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GREASE

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This invention relates to lubricating greases and to a process for preparing the same.

By the expression "lubricating grease" is meant a semi-solid lubricant comprising a mixture of a soap, such for instance as a calcium soap or a sodium soap made from tallow, and a lubricating oil, such for instance as a mineral oil of medium viscosity, which mixture may or may not be an emulsion. According to their constitutions and uses, they are known variously as "cup greases", "driving journal compounds", "fiber greases", "gear greases", "axle greases", and by many other names.

Typical of such lubricating greases, and of the methods commonly employed in their manufacture, is the following:

To about 90 pounds of stearic acid (single pressed), or to an equivalent amount of good stearine or tallow, in a steam-jacketed kettle provided with a stirrer, is added nearly a like quantity, say 100 pounds, of steam-refined cylinder stock, and the resulting mixture is agitated until a homogeneous mixture results. To this homogeneous mixture there is then added sufficient caustic soda solution (say, 50% solution) to saponify all the saponifiable constituents thereof, and the mixture is then heated, with constant stirring, until not more than about 1% of water remains in the mass. The progress of the reaction is indicated by the evolution of steam, and the heating temperature is so regulated that the reaction mixture does not boil over. The resulting extremely viscous, sometimes crumbly, mixture is then withdrawn into suitable containers in which it, upon cooling, solidifies. This product, a so-called "driving journal compound", has a dark brown to black color, and a fibrous fracture, is sticky and harsh to the touch, and may be "worked" between the fingers to a rather stiff but slightly spongy mass. It begins to flow readily at about 475° to 500° F.; at temperatures substantially below this flow point it does not readily yield lubricant films. In use, a cake of the material is placed in the "cellar" of a locomotive driving journal upon a spring-actuated feeding device which forces the cake against and through a perforated plate or coarse screen (e. g., one having openings from ⅛ to ¼ inch) which plate or screen is immediately under the bearing surface of the journal.

Lubricating greases similar to the above-described have various disadvantages, aside from that just noted, including chiefly a tendency to "leak" or give up their contents of lubricating oil more readily than their contents of soap, with the result that the partially used cake or mass has a too-high soap content and an unduly high melting point so that the journal itself must be heated to still higher temperatures before the mass will feed properly and form an interface. It is the common practice to evaluate such greases on the basis of the relative value of their lubricating oil constituents, as it is commonly understood that the lubricating value of the grease is dependent mainly upon the oil therein: consequently in well made greases only high grade lubricating oil stocks commonly are employed.

I have found that the above, and other disadvantages may be overcome, and that a very material economy may be secured, by preparing lubricating greases from lubricating oils and soaps of certain acidic mixtures obtained by the partial, liquid-phase, oxidation of hydrocarbons of mineral origin. The lubricating greases embodying the present invention readily give off lubricant films at temperatures materially below their flow points; do not "leak" their lubricating oil contents but persist as constant compositions; and are further characterized by an unctious rather than a sticky feel, slipperiness, a conchoidal fracture, and a rubbery as opposed to fibrous structure.

As starting material for the preparation of the soaps employed in preparing my greases I use acidic mixtures, consisting essentially of relatively high-molecular-weight carboxylic acids soluble in petroleum hydrocarbons but insoluble in water, which acidic mixtures are found in and may or may not be separated from reaction mixtures from the partial oxidation of such hydrocarbon mixtures as 36–40° Baumé petroleum distillate, 45° Baumé petroleum distillate, and other mineral hydrocarbons, including paraffin wax, but especially the semi-solid product, known variously as "dark green petrolatum", "Sharples wax", or "amorphous wax", which is obtainable from crude petroleum oil by diluting the topped crude with a relatively large amount of gasoline, chilling the mixture to say 30 to 40° below zero F., and centrifuging liquids from the so-chilled mass.

