

2,828,260

INORGANIC GEL-THICKENED LUBRICANT OF GOOD TEMPERATURE SUSCEPTIBILITY AND DYNAMIC WATER STABILITY CHARACTERISTICS

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This invention relates to an aerogel-thickened lubricant of good temperature susceptibility and water resistance characteristics.

Mineral lubricating oils thickened with a calcium or sodium soap are the most commonly used lubricants. The so-called soda base greases have relatively good stability at reasonably elevated temperatures but deteriorate readily in the presence of water, presumably due to the high solubility of the soda base soap in water. Calcium soap greases have better resistance to water but tend to lose their consistency or thin out at

elevated temperatures. Both types of soap base greases break down at temperatures of the order of 300 to 400° F. and this breakdown is accompanied by an irreversible change in the grease structure so that on cooling the grease is found to have lost its greaselike 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

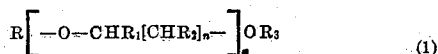
Soap or other thickener	Appearance at 400° F.	Appearance after cooling
Aluminum.....	Very gummy and soft.	Hard and lumpy.
Lithium.....	Liquid.....	Do.
Calcium.....	do.....	Hard—separation of soap.
Sodium.....	do.....	Solidifies hard mass.
Do.....	do.....	Soupy.
Sodium-calcium.....	do.....	Complete separation of oil plus 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 thin out upon stirring and this is undesirable in field applications where a grease is agitated or worked while subject to a high temperature. Aerogel greases also reveal an unsatisfactory dynamic water resistance and this again is unsatisfactory in field applications where the grease is agitated or worked in the presence of water. The grease may emulsify with water to the point of inversion to an oil-in-water emulsion, at which point the grease characteristics are lost.

In accordance with the invention water-insoluble oil-miscible or -dispersible polyalkylene glycol diethers characterized by a viscosity at 100° F. within the range of 40 to 500 SSU are employed in conjunction with an alkylol or amino imidazoline in thickened lubricant compositions comprising a lubricating oil thickened with a nonabrasive inorganic thickening or filling agent and particularly finely divided silica, a silica aerogel being illustrative. The thickened lubricants so prepared have

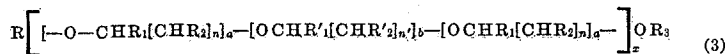
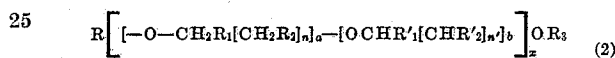
excellent temperature susceptibility properties and excellent dynamic water resistance, attributable to the presence of the alkylol or amino imidazoline and the polyalkylene glycol diether.

The polyalkylene glycol diethers are characterized by the following general formula:

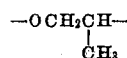


where n is an integer having the value of one or more, preferably one, two or three, x is an integer taken in sufficient number to produce an ether having the prescribed viscosity, R_1 and R_2 are hydrogen or lower alkyl groups, and R and R_3 are each lower alkyl groups. When n is one, preferably at least one of R_1 and R_2 is a lower alkyl group, preferably methyl. The lower alkyl group can have from one to about five carbon atoms such as methyl, ethyl, propyl, butyl or amyl and can have either a straight or branched chain. Preferably, one of R_1 and R_2 is hydrogen and one is a methyl group, and R and R_3 can be methyl, ethyl or isopropyl.

Within the above Formula 1 and worthy of especial mention are the mixed ethers of the types:



where a , b , and x are integers taken in sufficient number to produce an ether having the prescribed viscosity, and n and n' , R_1 and R'_1 , and R_2 and R'_2 can be the same or different, and are defined as in Formula 1. Preferably, when the " a " units are $-OCH_2CH_2-$ and the " b " units



the ratio of $a:b$ is 75 to 25 of " a " to 10 to 90 of " b ."

These ethers are obtained by reaction of the alkylene oxide with water or a glycol, and with a monohydric alcohol, desirably in the presence of a catalyst. The reaction which takes place seems to be a simple addition wherein the alkylene oxide is converted to the corresponding oxyalkylene groups or radicals. The glycol may itself be prepared by reaction of the alkylene oxide with water. Thus, water can be regarded as the ultimate starting material. The molecular weight of the polymer obtained will depend upon the relative proportions of alkylene oxide, water and monohydroxy aliphatic alcohol.

