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THICKENED LUBRICANTS

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This invention relates to an aerogel grease of good high temperature stability and water resistance.

While the word "grease" has usually been employed to describe an oil thickened with a soap, it is here used in a broader sense to include any thickened lubricant.

It is generally known that soap-base greases break down at high temperatures, of the order of 300 to 400° F. This breakdown is accompanied by an irreversible change in the grease structure, so that upon cooling the grease is observed to have lost its grease-like characteristics. The aerogel greases usually are far superior to the soap-base greases in stability at high temperatures as the following table shows:

TABLE I

Soap or Other Thickener	Appearance at 400° F.	Appearance After Cooling
Aluminum	Very gummy and soft.	Hard and lumpy.
Lithium	Liquid	Do.
Calcium	do	Hard—separation of soap.
Sodium	do	Solidifies hard mass.
Do	do	Soupy.
Sodium-Calcium	do	Complete separation of oil+soap.
Silica Aerogel	Unchanged	Unchanged except somewhat thinner.
Do	do	Unchanged, upon stirring, breaks down into a heavy liquid.

However, after heating at high temperatures some aerogel greases tend to lose consistency upon stirring. This is undesirable because there are many field applications where a grease is agitated or worked while subject to a high temperature and it is important that the grease retain its consistency under these conditions and subsequent thereto.

Accordingly, it is the object of the present invention to provide an aerogel grease having improved stability at high temperatures, particularly after working at high temperatures.

In accordance with the invention, these objects are accomplished by incorporating a water-miscible or water-soluble polyhydric alcohol in an aerogel grease composition comprising a lubricating oil thickened with a non-abrasive, inorganic thickening or gelling agent, and particularly finely divided silica, a silica aerogel being illustrative. Thickened lubricants so prepared have excellent temperature susceptibility properties.

The grease is also rendered more or less resistant to deterioration by water by incorporating a hydrophobic cationic surface-active water stabilizer therein in the form of Amine "O," 1-β-hydroxyethyl 2-heptadecenyl imidazoline.

The presence of the polyhydric alcohol in an amount to obtain improved high temperature stability does not markedly affect the consistency of the thickened lubricant, i. e., the amount of the inorganic gelling agent to impart a given consistency to the thickened lubricant is not materially modified. Furthermore, the inclusion of

the polyhydric alcohol will not effect a change in the consistency of the thickened lubricant upon storage. The polyhydric alcohol likewise does not affect the water-resistance imparted to the grease by the hydrophobic cationic surface-active water stabilizing agent.

Due to the inorganic nature of the gelling agent, the thickened lubricant has excellent storage stability. This is to be contrasted with the heat susceptibility and deterioration of fatty materials in soap-base greases.

The preparation of the grease is simple and readily adaptable to continuous operation, as contrasted with the involved grease-making techniques which are often considered in the industry as an art.

The oil stock used in making the thickened lubricant may be widely varied, as contrasted with present grease-making requirements in which the oil in many cases must meet certain critical specifications.

In addition, the avoidance of the use of soap permits the manufacturer to be independent of the fat supply, which is important in periods in which fats and soaps are scarce and, many times, of pronounced non-uniformity.

The inorganic gelling agent to be used in making the thickened lubricant in accordance with this invention may be any inorganic material which forms a gel with a lubricating oil and which is so finely divided as to be non-abrasive. The preferred materials are the aerogels, which may be formed from any material not incompatible with oil, such as silica, alumina, and other gel-forming metal oxides.

A series of silica aerogels which can be used as the inorganic gelling agent of the invention are marketed under the trade name "Santocel."

Santocel C is prepared from a sodium silicate solution in the following way: The solution is neutralized with sulfuric acid and then allowed to stand until the mixture sets to form a hydrogel. The by-product sodium sulfate is washed out by the repeated washings with water. The continuous water phase in this hydrogel is then replaced by continued washing with alcohol until an alcogel is formed. In order to remove the liquid phase without a collapse of the gel structure, the alcogel is placed in an autoclave which is then heated above the critical temperature of the alcohol and the pressure is allowed to increase to a point above the critical pressure of the alcohol. The vent valve is then opened and the alcohol allowed to escape. Under these conditions, the silica gel structure remains practically undisturbed and the liquid phase of the gel is replaced with air. The material is then reduced in particle size by blowing it through a series of pipes containing sharp bends with jets of compressed air. Santocel C has a secondary agglomerate particle size of about 3 to 5 microns.

Santocel A is prepared as set forth for Santocel C up to the point of removal of the product from the autoclave. This material is run through a continuous heating chamber where it is heated for ½ hour to a temperature of about 1500° F. to eliminate the last traces of volatile material. It is then broken down in a reductionizer or micronizer to a particle size of about 1/16 inch in diameter. The solids content of the original hydrogel used in preparing Santocel C is approximately 25% higher than that of Santocel A.

