

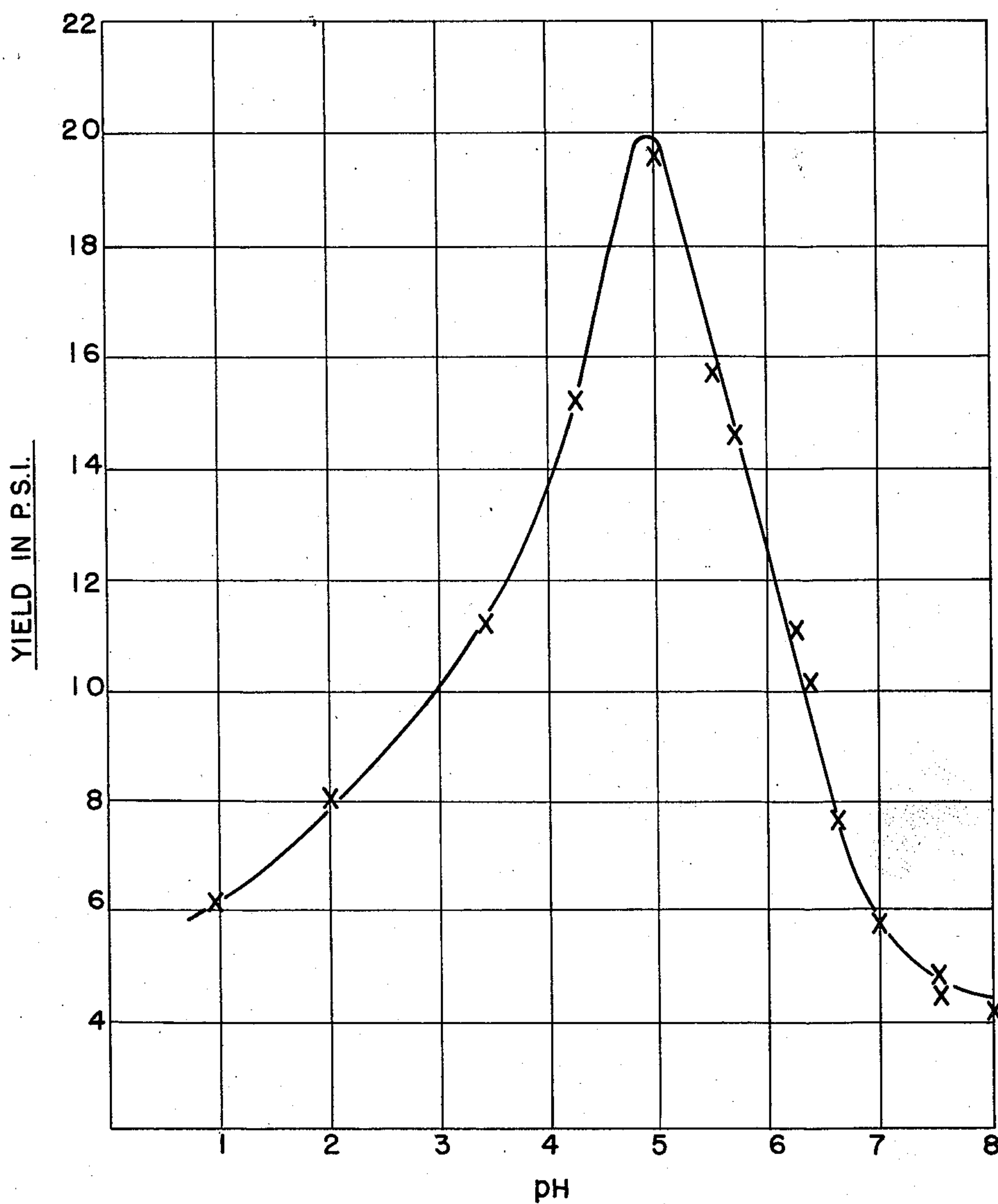
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LUBRICATING GREASE CONTAINING WATER REPELLENT AEROGEL

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LUBRICATING GREASE CONTAINING WATER REPELLENT AEROGEL

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The present invention relates to lubricating grease containing aerogels. It relates more particularly to greases formed primarily of lubricating oils, especially mineral base lubricating oils, thickened to a grease consistency with an inorganic gel which has been rendered effectively water repellent so as to increase substantially the resistance of the grease to moisture and liquid water.