Thus, the starting material for the preparation of these soaps may be the whole mass, resulting from the protracted oxidation of paraffin wax, or it may be an acidic mixture separated from such mass by appropriate methods hereinafter to be described more fully, or the whole mass resulting from the oxidation of Sharples wax, for instance, an oxidized Sharples wax having

a saponification value of from about 110 to about 175 or an acidic mixture separable therefrom or it may be an acidic mixture separable from the reaction mixture from the partial oxidation of one or another of the other mineral hydrocarbons referred to above.

The process of oxidation, which forms no part of the present invention, and the compositions of the resulting reaction mixtures, are fully described in my U. S. Patent No. 1,768,523. These reaction mixtures consist essentially of the aforesaid petroleum-soluble high-molecular-weight saturated aliphatic carboxylic acids, unsaponifiable but readily emulsifiable oxygen-compounds of hydrocarbons including compounds of alcoholic and/or ketonic constitution, and unoxidized hydrocarbons, all in varying amounts. Preferably I oxidize under such conditions and for such a period of time that the reaction mixture has a saponification equivalent of from about 110 or 120 to about 175.

From the aforesaid reaction mixtures I may, and preferably do, separate a product rich in, or substantially consisting of, the said aliphatic carboxylic acids by one of a number of operable methods including the following preferred methods:

I. Saponification method

To the reaction mixture is added sufficient saponifying agent, e. g., caustic soda solution, to saponify all of the saponifiable constituents thereof, the resulting soapy solution is separated from oily, unsaponified and non-emulsified components of the mixture, and the soapy solution is treated with an amount of an acid, e. g., sulphuric acid, sufficient to decompose or "break" the soaps precipitating the water-insoluble organic compounds thereby released, and separating the precipitated organic compounds from the aqueous solution. The organic compounds which constitute the separated mixture consist essentially of the aforesaid high-molecular-weight aliphatic carboxylic acids together with a material amount of unsaponifiable, non-acidic, oxidized hydrocarbons which readily emulsify with the aforesaid soaps and persistently associate with them.

II. Alcoholic separation method

The aforesaid reaction mixture, or the soapy solution described in Method I above, is treated with alcohol (e. g., 85% to 95% ethyl alcohol of commerce) in amount sufficient to dissolve the saponifiable, or saponified, as the case may be, constituents thereof, the alcoholic solution is separated from the constituents insoluble in alcohol, and the solvent is removed (as by distillation) from the so-separated compounds. By this method a resulting product is obtained which is considerably richer in, or consists substantially of, the aforesaid acids.

By whichever of the above methods produced, the product rich in the aforesaid acids may readily be saponified by treatment with an appropriate amount, that is, the theoretical amount, of an alkaline saponifying agent such as caustic soda to neutralize the acidic constituents thereof, whereby to produce soaps (or neutral products consisting largely or essentially of soaps) of the acids, which soap mixture, or soapy mixture, is freely soluble in or miscible with the commonly known and used lubricating oils or their equivalents to the production of lubricating greases having the desirable properties hereinbefore described.

Illustrative of the manner in which the greases forming the basis of the present invention are prepared is the following:

Example I

80 pounds of an acidic mixture separated according to Method I above from a reaction mixture produced by the oxidation of dark green petrolatum of 145–155° F. melting point, or "Sharples wax", in the manner set out in U. S. Patent No. 1,768,523, the oxidation being stopped when the reaction mixture showed a saponification equivalent of 170, and containing, say, 20 pounds of water, is dehydrated either by evaporation treatment at a temperature of about 300° F. or by heat treatment at about 248° F. in admixture with a relatively small quantity of a steam-refined lubricating oil stock (10 pounds), and the dehydrated mixture is saponified by treatment with 14.4 pounds of a 50% caustic soda solution, either at rocm temperature or at an elevated temperature of the order of 200° F., with thorough stirring. To the dehydrated mixture there is then added, with agitation and while the mixture is maintained at a temperature above about 220° F., an amount of the lubricating oil stock sufficient to bring the total content of lubricating oil to the proportion desired, say 40 pounds. I may, and preferably do, subject the mixture to a milling treatment or its equivalent to smooth out any lumps or granules in the grease product. The resulting composition is then drawn off into suitable molds or other containers and there solidified by cooling.