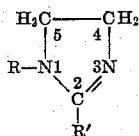
From various analyses it has been determined that these polyalkylene glycol ethers are complex mixtures of compounds having polyoxyalkylene chains of different lengths and different internal configurations, and although the materials are characterized as diethers, they may contain a small proportion of chains having hydroxyl groups at each end and of chains having one alkyl group at each end, i. e., monoethers. If mixed alkylene oxides are employed as the starting material the chains will contain complex mixtures of the mixed alkylene oxide radicals in various combinations, depending upon the relative proportions of the alkylene oxides, and a given chain may have several oxyalkylene units of the same type together or intermingled with other oxyalkylene units in any order or combination. Thus the above formulae for the mixed ethers are merely suggestive of the types of combinations that may be found.

The important criterion from the standpoint of the invention is the viscosity of the ether, and this should be within the range from 40 to 500 SSU at 100° F.

Polyethylene and mixed polyethylene-1,2-propylene glycol dimethylethers are preferred.

Thus it will be understood that there can be employed in accordance with the invention mixtures of these glycol ethers with monohydroxy monoethers and even dihydroxy compounds which are present in the mixture following condensation and/or etherification of the alkylene oxide, but at least the major proportion and preferably upwards of 85% is the diether. Reference is made to U. S. Patent No. 2,425,845, to Toussaint et al., dated August 19, 1947, which describes methods for the manufacture of the glycols and to U. S. Patent No. 2,425,755, to Roberts et al., dated August 19, 1947, which describes the preparation of the monoethers. The diethers are obtained by methods analogous to the monoethers, using twice the amount or more of the monohydric alcohol.

The imidazoline should be surface-active, oil-dispersible and water-insoluble and has the following structure:

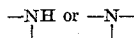


Many of the compounds having the above general structure are also capable of improving the high temperature stability of lubricating oils thickened with inorganic thickening or gelling agents, such as silica aerogels.

In the above formula, R is a hydrophilic group. Especially satisfactory hydrophilic groups are alkylol groups and aliphatic, cycloaliphatic or mixed cycloaliphatic amino groups having at least one basic nitrogen atom.

The alkylol group can bear one or more hydroxyl groups.

The amino group preferably has at least two basic nitrogen atoms, which can be primary, secondary or tertiary, in any combination of the three. Where one or more of the nitrogens is primary, i. e., —NH_2 , they can be attached at any position in an aliphatic chain or on a cyclic ring. Where one or more of the nitrogens is secondary or tertiary, i. e.,



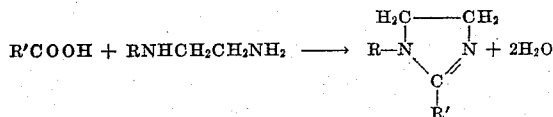
they can be substituted in a straight or branched aliphatic chain, or in heterocyclic ring, which can itself bear alkyl, alkylene, hydroxyalkyl or hydroxyalkylene groups, desirably in the 1-position, as in the above imidazoline ring. See U. S. Patent No. 2,655,476, dated October 13, 1953, to Everett C. Hughes and Ernest C. Milberger.

Thus R can be a hydroxyethyl group, a mono-, di- or triethylene amino group, a 1-alkylene-imidazoline group, or a 1-alkylene amino imidazoline group.

R' is an alkyl, hydroxyalkyl, alkylene or hydroxyalkylene group.

R', which is derived from an acid, can have from eleven to twenty-one carbon atoms, such as undecyl, tridecyl, abietyl, pentadecyl, undecenyl, heptadecyl, ricinoleyl, and heptadecenyl.

The alkylol imidazolines are prepared by reaction of aliphatic acids and hydroxy diamines followed by cyclization, in the following way:

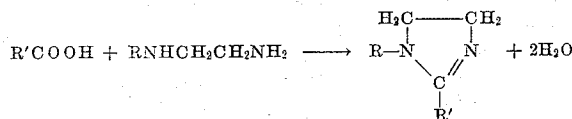


Alkylol imidazolines in which R is from one to about six carbon atoms, such as hydroxyethyl and hydroxyisopropyl, are readily available and are preferred. The chain length for R is dependent upon the alcoholic (polar) character of the group; the larger the number of carbon atoms, the more the group takes on the character of a hydrocarbon and loses its alcoholic character. An upper limit of about eighteen carbon atoms for R is indicated by this requirement.

Amine "O," 1-β-hydroxyethyl-2-heptadecenyl imidazo-

line, and analogous compounds as described in application Serial No. 240,452, filed August 4, 1951, now U. S. Patent No. 2,711,393, patented June 21, 1955, have been found to be particularly effective alkylol imidazolines in the thickened lubricants of the invention.