In copending applications, Serial Nos. 66,130, 66,131, 66,132 and 66,133, filed December 18, 1948, now U. S. Patent Nos. 2,583,603, 2,583,604, 2,583,605 and 2,583,606, respectively, the present inventors have disclosed various modifications of a basic invention wherein the customary soaps which have long been used may be largely or entirely replaced with inorganic gel as the thickening agent. This is accomplished by replacing the aqueous liquid component of the normal gel with a mutual solvent for water and oil, such as a ketone, e. g., acetone, and then replacing the mutual solvent with a lubricating oil. The prior art had made broad suggestions of such a procedure, but the present inventors found that the resulting lubricants were markedly deficient in water resistance. Hence, they discovered and disclosed in said applications various methods by which such greases could be improved in water resistance.

According to the present invention, the yield value as well as the quality of lubricating greases prepared by exchanging the solvent in silica aquagel is greatly affected by the conditions under which the aquagel is prepared. Apparently this is related to the surface properties of the aquagel particles which are formed under various conditions of gel precipitation.

Silica aquagels are commonly prepared by precipitation with acid from aqueous solutions of sodium silicate. When the acids are added to the sodium silicates (usually the latter are employed in solutions of about 1.185 specific gravity) the aquagel will form anywhere in the pH range of 1.0 to 8.5. The time required for the sol-gel transformation varies with pH, being a minimum at about pH 8.0.

When these gels are solvent exchanged, e. g., first with acetone and then with mineral lubricating oil (or alternatively the acetone is replaced with a light naphtha and thereafter with the lubricating oil), there is a wide variation in the yield (i. e., consistency, or hardness, of grease for a given gel content). This variation appears to be in large measure a function of the pH value at which the gel is finished prior to washing with water and solvent exchange.

The attached drawing shows a graph of the yield of grease prepared by this method using silica gels maintained at different pH conditions prior to solvent exchange. It will be observed that a sharp maximum occurs at a pH value of about 5. Thus, the yield was only 6 units for silica aquagel prepared under the highly acidic conditions of pH 1 and was even less for gel prepared under the mildly alkaline conditions of pH 8. In between, the values showed a yield of 8 at pH 2, a yield of 11 at pH 3.5, a yield of 15.2 at pH 4.3 and a maximum of

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about 19.7 yield at pH 5. As the pH value was further increased to 5.5, the yield dropped to 15.7. At pH 5.75 it dropped further to 14.6 and still further to values of 11.2 and 10.2, respectively, for pH values of 6.3 and 6.4. At pH 6.6 it was only 7.6 and at pH 7 it was 5.6. At pH 7.5, the yield was 4.8 and it dropped to about 4.4 at pH 8. It will be noted that optimum results were obtained at a sharply defined pH value which lies above 4.3 and below 5.5.

The solvent exchanged silica aquagel may also be converted into an aerogel by a method similar to that of Kistler (U. S. Patent No. 2,093,454, issued September 21, 1937) and described completely in our copending application, Serial No. 275,016, filed March 5, 1952, now Patent No. 2,805,961. This method differs from that of Kistler essentially in the addition of water-proofing ingredients, such as polymerizable organic compounds of the type of modified alkyd resins, drying oils, etc., to the solvent-exchanged aquagel prior to autoclaving. The silica is then added to the oil in a suitable quantity and the finished grease obtained by shearing the system. Results similar to those obtained by the first method of preparing grease via the solvent exchange method were obtained.

