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GREASE COMPOSITIONS

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This invention relates to improved grease compositions. More particularly, it is concerned with greases gelled with inorganic colloids and exhibiting outstanding properties with respect to water resistance and a particular type of corrosion.

Greases have been developed which contain inorganic gelling agents such as silica aerogel or other forms of colloidal oxides, such as colloidal alumina. The principal advantage of such greases over the corresponding soap gelled greases is the lack of any phase change during heating of the grease. It has been determined that the essential limiting factor in the use of greases gelled with inorganic colloids is the temperature at which the lubricating base either volatilizes or decomposes. As opposed to this, soap greases are limited in their utility to the temperature at which such phase change takes place in the grease that the latter becomes unduly soft and even fluid.

While the two component system of, for example, colloidal silica and lubricating oil possess this advantage with respect to lack of phase changes, such compositions are inherently water sensitive. Hence, without further modification, these greases cannot be used where they come in contact either intentionally or otherwise with water. Under hydrous conditions such greases disintegrate to form precipitated silica and the fluid lubricant. In accordance with the disclosures of a copending U. S. patent application, Serial No. 782,694, filed October 28, 1947, in the name of Fred H. Stross, these water sensitive greases may be made substantially resistant to such deleterious action by the addition thereto of cationic hydrophobic surface active agents. The addition of such materials protects the subject greases from disintegration by water attack but three-component systems are still deficient in one particular respect.

One of the characteristics which most greases must satisfy is minimum development of corrosion of metallic surfaces to which the greases are applied. Corrosion may be respectively divided into two principal types according to the conditions under which it occurs: "dynamic corrosion" specifies the type of corrosion which occurs during active lubrication of a metal surface, while "static corrosion" is regarded here as the corrosion which occurs on a greased metal surface either prior to or subsequent to dynamic operation.

In attempting to overcome these two detrimental characteristics it has been determined

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that the same treatment or modification of a grease does not necessarily overcome both dynamic and static corrosion. In investigating these phenomena, it has been determined moreover, that additives employed for the purpose of correcting corrosion must be present only in critical limited amounts. While the lower limits of such additive concentration is dependent only upon effective elimination of corrosion, the upper limit of anti-corrosive additive is fixed by the adverse effect that excessive amounts of the additive have upon the consistency of the grease. If amounts of the additives to be defined hereinafter exceed the range defined, the greases become unduly soft or in fact may fluidize on heating and run out of a bearing or off of a surface.

It is an object of the present invention to provide improved greases gelled with inorganic colloids. It is another object of the present invention to provide greases exhibiting substantially no static corrosion characteristics. It is a further object of the present invention to provide greases showing substantially improved water resistant characteristics. Other objects and advantages will become apparent during the following discussion.

Now, in accordance with the present invention, it has been found that the "static corrosion," as defined hereinbefore, exhibited by greases gelled with inorganic colloids can be corrected by the combined addition thereto of a water-soluble inorganic nitrite and a cationic hydrophobic surface active agent. It has been established that the combination of these two additives is essential, since the use of either one in the absence of the other does not result in a satisfactory grease. Still in accordance with this invention, the additives are only satisfactory within critical ranges, as more fully discussed hereinafter.

The nitrites useful in the composition of the present invention include especially ammonium nitrite, alkali metal nitrites, such as sodium nitrite, potassium nitrite and lithium nitrite; alkaline earth metal nitrites, such as barium, calcium, and magnesium nitrites and heavy metal nitrites, such as copper nitrite, iron nitrite, and lead nitrite; as well as amphoteric metal nitrites, such as aluminum nitrite and zinc nitrite. As pointed out in the statement of the invention given before, the proportion of the nitrite in the subject greases has been found to be critical for the desired effect. The minimum amount must be sufficient to provide effective protection against static corrosion and the maximum amount per-

missible is such as to avoid appreciable softening of the grease. In this respect, it has been determined that the proportion of nitrite is critical with respect to the inorganic gelling agent and not with respect to the total grease composition. In order to be effective for the present purpose and not to cause disadvantageous softening of the grease, the nitrite should be present in an amount between about 1% and about 20% by weight of the inorganic gelling agent. The most favored concentration range is between 3 and 15% by weight based on the inorganic gelling agent, while optimum amounts are generally within the range of 3-6%.