AR is a modification of A, differing only in that the material is reductionized to about the same particle size as C, approximately 1 to 6 microns in diameter.

ARD is a modification of AR, differing only in that ARD is densified by extracting air under vacuum, and therefore has a smaller volume than AR.

AX is an A which has not been devolatilized.

CDv is a C which has been devolatilized as set forth for A. CDv is reductionized before being devolatilized.

CDvR differs slightly from CDv in that the CDvR has been devolatilized just after heating in the autoclave and then reductionized. It differs from CDv in that the latter is reductionized before being devolatilized.

The primary differences between the A's and the C's are as follows:

(1) The C's are prepared from a sodium silicate solution containing 25% more silica than the A's. Therefore, in general the A's are lighter and composed of smaller particles than the C's.

(2) The A's have undergone a devolatilization step in their preparation.

The following are the bulk densities of preferred silica aerogels:

	Density, grams per ml.
AR	0.029
ARD	0.056 to 0.064
C	0.082

In general, AR and ARD show superior gelling ability and the A's in general are better than the C's. Silica aerogels which have been devolatilized generally have a higher gelling efficiency than the undevolatilized aerogels.

Other types of inorganic gelling agents which may be used include a Fumed Silica. It is finely divided and appears very much like an aerogel. It is made by a combustion or vaporization process, as a source of white "carbon black" for the rubber industry. The particles are several microns in size and porous in nature.

Another material is "Linde Silica Flour." It is very similar in physical appearance to the silica aerogel. The particle size of the silica is purported to be 0.01 to 0.05 micron and to be manufactured by burning silicon tetrachloride and collecting the combustion product on cool plates analogous to the production of carbon black. The particles are thought to be aggregates or clusters of particles rather than of sponge-like character.

Still another inorganic gelling agent known is "Ludox" silica which is known as a silica sol, and silica derivatives thereof. It has a particle size of the order of 0.01 to 0.03 micron.

In preparing thickened lubricants it is necessary to remove the water from the sol and replace it with an oil. This is possible by formulating the lubricant and removing the water by flash distillation or azeotropic distillation.

No attempt is made to enumerate all of the inorganic gelling agents which will be suitable, nor to present examples of all of them since the novel aspects of the invention reside in imparting high temperature stability to the lubricant rather than the use of novel gelling agents, per se.

The lubricating oil to be used in the process may have any lubricating viscosity. It may be raw oil, acid-refined, or solvent-refined, as required for the particular lubricating need.

The nature of the base oil has been found to make little difference in the relative consistencies of the thickened lubricants and conventionally (acid) refined oils produce slightly thicker lubricants than solvent-refined oils. Excellent working stability is obtained regardless of the type of the base oil. An increase in the viscosity of the base oil, as might be expected, brings increased viscosity to the thickened lubricant and minimizes bleeding. The change is relatively small and fairly linear. The viscosity of the oil does not affect the working stability of the lubricant.

The relative proportions of the inorganic gelling agent and the oil will vary somewhat depending upon the desired body in the thickened lubricant, the gelling ability of the inorganic gelling agent and the viscosity of the oil used. It has been noted, for instance, that with the Linde Silica Flour, the lubricants are somewhat harder, i. e., have a lower penetration than lubricants containing the same weight of Santocel. Lubricants made with low viscosity oils require a somewhat larger amount of the inorganic gelling agent to give a lubricant of the same

penetration. The thickened lubricant may vary in consistency from the consistency of a slightly thickened oil to a solid or semi-solid of grease-like consistency. In general, the amount of the inorganic gelling agent falls within the range of 5 to 20%, and in most cases would fall within the range of 7 to 12%.

The amount of the inorganic gelling agent, as might be expected, affects the consistency of the thickened lubricant in that an increase in its concentration brings a corresponding increase in consistency. The range is fairly linear and the amount of the gelling agent can be selected with relation to the consistency desired in view of the information in the following examples. While the difference is slight, the lubricants made with lower concentrations of gelling agent possess better working stability, while lubricants with larger amounts of gelling agent show slightly improved temperature susceptibility characteristics. The bleeding tendencies are decreased by increasing concentrations of the gelling agent.

In general, the properties of the thickened lubricants are remarkably independent of the composition variables and are not critical. The relative concentration of the gelling agent effects the most significant alteration, particularly with regard to the final consistency of the product. This permits the manufacture of thickened lubricants having a wide variety of consistencies.

A wide variety of water-miscible or water-soluble polyhydric alcohols can be employed in accordance with the invention to improve the high temperature stability of aerogel-base greases. Alcohols which are water-immiscible, i. e., are oleaginous in character, cannot be used, because they are hydrophobic. The alcohol must be hydrophilic, i. e., not oleaginous, for reasons which will be apparent from the theory of the action of the alcohol, set forth later.