The most critical pH conditions are those maintained during a gel conditioning stage of the gel formation process, that is, immediately prior to water washing and solvent exchange. This conditioning involves diluting the precipitated product with a suitable amount of water to give a slurry that is readily handled. Where the silica aquagel contains 3 to 5% water of SiO_2 about $\frac{1}{4}$ to $\frac{1}{2}$, preferably $\frac{1}{3}$, of its volumes of water is used. The pH of the dispersion is adjusted to about 5.0 allowing the product to age by standing, preferably at room temperature, for periods of about $\frac{1}{2}$ hour up to 2 days before washing.

For example, optimum results will be obtained in accordance with the invention when the gel is precipitated at a pH of about 5 and thereafter aged or conditioned at about the same pH, followed by water washing and solvent exchange. However, a silica gel of similarly high yield value is obtained independent of the pH at which the gel is actually precipitated, provided aging or conditioning of the gel takes place at a pH of about 5. In other words, a silica gel precipitated at any pH may be conditioned during the aging or setting stage to an optimum pH conducive to a maximum yield value.

The yield values mentioned above are based on an arbitrary system, but they are directly proportional to the Bingham yield value or the Goodeve coefficient of thixotropy of the oil-gel system.

These yield values of the grease were obtained as follows:

Acetone-wet silica gel containing 5.76% equivalent dry solid was dispersed in 94.24 grams of 300 viscosity 95 V. I. mineral lubricating oil by means of a colloid mill after flashing off the acetone from the oil. Plasticity measurements were carried out by extruding the grease at room temperature under several pressures through a capillary viscometer having a length of 2.45 cm. and a diameter of 0.089 cm. The weight of grease extruded at various pressures is determined. The pressure in p. s. i. was plotted as abscissa with rate of flow as ordinate. The linear portion of this curve is extended to the abscissa (i. e., to zero rate of shear). The value of the pressure at this point is referred to as the yield value of the grease (see ASTM D-1092-51, page 561). This value may be converted into Bingham yield value by multiplying by the appropriate constant characteristic of this instrument.

There is no simple mathematical relationship between yield value and ASTM worked penetration, but the two may be correlated by setting up a number of graphs,

obtained by preparing a number of greases of different thickener content and measuring both their worked penetration and yield value. Having obtained the relationship of penetration and yield value, one may take from the curves the penetration value corresponding to any yield value, for example as follows.

To correlate the yield values reported above to ASTM penetration values, three silica greases were prepared of variable silica content, i. e., 6, 7.5, and 9%. The worked penetration value of each grease was obtained and a curve No. 1 set up with percent silica as abscissa and worked penetration as ordinate. The silica used to establish this basic relationship was a commercial material and does not represent the improved silica of the present invention.

The penetration values of these greases were correlated to the corresponding yield values as indicated above. The results were as follows:

Grease	SiO ₂ , percent	Penetration	Yield value, dynes/sq. cm.
A-----	9	273	14.9 × 10 ³
B-----	7.5	309	10.6 × 10 ³
C-----	6	342	7.1 × 10 ³

These results may form the basis for a graph No. 2 relating yield value and worked penetration.

These correlations and the correlation of yield value vs. pH, illustrated in the drawing of this application, may be used as follows: At a given pH the yield value is read from the graph of the accompanying drawing. This yield value is converted to worked penetration by reference to graph No. 2. With this knowledge, graph No. 1 is referred to and the point is plotted thereon. Now a line is drawn parallel to the present line on graph No. 1 but through the point just plotted. In doing this, it is assumed that the worked penetration/% silica curve has the same slope for all silicas (i. e. all those prepared in a similar manner but at different pH values). Having this curve the % silica (at this pH) required to obtain any value of worked penetration may be read off. The process is repeated for other pH values. By this method, the following figures were obtained showing the percent silica required (maintained at different pH values) to obtain a grease of given consistency.