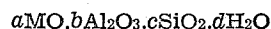
The inorganic gelling agents contemplated for use in the present invention comprise two principal classes. One of these includes substantially amorphous gelling agents, while the other comprises gelling agents which have recognizably crystalline structures. The amorphous gelling agents include silicates, oxides, hydroxides, synthetic zeolites, mixed silicate-silica gels and mixed silicate-hydroxide gels, as well as complex mixtures of these various types. The crystalline gelling agents include especially natural and synthetic montmorillonites. The gelling agent may be especially recognized as having an exceedingly finely divided character, the average particle size diameter of which is usually about 100 millimicrons or less. Dependent upon the process by which the gelling particles are prepared, the latter may have a considerable variation in surface area. Aerogels, for example, which are suitable for use in the present compositions have surface areas of approximately 300-400 sq. meters per gram. On the other hand, colloids prepared as described hereinafter according to the "direct transfer process" have surface areas ranging from about 300 to 1,000 sq. meters per gram. Coarser particles still useful as gelling agents are those prepared by burning organic silicates and the like to produce finely-divided ash residues of silica having particle sizes ranging from about 5 to 100 millimicrons diameter (50 to 1,000 Å.) and surface areas of about 100 to 200 sq. meters per gram. The simple colloidal materials useful as gelling agents include especially oxides, such as silica, magnesia, alumina, and calcium, copper, barium or strontium oxides and mixtures thereof. Particularly favored are those mixtures containing at least 3% by weight of an alkaline earth metal, such as magnesium. Hence, a suitable mixture comprises at least 3% magnesium and 97% silica.

The alkaline earth metals present in each of these classes of gelling agents include magnesium, calcium, strontium, barium and beryllium. Magnesium has been found to give the most favorable effects, while calcium also promotes the best qualities in a grease. While the critical limits have been set at between 2% and 25%, based on the weight of the inorganic gel components, of an alkaline earth metal, it is preferred that the latter be present in an amount between 3% and 20%. Amorphous gels such as those described hereinafter possess optimum properties as grease-forming agents when they contain between 3% and 20% by weight of the alkaline earth metal while the crystalline materials exhibit optimum properties when they contain from 7% to 20% of the alkaline earth metal.

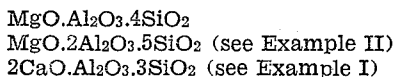
It will be understood that the colloidal substances with which this invention is concerned are not subject to exact description regarding the presence or absence of silicate or hydroxide. In

this respect, it is not possible to determine with accuracy whether magnesium silicate, for example, comprises a mixture of magnesium hydroxide together with silica or whether an actual silicate structure is formed. However, in accordance with the most accepted authorities, it appears probable that gels may be prepared having "pure" silicate structures such as magnesium silicate, calcium silicate and barium silicate. These are most easily prepared by the addition of an alkaline earth metal salt to sodium silicate solution in an amount sufficient to form the stoichiometric compound. Mixtures of silicates with silica having a reduced but sufficient amount of the alkaline earth metal present may be prepared by the addition of an alkaline earth metal salt to sodium or potassium silicate solution, the silicate being present in an excess over the amount required to form the alkaline earth metal silicate. Preferably, acid such as sulfuric acid is then added to this mixture to cause gelation of the colloid at a pH between about 6.5 and 8.5; hence, mixtures of magnesium silicate, calcium silicate or barium silicate with silica may be prepared.

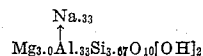
The alkaline earth metal salts useful for the preparation of the subject gels include especially the water soluble sulfates, chlorides or nitrates of the metal. Typical suitable members include calcium chloride and magnesium nitrate. Another class of inorganic gelling agents useful for the production of the present composition are the synthetic zeolites which comprise aluminum silicates having exchangeable alkaline earth metal ions. A typical preparation of such zeolites comprises the formation of aluminum silicate by reaction of sodium aluminate and sodium silicate followed by steeping the resulting gel in an alkaline earth metal salt such as magnesium chloride. The complex silicates which result from this type of preparation may be expressed by the general formula:



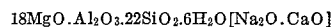
wherein M is an alkaline earth metal and a , b , c , and d are whole numbers such that various ratios of the three different oxides may be present. Preferably, the synthetic zeolites contain an alumina-to-silica molar ratio between 1 to 3 and 1 to 4. Also, it is preferable that the alkaline earth metal oxide and silica be present in the zeolites in a molar ratio between 0.5 to 4 and 2 to 4. Typical zeolites meeting the above requirements include the following structures:



The gels described hereinbefore are those having predominantly amorphous structure. The other class of suitable inorganic gelling agents comprises those having a highly organized crystalline structure as shown by their X-ray diffraction patterns. The two principal types of natural products meeting the critical alkaline earth content specified hereinbefore are the saponites and hectorites. Saponite is represented in its ideal structure in the two following forms:



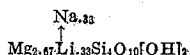
or



The most effective member of this series is hectorite which is a natural clay found princi-

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pally at Hector, California. This material is the end member of the montmorillonite series and comprises mainly magnesium silicate containing appreciable amounts of lithium and fluorine. It is represented in the following formulae:



or



It will be understood that no exact formula can be ascribed to these naturally occurring substances, since nearly every specimen will give a different analysis. It is pertinent to point out that many naturally occurring montmorillonites contain too low a natural content of alkaline earth metal to meet the present critical specifications. For example, Wyoming bentonite, which is sometimes called montmorillonite, contains about 1% magnesium. However, when this material is converted to an aliphatic ammonium bentonite complex which, in turn, is used as a grease-forming agent, the greases which result exhibit high emulsification characteristics.

It has been found possible to convert these low grade naturally occurring substances for use in the present compositions by treating them for extended periods of time with alkaline earth metal salts. Wyoming bentonite, for instance, may be dispersed in water to form a dilute hydrosol to which is added an alkaline earth metal salt such as magnesium chloride in an amount between about 5% and about 20%. This mixture is allowed to stand at a temperature between about 20° and 125° C. for a period of time ranging from about 1 to 60 hours. At the end of this period, the hydrosol is converted to an aliphatic ammonium clay complex by treatment with an ammonium salt such as dimethyldicetyl ammonium chloride, thus forming the gelled complex which may be subsequently washed free of chloride ions. Analysis of this material indicates that some of the alkaline earth metal has entered the clay complex, raising the alkaline earth metal content to a level within the critical range required in the present compositions.

Reference is made to the publication by Ross and Hendricks published by the United States Government Printing Office, 1945, entitled "Minerals of the Montmorillonite Group," pages 34 and 35. Tables 1 and 4 thereof describe numerous montmorillonites which are suitable for use in the present compositions and which contain the critically defined concentrations of alkaline earth metals together with the sources from which these clays were obtained. Further reference is made to the book by C. E. Marshall "The Colloid Chemistry of the Silicate Minerals" published by Academic Press Incorporated, 1949, and especially to page 59 thereof, Figure 25, which shows an idealized crystalline structure of the subject montmorillonites.

Many of these naturally occurring substances contain non-colloidal materials which interfere with their optimum function as gelling agents; hence, at times it is preferable to synthesize similar materials such as by the methods described by Strese and Hofmann, Z. Anorg. Allegem. Chem. 247, 65-95 (1941). According to the latter workers, magnesium silicate gels having crystalline structures may be prepared by hydrothermal treatment of magnesium silicate chloride.

While Strese and Hofmann are concerned espe-

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cially with the preparation of synthetic magnesium montmorillonites, it is possible to utilize the same general technique in the preparation of other alkaline earth metal synthetic montmorillonites such as barium, calcium, beryllium or strontium montmorillonites. An improvement over the process as described by Strese and Hofmann comprises the initial formation of colloidal magnesium silicate gel at temperatures between about 10° and 40° C. rather than at the boiling point recommended by these authors. Hence, a preferred process for the preparation of the colloidal gel comprises slow addition of dilute alkaline earth metal salt solution to an alkali metal silicate solution at about room temperature. The gel which sets may be washed and dried generally as described by Strese and Hofmann. It is then heated at temperatures between about 150° and 400° C. for periods between twelve and ninety-six hours at pressures of 200-1,000 lbs. per square inch in the presence of dilute alkali metal hydroxide solution. The resulting metal when examined by X-ray diffraction techniques exhibits typical montmorillonite patterns.