Provided the polyhydric alcohol is hydrophilic, it may have from 2 to 8 carbon atoms and must contain at least two hydroxyl groups. It may contain as many as four hydroxyl groups, those having two and three hydroxyl groups being most available and therefore being preferred. Other polar groups, such as one or more ether or amino groups, may also be present. The two- and three-hydroxyl polyhydric alcohols are employed in the examples because of their low cost and availability. The polyhydric alcohol may contain other inert substituents, such as halogen, which have been found not to reduce the activity of the compounds. Exemplifying compounds within the scope of the invention are ethylene glycol, diethylene glycol, glycerol α-monomethyl ether, glycerol, dulcitol, erythritol, pentaerythritol, mannitol, sorbitol, glycerol chlorohydrin, 1-methyl glycerol, trimethylene glycol, butanediol-2,3, pinacol, propylene glycol, butantriol, and polymeric dihydroxy (glycol) polyethers derived by condensation of ethylene oxide or propylene oxide, containing from two to ten oxide units.

The polyhydric alcohol need not be oil-soluble, but should be oil-dispersible. It should have a minimum boiling point of about 150° C. since its primary purpose is to stabilize the grease at high temperatures.

The polyhydric alcohol is incorporated in the aerogel-base grease in an amount to impart high temperature stability. Ordinarily a concentration of polyhydric alcohol ranging from 0.25 to about 1% by weight of the aerogel-base grease gives satisfactory results. There is no reason to employ more polyhydric alcohol than is necessary, but excessive amounts do no harm, and amounts up to 5% or even higher have been successfully employed.

The amount of hydrophobic cationic surface-active agent to impart water-resistance to the aerogel grease in the form of 1-β-hydroxylethyl-2-heptadecenyl imidazoline will vary from 0.1% to about 5%, depending upon the water-stabilizing effect desired, the amount and nature of the gelling agent used, and the economics involved.

In some instances, the composition containing the polyhydric alcohol high temperature stabilizer may not dis-

play a long life when used continuously at high temperatures. A breakdown in high temperature stability at high temperatures if it appears is due to a decomposition, through oxidation, of the polyhydric alcohol stabilizer of the invention. In such circumstances, it is desirable to include in the composition an antioxidant for the polyhydric alcohol stabilizer. Conventional amine antioxidants which are more readily oxidized than the polyhydric alcohols of the invention can be employed for this purpose. Tetramethyldiaminodiphenylmethane is a particularly desirable antioxidant for the polyhydric alcohols of the invention. Only small quantities are required, and ordinarily an amount ranging from 0.1 to about 1% by weight of the aerogel base grease is ample. There is no reason to employ more antioxidant than is necessary to produce the desired effect, but excessive amounts do no harm and amounts up to 5% can be used, if desired.

The composition is made simply by mixing the inorganic gelling agent, the oil, a polyhydric alcohol and the cationic water stabilizer in any order or manner.

In one embodiment, the polyhydric alcohol and the cationic water stabilizer, can be incorporated with the inorganic gelling agent either by mixing directly or, if desired, by dissolving them in a solvent, mixing the solution with the gelling agent and evaporating the solvent.

Generally, the polyhydric alcohol and cationic water stabilizer are dispersed in the oil and the inorganic gelling agent added thereto and mixed therewith. Any simple mixing technique can be employed and, if desired, the mixture can be homogenized in a colloid mill, although this is not necessary.

The composition of the invention is not limited to the oil, gelling agent, cationic water stabilizer, and polyhydric alcohol. Any of the materials conventionally added to lubricants and greases may be included. The expression "consisting essentially of" as used herein is intended to refer to the components which are essential to the composition, namely, the oil, the inorganic gelling agent and the polyhydric alcohol, and the expression does not exclude other components from the composition which do not render it unsuitable for lubrication, such materials being, for instance, the cationic water stabilizer, high polymers to modify viscosity or viscosity index, materials to impart tackiness, lubricating solids such as graphite, antioxidant additives, corrosion inhibitors of various types, sulfur, additives, to render the lubricant suitable for use in gears, for cutting, grinding, etc.

The following examples illustrated preferred embodiments of the invention. In the examples, water-resistant thickened lubricants are prepared to show the absence of an effect of the polyhydric alcohol on the water resistance of the grease.

Examples 1 to 6

The base grease used in Examples 2 to 6 was a commercial water-resistant aerogel grease of the following formulation:

	Percent
Santocel C	10.0
Amine "O" [1]	1.0
Paratac [2]	2.0
Paraflow [3]	0.5
Methane base	0.5
Red dye	0.02
Solvent-extracted neutral oil (250 SSU at 210° F.)	85.98

[1] (1-β-hydroxyethyl-2-heptadecenyl-imidazoline).
[2] An isobutylene polymer sold by the Enjay Company, Inc. and commonly used in compounding greases.
[3] A Friedel-Crafts reaction product, useful as a pour point depressant and sold by the Enjay Company, Inc.