The amino imidazolines are prepared by reaction of aliphatic acids and polyamines followed by cyclization in the following way:



Amino imidazolines in which R has two basic nitrogen atoms and from four to about twenty carbon atoms, such as diethylene diamino and triethylene triamino, and the alkyl-substituted N-alkylene and N-alkylene-amino imidazolines (wherein R is attached to the imidazoline nucleus of the general formula through the N-alkylene or N-alkylene-amino group), are readily available and are preferred. The chain length for R is dependent upon the basic (polar) character of the group, the larger the number of carbon atoms, relative to the number of amino nitrogens, the more the group takes on the character of a hydrocarbon and loses its basic or amine character. An upper limit of about five carbon atoms per amino nitrogen is indicated by this requirement, with about a maximum of thirty carbon atoms for the R group.

The amino imidazolines described in U. S. Patent No. 2,655,476 have been found to be particularly effective in the thickened lubricants of the invention.

The presence of the polyalkylene glycol ether in an amount to obtain improved high temperature and dynamic water 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 polyalkylene glycol ether will not effect a change in the consistency of the thickened lubricant upon storage.

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 manufactured by Monsanto Chemical Company and 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 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 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 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 ½₁₆ 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 marketed by B. F. Goodrich Company. 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" marketed by Linde Air Products Co. 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 from Du Pont 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.

The silica from Columbia-Southern Chemical Corporation also is useful. These have the following properties:

Wet screen retained 325 mesh, percent	Brunauer-Emmett-Teller nitrogen absorption surface area, m. ² /gm.
0.004 -----	257.0
0.01 -----	236.5
0.02 -----	ca. 210.0
0.008 -----	215.5
0.004 -----	228.0

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 water-proofing 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% by weight of the thickened lubricant.

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 amount 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, par-

ticularly 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-insoluble polyalkylene glycol diethers can be employed in accordance with the invention. The molecular weight and chain length of the diether are not critical except as they affect viscosity. Any polyalkylene glycol diethers having a viscosity at 100° F. within the range of 40 to 500 SSU can be employed in the composition of the invention.

The following are a few typical polyalkylene glycol diethers in accordance with the invention:

- (1)
$$R-[O-CH_2-\underset{\text{CH}_3}{\underset{|}{CH}}-]_x-OR_3$$
- (2)
$$R-[O-CH_2CH_2CH_2CH_2-]_x-OR_3$$
- (3)
$$R-[O-CH_2CH-]_x-OR_3$$

$$\text{C}_2\text{H}_5$$
- (4)
$$R-[O-CH_2CH_2CH_2CH_2-]_x-OR_3$$
- (5)
$$R-[O-\underset{\text{CH}_3}{\underset{|}{CH}}-\underset{\text{CH}_3}{\underset{|}{CH}}-]_x-OR_3$$
- (6)
$$R-[OCH_2\underset{\text{CH}_3}{\underset{|}{CH}}CH_2-]_x-OR_3$$
- (7)
$$R-[OCH_2CH_2]_a-[OCH_2\underset{\text{CH}_3}{\underset{|}{CH}}]_b-OR_3$$
- (8)
$$R-[OCH_2CH_2CH_2]_a-[O-\underset{\text{CH}_3}{\underset{|}{CH}}CH_2]_b-OR_3$$

Exemplifying specific diethers within the scope of the invention are the Ucon DLB and DLB-X series of polyalkylene glycols, available from the Union Carbide and Carbon Corporation. These are mixed polyethylene-1,2-propylene glycol dimethyl ethers, of the form of No. 7, above, which have the following properties:

TABLE II

Standard grade	DLB-47-E	DLB-67-E	DLB-50-B	DLB-144E DLB-190-B DLB-200-B	DLB-265-BX
Viscosity:					
Saybolt seconds at—					
210° F.-----	33.9	37.9	34.7	56.64	61.89
100° F.-----	47.4	67.0	52.0	203	265
0° F.-----	275	870	500	590C	47,200
Centistokes at—					
210° F.-----	2.3	3.5	2.52	9.25	10.76
100° F.-----	6.6	12.3	8	43.93	57.22
0° F.-----	59.7	189	109	1,350	2,465
-20° F.-----	140	500	270	4,500	10,300
-40° F.-----	340	1,900	905		
Viscosity index (A. S. T. M. D-567-41)	173	177	159	157	149
Pour point, ° F. (A. S. T. M. D-97-39)	-80	-80	<-70	<-76	-72
Flash point, open cup, ° F. (A. S. T. M. D-92-45)	330	270	270	395	485
Do-----	340		335	455	555
Density, g./cc. at—					
210° F.-----	0.874	0.890	0.876	0.9235	0.9145
100° F.-----	0.923	0.937	0.925	0.9700	0.9610

The polyalkylene glycol diether should be oil-dispersible.

