Patented Jan. 30, 1940 2,188,864

UNITED STATES PATENT OFFICE

2,188,864

GREASE AND METHOD OF MAKING THE SAME

Samuel Edward Jolly, Prospect Park, Pa., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

No Drawing. Application August 13, 1938, Serial No. 224,727

5 Claims. (Cl. 87—9)

This invention relates to grease and method of making the same, and has particular reference to a grease of the type known as block grease, which may be defined as a grease having an A. S. T. M. penetration of not more than 90 at 77° F.

Solid, substantially anhydrous, high melting point greases are used for the lubrication of open type bearings which run at elevated temperatures due to radiated or conducted heat in addition to the heat developed by friction between the metal surfaces. These conditions exist, for example, on the dryer rolls of paper machines, driving journals on locomotives, hot necks on rolling mills, and the like. In most cases, the lubrication is applied in the form of a cake or block held in contact with the rotating shaft by means of a spring.

A satisfactory lubricant for use under these conditions should have certain definite characteristics. It should have a melting point in excess of the maximum operating temperature of the bearing and should not soften appreciably at temperatures much below its melting point. This prevents excessive consumption of the lubricant. In spite of the high melting point, however, the lubricant should maintain an oily surface of contact in the bearing at ordinary temperatures. This prevents a high starting torque and provides lubrication over the entire range of operation. The lubricant should also be stable. That is, it should show no tendency towards separation of the soap from the oil. Sweating or separation of the oil leaves a hard soap residue with little or no lubricating properties which may result in seized or scored bearings. The lubricant should be hard enough to form a cake or block which will not be broken in storage, handling or use, and it should not be brittle or crumbly.

The high temperatures under which lubricants of this type are used, usually in excess of 350° F., preclude the use of calcium soaps in their manufacture. Sodium soaps are nearly always used since they have the desired high melting point and are stable at the high temperatures encountered. Sodium base greases show a smaller change in consistency with increase in temperature up to the melting point than do other types of greases. Under certain conditions, mixtures of calcium and sodium soaps may be used in the greases.

The usual greases heretofore used for this type of lubricant contain 25% to 50% of the sodium soap of tallow, stearic acid, hydrogenated fatty acids or the sodium soaps of a mixture of these components incorporated in a suitable mineral oil. Various types of mineral oils may be used in these greases, but oils having high flash and fire points are preferable. These greases are manufactured in an anhydrous or substantially anhydrous condition, as the usual operating temperatures are above the boiling point of water. Free alkali content may range from 0.1 to 1.0%, though the normal range is from 0.1 to 0.5%. When the sodium soaps of these materials are incorporated in oil, a fibrous, spongy product is obtained the character of which may be somewhat altered by the conditions of manufacture.

In accordance with the present invention, it is found that an improved lubricant of this general type can be made by employing a mixture of stearic acid, tallow or hydrogenated fatty acids together with the water-insoluble products obtained by the oxidation of aliphatic hydrocarbons. These water-insoluble oxidation products contain acids, esters, intermediate oxidation products and unoxidized hydrocarbons, and may be used as produced, but it is preferred to use a purified product from which the unsaponifiable material has been separated. It is also found that the material obtained by an alcoholysis treatment and having substantially the same saponification and acid values, gives valuable products. The oxidation products of slack wax or the purified saponifiable material obtained from the oxidation products of slack wax may be successfully employed.

The employment of these oxidation products in combination with certain vegetable or animal fats or fatty acids, or hydrogenated fatty acids, for the manufacture of grease, yields a product having desirable properties not possessed by a grease made from either of the materials alone. The presence of the soaps of the oxidation products produces a lubricant of increased stability against sweating or leaking of oil. The grease has a shorter fiber and is harder (i. e., has a lower penetration) than a grease made from the sodium soap of tallow, stearic acid, hydrogenated fatty acids or mixtures of these components. Greases made from the mixture of oxidation products and vegetable or animal fats or fatty acids have a desirable oiliness at ordinary temperatures not possessed by a grease made without the presence of oxidation products. The additional hardness results in economy of operation, since the consumption of the lubricant is materially lessened. These greases or films of the greases adhere very well to metallic surfaces.

