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## GREASE MANUFACTURE

Walter H. Peterson, Point Richmond, Calif., as-  
signor to Shell Development Company, San  
Francisco, Calif., a corporation of Delaware

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This invention relates to the preparation of greases and similar compositions. More specifically, the invention is concerned with improvements in the process for the preparation of greases comprising or containing inorganic col-  
loids and lubricating oils.

Greases comprising lubricating oils gelled with inorganic colloids incorporated therein have been described previously by Munch (German Patent 451,055) and Kistler (U. S. Patent 2,260,625). The inorganic colloidal materials in most cases have been various forms of silica. Kistler, for example, shows the use of silica aerogels, while Munch was the first to describe silica greases prepared by the displacement of water from silica hydrogel using volatile organic liquids which in turn were displaced with a mineral oil. In comparison with ordinary greases, the lubricating oil-inorganic gel greases possess the outstanding characteristic of structural stability at elevated temperatures. This property makes such greases of particular interest in the lubricating of ball bearings and other machinery parts, as well as in turbojet engines and in steel rolling mills.

One of the shortcomings of such systems is that they are sensitive to the presence of water, apparently due to the hydrophilic nature of the gel surfaces. Hence, the unmodified greases prepared according to the two publications given above have been found to be unstable if employed in the presence of water. The end result is the disintegration of the grease structure, resulting in the precipitation of silica and the separation of an oil phase.

Various means have been taken to correct this characteristic. The addition of various protective compounds is described in several copending patent applications. Patent application Serial No. 782,694, filed October 28, 1947, in the name of Fred H. Stross (now Patent No. 2,554,222 dated May 22, 1951), describes the use of amines for this purpose. A similar result was obtained by the addition of hydrophobic soaps as disclosed in patent application Serial No. 782,695, filed October 28, 1947, by the same inventor (now abandoned). Greases of amphoteric metal such as alumina may be water-proofed by the addition of high molecular weight acids, as shown by copending patent application Serial No. 91,229, filed May 3, 1949, filed in the names of Fred H. Stross and Stanley T. Abrams. One of the most promising types of additives to be utilized for the subject purpose includes hydrophobic hydroxy compounds exemplified by the glycerides of 12-hydroxy stearic acid. These are disclosed in patent application Serial No. 82,905, filed March 22, 1949, in the name of W. H. Peterson (now Patent No. 2,573,650 dated October 30, 1951). The present application is a continuation-in-part of the latter application, Serial No. 82,905.

In utilizing these various water-proofing agents, it has been the normal practice to in-

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corporate the agent either in the inorganic gel or more usually in the lubricating oil. Following this, the three major ingredients, namely, additive, gel and oil, were stirred and subjected to shearing in order to produce a satisfactory grease structure. At times, moderate amounts of warming have been employed. The major purpose for heat, as used in the past, has been to thin the oil so as to more easily incorporate the addition ingredients therein.

It is an object of the present invention to improve the water-resistance of greases gelled by the presence of inorganic colloidal material. It is a further object of the present invention to improve the process for the preparation of such greases. It is an additional object to provide improved water-resistant lubricating greases showing an unexpected response to water-proofing agents. These objects will be more fully understood and other objects will become apparent from the following description of the invention.

Now, in accordance with this invention, it has been found that the water-resistance and other characteristics of greases gelled with inorganic colloidal materials are substantially improved when the ingredients are heated for a period between about 20 and about 180 minutes at a temperature between about 120° C. and about 220° C., preferably between 165° C. and 200° C. Still in accordance with this invention, it has been found that this heat treatment is especially effective if a surface active hydrophobic material useful as a water-proofing agent is present during a substantial part of the heating period. Another feature of the present invention comprises the improvement in gelling power of inorganic colloids caused by the subject heat treatment. Again, in accordance with this invention, it has been found that the heat treatment is of maximum benefit when the inorganic colloidal material has been treated with 1-30% by weight of an acid such as phosphoric acid or boric acid previous to incorporation in the mixture of grease-forming ingredients.

