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2,944,970

HIGH TEMPERATURE GREASE COMPOSITIONS CONTAINING SALICYLIC ACID DERIVATIVES

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No Drawing. Filed July 12, 1954, Ser. No. 442,907

10 Claims. (Cl. 252—18)

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 useful as the lubricating medium and soaps of fatty acids or of hydroxy fatty acids are commonly employed as gelling agents. The present invention does not deal with greases containing a major amount of soap as the gelling agent. It is directed, instead, to grease compositions, plastic solids or jellies in which are combined said lubricating properties and most especially the ability to lubricate for extended periods at relatively high temperatures, especially in excess of about 200° C.

Greases have been prepared heretofore which utilize a number of non-soap gelling agents which have a particular advantage over soap base greases in that they do not pass through a "phase change" which may drastically alter the consistency of the grease and even destroy the grease structure. As opposed to this undesirable property of soap greases, the greases with which the present invention deals retain their grease-like structure at elevated temperatures. Past experience, in fact, has shown that the limiting property of the present greases does not comprise the change in consistency of the grease due to an alteration in the gelling agent per se, but rather upon the instability of the lubricating medium at elevated temperatures. Consequently it will be seen that while the use of non-soap gelling agents such as those described hereinafter should enable them to operate at elevated temperatures, there is still a limitation upon such use, due to the instability of the component of the grease other than the gelling agent. Such non-soap gelling agents comprise amorphous colloidal gels such as silica or the like or onium clays all to be described more fully hereinafter.

Other suitable high temperature gelling agents include various forms of grease-forming colloidal carbon blacks or acetylene blacks.

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 temperatures must contain a major amount of relatively high boiling oleaginous fluids. This can be accomplished by the use of certain high molecular weight synthetic materials but with the inherent disadvantages of high cost and lack of lubricity.

The experience of oil compounders in the use of various anti-oxidant materials such as amines and phenols has proved to be of substantially little value when attempting to solve the problem of instability of the subject type of greases, especially when high temperature use is considered. The presence of the colloidal gels especially of the silica gel type appears to catalyze

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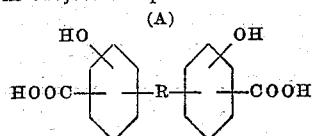
decomposition of lubricating oils which in their absence might be stable at the same temperatures. The presence of such well-known anti-oxidants such as 2,6-ditertiarybutyl-4-methylphenol or other alkylated phenols such as tritertiarybutyl phenol has proved to be of no help since these materials do not stabilize the greases against decomposition at temperatures in the order of 400° F. or above. The same may be said of aromatic amines such as the well-known phenyl-alpha-naphthylamine or other diaryl amines such as diphenylamine, phenyl-beta-naphthylamine and the various dinaphthylamines. These latter materials may provide adequate protection at relatively low operating temperatures in the order of 100–250° F.; however, when utilized in the subject grease compositions at relatively high temperatures in the order of 400° F. and above, it has been found that these amines and phenols, far from stabilizing the subject compositions actually appear to be pro-oxidant materials. Hence, their use for the present purpose is of little value and may in fact be harmful.

It is an object of the present invention to provide grease compositions particularly useful at temperatures in the order of 400° F. and above. It is another object of this invention to provide grease compositions which maintain their structure and lubricating properties at relatively highly elevated temperatures. It is a further object of this invention to provide grease compositions which remain plastic at high temperatures in the substantial absence of aromatic amines and phenols. Other objects will become apparent during the description of the invention.

Now, in accordance with the present invention, it has been found that grease compositions having unexpectedly high stability at elevated temperatures may be prepared by dispersing a gelling proportion of a colloidal gel of inorganic origin in a lubricating oil together with a stabilizing proportion of an alkylene bis(hydroxy benzoic acid), or the metallic salts of a hydroxy benzoic acid. More particularly, the stabilizing materials utilized in the present invention are preferably the alkylene bis(salicylic acids) or the polyvalent metal salts of alkyl salicylic acids all as more particularly described herein-after.