The improved greases need not have solely a sodium base, but for certain purposes, may have a mixed base, for example, sodium and calcium.

The preferred method of preparation of these greases is to effect the saponification in the absence of oil by heating the saponifiable mixture with aqueous sodium hydroxide under pressure to a temperature of about 175° C. for approxi-

mately three hours. The oil-free soap is then dehydrated by heating it to a temperature of about 225° C. Approximately one-fourth of the required amount of oil is then added to the soap and agitation effected until a homogeneous product is obtained. The remainder of the oil is finally added and the product heated to a temperature in excess of 260° C. Agitation is continued during cooling until the grease begins to thicken. It is then transferred to forms and allowed to solidify.

The above general method of preparation is merely cited by way of example, since the saponification may be carried out in the presence of all or part of the oil which is to be ultimately incorporated in the grease. To eliminate difficulties due to foaming, it is preferable to carry out the saponification in the absence of oil and to add the oil to the nearly anhydrous soap. Dehydration at some stage of the process is desirable inasmuch as the grease is to be subjected to elevated temperatures in use and the presence of any substantial amount of water may cause breakdown by reason of the liberation of steam. To this end, the grease should be heated to a temperature in excess of about 250° C. The saponification may be carried out at atmospheric or superatmospheric pressure.

The oils used may vary quite considerably, and in general it may be said that the oils used may be of the numerous types employed in the formation of block greases involving solely the sodium soaps of fatty acids. For example, it has been found that an oil having a viscosity of 155 seconds Saybolt at 210° F., and a fire point of 595° F. is quite satisfactory. The viscosity is not particularly material, since the nature of the grease is more dependent upon the soap used than the oil used. In general, however, the oil should have a flash point in excess of about 400° F. Oils having this property will be found quite satisfactory.

As an example of a grease made in accordance with the invention, a mixture of 950 grams of stearic acid and 950 grams of the water-insoluble saponifiable material obtained from the oxidation products of paraffin wax was charged into an autociave. The saponifiable material obtained by oxidation had a saponification value of 133 and an acid value of 69.2. The mixture was saponified by heating with 290 grams of sodium hydroxide dissolved in 500 grams of water at a temperature of 175–180° C. for three hours. The soap was dehydrated by prolonged heating and ultimately its temperature was raised at 220° C. 3060 grams of mineral oil were then added and the resulting mixture heated to 265° C. and then poured into a mold and allowed to solidify. The product obtained, containing 40% of soap, based on the final grease, of which 20% was the soap of stearic acid and 20% the soap of the water-insoluble oxidation materials, had the following characteristics:

Free alkali	0.48 percent (NaOH)
Water	Trace
Melting point	410° F. (drop method)
A. S. T. M. penetration, at 77° F.	24

As a further example, another grease was made under the same conditions as the grease of the preceding example, but containing a total of 33% of soap based on the final grease, 16.5% being the sodium soap of stearic acid and 16.5% being the sodium soap of paraffin acids which had been treated by alcoholysis to produce a product having substantially the same saponification and acid values (saponification value 149.5, acid value 145.7). This grease had the following characteristics:

Free alkali	0.37 percent (NaOH)
Water	Trace
Melting point	403° F. (drop method)
A. S. T. M. penetration, at 77° F.	25

