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HIGH TEMPERATURE INORGANIC GEL GREASE COMPOSITIONS

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This invention relates to improved grease compositions. More particularly, it is concerned with greases exhibiting exceptionally high stability at elevated temperatures.

Grease compositions ordinarily comprise a liquid medium and a gelling agent therefor. The liquid medium is preferably one possessing lubricating properties and the gelling agent is ordinarily a soap or a colloidal material of inorganic origin. Mineral lubricating oils are primarily useful as the lubricating medium and soaps, such as those of fatty acids or hydroxy fatty acids, are commonly employed as gelling agent.

The present invention is directed to grease compositions containing gelling agents of inorganic origin as one of the essential constituents. Greases have been prepared heretofore which utilize amorphous colloidal gels, such as silica and the like, or which employ clays or onium clays as the grease-forming material. The latter clays comprise high base-exchange clays which have been converted to oleophilic materials by base exchange with oleophilic onium compounds such as quaternary ammonium materials or their phosphonium, sulfonium or stibonium analogs.

Greases gelled with ordinary soaps are useful for operation under relatively mild temperature conditions but at elevated temperatures, in the order of 200° F. or higher, soap greases rapidly soften and eventually become fluid. This is apparently due to phase changes which occur in the soap fibers as they change from one crystal form to another. Greases gelled with colloids of inorganic origin exhibit the advantage of maintaining their consistency over a far wider temperature range. Due to their inorganic character, the gels do not pass through phase changes at temperatures below about 500° C. but maintain the original structure of the grease substantially in its original state. Hence, the limiting character of such greases is not the softening thereof but instead is dependent upon the thermal and oxidation stability and volatility of the liquid component of the grease.

High temperature greases containing gelling agents of inorganic origin may utilize either mineral oil lubricants or synthetic fluids as the liquid phase. Since volatility is one of the limiting characteristics, any greases to be employed at high temperature must, of course, contain a major amount of high boiling oleaginous fluid.

Greases to be used at elevated temperatures for many purposes must be of relatively low cost if they are to be economically practical. Hence, it is highly desirable to employ a petroleum oil fraction as a major or sole component of lubricating oil phase of high temperature greases, but lubricating oils exhibit rapidly increasing decomposition when subjected to heat and oxidation influences. The addition of ordinary anti-oxidants, such as alkyl phenols or aromatic amines, has been found to be substantially ineffective above about 300° F. In fact, the course of oxidation at such elevated temperatures appears to be actually accelerated by these materials rather than retarded.

It is an object of the present invention to provide grease compositions useful at high temperatures. It is another object of this invention to provide grease compositions which maintain their structure and stability at elevated temperatures. It is a further object of this invention to provide grease compositions utilizing mineral oil fractions as a major component of the lubricating oil phase but which are stable when employed at high temperatures. Other objects will become apparent during the following description.

Now, in accordance with this invention, it has been found that greases gelled with a thickener of the group consisting of silica-containing inorganic amorphous colloids, clays and onium clays can be made remarkably stable to decomposition at elevated temperatures (even at as high as 300–450° F.) by the combination of from about 1% to about 25% by weight, based on the total grease, of carbocyclic hydrocarbons having molecular weights within the range of from about 300 to about 750, and from about 0.5% to about 20% by weight, based on the total composition, of a basic inorganic zinc compound, such as zinc oxide, zinc hydroxide, zinc borate and zinc carbonate, the balance of the composition comprising a major proportion of a lubricating oil.

The zinc compounds are preferably utilized in amounts between about 2.5% and about 10% by weight of the total grease. They should be utilized in the form of finely divided particles, such as utilized for paint pigments or the like, and preferably have particle sizes less than about 10 microns. Such finely divided powders can be easily incorporated in greases by milling or other shearing means, or may be formed in situ.