Percent silica			Penetration
pH 4	pH 5	pH 6	
7.8	6.3	7.9	280
6.9	5.5	7.0	300
5	3.5	5.1	350

It will be seen that about 25-40% more silica is required at pH 4 or 6 than at pH 5 for a desired penetration of 280-350.

It will, of course, be understood that greases prepared from silica gels prepared as above may be subjected to the other treatments described in the copending applications mentioned above. Thus the water-proofing of the gel, before or after its incorporation in oil, is a particularly desirable step. It is quite essential if the grease is to be used under conditions where it comes into contact with any appreciable quantities of moisture, even in the air.

Hence the type of moisture-proofing in the above applications, and especially that described in detail in Serial No. 66,132, should normally be applied. This may be accomplished by milling from 10 to 100% by weight, based on the dry weight of silica gel, of resin possessing some oil solubility, preferably an alkyd resin, into the grease. A specifically preferred resin is a so-

called "modified" alkyd resin, such as the resins formed by condensation of glycols or glycerol with phthalic anhydride, modified by inclusion of 2 to 50%, based on the weight of the condensing reactants of linseed oil, the unsaturated acids derived from linseed oil, or oleic acid, or mixtures thereof. These modifiers incorporate long chains into the polymeric resins and improve their oil solubility. Such treatment of the resins improves the compatibility of the resin-coated silica gel with the lubricating oil. The gel will usually form about 4 to 25% of the weight of the grease (based on dry weight of aquagel). Other methods of water-proofing may be used but, in general, it is desirable to overcome the normal hydrophilic properties of the gel by coating it with some relatively oleophilic and water repellent material.

It will, of course, be understood that the oils used, as well as other ingredients, may be any of those known in the prior art as being suitable for grease compositions. Mineral oils of 50 to 5000 SSU viscosity at 100° F. may be employed, but synthetic oils, such as the esters of dibasic acids, complex esters formed from a combination of mono- and di-functional acids and alcohols, polyglycols or glycol-ethers, silicone oils, etc., may be used alone or in combination with each other or with mineral oil as the liquid component of the grease. Suitable mutual solvents must be chosen in each case, as will be obvious. The ethers and ketones, especially acetone, are usually preferred, especially when mineral base lubricating oil is used, but other solvents such as lower alkyl alcohols, i. e., water-soluble alcohols, may be preferable or necessary for some of the synthetic oils. When such alcohols are used, it is not always necessary to remove all the water of gelation. Any residue may be flashed off with the alcohol after the lubricating oil is incorporated into the gel.

The invention will be more readily understood by referring to the following specific examples.

EXAMPLE I

100 grams of sodium silicate having a specific gravity of 41 Baumé containing 28.7% SiO₂ and 8.9% Na₂O were diluted to 450 cc. with distilled water. While stirring, the sodium silicate was precipitated with 500 cc. dilute sulphuric acid containing 22 grams of 1:1 H₂SO₄-water solution. Several minutes after the last trace of the acid was added, the silica-sol had a pH of 5.00. After standing at room temperature for 24 hours at this pH, the silica-aquagel was broken in one liter of distilled water in a Waring blender and filtered. After four similar washings, the silica aquagel was substantially free of sodium sulphate.

The silica aquagel was then mixed with one liter of acetone and filtered. The partially acetone-wet silica aquagel was then placed in a fritted glass funnel and fresh acetone was cycled through it continuously by distilling through a packed column until the water contained in the aquagel was completely replaced by acetone. A portion of the silica-acetone gel containing 5.76 grams equivalent of solid silica was then dispersed in 94.24 grams of mineral oil having a viscosity of 300 SSU at 100° F. and a viscosity index of 95. After flashing off the acetone and passing the mixture through a colloid mill, the yield value of the grease was determined as previously described. It had a very satisfactory structure and consistency.