The above-described dehydration step is not essential and, of course, is not practiced in the case where the acidic starting material contains practically no water.

The lubricating grease so produced is a driving journal compound having a melting point of about 540° F. but begins to deform at about 460–475° F.: it is much more unctious to the touch than a sodium stearate grease, is not sticky, and does not "leak" its lubricating oil constituent either in storage or under the conditions of use, breaks (cold) with a conchoidal fracture, and is slippery to the touch. From the standpoint of economy, it may be prepared at an actual cost materially below that of the commonly used sodium stearate grease.

The foregoing specific example may be modified by the substitution of an acidic mixture separated from the reaction mixture produced by the oxidation of paraffin wax or of one or another of the various distillates of petroleum, or by the substitution of the acidic reaction mixtures as such, for the acidic mixture there specifically disclosed. As was indicated in the foregoing general description of the invention, I may subject the oxidized masses, as such, to saponification treatment, whereby to transform into soaps their whole content of saponifiable constituents, thereby producing a soapy product consisting of, on the one hand, the said soaps and, on the other hand, unsaponifiable compounds, both oxygenated and non-oxygenated, which unsaponifiable compounds are found to be miscible with the soaps and with the soap-lubricating oil mixtures. The resulting saponified mixtures are then compounded with suitable amounts of lubricating oil, in the manner described in the foregoing specific example, to the production of greases.

The relative consistency or hardness of the greases forming the basis of the present invention may be modified in any one of several ways:

for example, by increasing the content of lubricating oil, or by using as the soap-forming material an acidic product containing more of the unsaponifiable oxidation products above described. Thus, there may be made in substantially the same manner relatively softer greases, having lower melting and deforming points, including cup greases, roller bearing greases, greases adapted for use in lubricating floating bushing bearings, and the like. Also, a relatively very hard grease may be prepared by combining with the soap described in Example I above a suitable amount, say 40%, of unoxidized dark green petrolatum or "Sharples wax". This latter, while having a high melting point, has good lubricating properties, is readily deformable and has a high unctiousness.

The invention is not restricted to the use of sodium soaps but includes the preparation of lubricating greases from the calcium, potassium, lead, aluminum, magnesium, and various other metallic, soaps of the acidic mixtures herein described. Illustrative thereof is a "lime cup grease" prepared by combining a "low cold test" petroleum lubricating oil of about 200 viscosity (at 100° C.) with the soap produced by treating with calcium hydroxide the acidic mixture obtained from oxidized paraffine wax. This latter is a transparent, light-colored, grease of excellent lubricating properties.

The grease from the calcium soaps of the "petroleum acids" are prepared in a manner similar to that commonly employed in the making of "lime greases" from stearic acid or tallow, it being desirable, however, on account of the tendency of the calcium hydroxide to "seize" the "petroleum acids" to mix a small amount of lubricating oil stock with the acids before adding the calcium hydroxide, and then to introduce the latter into the mixture as an emulsion of the calcium hydroxide in a further amount of the lubricating oil: after the soap is well dispersed the necessary further additions of lubricating oil may be made. This reaction preferably is conducted at a temperature below 212° F. and under vigorous agitation. The resulting products are remarkably unctious, of short shear, and of a more or less buttery consistency.

Example II

A 'leaded transmission grease" may be prepared by the following method:

The oxidation reaction mixture obtained from "Sharples wax" is saponified in the manner set out in Example I above, the soap solution is separated from unsaponifiable constituents of the reaction mixture and is largely diluted with water whereby to precipitate emulsified but unsaponified bodies persisting with the soap solution, and the resulting purified soap solution is treated with an appropriate amount of a lead salt, such, for instance, as lead nitrate, in aqueous solution. Thereby there is precipitated a mixture of lead soaps of the acids, which mixture may be dehydrated in known manner at about 245° to 265° F. These lead soaps are admixed without difficulty, in the warm, with a lubricating oil stock, producing what apparently is a true solution of the lead soaps in the oil.