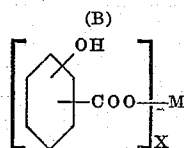
The present invention is predicated upon the fact that these stabilizing substances produce grease compositions which remain plastic for extended periods even in temperatures in excess of 400° F., in spite of the fact that the unmodified greases carbonize and substantially decompose after relatively short periods at these same temperatures. These relative properties will be described in greater detail in the operating examples which follow hereinafter. The stabilizing effect of the subject classes of material is especially surprising since their presence even in the amounts necessary for effective stabilization does not result in any substantial softening of the grease. This phenomenon is especially unexpected in view of the fact that these materials are primarily known as detergents and consequently would be expected to cause softening of the grease compositions or even liquefaction thereof. However, contrary to this expected result, it has been found that the materials, if anything, actually provide further stiffening of the grease compositions thereby improving rather than degrading their properties at elevated temperatures.

The two general classes of materials especially effective for use in subject compositions are as follows:



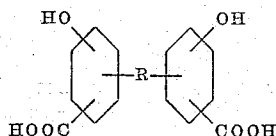
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wherein R is an alkylene hydrocarbon radical.



wherein M is a polyvalent metal radical, preferably divalent and X is an integer identical with the valency of the metal M.

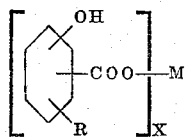
The preferred class of substances especially useful for the present purpose comprise the alkylene bis(hydroxy benzoic acids), and particularly the alkylene bis(salicylic acids). It will be understood that the materials of this particular class are rarely obtained in their pure state. They comprise in most cases complex mixtures of analogues and homologues especially with respect to the relative positions of the substituents directly attached to the two aromatic rings. The rings may be the same or different and may contain alkyl substituents of varying lengths. Moreover, mixtures of alkyl radicals, i.e. more than one alkyl radical, may be present on one or both of the aromatic nuclei. The preferred substances are the alkylene bis(hydroxy-benzoic acids), which have the following configuration:



Typical species of this class are methylene bis(salicylic acids); ethylene bis(salicylic acids); propylene bis(salicylic acids); methylene bis(isopropyl salicylic acids); methylene bis(C₁₄₋₁₈ alkyl salicylic acids); and decylene bis(salicylic acids).

Other alkylene bis(hydroxy aromatic acids) suitable for the present purpose include methylene bis(gallic acids); ethylene bis(vanillic acids); methylene bis(protocatechuic acids); and propylene bis(tannic acids). It is found to be particularly suitable if the alkylene radical acting as the link for the two hydroxy carboxy aromatic nuclei contains between 1 and about 10 carbon atoms. Moreover, any alkyl substituents on the aromatic nuclei should have between about 3 and about 24 carbon atoms each and may be either straight chain or branch chain alkyl radicals. Either one or both of the nuclei may be alkylated in this manner.

Also effective for the present purpose are the polyvalent metal salts of salicylic acids and preferably of alkylated salicylic acids wherein the alkyl radical (including isoalkyl) contain between 3 and 24 carbon atoms each. Preferably alkaline earth metal radicals are used in the preparation of such salts, however, amphoteric metals such as zinc, aluminum and tin may be applied. Suitable metallic radicals therefor include those of beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, aluminum, and tin. The following list of salts of alkylated salicylic acids denotes typical species which may be employed for the present purpose.



R is an alkyl (including isoalkyl) radical of 3-24 C's, in varying positions, M is a polyvalent (preferably divalent) metal radical and X is an integer equivalent to the valency of the metal M. Suitable species of this class include the following: Ca di(isopropyl salicylates); Zn di(isobutyl salicylates); Zn di(C₁₄₋₁₈ alkyl salicylates); Mg di(isopropyl salicylates); Ca di(3,5,5-trimethylhexyl salicylate); and Ba di(2,4,4-trimethyloctyl salicylate).

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While the salicylates have been specified in the above list, the corresponding meta- and para-benzoic acid derivatives may be employed. The length of the alkyl radical will depend in part upon the solubility required of the stabilizing material, as well as upon the temperature to which the greases will eventually be subjected. The higher the expected operating temperature of the grease, the larger the alkyl radical should be so as to reduce the volatility of the compound. Solubility, however, is not a major requirement in many cases since it appears to be necessary only to disperse the materials even in suspended form in the greases rather than requiring their complete solution in the grease composition.