As still another example, there may be cited the preparation of a grease from a mixture of 950 grams of tallow and 950 grams of the water-insoluble saponifiable material obtained from the oxidation products of paraffin wax. This mixture was saponified with 290 grams of sodium hydroxide dissolved in 500 grams of water at a temperature of 170–175° C. for three and one-half hours. The saponifiable material from the oxidation products of paraffin wax had a saponification value of 133. The oil-free soap was dehydrated and heated to a temperature of 225° C. 3060 grams of mineral oil having a flash point of 510° F. was added and the product heated to 275° C. and then cooled in molds. This grease contained 40% of soap: 20% being the sodium soap made from the tallow and 20% the sodium soap of the acids obtained by the oxidation of paraffin wax. The grease had the following characteristics:

Free alkali	0.6 percent (NaOH)
Water	Trace
Melting point	460° F. (drop method)
A. S. T. M. penetration, at 77° F.	28

As an example of a block grease prepared from the oxidation products of slack wax, there may be cited a grease made under conditions similar to those outlined above and containing a total of 40% of sodium soaps, 20% being the sodium soap of stearic acid and 20% the sodium soaps of the water-insoluble acids obtained by the oxidation of slack wax. This grease was found to have the following characteristics:

Free alkali	0.65 percent (NaOH)
Water	Trace
Melting point	419° F. (drop method)
A. S. T. M. penetration, at 77° F.	24

Another grease made under similar conditions and containing a total of 40% of soaps, 20% of the soap being a sodium soap made from tallow and the remaining 20% the sodium soaps of the water-insoluble acids obtained by the oxidation of slack wax, had the following characteristics:

Free alkali	0.59 percent (NaOH)
Water	Trace
Melting point	430° F.
A. S. T. M. penetration, at 77° F.	26

The greases of both of the above examples were prepared from water-insoluble oxidation products of slack wax having a saponification value of 130, the unsaponifiable material having been removed by saponification of the original oxidation products followed by the acidic precipitation of the acids.

As an example of a mixed base grease there may be cited a grease containing a total of 40% of soaps, 30% being the sodium soap of stearic acid and 10% the calcium soap of the acids ob-

tained from the above-mentioned water-insoluble oxidation products of slack wax. This grease had the following characteristics:

Free alkali	0.66 percent (NaOH)
Water	Trace
Melting point	394° F.
A. S. T. M. penetration, at 77° F.	23

This grease shows a considerable lowering in the melting point due to the presence of the calcium soaps. However, it has a very low solubility in water, and consequently is of a type useable in certain cases where there might be a small amount of water in contact with the grease during its use. Such a condition exists, for example, very often in the case of the lubrication of beaters in paper mills where water leaks through the packing along the shaft which is being lubricated. At ordinary temperatures in such case, the penetration is quite low and the lowered melting point is not a disadvantage. In the case of wax base greases in accordance with the invention, the sodium soap should be not less than about 60% of the total soap content if the other soap is a calcium soap. For example, it has been found that if the total soap content is 55% of the grease the maximum amount of calcium soap should be around 20% of the final grease. On the other hand, with a total soap content of about 30% the maximum content of calcium soap should be about 5%. As the total soap content is lowered it is necessary that the proportion of calcium to sodium soap should be kept decreasingly low to avoid an undue softening.

It has been found that greases provided in accordance with the present invention, whether containing a single base of a mixture of bases, should conform to the following requirements: They should have an A. S. T. M. penetration at 77° F. of not more than 90 and preferably not more than about 30. They should have a total soap content of not less than 25% and not more than 55% of the weight of the finished grease. The soaps of fatty acids should be present in amounts not less than 15% and not more than 45% of the finished grease. The soaps of water-insoluble oxidation products of aliphatic petroleum hydrocarbons should form not less than 10% and not more than 40% of the finished grease. Within the limitations mentioned above the greases, so long as the content of sodium soap of either of the groups of acids is not less than about 60% of the total soap content, will have an A. S. T. M. penetration well within the limits of a satisfactory block grease. The greases, furthermore, have a desirable oiliness, and though hard, impart their oil to a shaft and its bearing for proper lubrication. They have a substantially increased stability against sweating or leaking of oil as contrasted with block greases made solely from the soaps of vegetable fatty acids. They have a shorter fiber and are harder than such greases. Their oiliness is quite sufficient at ordinary temperatures to provide proper lubrication when the parts are cold.