This base grease is referred to hereafter as the Aerogel W. R. Base Formula (Example 2). One of the polyhydric alcohols listed in the following table, in the amount stated in the table, was incorporated in this grease by blending it with the oil, and then mixing in the other components of the grease (Examples 3 to 6). The resulting grease compositions were tested for high temperature stability by measurement of micropenetrations before and after heating to 400° F. The results obtained were compared with the results for the base grease formulation above, and also with non-water-resistant aerogel grease containing 10% Santocel C and 90% No. 250 solvent-extracted neutral oil which did not contain Amine "O" (Example 1). This formula is referred to hereinafter as the Aerogel Base Formula.

The grease is prepared for the determination of high temperature stability by placing approximately 100 cc. of grease in a 150 ml. beaker. The beakers are heated to the test temperature by placing them in an aluminum block furnace. This furnace consisted of a solid block of aluminum heated by internal electrical heaters. Six holes, each large enough to accommodate a 150 cc. beaker, were drilled in the top of the block, together with a thermocouple, so that a measure of the temperature of the block could be obtained. In this manner, six beakers could be heated simultaneously. The beakers containing the grease were placed in the aluminum furnace and held there until the equilibrium temperature of the grease was 400° F. The samples were stirred at five-minute intervals during heating. After this the grease was allowed to cool to room temperature overnight and then was stirred vigorously with a spatula.

Kaufman micropenetration measurements were obtained on the grease before and after the test procedure (Industrial and Engineering Chemistry, Analytical Edition, volume 11, page 108, 1939), and the results are expressed in the table below as percent increase in penetration.

The following results were obtained on the aerogel-base greases tested, containing the polyhydric alcohols listed in the amounts stated:

TABLE II

Ex. No.	Additive	B. P. (° C.)	Percent Added	Kaufman Micropenetrations		
				Original	After Block	Percent Increase
1	None (Aerogel Base Formula).			122	243	100.0
2	None (Aerogel W. R. Base Formula).			123	Soup	
3	Glycerine	194.4	0.5	115	208	80.8
4	do	194.4	1.0	122	129	7.0
5	Ethylene Glycol	197.4	0.5	84	125	48.8
6	do	197.4	1.0	121	120	−0.8

The results show that an aerogel-base grease which does not contain Amine "O" in order to improve its water stability (Example 1) has a high temperature stability which while superior to soap types leaves much to be desired. When Amine "O" and other components are added to this base grease (Example 2) the stability at 400° F. is destroyed and the grease liquefies, and remains liquid after cooling. Through addition of glycerine and ethylene glycol in amounts ranging from 0.5 to 1%, the effect of the Amine "O" is completely overcome and the aerogel grease possesses a better high temperature stability than the original Aerogel Base Formula.

Examples 7 to 12

Aerogel greases were prepared by blending a polyhydric alcohol into the base oil and subsequently mixing this composition with Santocel and the other ingredients

to prepare the grease. These greases had the following composition:

Santocel AR or ARD	7.5%.
Amine "O" [1]	1.0%.
Paratac [2]	2.0%.
Paraflow [3]	0.5%.
Methane base	0.5%.
Red dye	0.02%.
Solvent-extracted neutral oil (250 SSU at 210° F.)	88.48%.
Polyhydric alcohol	0.5 to 1% by weight of the above.

[1] (1-heptadecenyl-2-β-hydroxyethyl-imidazoline.)
[2] An isobutylene polymer sold by the Enjay Company, Inc. and commonly used in compounding greases.
[3] A Friedel-Crafts reaction product, useful as a pour point depressant and sold by the Enjay Company, Inc.

These greases were subjected to the block test and the micropenetrations of the greases measured before and after heating at 400° F., the SOHIO micropenetration technique was employed. This required a very small sample of grease and a miniature cone and cup. The microcone employed was specially built, and its dimensions are compared in Table III with those of the standard ASTM cone, ASTM Designation 217–48, described on page 143 of the November, 1948 edition of D–2 Specifications for Petroleum Products. The cone and grease cup employed in obtaining the following test results required a minimum sample size of 35 ml.

TABLE III.—MICROCONE DIMENSIONS

	ASTM		Sohio	
	Cone	Cup	Cone	Cup
Diameter, mm	65	78	20	43
Height, mm	45		17	
Depth, mm		65		24.5
Surface, sq. mm	7,070	4,778	620	1,470
Volume, cc		290		35.6
Cone, diam./cup surface		0.0136		0.0136
Cone, height/cup depth		0.693		0.693
Wt. of assembly, gms	150		13 (calc'd)	
Wt. of assembly/sq. mm. cone surface		0.021		0.021

The following results were obtained:

TABLE IV

Ex. No.	Santocel	Additive (Percent Used)	Sohio Micropenetrations		
			Original	After Block	Percent Increase
7	"AR"	0.5% Glycerol	99	122 (124) (87)	23 (25) (−12)
8	"AR"	1.0% Glycerol	94	112	19.2
9	"AR"	0.5% Ethylene Glycol	90	125 (117)	39 (30)
10	"AR"	1.0% Ethylene Glycol	110	126 (110)	14.5 0
11	"ARD"	None	120	188	56.5
12	"ARD"	1.0% Glycerol	125	150	20

It will be noted that the grease containing glycerol and Santocel ARD (Example 12) has a better high temperature stability than the corresponding grease (Example 11) which did not contain glycerol. The high temperature stability of all of the greases containing a polyhydric alcohol was good.