The polyalkylene glycol diether is incorporated in the thickened lubricant in an amount to impart high temperature stability to the grease. Ordinarily, a concentration of polyalkylene glycol diether ranging from 0.25 to about 2.5% by weight of the thickened lubricant gives satisfactory results. There is no reason to employ more polyalkylene glycol diether than is necessary, but excessive amounts do no harm, and amounts up to 5% or even higher have been successfully employed.

In general, the concentration of the imidazoline should at least about 2.5% by weight of the aerogel but will vary depending upon the water stabilizing effect desired, the nature of the particular compound selected, the amount and nature of the gelling agent used, and the economics involved. Both static and dynamic water resistance tend to increase with time, so that an amount of imidazoline may be inadequate to impart the desired water resistance at once, yet after the grease has aged

for a few weeks or months it may display excellent water resistance. Preferably, from 4 to 14% imidazoline by weight of the aerogel is used, as such amounts usually impart excellent water resistance at once. A cheap compound, of course, can be used in much larger quantities than can an expensive compound, at the same total cost for the lubricant.

In some instances, the thickened lubricant may not display 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, and in such circumstances, it is desirable to include an antioxidant in the composition. Conventional amine antioxidants which are more readily oxidized than the components of the lubricant can be employed for this purpose. Tetramethyldiaminodiphenylmethane, available under the trade name "Calco MB," is a particularly desirable antioxidant. Only small quantities are required, and ordinarily an amount ranging from 0.1 to about 1% by weight of the thickened lubricant 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, the polyalkylene glycol diether, the cationic water stabilizer and the antioxidant in any order or manner.

In one embodiment, the polyalkylene glycol diether and, desirably, the cationic water stabilizer and antioxidant, can be incorporated with the inorganic gelling agent either by mixing directly, or if desired, by dissolving them in a volatile hydrocarbon solvent, such as pentane, adding oil, mixing the solution with the inorganic gelling agent, and then evaporating the solvent.

Generally, the polyalkylene glycol diether and, optionally, cationic water stabilizer and antioxidant, 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 mixing temperature is not critical, but is preferably in the range of 100° F. to about 250° F. At higher temperatures grease yield is affected. Mixing temperatures of 140° to 160° F. are preferred.

Mixing is continued until the components are thoroughly dispersed in the oil and the consistency has attained the desired level. Any type of mixing is satisfactory. High shear supplemental mixing at a high temperature is useful.

The composition of the invention is not limited to the oil, gelling agent, imidazoline and polyalkylene glycol diether. Any of the materials conventionally added to lu-

bricants and greases can 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, the imidazoline, and the polyalkylene glycol diether, 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 antioxidant, 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 illustrate preferred embodiments of the invention.

In the examples which follow the high temperature stability of the grease was determined by measurement of micropenetrations before and after heating to 400° F. in the "block" test. The grease was prepared for the determination of high temperature stability by placing approximately 100 cc. of grease in a 150 ml. beaker. The beaker was heated to the test temperature 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 reached 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. Micropenetration measurements were obtained on the grease before and after the test procedure. The cycle was repeated as many times as desired and the results are expressed by plotting the actual penetration against the number of cycles.

The static water stability was determined as follows: A 2 x 2 inch stainless steel plate was coated with a uniform layer of the grease, following which the coated plate was immersed in a beaker filled with tap water and boiled for thirty minutes.

The dynamic water resistance of the grease was determined as follows: One hundred and fifty grams of grease was weighed into the ASTM grease worker cup. The grease then was worked 300 strokes after which a Shell penetration was obtained. Fifty percent water by weight of the grease was added, followed by a second 300 stroke working cycle. A Shell penetration was again obtained and an observation made of the type of emulsion formed. If free water remained unemulsified this was noted. Whether the emulsion was an oil-in-water or water-in-oil type was readily apparent, for the water-in-oil emulsion was shiny in appearance while the oil-in-water emulsion had a dull matte surface. If the 50 weight percent of water had been completely emulsified and no emulsion inversion had occurred an additional 50% of water on the original weight of the grease was added, the grease worked an additional 300 strokes, in the presence now of 100% water, and another Shell penetration obtained. The grease was considered to have good dynamic water resistance if, at the conclusion of the second 300 stroke working cycle, in the presence of 50% water, the emulsion had not inverted, i. e., the emulsion remained of the water-in-oil type, whether or not the water added had been completely emulsified. Dynamic water resistance was considered excellent if inversion of the emulsion had not occurred at the end of the third 300 stroke working cycle, in the presence of 100% water.