The grease of the foregoing example was tested for penetration in the standard ASTM penetrometer. It had an unworked penetration of 200 mm./10 and a worked penetration (after 60 strokes in the ASTM 1/4" hole plate grease worker) of 210 mm./10. In both cases the grease was a clear, transparent slightly amber gel in appearance.

In order to test water repellancy of various grease samples an apparatus was devised consisting of an elongated grease worker of 50 cc. capacity fitted with a single

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orifice of 1/32" diameter. For this test about 10 grams of the grease and 40 cc. of water are placed in the worker and forced back and forth through the orifice. This test ordinarily is carried out for 50 cycles, passing the grease and water 100 times through the orifice. Greases which do not liquefy or disintegrate during such tests are considered to be satisfactorily water repellant. The test showed no oil separation when 50% by weight of the alkyd resin based on the silica was used as water-proofing agent.

EXAMPLE II

One hundred seventy-five grams of sodium silicate having a specific gravity of 41° Baumé containing 28.7% SiO₂ and 8.9% Na₂O were diluted to 1000 cc. with distilled water while stirring; the sodium silicate was precipitated with 1000 cc. of dilute sulfuric acid containing 38.1 grams of 1:1 H₂SO₄-water solution. Several minutes after the last traces of acid were added the silica sol, before gelation occurred, had a pH of 5. After ageing for 2 days at room temperature, circa 25° C., the gel was divided into three portions of 660 grams each.

Fraction (1) (Blank)

Fraction (2) was broken up with an additional 250 cc. of distilled water, stirred vigorously to break lumps of gel and the pH adjusted to 2.90 with an additional small amount of 1:1 H₂SO₄-water solution.

Fraction (3) was broken up as above, but treated with a small volume of 10% NaOH in order to raise the pH to 7.1. The slurries were allowed to stand for an additional 24 hours at room temperature. Meanwhile, Fraction (1), and subsequently Fraction (2) and Fraction (3) were washed with distilled water until no turbidity due to sulfate ions was obtained from the filtrate using BaCl₂-HCl reagent.

The gels were then solvent exchanged with acetone until the normal water content of the aquagel was completely replaced with acetone as described in Example I.

A portion of the silica-acetone amorphous gel containing 5 grams equivalent of solid silica was added to 95 grams of mineral oil having a viscosity of 300 SSU at 100° F. and a viscosity index of 95. After the acetone was flashed off, the system was homogenized by passing through a colloid mill. The variation of yield value with pH is shown below:

pH	Penetration	Yield value, dynes/cm. ²
5.0 (Fraction 1)-----	276	16.3 × 10 ³
2.9 (Fraction 2)-----	302	11.3 × 10 ³
7.1 (Fraction 3)-----	286	13.2 × 10 ³

These data demonstrate that changing the pH during the conditioning stage from the critical pH 5 substantially alters the yield value of a gel precipitated at pH 5.

EXAMPLE III

One hundred seventy-five grams of sodium silicate having a specific gravity of 41° Baumé containing 28.7% SiO₂ and 8.9% Na₂O were diluted to 1 liter with distilled water. While stirring, the sodium silicate was precipitated with 1 liter of dilute sulfuric acid containing 37.0 grams of 1:1 H₂SO₄-water solution. Several minutes after the last traces of acid were added, the silica sol, before gelation occurred, had a pH of 6.55. After standing at room temperature for 24 hours, the gel was divided into portions of 475 grams each and broken up with 250 cc. of distilled water.

Fraction (1), the original sample, served as a blank.

Fraction (2) and Fraction (3), while stirring vigorously, were treated with a small volume of 1:1 H₂SO₄-water solution dropwise until a pH of 5.00 and a pH of 4.00 were reached, respectively. The suspensions were allowed to stand for 24 hours, then washed with distilled

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water until substantially free of sulfate ions as previously described. The gels were then solvent exchanged with acetone until the normal water content of the aquagel was replaced by acetone as described in Example I.