The carbocyclic hydrocarbons may be monocyclic or polycyclic, have molecular weights between about 300 and about 750, and preferably comprise higher aromatics or naphthenes. Typical donors are as follows:

2-methylnaphthalene
2,6-dimethylnaphthalene
2,3-dimethylnaphthalene
n-Propylcyclohexane
Cis-1,3-dimethylcyclohexane
Trans-1,4-dimethylcyclohexane
Cyclohexene
1-methyl cyclohexene
Δ^{4}-tetrahydrophthalic acid
$\Delta^{1:3}$-cyclohexadiene
$\Delta^{1:4}$-cyclohexadiene
$\Delta^{1:4}$-dihydronaphthalene
Δ^{1}-dihydronaphthalene
Δ^{2}-dihydronaphthalene
Isopropylcyclohexane
Amylcyclohexane
Triethylcyclohexane
Cis-decalin
Trans-decalin
Hexahydroindane
Cyclopentylcyclohexane
Bicyclohexyl
Amyldecalin
Abietanes

The proportion of carbocyclic hydrocarbon material required for effective stabilization of the present compositions is relatively insignificant but should be at least about 1% by weight of the final grease composition. The carbocyclic hydrocarbons may be a lubricant per se or may be added together with other lubricating components. Preferably the carbocyclic hydrocarbon is present in an amount between 5% and 25% of the weight of the grease composition. In most cases the carbocyclic hydrocarbon comprises more than one of the above types of compounds, but the use of single carbocyclic hydrocarbons is also contemplated. Cycloaliphatic (naphthenes) are preferred and especially those having molecular weights in the range of 300–750. In the case of certain lubricating oil fractions, such as bright stock, cylinder stock, and the like, the naphthenes may occur naturally, but in other instances, such as in synthetic lubricating materials, it may be necessary to add them. In the latter case, the naphthenes present in bright stock are suitable substances.

One aspect of the present invention comprises the process of operating and utilizing grease compositions at temperatures above about 300° F. in the presence of the above-described carbocyclic hydrocarbons and basic inorganic zinc compounds, whereby substantial protection against oxidative and thermal decomposition of the grease is accomplished. These essential zinc compounds and carbocyclic hydrocarbons may be combined with standard organic oxidation inhibitors so that the resulting compositions are not only protected against oxidation at temperatures above about 300° F., but also at lower temperatures encountered during operation. Thus, the present compositions may be modified by the presence of polynuclear aromatic amines such as phenyl-α-naphthylamine or by the addition of phenolic inhibitors such as 1,2-dihydroxybenzene and alkylated phenols.

Another desirable type of oxidation inhibitor to be included comprises one or more epoxy compounds and particularly glycidyl substances, such as glycidyl phenyl ether. Still further protection against degradation at elevated temperatures may be obtained by the inclusion at these temperatures of metallic sulfides, such as zinc sulfide, copper sulfide, tungsten sulfide, and the like. The latter type of materials appears to operate by coating the metallic surfaces with which the grease comes in contact, thereby masking the metal as a possible oxidation catalyst.

The major gelling agent in the subject greases is a colloid of inorganic origin, including silica-containing amorphous colloids, clays and onium clays utilized in amounts sufficient to gel the oil to a grease structure, normally in proportions of 1–15% by weight of the total grease. For the most part, such gelling agents include silica. Improvements in corrosion characteristics of the subject greases are obtained by combinations of silica with a minor proportion of an alkaline earth metal oxide such as magnesia or lime. It is believed that the mixed gelling agents chiefly comprise a mixture of silica with the alkaline earth metal oxide although some alkaline earth metal silicate may be present as well. Onium clays are prepared by dispersing high base-exchange clays, such as Wyoming bentonite, or hectorite, in water and adding thereto a quaternary onium compound such as dimethyl dioctadecyl ammonium bromide. The base exchange which occurs results in the formation of the so-called "onium clay" which preferably bears at least 50 milliequivalents of an onium radical per 100 grams of clay. Such onium clays are capable of swelling at least ten times their original dry volume in nitrobenzene. For this purpose the onium compound should bear at least one hydrophobic radical longer than 15 Angstroms and preferably having an area greater than 70 square Angstroms. For this purpose at least one of the organic radicals should contain more than about 10 carbon atoms in a straight chain. Other suitable onium compounds, which may be used in the formation of onium clays, include dodecyl ammonium acetate, triphenyl lauryl phosphonium bromide, didodecylethyl sulfonium bromide, decyltriphenyl arsonium bromide, as well as their analogs and homologs.