The following results are typical of the application of this test to conventional greases:

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TABLE III

5	Base grease	Shell penetrations			Comments
		Initial	50% H ₂ O	100% H ₂ O	
	Lithium hydroxystearate.	129	140	146	At 50%, all water emulsion with free water in drops. W/O. ¹ Free water at 100% W/O. ¹
10	Aluminum.....	155	166	-----	Considerable free water. W/O. ¹
	Lime.....	182	206	-----	Free water. W/O. ¹
	Barium.....	141	191	-----	Do. ¹
	Soda.....	120	77	-----	Do. ¹
15	Aerogel (Santocel ARD).	145	142	-----	Emulsion inverted to O/W. ²

¹ W/O means water-in-oil emulsion.

² O/W means oil-in-water emulsion.

These results show that the soap base greases tested were resistant to water, but the aerogel grease was not. Accordingly, an aerogel base grease that passes the test can be regarded as the equal of a soap base grease in dynamic water resistance under these test conditions, which closely approximate field conditions.

The ability of the grease to emulsify with free water to some extent is desirable, and therefore in evaluating the test results it is not necessary that the grease emulsify with water, but merely that it not emulsify with water to the point where inversion to an oil-in-water emulsion occurs.

The working or mechanical stability of the greases was evaluated by 10,000 strokes' working at room temperature in the ASTM grease worker and by four hours at room temperature in a grease working assembly wherein the grease sample was subjected to the severe working afforded by close intermeshing gears in an enclosed space. This approximates many field conditions for general ball and roller bearing and transmission greases. The measurements include a Sohio micropenetration of the grease before working, a Sohio micropenetration after working, plus a Sohio micropenetration after the grease has been allowed to stand for approximately twenty-four hours, and another after the set up in grease body has been disturbed by vigorous stirring with a spatula. The last two measurements offer further data on the ability of the greases to resist mechanical breakdown.

Examples 1 to 10

A group of greases was prepared having the following formulation:

	Percent
Santocel ARD.....	9.0.
Ucon lubricant.....	2.0.
Amine "O" ¹	Amount indicated in table below.
Paratac ²	1.0.
Paraflow ³	0.5.
Ortholeum ⁴	0.5.
Solvent extracted bright stock (2000 SSU at 100° F.) ⁵	89.2.

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 An antioxidant for mineral lubricating oils.

⁵ 46.5 volume percent solvent-extracted bright stock, 78 SSU at 210° F., and 53.5 volume percent solvent-extracted bright stock, 250 SSU at 210° F.

The oil-soluble additives, i. e., the Paratac, Paraflow and Ortholeum 300, were dissolved in the oil. The oil was brought to 95° F., the Amine "O" and Ucon added with thorough mixing and then the Santocel was blended in as rapidly as it was absorbed in the mixture. The total mixing time was sixty minutes at the temperature indicated in the table.

TABLE IV

Example No.	Percent Amine "O" ¹	Ucon polymer	Temp., ° F.		Final grease temp., ° F.	Initial Shell pen.	24 hr. Shell	ASTM penetration	
			Initial oil bath	Final oil blend				0 strokes	60 strokes
1-----	0	DLB 190-B	100	99	100	155	165	325	325
2-----	4	DLB 190-B	95	95	93	157	170	332	326
3-----	8	DLB 190-B	97	98	95	162	179	337	339
4-----	12	DLB 190-B	97	95	96	157	190	341	349
5-----	14	DLB 190-B	95	95	94	185	198	352	352
6-----	8	DLB 50-B	96	96	95	152	168	322	318
7-----	8	DLB 144-E	96	95	109	168	182	337	334
8-----	10	DLB 100	95	102	105	118	-----	283	295

¹ Based on weight of Santocel ARD.

The table shows that in many cases the grease yield decreases as the amount of Amine "O" increases and this is a linear decrease as is evident when the results are plotted on a graph. It would be concluded from this data that the smallest amount of Amine "O" required to give the desired water resistance should be employed.

The dynamic water resistance of these greases was evaluated by the tests described above and are summarized below:

TABLE V

Ex. No.	Percent Amine "O" ¹	Dynamic water resistance			
		Shell pens.		Comments	
		Orig.	100%		
1-----	0	-----	-----	Oil-in-water emulsion—inversion: complete breakdown of grease.	
2-----	4	-----	-----	Nearly inverted—free unemul. H ₂ O.	
3-----	8	162	146	70% Water-in-oil emulsion—30% free unemul. H ₂ O.	
4-----	12	157	149	50% Water-in-oil emulsion—50% free unemul. H ₂ O.	
5-----	14	185	197	30% Water-in-oil emulsion—70% free unemul. H ₂ O.	
6-----	8	152	146	75% Water-in-oil emulsion—25% free unemul. H ₂ O.	
7-----	8	168	144	80% Water-in-oil emulsion—20% free unemul. H ₂ O.	
8-----	10	136	122	Water-in-oil emulsion—free unemul. H ₂ O.	