The inorganic colloidal materials especially useful for grease formation include metallic oxides or hydroxides as well as treated clays as defined hereinafter. More specifically, the inorganic colloids capable of gel formation in lubricants are alkaline earth metal oxides and hydroxides, alkaline earth metal carbonates, alkali metal carbonates, polyvalent metal oxides such as silica, magnesia, alumina, ferric oxide, vanadium pentoxides and other heavy metal oxides, polyvalent metal sulfides such as ferrous sulfide and cuprous sulfide, and some metallic sulfates and phosphates. Mixtures of these materials may be employed, of which the most promising have been found to be synthetic zeolites such as magnesium silicates or aluminum silicates prepared by known methods.

Various naturally occurring colloidal inorganic compounds are also useful if employed as more



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particularly described hereinafter. These are ordinarily complex combinations of two or more metallic oxides roughly described as magnesium silicates, aluminum silicates, magnesium-aluminum silicates and the like, which may be considered to be chemical combinations of magnesium oxide with silicon dioxide or aluminum oxide with silicon dioxide, etc. Some representative naturally occurring materials which are particularly suitable are the bentonites, fuller's earth, Hectorite and Wyoming montmorillonite. The magnesium montmorillonites such as Hectorite have been found to be especially effective grease gelling agents, particularly when treated as described hereinafter.

In order to perform its function as a gelling agent, the inorganic colloid should be in a highly expanded form. One method for the preparation of colloidal materials comprises conversion of inorganic metalloidal halides or other combustible materials into aerosols, such as by burning silicon tetrachloride to form an aerosol of colloidal silica. Other typical methods for the preparation of expanded colloids include the aerogel formation described in the Kistler patent referred to above and also gels incorporated in oil without an intermediate drying step between hydrogel formation and grease formation. A typical method for the preparation of aerogels comprises forming silica hydrogel by the addition of sulfuric acids to sodium silicate solution. The aerogel is then prepared by displacing water from the hydrogel with a volatile organic liquid such as ethyl alcohol and heating the resulting organogel to a temperature above the critical temperature of the liquid contained therein while maintaining the pressure on the system sufficiently high to insure that the liquid phase will remain liquid until the critical temperature is reached. At this point, the liquid will be converted into the gaseous state without the formation of menisci at the gas-liquid interface.

In the preparation of greases without a drying step, one of the acceptable processes comprises formation of a hydrogel, displacement of water with a water-miscible organic solvent such as alcohol, and replacement of the alcohol with either a lubricating oil or another volatile oil-miscible solvent such as benzene. In the latter case, the benzene is then replaced by a lubricating oil. An improvement on both of these alternatives comprises the direct transfer of a hydrogel into oil without intermediate drying or intermediate organogel formation. It has recently been found that this direct transfer is possible by incorporating one of the hydrophobic surface active agents recited hereinafter together with the two major ingredients, namely, the inorganic gelling agent and lubricating oil and subsequently removing water.

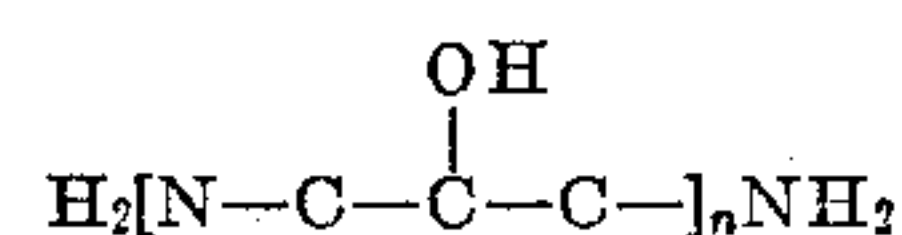
Various grease-forming base liquids may be utilized in the preparation of inorganic gel greases. In general, it is preferred to use the usual range of mineral lubricating oils which are employed in the preparation of ordinary soap greases. Synthetic liquid hydrocarbons may be used also including various alkylated aromatic hydrocarbons such as tertiary butyl naphthalenes, polymerized olefins such as suitable liquid polyethylenes, polybutylenes, polycetenes and the like. Various other oleaginous liquids including natural occurring materials such as vegetable and animal oils and synthetic lubricants may be used. Examples of the latter class include the diesters of dicarboxylic acids such as bis(2-ethylhexyl)

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sebacate, bis(methylethyl) succinate; the inorganic esters such as the phosphate esters including tributyl phosphate, trioctyl phosphate, tricresyl phosphate and dioctyl cresyl phosphate. Mixtures of such lubricants may be employed as well. For special purposes involving high temperature use or for analogous utility, the polymeric silicones may be used with advantage.