Examples 13 to 16

An aerogel water-resistant grease of the following formula was made up:

	A	B
	Percent	Percent
Santocel ARD	8.0	8.0
Amine "O" [1]	0.8	0.8
Paratac [2]	1.0	1.0
Paraflow [3]	0.5	0.5
Methane Base	0.5	0.5
Bright Stock (78 SUS at 210° F.)	89.2	88.2
Polyhydric alcohol		1.0

[1] (1-β-hydroxyethyl-2-heptadecenyl-imidazoline.)
[2] An isobutylene polymer sold by the Enjay Company, Inc. and commonly used in compounding greases.
[3] A Friedel-Crafts reaction product, useful as a pour point depressant and sold by the Enjay Company, Inc.

Formula A is called the "Aerogel Water-Resistant Base Formula" in the table which follows. Formula B is the water-resistant formula modified by addition of 1% polyhydric alcohol in accordance with the invention (and reducing the bright stock accordingly) in order to prepare an aerogel grease which is not only water-resistant but also stable at high temperatures.

In preparing these greases, the Amine "O" and the polyhydric alcohol to be tested were dissolved in a stock solution of the base oil containing the other components. The Santocel was added to this solution and completely wetted by stirring. The grease was prepared at 95° F. by mixing for the time indicated in the following table, the time being varied so as to approximate the final penetration of the aerogel water-resistant base formula. If this time is the same as or longer and/or if the original penetration is the same as or less than that of the base formula, it is evident that the polyhydric alcohol has either no or a beneficial effect on yield.

The penetration of the grease was taken before and after heating in the block described in Example 1, in accordance with the Shell Microcone Penetration Test (Institute Spokesman (NLGI) volume VI, Number 12, page 1, 1943).

TABLE V

Ex. No.	Additive	Mixing Time, Minutes	Immed. Shell Pen.	High Temperature Stability			Water Stability
				No. Cycles	Shell Penetration		
					Initial	Final	
13	Aerogel Base Formula.*	40	159	5	157	202	None.
14	Aerogel W. R. Base Formula.	30	159	4	171	267	Good.
15	Ethylene Glycol.	20	159	4	167	201	Do.
16	Glycerol	30	165	5	168	205	Do.

*Same formula as Example 1.

The results show that incorporating the Amine "O" in the aerogel base formula appreciably increases the penetration and thus reduces the high temperature stability. This effect of the Amine "O" is, however, overcome by the polyhydric alcohols added to the aerogel water-resistant base formula.

Examples 17 to 26

Aerogel greases were prepared as set forth in Formula A of Examples 13 to 16, employing from 0.5 to 5% glycerol and from 0.5 to 2% ethylene glycol as the polyhydric alcohol. In formulating these greases, the base oil content shown in Formula A of Examples 13 to 16 was reduced by the amount of polyhydric alcohol added.

These greases were tested in accordance with the Shell Microcone Penetration Test before and after heating in

the aluminum block to 400° F. The following results were obtained:

TABLE VI

Ex. No.	Additive	Percent	Mixing Time, Minutes	High Temperature Stability			Water Stability
				No. Cycles	Shell Penetration		
					Initial	Final	
17	Aerogel Base Formula.*	------	40	5	157	202	None.
18	Aerogel W. R. Base Formula.	------	30	4	171	267	Good.
19	Glycerol	0.5	30	3	170	215	Do.
20	do	1.0	30	5	168	205	Do.
21	do	2.0	15	7	164	189	Do.
22	do	3.0	25	7	149	194	
23	do	5.0	25	7	166	186	
24	Ethylene Glycol.	0.5	30	3	171	214	Do.
25	do	1.0	20	4	167	201	Do.
26	do	2.0	30	6	127	131	Do.

*Same as formula in Example 1.

These data show that increasing the amount of glycerol beyond 2% has no appreciable effect upon the high temperature stability, although it does no harm. In each case the ethylene glycol and glycerol overcome the effect of the Amine "O" on the high temperature stability of the aerogel grease, and in Examples 21, 22, 23 and 26 the high temperature stability is improved, compared to the original Base Formula (Example 17).