While the polyvalent metal salts of alkylated salicylic acids are preferred above other derivatives of similar nature, the following polyhydroxy benzoic acid derivatives may be used in place of or in addition to such materials: metal salts of alkyl dihydroxybenzoic acids (alkyl protocatechuic acid salts), e.g. Ca di(dihydroxyisopropylbenzoic acids); Mg di(dihydroxyoctadecylbenzoic acids); and Cd di(dihydroxytetradecylbenzoic acids).

The stabilizing agents are to be employed in the present grease compositions in amounts varying from about 1% to about 10% by weight of the total grease. They should be dispersed uniformly through the grease composition in a relatively fine state of subdivision such as by means of passing through a colloid mill or a paint mill and the like preferably after being combined with the preformed grease made of the components to be described herewith.

The compositions of this invention contain as the major gelling agent from about 2% to about 20% by weight of a colloid of inorganic origin. Usually between 5% and about 15% by weight of said colloids provide the composition with a suitable grease consistency. For the most part, such gelling agents include grease-forming amorphous colloidal materials including silica, alumina, magnesia, lime and combinations thereof in the form of voluminous precipitates having their normal liquid content, e.g. water, replaced by a lubricating oil. In addition to the amorphous colloidal substances useful for the present purpose, clays, onium clays, or carbon blacks having high absorptive capacity are also satisfactory. Improvements in corrosion characteristics of the subject greases are obtained by combinations of silica with a minor proportion of an alkylene earth metal oxide such as magnesia or lime.

The onium clays are prepared and utilized in accordance with the disclosures of the Jordan patent, U.S. 2,531,440. Preferably these 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 dioctadecylammonium bromide. The base exchange which occurs causes the formation of the so-called "onium clay," which preferably bears at least 15 milliequivalents of an onium radical per hundred grams of clay. Such onium clays are capable of swelling at least ten times their original dry volume in nitrobenzene. For the present purpose, the onium compound should bear at least one hydrophobic radical longer than about 10 angstroms and preferably has a surface area greater than about 35 square Angstroms. Thus, at least one of the organic radicals of the onium compound should contain greater than about 10 carbon atoms in a straight chain. Other suitable onium compounds which may be used in the formation of onium clays include dodecylammonium acetate, triphenyl laurylphosphonium bromide, didodecylethylsulphonium bromide, decyltriphenylarsonium bromide, as well as their analogs and homologs of which the ammonium compound is preferred.

The amorphous gelling agents are preferably incorporated in the mineral lubricating oil while in a highly expanded state of subdivision. The bulk density of the amorphous gelling agents, such as silica and the like,

should be between about 0.05 and 0.25 gram per cubic centimeter such as can be obtained by the "aerogel" technique or by solvent transfer methods. According to the aerogel process, a gel such as silica hydrogel is dehydrated by solvent displacement with a low boiling liquid having a low critical temperature, such as acetone or ethyl alcohol. The organogel so prepared is heated under pressure in a closed autoclave, or other pressure equipment, above the critical temperature of the solvent, at which time 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.

Low density fines from pigment grinding processes or from catalyst preparations may be used. Also, aerosol processes, such as the burning of silicon tetrachloride and the like may be utilized. Other processes which may be employed to create similar substances 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 to form a grease structure. A still further process comprises admixing 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 separates, incorporation of this 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 waterproof properties which it would not otherwise possess.

Any of the well-known mineral oil or synthetic lubricating oil lubricating bases (and mixtures of mineral oil with synthetics) well-known for their use in grease compositions may be employed in the present instance. Suitable synthetic substances include particularly the aliphatic diesters such as the sebacates, azelates, adipates and the like including bis(2-ethylhexyl)sebacate, bis 3,5,5-trimethylhexyl-adipate; the corresponding tetraalkyl silicates, phosphorus esters including particularly the aliphatic and aromatic phosphates, phosphonates and phosphinates, e.g. tricresylphosphate, trioctylphosphate, diphenylcresylphosphate, dicresyloctylphosphate; fluorocarbons, silicones and the like. Mineral lubricating oils are preferred and residual oils such as cylinder stocks or bright stocks are particularly useful due to their physical properties making them especially suitable in grease compositions to be used at elevated temperatures.

