated above about 300° F., the cooling prior to hydration approximates 200° F. and the heating after hydration is in the vicinity of 270° F.
3. A method for the manufacture of a barium soap grease composed of a major quantity of an asphaltic base mineral lubricating oil and a minor quantity of a basic barium soap comprising saponifying a fatty saponifiable material with barium hydroxide in proportions to yield a preponderance of basic barium soap, adding a portion of the mineral oil to be combined with the soap in the final grease heating the batch at a temperature and for a time sufficient to produce the basic barium soap, adding the rest of the asphaltic base mineral oil having adequate solvent power for barium soap, heating the mixture in excess of about 300° F., and cooling the grease.
4. A method according to claim 3 including the additional step of working the cooled grease to a uniform consistency.
5. A lubricating grease comprising a major quantity of a mineral lubricating oil and a minor quantity of a basic barium soap.
6. The grease as in claim 5 wherein the oil is an asphaltic base oil.
7. The grease as in claim 5 wherein the oil is a naphthenic base oil.
8. A lubricating grease comprising a major quantity of a mineral lubricating oil and a minor quantity of barium soaps, the preponderant proportion thereof being basic barium soap.
9. The grease as in claim 8 wherein the oil is an asphaltic base oil.
10. The grease as in claim 8 wherein the oil is a naphthenic base oil.
11. The grease as in claim 5 wherein the melting point thereof is above 250° F.
12. The grease as in claim 5 wherein the oil

is an asphaltic base oil and the melting point of the grease is above 250° F.

13. The grease as in claim 8 wherein the melting point thereof is above 250° F.

5 14. The grease as in claim 8 wherein the oil is an asphaltic base oil and the melting point of the grease is above 250° F.

10 15. A lubricating grease comprising a minor proportion of a mixture of basic and normal barium soaps incorporated in a mineral lubricat-

ing oil having solvent power for said soaps, the basic barium soap constituting a preponderant proportion of the total soap, the oil being present in major proportions to impart lubricating characteristics to the grease.

16. A grease according to claim 15 wherein the lubricating oil is a naphthenic base mineral oil. 5

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