A portion of the silica-acetone amorphous gel containing 5 grams equivalent of solid silica was added to 95 grams of mineral oil having a viscosity of 300 SSU at 100° F. and a viscosity index of 95. After the acetone was flashed off, the silica-oil system was homogenized by passing through a colloid mill. After removal of entrapped air, the following penetration values were obtained:

pH:	Penetration
6.55 (Fraction 1) -----	339
5.00 (Fraction 2) -----	279
4.00 (Fraction 3) -----	294

EXAMPLE IV

A batch of 175 grams of sodium silicate was precipitated with 39.8 grams of 1:1 H₂SO₄-water solution and a pH of 2.50 was obtained. After standing until gelatin occurred, this ample was divided into four fractions of 475 grams each and broken up with 250 cc. of distilled water.

Fraction (1), the original sample, served as a blank.

Fraction (2), Fraction (3) and Fraction (4) were treated with varying quantities of 10% NaOH until the following pH's were reached respectively: 3.90, 5.00 and 7.00. The slurries were allowed to stand for 24 hours at room temperature and then were washed, solvent exchanged with acetone and formulated into greases as described above.

	Result	Penetration
pH:		
2.50 (Fraction 1)-----		364
2.90 (Fraction 2)-----		326
5.00 (Fraction 3)-----		272
7.00 (Fraction 4)-----		330

Examples III and IV demonstrate that a maximum yield value is obtained with silica base greases independent of the pH at which the silica is precipitated, provided that the silica is conditioned to pH 5 after precipitation.

A particular advantage of silica gel as a thickener in lieu of soap is its stability at very high temperatures. There are other advantages, however. Soaps used in conventional greases are much less compatible with lubricating oils of high viscosity index than with those of low viscosity index. Consequently it is almost a universal custom in the lubricating grease industry to use oils of low viscosity index. Obviously it would be preferable, for many uses, to employ oils of higher viscosity index. When silica gel is used as the thickener, the latter oils are just as compatible as those of lower viscosity index. Hence the manufacturer is not restricted in his choice of oils, but may use those which are most suitable without concern as to compatibility with the thickener. Thus, oils of 95 V. I. or higher may be used when desired.

Obviously the usual oil and grease additions such as antioxidants, mutual deactivators, viscosity index improvers, and the like may be added to lubricants of the present invention in usual proportions.

This application is a continuation-in-part of copending application Serial No. 259,306, filed November 30, 1951, now abandoned.

What is claimed is:

1. A process of preparing a silica gel base lubricating grease whereby an increased thickening effect is obtained per given amount of silica gel which comprises acidifying an aqueous sodium silicate solution to precipitate a silica aquagel, conditioning said silica aquagel at a pH of 5 for a time in the range of 1/2 to 48 hours, washing the gel so conditioned with an aqueous medium, exchanging the water in the gel so washed with a mutual solvent

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for water and lubricating oil, and thereafter replacing said mutual solvent with a lubricating oil, the proportion of said gel being sufficient to thicken said lubricating oil to a grease consistency.

2. The process of claim 1 wherein said proportion of gel is in the range of 4 to 25 wt. percent.

3. The process of claim 1 wherein said lubricating oil is a mineral lubricating oil.

4. A process for preparing a silica gel base lubricating grease whereby an increased thickening effect is obtained per given amount of silica gel which comprises acidifying an aqueous sodium silicate solution having a specific gravity of 1.185 with sulfuric acid, precipitating and forming thereby a silica aquagel, diluting said aquagel with water, conditioning said aquagel at a pH of 5 for a time in

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the range of ½ to 48 hours, washing the aquagel so conditioned with an aqueous medium, replacing the water in the aquagel so washed with acetone, and then replacing said acetone with a mineral lubricating oil, the amount of silica gel in the final composition being in the range of 4 to 25 wt. percent to obtain a grease structure.

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