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 particularly suitable and preferable mineral oils comprises the fraction thereof generally termed "bright stocks," and particularly bright stocks having a viscosity index of at least 60. The term "bright stock" is one which is well recognized in the art of refining mineral oils. To obtain the desired fraction, crude oils are usually subjected to distillation under ordinary 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 steam distillation, usually under a vacuum. Under these conditions, gas oil and waxy 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 deasphalted and dewaxed oil is treated with a solvent for the purpose of reducing or removing the aromatic fractions. The solvent extraction and dewaxing can be reversed in sequence if desired. Clay contact treatment or percolation may be employed to clean up the oil fol-

lowing 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 suitable for use in the present compositions should have the following ranges of properties:

Table I.—Properties of bright stocks

Viscosity, SUS, 100° F.....	>1,250, usually 1,250-11,000, preferably 1,500-3,500.
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.

The tables which follow give the properties of typical bright stocks which are useful in the compositions of this invention.

Table II.—Examples of typical bright stocks

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

Table III.—Specifications for typical Mid-Continent bright stocks

	Unfiltered		Clay 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 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 constituent 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 in its preferred embodiment 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.

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 purpose. Hence, the best definition with respect to essential characteristics of mineral oil suitable for the present compositions comprises those having an aromatic hydrocarbon content

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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.

While the essential ingredients of the subject grease compositions now have been described, further improvements in the stability of the greases at elevated temperatures may be accomplished by the supplementary presence of other stabilizing substances including heavy metal sulfides, acid salts of phosphoric acids, hydrogen donor materials such as zinc carbonates, and most particularly acids of the type utilized in the formation of the metallic stabilizing salts described hereinbefore. Such acids include especially the alkyl salicylic acids but also contemplate the use of analogs and homologs thereof as well as isomeric materials. Suitable species of materials include the isopropyl hydroxybenzoic acids, n-hexylhydroxybenzoic acids, and more desirably, those hydroxy aromatic carboxylic acids bearing at least one alkyl substituent containing at least ten carbon atoms. The reason for this minimum chain length, of course, is to decrease the volatility of the material so that it will remain in the grease composition during high temperature operation. Suitable substances for this purpose include especially dodecyl-ortho-hydroxybenzoic acids, tetradecyl-meta-hydroxybenzoic acids, and octadecyl-para-hydroxybenzoic acids as well as the corresponding gallic acids, vanillic acids, tannic acids and the like, containing substituents of ten or more carbon atoms so as to minimize volatility. The presence of these materials enhances the stabilizing effect of the salts and/or of the alkylene bis(hydroxyaromatic carboxylic acids). The molar ratio of the above acids to the essential stabilizer described hereinbefore is preferably between 1:4 and about 4:1 with the optimum range being between 1:2 and 2:1.

A film of the grease composition, approximately 0.013 inch in thickness, is spread on a sanded steel plate and heated for six hours at 200° C. in an atmosphere of circulating air. Greases comprising a mineral oil bright stock and 10% of a silica aerogel turn to hard lacquer under such conditions. When a corresponding grease is modified with 5% by weight of methylene bis(salicylic acid) and heated under the same conditions, the film of grease remains plastic and appears to be substantially unchanged from its condition at the start of the test. Similar results may be obtained by the modification of silica aerogel bright stock grease with 5% by weight of zinc bis(isopropylsalicylate). Still more satisfactory results may be obtained by modifying the same type of grease with about 4% by weight of the calcium salt of C₁₄₋₁₈ alkyl salicylic acids. The use of this relatively non-volatile material stabilizes the grease composition for longer periods than can be obtained by the use of the two stabilizing agents mentioned above.

Another test for investigating the stability of the present compositions comprises operating a bearing rig (packed with the grease being tested) at 400° F. to failure (involving a high noise level or stalling of the rig). In this test the rig is operated for four hours at ambient temperature and then raised to 400° F. for 10 hours. The machine is then stopped for ten hours and the cycle then repeated.