In accordance with the basic concept of the present invention, these two principal ingredients are heated together at a temperature between about 120° C. and 220° C. for a period between about 20 and about 180 minutes. The preferred ranges within which optimum effect has been obtained include a temperature range of about 165 and 200° C. and the preferred heating period is between 30 minutes and 120 minutes. The heating may be conducted at atmospheric pressure or under vacuum or superatmospheric pressure. If the grease is to be formed from an inorganic alcogel the heating period is conveniently conducted under vacuum so that alcohol is withdrawn simultaneously during the heat treatment. The mixture of ingredients may be stirred during the heating period or may be subjected to shearing such as milling for the purpose of creating a proper dispersion of the gel throughout the lubricating oil so as to create a grease structure.

The present process is especially applicable to the preparation of greases containing hydrophobic surface active agents of the classes referred to hereinbefore and fully described in the copending patent applications enunciated herein. Preferred classes of these surface active agents include especially hydrophobic cationic surface active agents such as higher aliphatic amines, quaternary ammonium compounds and polyamines as well as their salts and amides. Typical species include heptadecyl amine, dimethyl benzyl octadecyl ammonium chloride, amines obtained by the ammonolysis of chlorinated paraffin wax, higher fatty acid salts of polymeric adducts such as those derived from acrolein and ammonia and from diallyl amine and hydrogen sulfide; and higher fatty acid partial amides of polyalkylene polyamines such as oleic acid amide of tetraethylenepentamine. An especially preferred type of polymeric amine for use in the present invention may be obtained by reaction of ammonia with epichlorhydrin resulting in the formation of a linear alkylene polyamine bearing hydroxyl substituents. The principal product of such a reaction normally has the general formula



wherein  $n$  is an integer between 2 and 10. In order to be effective as a water-proofing agent for the subject greases, this particular type of polyamine should be in partial amide formation with a hydrophobic organic acid such as the higher fatty acids derived from animal and vegetable oils. Another highly effective type of hydrophobic agent comprises the condensation products of a polyamine with alkyl or alkenyl substituted succinic or succinamic acids or their anhydrides or acid esters. Typical species include the reaction products of ammonia and epichlorhydrin condensed with octadecenyl succinic acid. Another preferred species of this category include the condensation products of alkaline diamines with the same classes of acids. Typical of these are the condensation products of dodecenyl succinic anhydride and ethylene diamine



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and octadecenyl succinamic acid and ethylene diamine. When amphoteric metal gels are used as the gelling agent, it has been found that water insoluble organic acids provide outstanding water resistance. These are typified by tetradecane-1-phosphinic acid, petroleum hydrocarbon sulfonic acids, stearic acid and the like.

In the production of water-resistant greases from metallic gels such as silica, water-insoluble soaps such as aluminium stearate, aluminum 12-hydroxy stearate, lead stearate and the like, may be used.

As stated hereinbefore, the combined effect of incorporating one of these hydrophobic water-proofing agents together with the heat treatment forming the basis of the present invention, provides greases exhibiting outstanding resistance to the deleterious action of water. Greases prepared according to the present process are preferably those containing 2-10% by weight of the inorganic gelling agent based on the total grease composition and 10-50% by weight of the inorganic gelling agent of one or more of the water-resistance improving materials.