The above materials are dispersed in colloidal gel form in lubricating oils for the preparation of the present greases. While mineral lubricating oils are suitable for use in more instances, synthetic lubricants may be used in place of or in addition to mineral lubricating oil. The list which follows gives typical species of the varieties which may be employed. Generally, these include oxyalkylene polymers, silicone fluids, organic phosphates, polymerized olefins and esters of dicarboxylic acids.

LUBRICATING OILS

- Mineral lubricating oil, preferably viscosity of 300-350 SSU at 100° F.
- Propylene oxide polymers having average molecular weights of 200 to 1,500
- Ethylene oxide-propylene oxide copolymers
- Trimethylene glycol polymers
- Ethylene glycol-trimethylene glycol copolymers
- Silicone fluids
- Tricresyl phosphate
- Trioctyl phosphate
- Diphenylresyl phosphate
- Diphenyloctyl phosphate
- Di(2-ethylhexyl) sebacate
- Diocetyl caprylate
- Polymerized olefins
- Di(3-methylheptyl) adipate
- Polyvinyl caprylate

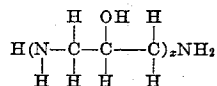
In accordance with the present invention, the essential ingredient promoting the water resistance of the above greases is a cationic hydrophobic surface active agent. The agent should be present in an amount dependent upon the inorganic gelling agent and not upon the total of the ingredients contained in the grease composition. Consequently, in providing for resistance against disintegration by the action of water, the agent should be present in an amount between 10% and about 75% by weight based upon the inorganic gelling agent. These water proofing materials include high molecular weight amines, amine salts and quaternary ammonium compounds, as well as amides, and amino amides. In the case of substantially neutral inorganic gelling agents, such as silica, the water proofing material appears to be simply absorbed on the gel surface. When ion exchange materials, such

as the zeolites and clays are being utilized, an ion-exchange reaction appears to occur between inorganic gel and the amino compound. For the present purpose, however, in order to simplify the description, especially in the claims, this apparent ion-exchange reaction, while assumed to take place is not exactly described since it is not capable of clear definition. It appears, however, that clays and quaternary ammonium compounds, for example, when contacted to react form what may be termed an amino clay. However, in the present case, the compositions are described as inorganic gels containing cationic surface-active agents by which it will be understood that the latter is either absorbed on or present in ion-exchange relationship to the inorganic gelling agent.

Preferred amines useful as hydrophobic agents include especially aliphatic fatty amines having from 10 to 30 carbon atoms. These include octadecylamine, dodecylamine and other amines, preferably of the primary and secondary varieties which are analogous or homologous to the above. In the water-proofing of mixtures of oxides, silicates, clays or zeolites, the use of polyamines or quaternary ammonium compounds is preferred.

In the treatment of natural clays, as well as of the synthetic materials, a preferred category of surface-active agent comprises the quaternary ammonium salts broadly described as tetra-alkyl ammonium halides. At least one and preferably two of the alkyl radicals have a chain length of at least twelve carbon atoms, and optimum results are obtained if two of the alkyl radicals have chain lengths between fourteen and eighteen carbon atoms. Representative preferred substances are dimethyldihexadecylammonium chloride and dimethyldioctadecylammonium chloride and mixtures thereof.

While the quaternary ammonium salts described above are preferred, salts of high molecular weight amines, either primary or secondary, may be used. Preferably, these are salts of hydrohalide acids such as hydrochloric acid or water-soluble carboxylic acids such as acetic acid, and the amines contain at least one aliphatic radical having from twelve to twenty-four carbon atoms. Other water-soluble acids may be used to form the salts, such as hydrobromic acid, propionic acid and lactic acid. The cationic materials need not be completely water-soluble for application to the silicate hydrosols. They are, in fact, for the most part, water-dispersible rather than water-soluble. This is particularly true when two or more of the alkyl radicals have twelve or more carbon atoms or when the amines are polymeric in nature such as in the case of acrolein-ammonia condensation products. Acrolein-ammonia condensation products such as those just referred to have molecular weights between about 100 and 350 and a general structure as follows:



wherein x is an integer sufficient to provide a molecular weight within the recited range. Any of the hydrogen atoms on either the carbon or nitrogen atoms may be replaced with hydrocarbon radicals preferably having from one to six carbon atoms. The following list of cationic surface-active agents gives typical species which may be employed for providing the recited silicates with hydrophobic surfaces:

CATIONIC SURFACE-ACTIVE HYDROPHOBIC AGENTS

A. Quaternary ammonium salts

- 5 Trimethyldodecylammonium chloride
- Trimethyltetradecylammonium chloride
- Trimethyloctadecylammonium chloride
- Triethylhexadecylammonium chloride
- Dimethyldihexadecylammonium chloride
- 10 Dimethylcetylaurylammonium chloride
- Dimethylaurylstearyl ammonium chloride
- Diethyldioleyl ammonium chloride
- Dimethyldiheptadecyl ammonium chloride
- 15 Dimethyloctadecyloctadecenyl ammonium chloride

B. Amine salts of inorganic acids

- Tetradecylammonium chloride
- Octadecylammonium bromide
- 20 Octadecenyl ammonium chloride
- Methyloctadecyl ammonium chloride
- Ethylhexadecyl ammonium bromide
- Dioctadecyl ammonium chloride
- Octadecylheptadecyl ammonium bromide
- 25 Dihexadecyl ammonium chloride
- Ditetradecyl ammonium bromide
- Octyloctadecyl ammonium chloride

C. Amine salts of organic acids

- 30 Octadecyl ammonium acetate
- Heptadecyl ammonium propionate
- Hexadecyl ammonium acetate
- Dioctadecyl ammonium acetate
- Octadecenyl ammonium acetate
- 35 Heptadecyl ammonium acetate
- 12-hydroxystearyl ammonium acetate
- 10-ketolauryl ammonium acetate
- Oleic acid salt of 2-heptadecylimidazoline

D. Miscellaneous amino compounds

- 40 Acrolein-ammonia condensation products
- Diallylamine- H_2S condensation products
- Epichlorohydrin-ammonia condensation products, described in copending patent application Serial No. 133,962, filed December 12, 1949.
- 45

The general process for the preparation of these greases comprises dispersion of the agent in the lubricating oil followed by milling to produce a grease structure. A number of processes are available to create the proper type of dispersion. The earliest known variety comprises producing a hydrogel of the colloid, replacing water with a water-miscible solvent such as alcohol or acetone, displacing the latter with an oil-soluble solvent such as pentane, adding the resulting organogel to lubricating oil and subsequently removing the oil-soluble solvent. The resulting oleogel may then be milled to produce a grease structure.

60 An alternative process for the preparation of these greases comprises the formation of aerogels which are subsequently dispersed in a lubricating oil. According to this particular process, a hydrogel is initially formed from which water is displaced with low boiling liquids, after which the organogel is placed in an autoclave and heated above the critical temperature of the liquid which is present, and then the liquid is flashed off, above the latter temperature, the resulting dry gel remaining in a highly expanded state substantially as it was originally formed, as opposed to the xerogel structure which results if gels are dried below the critical temperature of the liquid present.

75 A more practical process for the preparation of

these lubricants comprises the "direct-transfer" technique entailing the following steps: A hydrogel is formed to which is added a water-repellent agent such as an amine, after which the mixture is stirred with lubricating oil under conditions which permit the removal of water, such as by heat, vacuum or both. Under these conditions, the resulting anhydrous gel is preferentially wet by the lubricating oil, thus avoiding the expensive steps of solvent-displacement or of aerogel formation. The resulting greases are not only highly water-proof, but appear to give substantially the same yield as greases prepared by either of the two preceding methods. Generally, preferred hydrogels contain 1.5 to 4% colloid and optimum washing characteristics and grease yield occur when the colloid concentration in water is 2.3 to 2.8%.

Still a fourth method for the preparation of the subject greases depends upon the water-repelling action which follows the complex formation occurring between cationic surface-active agents and the crystalline or zeolitic colloids. The resulting "aminogel" even though it is in aqueous form may be added directly to lubricating oil and water subsequently removed. Alternatively, the aminogel may be dried prior to incorporation in lubricating oil. Finally, the greases may be prepared by the forming of several greases and subsequently mixing them in desired proportions.