Examples 27 to 37

A large number of aerogel greases were prepared as follows: A fixed quantity of oil (78 SSU at 210° F. solvent-extracted bright stock) was weighed out into a 400 ml. beaker. 0.8% Amine "O" was added, and 1% of the alcohol additive was incorporated in the base oil. The oil mix, was heated to 130° F. while being mixed with a Lightnin' stirrer, and 8% Santocel ARD was mixed in with hand stirring. The resulting grease was allowed to stand overnight. An original penetration was then obtained using the Shell Microcone Penetration Test and the grease was then subjected to the block test. Grease samples exhibiting some degree of high temperature stability were cycled three or four times. Each sample was tested also for water stability and given a visual rating for consistency while at 400° F.

The alcohol additives tested included monohydric and polyhydric alcohols. Ethylene glycol and glycerol were included to evaluate the results obtained. Data from these tests are given in the following table:

TABLE VII

Ex. No.	Additive	"Block" Test Shell Penetrations					Water Stability
		Orig.	1	2	3	4	
	Aerogel W. R. Base Formula.	139	200	226	-----	-----	Good.
	Monohydric Alcohols						
27	2-Ethylhexanol	128	290	-----	-----	-----	Do.
28	Lauryl alcohol	135	298	-----	-----	-----	Do.
29	5-Ethylnonanol-2	156	299	-----	-----	-----	Do.
30	Heptadecanol	128	269	-----	-----	-----	Do.
31	Cetyl alcohol	126	298	-----	-----	-----	Do.
	Polyhydric Alcohols						
32	Diethylene glycol	135	178	180	195	-----	Do.
33	Triethylene glycol	127	179	186	190	195	Fair.
34	Ethylene glycol	114	139	165	184	184	Good.
35	Pentanediol-1,5	146	186	197	-----	-----	Do.
36	Glycerol	130	147	158	168	173	Do.
37	Trimethylol propane	154	194	194	207	-----	Do.

Without exception, the five monohydric alcohols tested were unsatisfactory under high temperature conditions. The initial penetrations for ethylene glycol, diethylene glycol, triethylene glycol and glycerol are lower than that of the control grease, and indicate that these compounds have no deleterious effect on grease yield. All of the polyhydric alcohols tested exert a stabilizing effect at high temperatures.

Examples 38 and 39

Additional greases were prepared from a blend of bright stocks to produce an oil of approximately 2000 SSU at 100° F. High temperature instability of aerogel greases is aggravated when a heavy base oil is used, and thus this provides a severe test of the high temperature stabilizing effect of the additives of the invention.

The test greases were prepared as outlined in the preceding Examples 27 to 37. The results are given in the following table:

TABLE VIII

Ex. No.	Additive	"Block" Test, Shell Penetrations				Water Stability
		Orig.	1	2	3	
38	Glycerol	162	180	186	193	Good.
39	Ethylene glycol	158	165	172	186	Do.

It is evident that the polyhydric alcohols are capable of increasing high temperature stability, even when a heavy base oil is employed.

Examples 40 to 44

	A	B
	Percent	*Percent*
Santocel C	10.0	10.0
Amine "O" [1]	1.0	1.0
Paratac [2]	2.0	2.0
Paraflow [3]	0.5	0.5
Methane base (Calco MB) [4]	0.5	0.5
Red dye	0.02	0.02
Glycol	------	0.5 to 1.0
Solvent-extracted neutral oil (250 SSU at 100° F.)	85.98	84.98 to 85.98

[1] 1-β-hydroxyethyl-2-heptadecenyl-imidazoline.
[2] An isobutylene polymer sold by the Enjay Company, Inc. and commonly used in compounding greases.
[3] A Friedel-Crafts reaction product, useful as a pour point depressant and sold by the Enjay Company, Inc.
[4] Tetramethyldiaminodiphenylmethane.

The base grease used in Examples 41 to 44 was the commercial water-resistant aerogel grease of Formula A. This base grease is referred to hereafter as the Aerogel W. R. Base Formula (Example 41). To prepare Examples 42 to 44, one of the glycols listed in the following table, in the amount stated in the table, was incorporated in this grease by blending it with the oil, and then mixing in the other components of the grease. The resulting grease compositions were tested for high temperature stability by measurement of micropenetrations before and after heating to 400° F. as in Examples 1 to 6. The results obtained were compared with the results for the W. R. base grease formulation above, and also with non-water-resistant aerogel grease containing 10% Santocel C and 90% No. 250 solvent-extracted neutral oil which did not contain Amine "O" (Example 40). This latter formula is referred to hereinafter as the Aerogel Base Formula.