The amorphous gelling agents are preferably incorporated in the lubricating oil while in a highly expanded state of subdivision. The density of the amorphous gelling agents, such as silica and the like, should be between about 0.01 and 0.2 gram per milliliter such as can be obtained by the "aerogel" technique. According to the latter process, silica gel is dehydrated by solvent displacement with a low boiling liquid such as acetone or alcohol. The organogel so prepared is heated in an autoclave, or other pressure equipment, above the critical temperature of the solvent at which point the pressure is released and the solvent flashed off, leaving the silica or similar gel in a highly expanded form particularly useful for the formation of grease structures with lubricating oils. Other processes which may be employed to create similar substances substantially equivalent or superior to aerogels include the solvent transfer process wherein the organogel referred to above is added to a mineral lubricating oil, after which the more volatile liquid is removed by distillation. The oleogel which remains may then be milled into a grease structure. A still further process comprises admixture of the hydrogel of silica or the like with a hydrophobic surface-active agent, such as a high molecular weight amine or partial amide, filtration of a major proportion of the water which thereupon separates, incorporation of the concentrated modified hydrogel with mineral oil and subsequent removal by distillation or settling of water from the resulting mixture. The latter process is preferred due to its economy and convenience. Moreover, the presence of the hydrophobic surface-active agent provides the grease with waterproofed properties which it would not otherwise possess.

While it is possible to improve the oleophilic character of the gelling agents described herein by chemical reaction between base exchanging gelling agents such as clay and onium compounds, this is not essential. If a hydrophobic or oleophilic grease composition is desired, it is merely necessary to absorb on the surface of the gelling agents (amorphous colloids or clays) a hydrophobing proportion of a catonic hydrophobic surface-active agent. The amounts and identities of these agents are described in such patents as U. S. 2,554,222, U. S. 2,623,852 and U. S. 2,623,853.

The lubricating oil to be employed in the subject greases may be of either natural or synthetic origin. Mineral oils particularly useful are preferably residual oils commonly known as cylinder stocks or bright stocks.

While the present invention is not to be confined to the use of a mineral oil derived from any particular source or by any particular refining process, the usual source of suitable mineral oils comprises the fraction thereof generally termed "bright stocks," and particularly bright stocks having a viscosity index of 60–105. The term "bright stock" is one which is well recognized and commonly used in the art of refining mineral oils. To obtain the desired fraction, suitable lubricating stock crude oils are usually subjected to distillation under ordinary atmospheric or slightly reduced pressures in order to obtain a "long residue" comprising the fraction which does not distill under these conditions without substantial decomposition. The long residue is then subjected to vacuum distillation, often in the presence of steam. Under these conditions, gas oil and distillate lubricant fractions distill over, leaving what is normally termed a "short residue" or a "steam refined stock," also known as "cylinder stock." The steam refined stock is then deasphalted (if an asphaltic crude is employed) and subjected to dewaxing operations to remove microcrystalline or macrocrystalline waxes. Following this, the dewaxed oil is treated with a solvent for the purpose of removing at least a portion of the aromatic components, except for a very highly paraffinic oil. Clay contact treatment or percolation may be employed to clean up the oil following any one or all of these separate operations. The raffinate which remains after deasphalting, dewaxing, extraction, and clay treatment is generally called "bright stock," The bright stocks for use in the present compositions should have the ranges of properties given in Table I:

TABLE I

Properties of bright stocks

Viscosity, SUS, 100° F., >1250, usually 1250–11,000, preferably 1500–3500
Viscosity, SUS, 210° F., >75, usually 125–325, preferably 150–250
Viscosity index, >+60, preferably +85–110
Aniline point, °C., >100 preferably >115
Flash, °F., >475, preferably >500
Fire, °F., >550, preferably >600
Pour point, °F., maximum, 25 preferably lower than 15
Percent aromatics <15, preferably <10—opt. <5
Percent naphthenes, <35
Percent paraffins, at least 60

Tables II and III give the properties of typical bright stocks which are useful in the compositions of this invention:

TABLE II

Examples of typical bright stocks

	SUS		Viscosity Index	Ring Analysis			Ratio of Paraffins to Naphthenes	Aver. Mol Wt.	Aver. Rings per Mol
	100	210		Aromatic	Naphthenes	Paraffins			
Mid Continent Bright Stock, Conventional Extraction	3,650	164	77	13	17	70	4.1	685	3.7
Mid Continent Bright Stock, Mild Extraction	2,569	141	85	9	19	72	3.8	685	3.4
Mid Continent Bright Stock, Heavy Extraction	2,049	131	93	3	21	76	3.62	675	2.9
Pennsylvania Bright Stock	2,109	144	102	5	16	79	4.95	730	3.0
Gulf Coastal Bright Stock	1,251	85	63	4	35	61	1.74	515	3.4

TABLE III

Specifications for typical Mid-Continent bright stocks

	Unfiltered		Filtered
Gravity, ° API, minimum	25.5	24.5	25.5
Color, NPA	8+	Dark Green	6.7
Pour Point, ° F., maximum	10	10	10
Flash, ° F., minimum	540	580	545
Fire, ° F., minimum	615	655	610
SUS at 210° F	150–170	200–215	150–160
Viscosity Index, minimum	90	90	90

It will be understood from the above analyses that the source or treatment of a particular mineral oil is not as important for the present purpose as the final properties of the mineral oil to be used in these compositions. For example, it is possible to vary the extent of solvent extraction dependent upon the original aromatic content and the requirements of the specific use of the final product, as well as upon the necessity or desirability of deasphalting, clay treating, acid treating, and the like. Hence, it will be recognized that the present invention is predicated upon the use of a mineral oil fraction having the above-defined ranges of properties and not upon the source or treatment of such oil.

In addition to their naphthenes, the two most important inherent properties of a mineral oil suitable for the present use comprise the aromatic content and the viscosity characteristics. The aromatic content has a large influence upon the sensitivity of the oil to thermal changes and the viscosity of the oils defines their suitability for their present purposes. Hence, the best definition with respect to essential characteristics of mineral oils suitable for the present compositions comprises those having an aromatic hydrocarbon content less than about 15% by weight and having a viscosity of between about 1250 and about 11,000 SUS at 100° F. Having defined these particular properties, the other properties such as flash, fire, aniline point, and viscosity index usually are largely dependent upon them.

In addition to the bright stocks and the like described above, synthetic lubricants can be utilized, including especially the ester type of lubricant and aliphatic polyethers. Representative classes of esters which may be employed are carboxylates, phosphates, and silicates. Polyethers comprise polyalkylene oxides and polyalkylene glyocols which may have either or both ester or ether end groups. All of these classes of materials have been fully described in the lubricating oil art. For the present high temperature greases species should be selected showing a suitable viscosity at the temperature contemplated during the use of the grease. Preferably they should exhibit an evaporation rate of less than about 5% at 400° F. in 8 hours.