¹ Based on weight of Santocel ARD.

It is evident that 8% Amine "O" by weight of the Santocel was sufficient to impart good water resistance. The results for Examples 3, 4, 5, 6, 7 and 8 are to be contrasted with Example 1 which did not contain Amine "O" but did contain 2% of the Ucon lubricant. This shows that the Ucon lubricant alone, even at a concentration of 2%, is not able to impart the necessary dynamic water resistance.

As an additional comparison two greases were prepared containing 5 and 15% Amine "O," respectively, by weight of the Santocel, and no Ucon oil. These greases had the following composition:

	Example 9	Example 10
	Percent	Percent
Santocel ARD-----	10.0	10.0
Amine "O"-----	0.5	1.5
Paratac-----	1.0	1.0
Parafflow-----	0.5	0.5
Ortholeum 300-----	0.5	0.5
Solvent extracted bright stock (78 SSU at 210° F.)-----	87.5	86.5

These greases were subjected to the static and dynamic water resistance and the high temperature stability tests. Example 9 had borderline static stability and very poor dynamic water resistance. Example 10 had excellent static and dynamic water resistance. Both these greases showed very poor high temperature stability. This shows that very large amounts of Amine "O" in the absence of Ucon oil are required to give an adequate dynamic water resistance, but that when such large amounts of

15 Amine "O" are used, the grease has very poor temperature susceptibility properties.

In contrast, Examples 1 to 7, inclusive, passed the "block" (high temperature stability) test:

TABLE VI

Example No.	"Block" test			
	1(24)	2(24)	3(24)	4(24)
1-----	226	241	258	265
2-----	223	236	248	258
3-----	274	285+	285+	285+
4-----	279	285+	285+	285+
5-----	286+	285+	285+	285+
6-----	278	285+	285+	285+
7-----	285+	285+	285+	285+
8-----	285+	285+	285+	285+
9-----	285+	285+	285+	285+
10-----	285+	285+	285+	285+
11-----	285+	285+	285+	285+
12-----	285+	285+	285+	285+
13-----	285+	285+	285+	285+
14-----	285+	285+	285+	285+
15-----	285+	285+	285+	285+
16-----	285+	285+	285+	285+
17-----	285+	285+	285+	285+
18-----	285+	285+	285+	285+
19-----	285+	285+	285+	285+
20-----	285+	285+	285+	285+
21-----	285+	285+	285+	285+
22-----	285+	285+	285+	285+
23-----	285+	285+	285+	285+
24-----	285+	285+	285+	285+
25-----	285+	285+	285+	285+
26-----	285+	285+	285+	285+
27-----	285+	285+	285+	285+
28-----	285+	285+	285+	285+
29-----	285+	285+	285+	285+
30-----	285+	285+	285+	285+
31-----	285+	285+	285+	285+
32-----	285+	285+	285+	285+
33-----	285+	285+	285+	285+
34-----	285+	285+	285+	285+
35-----	285+	285+	285+	285+
36-----	285+	285+	285+	285+
37-----	285+	285+	285+	285+
38-----	285+	285+	285+	285+
39-----	285+	285+	285+	285+
40-----	285+	285+	285+	285+
41-----	285+	285+	285+	285+
42-----	285+	285+	285+	285+
43-----	285+	285+	285+	285+
44-----	285+	285+	285+	285+
45-----	285+	285+	285+	285+
46-----	285+	285+	285+	285+
47-----	285+	285+	285+	285+
48-----	285+	285+	285+	285+
49-----	285+	285+	285+	285+
50-----	285+	285+	285+	285+
51-----	285+	285+	285+	285+
52-----	285+	285+	285+	285+
53-----	285+	285+	285+	285+
54-----	285+	285+	285+	285+
55-----	285+	285+	285+	285+
56-----	285+	285+	285+	285+
57-----	285+	285+	285+	285+
58-----	285+	285+	285+	285+
59-----	285+	285+	285+	285+
60-----	285+	285+	285+	285+
61-----	285+	285+	285+	285+
62-----	285+	285+	285+	285+
63-----	285+	285+	285+	285+
64-----	285+	285+	285+	285+
65-----	285+	285+	285+	285+
66-----	285+	285+	285+	285+
67-----	285+	285+	285+	285+
68-----	285+	285+	285+	285+
69-----	285+	285+	285+	285+
70-----	285+	285+	285+	285+
71-----	285+	285+	285+	285+
72-----	285+	285+	285+	285+
73-----	285+	285+	285+	285+
74-----	285+	285+	285+	285+
75-----	285+	285+	285+	285+