The addition of an inorganic nitrite to greases containing both cationic surface-active agents and inorganic colloids results in a grease exhibiting what is apparently a synergistic effect, especially with respect to water resistance. This is demonstrated by the information contained in the examples given hereinafter and especially by Examples I and II. In accordance with these examples, greases were prepared which contained either nitrite or amino compound and in both cases the resulting grease was found to be unsatisfactory. However, as shown in the examples, greases containing a combination of both of these materials exhibited satisfactory operating properties as measured by two distinctly different test methods. These test methods are described as the "Roller Bearing Corrosion Test" and the "West Wheel Bearing Test."

The Roller Bearing Corrosion Test was conducted by lubricating a small bearing in a drill press at 120% of the rated load for periods between 35 minutes and 15 hours. The bearing was lubricated with the grease being tested (approximately 1.2-1.4 g.) and containing 4 cc. of water. Subsequent to operation under these conditions, the bearing was removed, placed in a Petri dish covered with water from the test run and left overnight. It was then inspected for corrosion which had developed during this static period. The bearings were rated from 0 to 10, with 10 rating corresponding to substantially no rusting and 0 corresponding to heavy rusting. The bearings employed in this test were roller bearings. It was found that if excessive amounts of the nitrites were employed, the greases became water sensitive and softened, thus resulting in disintegration during operation in the presence of water. When the nitrites were employed within the limits described hereinbefore, the drill press bearing rating was substantially perfect when both the nitrite and amino compounds were present in the same grease. Examination especially of Examples I and II will indicate the synergistic nature of this invention which shows that the comparative three-component compositions would not be ex-

pected, if combined, to give the outstanding results obtained.

Three greases were prepared. Each of them contained lubricating oil gelled with silica, the grease being prepared by the direct transfer process described hereinbefore. The cationic surface-active agent utilized in the direct transfer was the $\frac{1}{3}$ partial amide of tall oil and the condensation product of epichlorohydrin and ammonia. Grease C may be prepared by dispersing silica aerogel in lubricating oil containing sodium nitrite. Grease B contained the surface-active agent but did not contain nitrite. Grease A was prepared by the direct transfer process and contained not only the condensation product but also sodium nitrite. The table given hereinafter shows the comparative results obtained when these three greases were tested by the Drill Press Bearing Test.

The Wet Wheel Bearing Grease Test equipment is made up of two Timken tapered roller bearings, adequately supported and provided with suitable grease retainers. Provision is made for loading the bearings, rotating at the desired speed, and injecting the desired quantity of water at periodic intervals into the test bearing compartment.

The rig consists of a Lauson engine block which is used for supporting the two Timken main bearings of this engine. These bearings were adopted as the test bearings since they are of the automotive wheel bearing type. The engine cover plates with slight modifications were also used. Specially made parts include the internal covers or grease retainers, and two adapters which hold the bearing cones and are taper bored to fit matching tapers on either end of a driving shaft. A $\frac{1}{4}$ H. P., 1750 R. P. M. motor drives the bearings at this speed. Four calibrated springs, each compressed to a predetermined length against the test bearing cover plate, give the desired total load (in thrust) on the bearing. Manual periodic injection of water into the test bearing is accomplished with a 25 ml. burette connected to the test compartment. A thermocouple contacting the outer race of the test bearing gives its equilibrium temperature throughout the test.

The cleaned test bearing (Timken Cone No. 15118, Timken Cup No. 15250X) is packed full with about 6 grams of the test grease. The internal surfaces of the cover plate and grease retainer are covered with a thin coating of the grease. The test section is assembled in place and then installed on the supporting block, the tapered end of the driving shaft fitting into the taper bored bearing cone adapter.

The machine is started at very light load and loaded, while running, to the test load in approximately 3 minutes. Individual injections of 2 ml. of water are made according to the following schedule: first injection, 5 minutes after start of test; all subsequent injections at $\frac{1}{2}$ hour intervals with the final injection made 10 minutes prior to termination of the test. In all, 12 ml. of water are introduced into the test bearing compartment in the $2\frac{1}{2}$ hour test.

The operating conditions are as follows:

- (a) Speed—1750 R. P. M.
- (b) Load—530 lbs. in thrust (rated load for the bearing)
- (c) Test time— $2\frac{1}{2}$ hours
- (d) Type water—distilled water+0.05% w. NaCl

At the end of the run, the test section is re-

moved from the machine and disassembled and the bearings rated for corrosion.