Suitable species include bis(2-ethylhexyl)sebacate, and the corresponding dialkyl esters of dicarboxylic acids, said acids having from 4 to 16 carbon atoms separating the carboxyl groups and the alcohol portion of said esters being derived from mono- or polyhydric alcohols containing at least about 4 carbon atoms, and preferably from 6 to 12 carbon atoms each. Phosphorus acid esters which may be employed include not only organic phosphates, but also phosphonates and phosphinates; corresponding phosphine oxides are also suitable. Phosphorous esters which have been found to be especially suitable include tricresyl phosphate, trioctyl phosphate, diphenyl cresyl phosphate, diphenyl octyl phosphate, dinonyl isooctenephosphonate, bis(phosphonoethyl)ether, and the like. Suitable silicon esters include the trialkyl silicates wherein each alkyl group has from 2 to 8 carbon atoms, such as tetrabutyl silicate and tetra-2-ethylhexyl silicate. The corresponding thiasilicates [e. g. tetra(7-methyl-4-thiaoctyl)silicate] are also useful and impart extreme pressure properties to the greases containing them. Alyklene oxide polymers may be prepared by known processes of polymerizing alkylene oxides or glycols such as propylene oxide or ethylene oxide or of copolymerizing ethylene oxide with propylene oxide. The resulting mixture of polymeric materials preferably has a molecular weight between about 200 and 2000, and contains polyoxyalkylene chains terminating in hydroxyl radicals. These may be modified by esterification or etherification for the preparation of polymeric derivatives having improved lubricating properties. Particularly desirable types include those in which at least about 25% by weight of the end groups are etherified with alcohols which have from 4 to 12 carbon atoms per molecule and wherein at least 25% of the terminal hydroxyls are esterified with aliphatic carboxylic acids having between 2 and 20 carbon atoms per molecule.

In demonstrating the effectiveness of the subject carbocyclic hydrocarbons combined with the zinc compounds for reducing the thermal and oxidative decomposition tendencies of greases, three types of tests were employed: In the first test, a film of the grease composition approximately 0.013 inch in thickness is spread on a sanded steel plate and heated for 6 hours at 400° F. in an atmosphere of circulating air. A grease consisting of 90% by weight of Mid-Continent bright stock containing 16% by weight of naphthenic hydrocarbons and silica aerogel in an amount of 10% by weight of the grease oxidizes to a hard lacquer under these conditions.

When the same grease is modified with 10% by weight of zinc oxide, and heated under the same conditions, the grease film remains plastic and appears to be substantially unchanged from its condition at the start of the test. Modification of the original silica-bright stock grease with 10% by weight thereof of zinc carbonate gives substantially the same degree of stabilization as obtained by the use of zinc oxide. In order to show that this phenomenon is not of wider applicability, a corresponding test, made with the same silica-bright stock grease modified by the presence of 10% by weight thereof of alumina, results in a grease film after the test period which is a very hard varnish having no grease-like properties remaining.

Parallel tests were made upon grease compositions comprising 92% by weight of the same bright stock lubricating oil gelled with 8% by weight of a dimethyl dioctadecyl ammonium clay, said ammonium clay having the trade name "Bentone 34." In the absence of any further modification, the film of grease after the test period is an extremely hard varnish. The addition of 10% by weight of zinc oxide to this grease before the test period results in a grease film upon testing which is stiffened somewhat but is not the hard varnish obtained by the unstabilized composition. The substitution of 10% zinc carbonate in place of zinc oxide results in a grease which remains plastic and is easily worked even after the test period. However, the substitution of 10% by weight of alumina for the zinc compounds provides no stabilization of the ammonium clay-bright stock grease, the heat tested grease film being very hard.

A second test comprises heating a diluted grease composition in a Dornte oxidation apparatus at 180° C. to determine the rate of oxygen absorption in the presence an iron catalyst. For this purpose the greases are diluted with additional quantities of the same mineral lubricating oil employed in the original grease in order to provide a fluid enough structure for oxygen to bubble therethrough. Under the conditions described a fluid grease comprising 2% silica and a mineral oil bright stock requires only 1.1 hours to absorb 1500 cc. of oxygen. A similar composition modified by the presence of 10% zinc carbonate is stable for approximately six times the period in which the uninhibited composition was tested.