The working stability of Examples 1 to 7 was determined by the four hour test in the gear grease worker. The results obtained appear in the following table:

TABLE VII

Example No.	Sohio micropenetration				Gain in penetration	
	Original	Wk'd. 4 hrs.	At rest	24 hrs. stirred	Wk'd. 4 hrs.	24 hrs. stirred
1-----	115	157	119	170	42	55
2-----	101	110	100	128	9	27
3-----	122	152	125	201	30	79
4-----	132	156	115	191	24	59
5-----	115	196	147	217	79	102
6-----	109	156	106	173	47	64
7-----	114	165	136	188	51	74

The changes of penetration shown in the table are of an order of magnitude indicating satisfactory mechanical stability.

These results show that greases containing Amine "O" alone even in amounts as high as 15% by weight of the Santocel or a Ucon lubricant alone have either satisfactory dynamic water resistance or satisfactory high temperature stability, but not both. On the other hand, greases containing both the Amine "O" and the Ucon oil have excellent static and dynamic water resistance as well as good high temperature susceptibility properties even though the amount of Amine "O" is as low as 8% by weight of the Santocel and the Ucon oil is in the same amount as when used alone. Evidently in the presence of the Ucon oil the Amine "O" is more effective in smaller amounts to impart dynamic water resistance while not affecting high temperature stability. The same effect is not obtained when diethylene glycol monoethyl ether ("Carbitol") is substituted for the Ucon oil, showing that this effect can be uniquely attributed to the poly-

alkylene glycol diethers of higher molecular weight. This is shown by the following:

Six greases were prepared having the following formulation:

Examples 11 to 16

	Percent
Santocel ARD.....	9.0
"Carbitol" (diethylene glycol monoethyl ether).....	2.0
Amine "O".....	Amount indicated in table below.
Paratac.....	1.0
Paraflo.....	0.5
Ortholeum 300.....	0.5
Mineral lubricating oil ¹ (2000 SSU at 100° F.).....	85.92

¹ 46.5 volume percent solvent-extracted bright stock (78 SSU at 210° F.), 53.5 volume percent solvent-extracted bright stock (250 SSU at 210° F.).

The Paratac, Paraflo and Ortholeum 300 were dissolved in the oil. The Santocel, Amine "O" and "Carbitol" then were blended and the preparation mixed at 95° F. for sixty minutes overall, including the time necessary to add the Santocel.

Shell penetrations were taken on all of the grease samples at the conclusion of the mixing cycle and a second Shell penetration obtained after the grease had stood overnight. The standard ASTM 0 and 60 stroke penetrations also were taken after the grease had stood overnight. The results are given in the following table:

TABLE VIII

Example No.	Amine "O" ¹	Initial Shell penetration	24 hr. Shell penetration	24 hr. ASTM penetrations	
				0 strokes	60 strokes
	Percent				
11.....	6	123	120	269	274
12.....	8	137	136	285	290
13.....	10	127	125	283	291
14.....	12	152	159	303	316
15.....	14	184	190	334	344
16.....	16	<282	<282	400	416

¹ Based on the weight of the Santocel.

The greases were tested for high temperature stability, and showed satisfactory high temperature stability characteristics after five cycles. Furthermore, those greases containing the higher amounts of Amine "O" which had given low grease yields stiffened with the heating during the test, compensating for the low yield therein.

The water resistance characteristics of the greases were checked by a static water test and the dynamic water test in the ASTM worker. The results are shown in the following table:

TABLE IX

Example No.	Percent Amine "O" ¹	Static 30-minute boiling water test	Dynamic water resistance		
			Shell pens.		Results
			Orig.	100% H ₂ O	
11.....	6	Very poor—considerable emulsion—loses grease characteristics.	-----	-----	Oil-in-water emulsion-inverted. Water-in-oil free H ₂ O—still adhesive. Water-in-oil emulsion small amount free H ₂ O—still adhesive.
12.....	8	Poor—considerable emulsion—loses grease-like characteristics.	-----	-----	
13.....	10	Good.....	-----	-----	
14.....	12	do.....	168	218	
15.....	14	do.....	208	120	
16.....	16	Very good.....	>280	108	

¹ Based on weight of Santocel ARD.