TABLE I

	Weight Percent	Wet Wheel Bearing Test	Roller Bearing Test
A. Silica.....	7.7	-----	-----
Epichlorohydrin-ammonia condensation product.....	3.5	-----	-----
NaNO ₂	0.25	7	10.
Lube Oil.....	88.55	-----	-----
B. Silica.....	7.7	-----	-----
Epichlorohydrin-ammonia condensation product.....	3.5	2	2.
Lube Oil.....	88.8	-----	-----
C. Silica.....	8.0	-----	-----
NaNO ₂	0.25	-----	grease disintegrated.
Lube Oil.....	91.75	-----	-----

EXAMPLE II

Three greases were prepared by gelling a lubricating oil with a mixture comprising 5% magnesia in the form of magnesium silicate and 95% silica. Greases D and E contained the same cationic surface-active agent employed in Example I. These greases were tested by the Wheel Bearing Test. The results obtained are given in Table II.

TABLE II

	Weight Percent	Wet Wheel Bearing Test Rating
D. MgO-SiO ₂	7.9	-----
Condensation Product.....	3.1	-----
NaNO ₂	0.25	10.
Lubricating oil.....	88.75	-----
E. MgO-SiO ₂	7.7	-----
Condensation product.....	3.5	2.
Lubricating oil.....	88.8	-----
F. MgO-SiO ₂	8.0	-----
NaNO ₂	0.25	grease disintegrated.
Lubricating oil.....	91.75	-----

EXAMPLES III-X

The following examples are typical compositions which are preparable according to the present invention. When greases are prepared in the proportions of ingredients described, they exhibit outstanding resistance to disintegration by water and also of substantially no static corrosion.

Example.....	3	4	5	6	7	8	9	10
Inorganic Colloid, percent based on grease:								
Silica.....			8	10				
Magnesia.....					12			
Magnesium silicate.....						6		
Aluminum oxide.....							7	
95% silica+5% mg. silicate.....								5
Wyoming bentonite.....	5							
Hectorite.....		4						
Cationic Agent, percent based on grease:								
Octadecylamine.....			2.5				3	
Dimethyldioctadecyl-ammonium chloride.....	2					3		
Heptadecylammonium acetate.....					3.5			1.5
Stearic acid diamide of tetraethylenepentamine.....		1.5		4				
Nitrite, percent based on grease:								
NaNO ₂	1.0	0.5						0.5
KNO ₂				0.75				
NH ₄ NO ₂					2.4		1.0	
Ca(NO ₂) ₂			0.25					
Ba(NO ₂) ₂						0.2		
Lubricating oil, percent based on grease:								
Mineral oil.....	92	94	89.25	85.25				
Trioctylphosphate.....					82.1			
Bis(2-ethylhexyl) sebacate.....						90.8		
Polymerized alpha-olefines, C ₄ -C ₁₆								93
Polymerized propylene oxide.....							89	

We claim as our invention:

1. A grease composition comprising the following ingredients in the stated percentages by weight:

5	Mineral lubricating oil	88
	Silica	8
	Magnesium silicate	0.5
	Partial fatty acid amide of epichlorohydrinammonia condensation product	3.2
10	Sodium nitrite	0.25

2. A grease composition comprising a major amount of mineral lubricating oil, 2-20% by weight based on said composition of a mixture of colloidal silica and colloidal magnesium silicate, said mixture having an average particle size less than about 100 millimicrons, 1-20% by weight based on the mixture of colloids of ammonium nitrite and 10-75% by weight based on said colloids of an aliphatic hydrophobic polyamine.

3. A grease composition comprising a major amount of mineral lubricating oil, 2-20% by weight based on said composition of a mixture of colloidal silica and colloidal magnesium silicate, said mixture having an average particle size less than about 100 millimicrons, 1-20% by weight based on the mixture of colloids of calcium nitrite and 10-75% by weight based on said colloids of an aliphatic hydrophobic polyamine.