TABLE IX

Ex. No.	Additive	B. P. (° C.)	Percent Added	Kaufman Micro-penetrations		
				Original	After Block	Percent Increase
40	None (Aerogel Base Formula).			122	243	100.0
41	None (Aerogel W. R. Base Formula).			123	Soup	
42	Diethylene Glycol.	245	0.5	108	185	71.2
43	do	245	1.0	121	209	72.6
44	Polyethylene glycol 900.		1.0	151	369	100+

The results show that an aerogel-base grease which does not contain Amine "O" in order to improve its water stability (Example 40) has a high temperature stability which, while superior to soap types, leaves much to be desired. When Amine "O" and other components are added to this base grease (Example 41) the stability at 400° F. is destroyed and the grease liquefies, and remains liquid after cooling. Through addition of diethylene glycol in amounts ranging from 0.5 to 1%, the effect of the Amine "O" is completely overcome and the aerogel grease possesses a better high temperature stability than the original Aerogel Base Formula. Polyethylene glycol 900 also overcomes the effect of the Amine "O" on high temperature stability.

Example 45

Aerogel water-resistant greases of the following formulae were made up:

	A	Example 45
	Percent	*Percent*
Santocel ARD	8.0	8.0
Amine "O" [1]	0.8	0.8
Paratac [2]	1.0	1.0
Paraflow [3]	0.5	0.5
Methane base (Calco MB) [4]	0.5	0.5
Bright stock (78 SSU at 210° F.)	89.2	88.2
Diethylene glycol		1.0

[1] 1-β-hydroxyethyl-2-heptadecenyl-imidazoline.
[2] An isobutylene polymer sold by the Enjay Company, Inc. and commonly used in compounding greases.
[3] A Friedel-Crafts reaction product, useful as a pour point depressant and sold by the Enjay Company, Inc.
[4] Tetramethyldiaminodiphenylmethane.

Example 45 is the water-resistant Formula A modified by addition of 1% diethylene glycol in accordance with the invention (and reducing the bright stock accordingly) in order to prepare an aerogel grease which is not only water-resistant but also stable at high temperatures.

In preparing these greases, the Amine "O" and the glycol to be tested were dissolved in a stock solution of the base oil containing the other components. The Santocel was added to this solution and completely wetted by stirring. The grease was prepared at 95° F. by mixing for the time indicated in the following table, the time being varied so as to approximate the final penetration of the aerogel water-resistant base formula. If this time is the same as or longer and/or if the original penetration is the same as or less than that of the base formula, it is evident that the ether has either no or a beneficial effect on yield. The penetration of the grease was taken before and after heating in the block described in accordance with the Shell Microcone Penetration Test (Institute Spokesman (NLGI), VI, 12, page 1 (1943)).

TABLE X

Ex. No.	Additive	Mixing Time, Minutes	Immed. Shell Pen.	High Temperature Stability			Water Stability
				No. Cycles	Shell Penetration		
					Initial	Final	
	Formula A	30	159	4	171	267	Good.
		30		4	171	267	Do.
45	Diethylene glycol.	20	168	4	173	220	Do.

The results show that the Amine "O" in Formula A appreciably increases the penetration and thus reduces the high temperature stability. This effect of the Amine "O" is, however, overcome by the glycol (Example 45).

Examples 46 to 48

A number of aerogel greases were prepared of the following formulations:

	A	B
	Percent	*Percent*
Santocel ARD	8.0	8.0
Amine "O" [1]	0.8	0.8
Paratac [2]	1.0	1.0
Paraflow [3]	0.5	0.5
Methane base (Calco MB) [4]	0.5	0.5
Bright stock (78 SSU at 210° F.)	89.2	88.2
Glycol		1.0

[1] 1-β-hydroxyethyl-2-heptadecenylimidazoline.
[2] An isobutylene polymer sold by the Enjay Company, Inc. and commonly used in compounding greases.
[3] A Friedel-Crafts reaction product, useful as a pour point depressant and sold by the Enjay Company, Inc.
[4] Tetramethyldiaminodiphenylmethane.

Formula A is Example 46 in the table which follows. Formula B is the water-resistant formula of Formula A, modified by addition of 1% glycol in accordance with the invention, reducing the bright stock accordingly, in order to prepare an aerogel grease which is not only water-resistant but also stable at high temperatures.

In preparing these greases, the Amino "O" and the glycol to be tested were dissolved in a stock solution of the base oil containing the other components. The Santocel was added to the solution and completely wetted by stirring. The grease was prepared at 95° F. by mixing for approximately 20 to 30 minutes, the time being adjusted to approximate the original penetration of Formula A.

The penetration of the grease was taken before and after heating in the block described in Example 1 in accordance with the Shell Micropenetration Test. After the data had been taken for four successive cycles, the average change in penetration per cycle was noted. The water stability of the greases was also determined. The following results were obtained:

TABLE XI

Ex. No.	Additive	Percent	"Block" test, Shell Pens.					Pen. Cycle	Water Stability
			Orig.	1st	2nd	3rd	4th		
46	Control with Amine "O"		139	200	226			43.5	Good.
47	Diethylene glycol	1.0	135	178	180	195	197	15	Do.
48	Polyethylene glycol 400	1.0	159	198				39	Do.