Substantially complete dehydration of the greases is essential as these greases are generally used where the temperature of operation exceeds the boiling point of water. If water is expelled from the grease the possibility of foaming and loss of lubrication is very great, especially when a heavy oil is used in the preparation of the grease. The maximum allowable content of water is not over 0.1%, and even less water is highly desirable. As pointed out above, the waterproof qualities of the grease may be substantially improved by using calcium soaps for form part of the soap mixture.

The limitations indicated above differentiate the satisfactory greases sharply from greases having compositions falling outside the given ranges. If less than 10% of the soaps of the oxidation products are used, the greases do not differ materially from greases made solely from the sodium soaps of stearic acid or tallow alone, i. e., they have the disadvantages of such greases heretofore described. On the other hand, if the finished grease contains more than about 40% of the sodium soaps of the oxidation products in combination with the sodium soaps of tallow or stearic acid, the resulting grease is unsatisfactory, being dense and hard and quite brittle and containing too little oil. Such a grease, furthermore, has a tendency to form a dry glazed surface in contact with a rotating shaft, resulting in poor lubrication. The same is true in general if the tallow soap content exceeds about 55%. The same is also true if the content of soaps of vegetable fatty acids is reduced below about 15%. If the total soap content falls below about 25% the grease becomes too soft and is unsuitable for use as a block grease.

Reference has been made above to the use of the water-insoluble products obtained by the oxidation of aliphatic hydrocarbons as the saponifiable materials used for the production of soaps used in the improved greases. It is found that the greases are relatively unsatisfactory if water-soluble materials are in the oxidized mixture used. The low molecular weight acids which are soluble in hot water produce soaps upon reaction with the alkali which are insoluble in, and incapable of homogeneous mixture with, mineral oils, when in an anhydrous condition. Accordingly, the products of oxidation are washed with hot water to remove the soluble constituents.

The various considerations indicated above, with respect to oxidized materials, are set forth in greater detail in the application of Jolly and McKee, Serial No. 99,642, filed September 5, 1936. Preferably, the oxidation products which are saponified for use in forming the block grease conform to the requirements therein, specified for the ordinary soft greases to which specific reference is made in that application.

The oxidation products and the separations of the products may be accomplished in various fashions, preferably as described in the applications of Alleman and Jolly, Serial No. 99,643, filed September 5, 1936. The hydrocarbon used as the starting point may be of any of various types, but is preferably one of high boiling point as, for example, a heavy lubricating oil, slack wax or paraffin wax. The hydrocarbon may be oxidized by the introduction of oxygen or air in a diffused condition into the oil while the latter is at a temperature between 120° C. and 160° C. At lower temperatures, the oxidation is quite slow. On the other hand, above about 170° C. the products are dark in color, and while the oxidation is rapid at first, the rate falls off towards the end of the run and the saponification value of the product decreases, indicating that decomposition has taken place. Preferably, the oxidation is started at a temperature of 160° C. to 165° C. until the saponification value reaches about 40. Then the temperature may be cut down to 150° C. to 155° C. for the remainder of the run, the temperature control being controlled

by control of the flow of air after cutting off external heat. The time for oxidation may vary, depending upon the saponification value desired in the final product and the nature of the oxygen supplied. For example, where a turbo-mixer is used the same results may be obtained in about twenty-four hours as require almost three times that period where the air is introduced through an ordinary type of diffuser. The details of the oxidation process, however, form no part of the present invention, and need not be described in greater detail.