4. A grease composition comprising a major amount of mineral lubricating oil, 2-20% by weight based on said composition of a mixture of colloidal silica and colloidal magnesium silicate, said mixture having an average particle size less than about 100 millimicrons, 1-20% by weight based on the mixture of colloids of sodium nitrite and 10-75% by weight based on said colloids of an aliphatic hydrophobic polyamine.

5. A grease composition comprising a major amount of a mineral lubricating oil, 2-20% by weight based on the grease composition of a colloidal silicate having an average particle size less than about 100 millimicrons, 1-20% by weight based on the silicate of an alkali metal nitrite and 10-75% by weight based on said silicate of an aliphatic hydrophobic polyamine.

6. A grease composition comprising a major amount of a mineral lubricating oil, 2-20% by weight based on the grease composition of a colloidal inorganic oxide having an average col-

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loidal particle size less than about 100 millimicrons, 1-20% by weight based on said oxide of an alkali metal nitrite and 10-75% by weight based on said silicate of an aliphatic hydrophobic polyamine.

7. A grease composition comprising a major amount of a lubricating oil, a minor amount, sufficient to at least thicken said oil of an inorganic colloid having an average particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of a cationic hydrophobic surface active agent and 1-20% by weight based on said colloid of an alkaline earth metal nitrite.

8. A grease composition comprising a major amount of a lubricating oil and a minor amount, sufficient to at least thicken said oil of an inorganic colloid having an average particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of an aliphatic quaternary ammonium hydrophobic surface active agent and 1-20% by weight based on said colloid of an inorganic nitrite.

9. A grease composition comprising a major amount of a lubricating oil and a minor amount, sufficient to at least thicken said oil, of an inorganic colloid having an average particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of a cationic hydrophobic surface active agent and 1-20% by weight based on said colloid of an alkali metal nitrite.

10. A grease composition comprising a major amount of a lubricating oil and a minor amount, sufficient to at least thicken said oil, of an inorganic colloid having an average particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of an aliphatic polyamine hydrophobic surface active agent and 1-20% by weight based on said colloid of an inorganic nitrite.

11. A grease composition comprising a major amount of a mineral lubricating oil, a minor amount, sufficient to impart a grease structure to said composition of an inorganic colloid having an average colloidal particle size less than 100 millimicrons, 10-75% by weight based on said colloid, of an aliphatic cationic surface active agent and 1-20% by weight based on said colloid of an alkali metal nitrite.

12. A grease composition comprising a major amount of a lubricating oil, a minor amount, sufficient to at least thicken said oil, of a colloidal silicate having an average colloidal particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of a cationic hydrophobic surface active agent and 1-20% by weight based on said colloid of an inorganic nitrite.

13. A grease composition comprising a major amount of a lubricating oil, a minor amount, sufficient to at least thicken said oil, of a colloidal

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inorganic oxide having an average colloidal particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of a cationic hydrophobic surface active agent and 1-20% by weight based on said colloid of an inorganic nitrite.

14. A grease composition comprising a major amount of a mineral lubricating oil, a minor amount, sufficient to at least thicken said oil, of an inorganic colloid having an average particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of a cationic hydrophobic surface active agent and 1-20% by weight based on said colloid of an inorganic nitrite.

15. A lubricating composition comprising a major amount of a lubricating oil, a minor amount, sufficient to at least thicken said oil, of an inorganic colloid having an average particle size less than about 100 millimicrons, 10-75% by weight based on said colloid, of a cationic hydrophobic surface active agent and 1-20% by weight based on said colloid of an inorganic nitrite.

16. A grease composition comprising the following ingredients in the stated percentages by weight:

Inorganic colloidal gel	----	2-20%.
Aliphatic hydrophobic poly-	10-75% (based on	
amine.	the inorganic	
	gel).	

Sodium nitrite	-----	3-15% (based on
		the inorganic
		gel).

Mineral lubricating oil	-----	Balance.
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17. A grease composition comprising the following ingredients in the stated percentages by weight:

Inorganic colloidal gel	-----	2-20%.
Aliphatic hydrophobic poly-	10-75 (based on	
amine.	the inorganic	
	gel).	

Sodium nitrite	-----	3-6% (based on
		the inorganic
		gel).

Mineral lubricating oil	-----	Balance.
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18. A grease composition according to claim 7 wherein the inorganic colloid is clay.

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