Example I

A silica alcogel was prepared by forming a hydrogel of silica having approximately a 5% silica content and replacing water by distillation in the presence of isopropyl alcohol. Five parts by weight of the silica alcogel (based on silica content) were added to 94 parts by weight of a mineral lubricating oil containing 1 part by weight of glyceryl 12-hydroxy stearate. The mixture was milled to disperse the alcogel in the lubricating oil after which the resulting composition was heated for one hour at one of the temperatures indicated in the table below. Five samples were treated in a similar manner, the sole variation being in the temperature of heating. After heating, the compositions were milled to a minimum grease penetration. A grease was also prepared having the same composition but was not given any heat treatment. All of the samples so prepared were subjected to a roll stability test in the presence of water. This test is intended to evaluate the mechanical stability of greases in contact with water such as may occur when wheel bearings are exposed to rain, cooling water, etc. In this method, 15 grams of water and 75 grams of the grease tested are kept in a rotating cylinder containing a weighted iron roller. The consistency of the grease is determined quantitatively before and at hourly intervals during rolling. The hours necessary to reduce the consistency of the grease to an arbitrary penetration has been taken as a measure of the mechanical stability of the grease sample in the presence of water. The following comparison was obtained by this method when the greases described above were tested.

Temperature of Heating, °C.	Water Roll Stability Test, Hours
157.....	5
162.....	4
172.....	10
191.....	8
211.....	6
No heating.....	2

Example II

Greases were prepared as described above containing 2% by weight of glycerol 12-hydroxy stearate, 5 parts by weight of silica and 93 parts

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of mineral lubricating oil. The samples so prepared were heated for one hour at the temperatures indicated below. For the purpose of comparison, a grease of the same composition was prepared but was not subjected to any heat treatment. The results given in the following table were obtained in the water roll stability test described above.

Temperature of Heating, °C.	Water Roll Stability Test, Hours
171.....	20.
192.....	Greater than 21.
210.....	Do.
No heating.....	2.

Example III

A grease was prepared having the same composition as that described in Example II. Part of the grease was not subjected to heat treatment while two portions thereof were heated at 170° C. for 26 and 83 minutes, respectively. The samples so prepared and treated were subjected to the water roll stability test described in Example I. The following data were obtained:

Time at 170° C., Minutes	Water Roll Stability Test, Hours
26.....	9
83.....	23
No heating.....	2

Example IV

Epichlorhydrin and about five molecular proportions of ammonia were reacted at about 40-60° C. for about one hour, the product was heated to about 140° C., and thereafter tallow fatty acids were added thereto and the mixture heated at 150° C. to 225° C. for about one hour to form the amide—the proportions being such as to form approximately the one-third amide. A grease was prepared containing about 2.5% of the partially saponified condensation product, 5% of silica and the remainder of mineral lubricating oil. The resulting grease was heated at a temperature of 170° C. for one hour. This grease was found to have a high resistance to disintegration by hot water, while a similar grease prepared from the same proportions of ingredients and heated at 130° C. for one hour had a substantially lower hot water resistance.

Example V

Alumina hydrogel was added to a mineral lubricating oil containing stearic acid after which the ingredients were heated with stirring for two hours at 150° C. Upon milling, a highly water resistant grease was formed containing 5 parts by weight of alumina, 2.5 parts by weight of stearic acid and 92.5 parts by weight of mineral oil.

Example VI

A silica alumina hydrogel containing about 10% alumina was added to mineral oil having alumina stearate dissolved therein. The mixture of components was heated for 30 minutes at 190° C. and then milled to a minimum grease penetration. The resulting grease contained 6% by weight of the silica alumina gel and 2% by weight of aluminum stearate. When subjected to the action of hot water for a period of 50 hours no disintegration occurred.



## Example VII

A grease was prepared by heating 4 parts by weight of silica alcogel and 1 part by weight of dimethyldioctadecylamine hydrochloride with 95 parts by weight of a mineral lubricating oil. The resulting composition was heated for one-half hour at 170° C. and exhibited good resistance to the action of hot water.

I claim as my invention:

1. In the process for the preparation of a grease comprising lubricating oil, a gelling amount of a colloidal metallic oxide gel in highly expanded form and capable of forming a grease with said oil and a hydrophobic surface active agent, the improvement which comprises heating said ingredients at a temperature between about 165 and about 200° C. for a period between about 30 minutes and about 120 minutes.

2. In the process for the preparation of a grease comprising lubricating oil, a gelling amount of a colloidal metallic oxide gel in highly expanded form and capable of forming a grease with said oil and a hydrophobic hydroxy fatty ester, the improvement which comprises heating said ingredients at a temperature between about 165° C. and about 200° C. for a period between about 30 minutes and about 120 minutes.