Instead of the above method, these lead soaps may be prepared by treating the separated acidic mixtures with lead carbonate or an equivalent lead salt, or, with less facility, even litharge. In the last-mentioned case, it is difficult to dissolve or suspend sufficient litharge in the acidic mixture to obtain as high a lead content in the resulting soap as is possible when practicing the double-decomposition method above described.

My researches with other metallic soaps of these "petroleum acids" has demonstrated that the soaps of iron, aluminum, manganese and other metals all are either soluble, or at least distensible, in lubricating oils whereby to make lubricating greases. Furthermore, soda-lime greases, and other so-called "mixed greases" and "sett greases" have been made in accordance with this process.

By the expression "a salt of a petroleum acid" as used in the appended claims I mean to include not only a single salt of a single isolated petroleum acid but also either salts of a plurality of petroleum acids or a saponified oxidation product of petroleum hydrocarbons rich in petroleum acids. By "petroleum acid" as used in the appended claims I mean a relatively high-molecular weight, saturated, aliphatic, carboxylic acid soluble in petroleum but insoluble in water, which acid was derived from an aliphatic hydrocarbon of mineral origin by controlled liquid-phase partial oxidation of the latter. See the disclosures in U. S. Patents 1,828,356, 1,863,004 and 1,770,876.

I claim:

1. Process which comprises treating with a saponifying agent a relatively high molecular weight saturated aliphatic petroleum acid derived from a reaction mixture obtained by the controlled partial oxidation of a mixture of aliphatic petroleum hydrocarbons and incorporating in the resulting soap a petroleum lubricating oil in an amount substantially greater than that of the soap but restricted to the production of a product which is solid to semi-solid at normal room temperature.

2. A lubricating grease composition consisting essentially of from about 35 to about 50% by weight of a hydrocarbon mixture of mineral origin and having lubricating properties containing dissolved therein from about 65 to about 50% by weight of oil-soluble salts of a mixture of relatively high molecular weight saturated aliphatic carboxylic acids derived from an aliphatic hydrocarbon mixture of mineral origin by controlled liquid-phase partial oxidation of the latter, said composition being a solid grease.

3. As a new product, a lubricating grease consisting essentially of a substantially anhydrous solution of a soap the acid radical of which is a saturated aliphatic carboxylic petroleum acid derived from a reaction mixture obtained by the controlled liquid phase partial oxidation of a mixture of aliphatic petroleum hydrocarbons and the basic radical of which is a metallic element of the group consisting of sodium, potassium, calcium, iron, aluminum, manganese and lead in a substantially anhydrous medium consisting of a mineral lubricating oil, which grease is semi-solid to solid at normal room temperature.

4. The product defined in claim 3 characterized in that the basic radical is sodium.

5. The product defined in claim 3 characterized in that the basic radical is calcium.

6. The product defined in claim 3 characterized in that the basic radical is lead.

7. Process which comprises reacting a dehydrated, saturated, aliphatic carboxylic petroleum acid compound derived from a reaction mixture obtained by the controlled liquid-phase partial oxidation of a mixture of aliphatic petroleum hydrocarbons with a reactive compound of a metal

of the group consisting of sodium, potassium, calcium, iron, aluminum, manganese and lead, whereby a salt of said metal and said acid is produced and dispersing the so-formed salt in a petroleum lubricating oil in such relative proportions as to yield a product which is solid to semi-solid at normal room temperature.

8. Process which comprises reacting a dehydrated sodium soap of a saturated aliphatic carboxylic petroleum acid derived from a reaction mixture obtained by the controlled liquid-phase partial oxidation of a mixture of aliphatic petroleum hydrocarbons with an alkaline saponifying agent in an amount to neutralize the said acid with formation of a soap therefrom, and dissolving the so-formed soap in a petroleum lubricating oil in such relative proportions as to yield a product which is solid to semi-solid at normal room temperature.

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