A third test for investigating the effect of the present compositions comprises utilizing the grease in a bearing rig operated at 400° F. to lubrication failure involving a high level or stalling of the rig. In this test the rig is operated for four hours at ambient temperature and then raised to the operating temperature of 400° F. for ten hours. The machine is then stopped for ten hours and the cycle then repeated. Under these conditions a silica-bright stock grease containing 10% silica gel and 90% bright stock lasts for only about four to six cycles. The addition of 10% zinc carbonate causes a 200 to 300% increase in cycle life.

This application is a continuation-in-part of application Serial No. 299,016, filed July 15, 1952, now abandoned, said application being a continuation-in-part of application Serial No. 170,248, filed June 24, 1950, now U. S. Patent 2,658,869.

We claim as our invention:

1. A grease composition consisting essentially of a major amount of a mineral lubricating oil containing 1 to 25% by weight, based on the total grease, of carbocyclic hydrocarbons having molecular weights within the range of from about 300 to about 750, a grease-forming proportion of a grease-forming gel of the group

consisting of amorphous inorganic colloids predominating in silica, hectorite and bentonite clays having adsorbed on the surface thereof a hydrophobing proportion of a cationic hydrophobic surface active agent, and onium hectorite and bentonite clays, and between about 0.5% and about 20% by weight of a compound selected from the group consisting of zinc oxide, zinc hydroxide, zinc borate and zinc carbonate.

2. A grease composition consisting essentially of a major amount of a mineral oil bright stock having a viscosity between about 1250 and about 11,000 SUS at 100° F., a viscosity index of 60–105 and containing 1–25% by weight, based on the total grease, of naphthenic hydrocarbons having molecular weights within the range of from about 300 to about 750, a gelling proportion of a grease-forming silica gel, and between about 0.5% and about 10% by weight of zinc carbonate.

3. A grease composition consisting essentially of a major amount of a mineral oil bright stock having a viscosity between about 1250 and about 11,000 SUS at 100° F., a viscosity index of 60–105 and containing 1–25% by weight, based on the total grease, of naphthenic hyrocarbons having molecular weights within the range of from about 300 to about 750, a gelling proportion of a grease-forming dimethyldioctadecyl ammonium bentonite clay gel, and between about 0.5% and about 10% by weight of zinc carbonate.

4. A grease composition consisting essentially of a major amount of a mineral oil bright stock having a viscosity between about 1250 and about 11,000 SUS at 100° F., a viscosity index of 60–105 and containing 1–25% by weight, based on the total grease, of naphthenic hydrocarbons having molecular weights within the range of from about 300 to about 750, a gelling proportion of a grease-forming silica gel, and between about 0.5% and about 10% by weight of zinc oxide.

5. A grease composition consisting essentially of a major proportion of a mineral lubricating oil containing 1–25% by weight, based on the total grease, of said oil of naphthenic hydrocarbons having molecular weights within the range of from about 300 to about 750, a gelling proportion of a silica grease-forming gel, and between about 0.5% and about 10% by weight of zinc carbonate.

6. A grease composition consisting essentially of a major proportion of a mineral lubricating oil containing 1–25% by weight, based on the total grease, of cycloaliphatic hydrocarbons having molecular weights within the range of from about 300 to about 750, a gelling proportion of a grease-forming dimethyldioctadecyl ammonium bentonite clay gel having adsorbed on the surface thereof a hydrophobing proportion of a cationic hydrophobic surface-active agent, and from about 0.5% to about 10% by weight of zinc carbonate.

7. A grease composition consisting essentially of a major amount of a mineral lubricating oil containing 1–25% by weight, based on the total grease, of carbocyclic hydrocarbons having molecular weights within the range of from about 300 to about 750, a grease-forming proportion of a grease-forming gel of the group consisting of amorphous inorganic colloids predominating in silica, hectorite and bentonite clays having adsorbed on the surface thereof a hydrophobing proportion of a cationic hydrophobic surface active agent and onium hectorite and bentonite clays, and between about 0.5% and about 20% by weight of a basic inorganic zinc compound.

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