3. In the process for the preparation of a grease comprising lubricating oil, a gelling amount of a colloidal metallic oxide gel in highly expanded form and capable of forming a grease with said oil and a hydrophobic amino surface active agent, the improvement which comprises heating said ingredients at a temperature between about 165 and about 200° C. for a period between about 30 minutes and about 120 minutes.

4. In the process for the preparation of a grease comprising a mineral lubricating oil, a gelling amount of colloidal silica gel in highly expanded form and capable of forming a grease with said oil and a glyceride of 12-hydroxy stearic acid, the improvement which comprises heating said ingredients at a temperature between about 165 and about 200° C. for a period between about 30 minutes and about 120 minutes.

5. In the process for the preparation of a grease comprising a mineral lubricating oil, a gelling amount of colloidal silica gel in highly expanded form and capable of forming a grease with said oil and a higher fatty acid amide of a condensation product of epichlorhydrin and ammonia, the improvement which comprises heating said ingredients at a temperature between about 165 and about 200° C. for a period between about 30 minutes and about 120 minutes.

6. The process which comprises mixing a lubricating oil, a colloidal metallic oxide gel in highly expanded form and capable of forming a grease with said oil and a hydrophobic surface active agent, heating the mixture so formed at a temperature between about 120 and about 220° C. for a period between about 20 minutes and about 180 minutes and shearing the heat treated mixture until a grease composition is formed.

7. The process which comprises mixing a lubricating oil, a colloidal metallic oxide gel in highly expanded form and capable of forming a grease with said oil bearing 1-30% of a mineral acid adsorbed thereon, and a hydrophobic surface active agent, heating the mixture so prepared at a temperature between about 120 and about 220° C. for a period between about 20 minutes and about 180 minutes, and shearing the heat

treated mixture until a grease structure is formed.

8. In the process for the preparation of a grease comprising mineral lubricating oil, a gelling amount of a colloidal metallic oxide capable of forming a grease with said oil, and a hydrophobic hydroxy fatty ester, the improvement which comprises heating said ingredients at a temperature between about 165° C. and about 200° C. for a period between about 30 minutes and about 120 minutes.

9. In the process for the preparation of a grease comprising mineral lubricating oil, a gelling amount of a colloidal metallic oxide capable of forming a grease with said oil, and a hydrophobic surface active agent, the improvement which comprises heating said ingredients at a temperature between about 165 and about 200° C. for a period between about 30 minutes and about 120 minutes.

10. In the process for the preparation of a grease comprising mineral lubricating oil and a gelling amount of a mixture of colloidal inorganic oxides capable of forming a grease with said oil and a hydrophobic surface active agent, the improvement which comprises heating said ingredients at a temperature between about 165 and 200° C. for a period between about 30 minutes and 120 minutes.

11. In a process for the preparation of a water resistant grease, the step comprising heating a composition comprising a lubricating oil, a gelling amount of an inorganic gel capable of forming a grease with said oil and from about 10% to about 50% by weight of the inorganic gelling agent of a non-metallic hydrophobic aliphatic hydroxy organic compound, said grease being heated at a temperature between about 120° and 220° C. for a period between about 20 minutes and about 3 hours.

12. In a process for the preparation of a grease, the step comprising heating a composition comprising a mineral lubricating oil thickened to a grease-like consistency by from about 2 to about 10% by weight, based on the total composition of an inorganic oxide gel in a highly expanded form having its normal liquid content replaced by said lubricating oil, and from 10% to 50% based on the gel of a non-metallic hydrophobic aliphatic hydroxy organic compound coating said gel, said composition being heated at a temperature between 120° and 220° C. for a period between about 20 minutes and about 3 hours.

13. In a process for the preparation of a water-resistant grease, the step comprising heating a composition comprising a lubricating oil, a gelling amount of an inorganic gel capable of forming a grease with said oil and a hydrophobic surface-active agent, said composition being heated at a temperature between about 120° and 220° C. for a period between about 20 minutes and 3 hours.

WALTER H. PETERSON.

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