The results show that incorporating the glycol in the control grease (containing Amine "O" but no glycol) appreciably increases high temperature stability, as evidenced by a reduction in penetration increase. This is best observable in the change in penetration per cycle noted in the above table. Diethylene glycol is most effective, but even the polyethylene glycol 400 gives a significant improvement in high temperature stability.

In the examples, the high temperature stability of the aerogel greases is tested by heating the greases to 400° F. This is an extreme test, inasmuch as the highest temperature to which a grease is subjected under even extraordinary conditions of use is about 300° F., but it was adopted as a suitable test standard by which to measure the high temperature stability of the greases because a grease stable at 400° F. will definitely have the stability necessary to withstand heating to 300° F. It will be understood that for normal purposes an aerogel grease need not be stable at temperatures above about 300° F., and that the greases of the invention at least meet this requirement. Where the term "high temperature stability" is used, it will be understood to mean that the aerogel grease is stable at at least 300° F.

The following hypothesis is given as a partial explanation of the reason to which is attributed the action of the polyhydric alcohol in improving the high temperature resistance of aerogel grease, but the invention is not to be bound thereby.

Silica aerogels are known to be in the form of an extremely finely divided material and it is thought that it is capable of forming a colloidal structure in the oil vehicle employed in an aerogel grease. Mixing or stirring in formulating the grease serves to disperse the secondary aerogel agglomerates throughout the body of the oil. The aerogel occupies a greater volume than the liquid oil vehicle, and because of this it is probable that the colloidal structure is aided somewhat by a close packing of the solid silica gel particles, perhaps with mechanical interlocking. It is thought that the basis of the structure is a tying together of the various silica aerogel particles by hydrogen bonding between hydroxyl groups which remain attached to individual silicon atoms in the silica gel molecule.

In setting up the colloidal grease structure, it is postulated that the distances between adjacent hydroxyl groups on different particles of silica aerogel may be too great in some circumstances to form a binding, attractive force between particles. In this event, water, which is always present in the aerogel structure, serves to bridge the gap between adjacent particles through hydrogen bonding between the compound and the hydroxyl groups on the adjacent silica aerogel particles. Thus the water in effect aids in setting up the colloidal grease structure, and may also link it together, at least in part.

When the grease under static conditions is submitted to temperatures high enough to volatilize the water no apparent effect is noticed at first, for there is no force to disarrange the structure. Consequently, penetration vs. temperature curves indicate that aerogel greases have excellent high temperature performance with a very low increase in consistency as the temperature is increased. However, when this static state is disturbed by stirring, the structure can and does collapse, due to the absence of the water which has been volatilized and which formerly served as the connecting links between adjoining silica particles. In consequence, the structure passes from a gel state to a colloidal sol state. This explains why the transformation of the heated aerogel grease from a grease-like condition to a soupy condition occurs only after stirring and why stirring thus brings about an apparently irreversible gel-to-sol transformation. This transformation may be reversed to some extent by adding water to the soupy grease, tending to substantiate this hypothesis, but it is not possible to return the grease to its original condition.

Thus, on the basis of this hypothesis, incorporation in the grease, in accordance with the invention, of a polyhydric alcohol which is not volatile at the temperatures to which the grease may be subjected leads to a partial or complete displacement of water in the aerogel by polyhydric alcohol, possibly before and in any event at the time water is volatilized at an elevated temperature. The low volatility of the polyhydric alcohol prevents its loss during heating and thus prevents destruction of the colloidal grease structure when the aerogel grease is stirred after it has been heated to high temperatures. It is also apparent from this that a hydrophobic polyhydric alcohol which is immiscible with water could not function in this way because it could not act as a substitute for water in the hydrophilic gel structure.

This application is a continuation-in-part of our applications Serial Nos. 119,752, filed October 5, 1949, 253,984, filed October 30, 1951, and 254,633, filed November 2, 1951, all three now abandoned.

We claim:

1. A water-resistant thickened lubricant of good temperature susceptibility properties, consisting essentially of a mineral lubricating oil of lubricating viscosity, an inorganic gelling agent imparting a grease-like consistency to the oil upon addition thereto, 1-β-hydroxyethyl-2-heptadecenyl imidazoline imparting stability against deterioration by water, and a water-soluble polyhydric alcohol imparting high temperature stability.

2. A water-resistant thickened lubricant of good temperature susceptibility properties in accordance with claim 1 wherein the polyhydric alcohol is glycerol.

3. A water-resistant thickened lubricant of good temperature susceptibility properties in accordance with claim 1 wherein the polyhydric alcohol is ethylene glycol.

4. A water-resistant thickened lubricant of good temperature susceptibility properties in accordance with claim 1 wherein the polyhydric alcohol is diethylene glycol.

5. A water-resistant thickened lubricant of good temperature susceptibility properties in accordance with claim 1 wherein the polyhydric alcohol is triethylene glycol.

6. A water-resistant thickened lubricant of good temperature susceptibility properties in accordance with claim 1 wherein the polyhydric alcohol is trimethylol propane.

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