If the grease did not pass the static test, the dynamic water test was not carried out since this would have been useless.

The results show that with "Carbitol" at least 10% Amine "O" is necessary for satisfactory performance in the static boiling water and that at least 14% is necessary in the dynamic water test. This shows that "Carbitol," diethylene glycol monoethyl ether having two ethylene glycol units, is not as effective as the higher polyalkylene glycol diethers such as the Ucons, which are polymers of ethylene and 1,2-propylene glycol units, in cooperating with the Amino "O" to give good dynamic water resistance.

The thickened lubricants of the invention are useful in many field grease applications. In the critical field of wheel bearing lubricants, these greases have performed very satisfactorily. Other successful field applications include chassis lubrication, general ball and roller bearing applications, foundry ladle trunnion bearings, phonograph bearings, textile spinning wheels, cam followers, kiln car bearings, farm equipment, worm gear-radar antennae, outdoor playground equipment, shaker screens and gears and mixing vessels.

The greases of the invention are characterized by their ease and reproducibility of preparation and their high static and dynamic water resistance and high temperature consistency stability. In addition they have excellent oxidation resistance and mechanical stability. All of these are requisites for a multipurpose lubricating grease,

Testing the high temperature stability of the thickened lubricants of the invention by heating the greases to 400° F 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 the temperature was adopted as a suitable test standard because a grease stable at 400° F. definitely will have the stability necessary to withstand heating to 300° F. It will be understood that for normal purposes the thickened lubricants of the invention 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 thickened lubricant is stable against loss of consistency at temperatures of at least 300° F.

The Shell penetrations are in accordance with the Shell Microcone Penetration Test, Institute Spokesman (NLGI), volume VI, Number 12, page 1 (1943).

The Sohio micropenetration technique employed required a microcone and cup. The microcone was specially built, and its dimensions are compared in Table II 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 test results required a minimum sample size of 35 ml.

TABLE X
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.....		0.136		0.136
Cone height/cup depth.....		0.693		0.693
Weight of assembly, gms.....	150		113	
Weight of assembly/sq. mm. cone surface.....		0.021		0.021

¹ Calculated.

All parts and percentages are by weight of the thickened lubricant unless otherwise indicated.

I claim:

1. A thickened lubricant of high temperature stability and good dynamic water resistance, consisting essentially of a mineral lubricating oil of lubricating viscosity as the major component, a finely-divided inorganic water-susceptible oil thickener in an amount sufficient to impart a grease consistency to the oil, a water-insoluble oil-miscible polyalkylene glycol diether having a viscosity at 100° F. within the range of from 40 to 500 SSU, and a water-insoluble oil-dispersible cationic surface-active imidazoline having an aliphatic group substituted at the 2-position and a hydrophilic group substituted at the 1-position of the imidazoline, said glycol diether being in an amount within the range from 0.25 to about 2.5% by weight of the thickened lubricant, and said imidazoline being in an amount within the range from 4 to 14% by weight of the inorganic water-susceptible oil thickener, each being in amounts sufficient in combination to impart high temperature stability and dynamic water resistance to the thickened lubricant.

2. A thickened lubricant in accordance with claim 1 in which the polyalkylene glycol diether is a mixed polyethylene-1,2-propylene glycol diether.

3. A thickened lubricant in accordance with claim 1 in which the imidazoline is 1- β -hydroxyethyl-2-heptadecenyl imidazoline.

4. A thickened lubricant in accordance with claim 1 in which the inorganic oil thickener is a silica aerogel.

5. A thickened lubricant of high temperature stability and good dynamic water resistance, consisting essentially of a mineral lubricating oil of lubricating viscosity as the major component, a finely-divided silica aerogel in an amount sufficient to impart a grease consistency to the oil, a water-insoluble oil-miscible mixed polyethylene-1,2-propylene glycol diether having a viscosity at 100° F. within the range of from 40 to 500 SSU, and a water-insoluble oil-dispersible cationic surface-active imidazoline having an aliphatic group substituted at the 2-position and a hydrophilic group substituted at the 1-position of the imidazoline, said glycol diether being in an amount within the range from 0.25 to about 2.5% by weight of the thickened lubricant, and said imidazoline being in an amount within the range from 4 to 14% by weight of the inorganic water-susceptible oil thickener, each being in amounts sufficient in combination to impart high temperature stability and dynamic water resistance to the thickened lubricant.

6. A thickened lubricant in accordance with claim 5, in which the imidazoline is 1- β -hydroxyethyl-2-heptadecenyl imidazoline.

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