Another preferable type of oxidation product to use in the preparation of these block greases is the oxidation product which has substantially the same saponification and acid values. This type of product is disclosed in my application Serial No. 192,070, filed February 23, 1938. As disclosed in said application, high molecular weight esters which are chiefly responsible for a difference between the saponification and acid values of the oxidation mixtures containing them may be broken down by alcoholysis into esters of low molecular weight alcohols which are then readily saponified with the production of soaps. In the use of products of this type the breakdown may be effected before the saponification which is to be used to form the soap, i. e., after alcoholysis saponification of the mixture may be effected followed by precipitation of the acids which may be washed and then resaponified to form the soap which is to be present in the grease or, alternatively, the products of the alcoholysis treatment may be saponified (along with the vegetable-acid material) at elevated temperatures of the type indicated above, at which temperatures the low molecular weight alcohol (generally methyl acohol) will be driven off. Immediately upon the completion of such saponification the oil may be added to form the grease.

What I claim and desire to protect by Letters Patent is:

1. A substantially anhydrous block grease having an A. S. T. M. penetration of at most 90 at 77° F. comprising a lubricating oil having a flash point in excess of 400° F. and a mixture of soaps of one or more high fatty acids of vegetable or animal origin and of water-insoluble saponifiable materials produced by the partial liquid phase oxidation of aliphatic petroleum hydrocarbons, said mixture of soaps forming not less than 25% and not more than 55% of the finished grease, the fatty acid soap content being not less than 15% and not more than 45% of the finished grease, the oxidation product soap content being not less than 10% and not more than 40% of the finished grease, and at least 60% of the total soap content being sodium soap.

2. A substantially anhydrous block grease having an A. S. T. M. penetration of at most 90 at 77° F. comprising a lubricating oil having a flash point in excess of 400° F. and a mixture of soaps of one or more higher fatty acids of vegetable or animal origin and of water-insoluble saponifiable materials produced by the partial liquid phase oxidation of aliphatic petroleum hydrocarbons, said mixture of soaps forming not less than 25% and not more than 55% of the finished grease, the oxidation product soap content being not less than 20% and not more than 70% of the total soap content, and at least 60% of the total soap content being sodium soap.

3. A substantially anhydrous block grease having an A. S. T. M. penetration of at most 90 at 77° F. comprising a lubricating oil having a flash point in excess of 400° F. and a mixture of soaps of one or more higher fatty acids of vegetable or animal origin and of water-insoluble saponifiable materials produced by the partial liquid phase oxidation of slack wax, said mixture of soaps forming not less than 25% and not more than 55% of the finished grease, the fatty acid soap content being not less than 15% and not more than 45% of the finished grease, the oxidation product soap content being not less than 10% and not more than 40% of the finished grease, and at least 60% of the total soap content being sodium soap.

4. A substantially anhydrous block grease having an A. S. T. M. penetration of at most 90 at 77° F. comprising a lubricating oil having a flash point in excess of 400° F. and a mixture of soaps of one or more higher fatty acids of vegetable or animal origin of water-insoluble saponifiable materials produced by the partial liquid phase oxidation of aliphatic petroleum hydrocarbons, said soaps including both sodium and calcium soaps, said mixture of soaps forming not less than 25% and not more than 55% of the finished grease, the fatty acid soap content being not less than 15% and not more than 45% of the finished grease, the oxidation product soap content being not less than 10% and not more than 40% of the finished grease and at least 60% of the total soap content being sodium soap.

5. A substantially anhydrous block grease having an A. S. T. M. penetration of at most 90 at 77° F. comprising a lubricating oil having a flash point in excess of 400° F. and a mixture of soaps of one or more higher fatty acids of vegetable or animal origin and of water-insoluble saponifiable materials having substantially the same saponification and acid values and produced by the alcoholysis of the products obtained by the partial liquid phase oxidation of aliphatic petroleum hydrocarbons, said mixture of soaps forming not less than 25% and not more than 55% of the finished grease, the fatty acid soap content being not less than 15% and not more than 45% of the finished grease, the oxidation product soap content being not less than 10% and not more than 40% of the finished grease, and at least 60% of the total soap content being sodium soap.

SAMUEL EDWARD JOLLY.