A grease comprising a mineral lubricating oil gelled with about 10% by weight of a hydrophobic onium clay lasted only two cycles in the above test. Addition of 10% (based on the grease) magnesium (diisopropyl salicylate) to the same grease extended the test life to ten cycles. The onium clay was produced by reaction of about six parts by weight of dimethyldioctadecylammonium bromide with ten parts by weight of Wyoming bentonite.

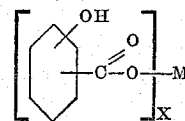
A second grease was prepared by addition of 5% by weight of surface-esterified silica to a mineral oil bright stock. This grease lasted four cycles in the above test,

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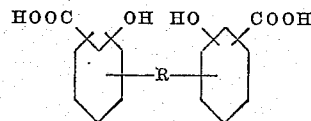
Addition of 5% by weight, based on the grease, of magnesium (diisopropylsalicylate) caused an increase in the life of the grease to ten cycles.

I claim as my invention:

1. A high temperature grease composition consisting essentially of a major proportion of a mineral lubricating oil, a gelling proportion of a non-soap colloidal gel of inorganic origin of the group consisting of amorphous inorganic oxides, clays and onium clays, and from about 1% to about 10% by weight of a hydroxy carboxy aromatic substance of the group consisting of

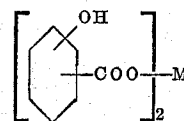


and



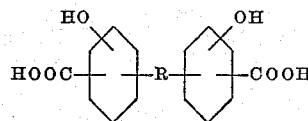
wherein the metal radical M is a polyvalent metal radical, X is an integer equivalent to the valency of the metal M, and the alkylene hydrocarbon radical R contains between about 1 and about 10 carbon atoms, the amount of said aromatic substance being sufficient to materially prolong the plastic life of the grease at high temperatures.

2. A high temperature grease composition consisting essentially of a major proportion of a mineral lubricating oil, an amount sufficient to impart a grease structure to said oil of an amorphous grease-forming inorganic colloidal gel of the group consisting of amorphous inorganic oxides, clays and onium clays, and as a high temperature stabilizer therefor from 1% to 10% by weight of a compound having the general formula



wherein M is an alkaline earth metal radical, the amount of said compound being sufficient to materially prolong the plastic life of the grease at high temperatures.

3. An improved lubricating grease composition consisting essentially of a major proportion of a mineral lubricating oil, an amorphous grease-forming inorganic colloidal gel of the group consisting of amorphous inorganic oxides, clays and onium clays, and from 1% to 10% by weight of a compound having a structural formula



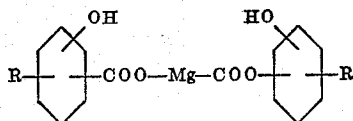
wherein R is an alkylene radical of from one to ten carbon atoms, said latter compound is present in said lubricant in an amount sufficient to materially prolong the plastic life of the grease at temperatures of about 250° F. and said colloidal gel is present in an amount sufficient to produce a composition having the consistency of a grease.

4. An improved lubricant consisting essentially of a residual mineral lubricating oil, a grease-forming proportion of an amorphous grease-forming inorganic oxide colloidal gel and from 1% to 10% by weight of an alkylene bis(salicylic acid), said alkylene radical containing between about 1 and about 10 carbon atoms.

5. An improved lubricant consisting essentially of a dispersion of a compound of bentonite and an aliphatic organic ammonium salt bearing at least one straight chain

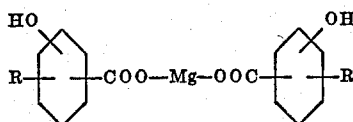
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substituted having at least 10 carbon atoms in a major amount of a mineral oil bright stock and a compound having a general formula



each of said aromatic nuclei bearing an alkyl radical R having between 3 and 24 carbon atoms each, said bentonite compound being present in said lubricant in an amount between about 2% and about 20% by weight of the total lubricant and wherein said aromatic compound is present in an amount between about 1% and about 10% by weight of the composition.

6. An improved lubricant consisting essentially of a grease-forming proportion of an onium clay compound in a major amount of a mineral oil bright stock and from 1% to 10% by weight of an aromatic additive having a general formula



each of the aromatic nuclei of said additive bearing an alkyl radical R having from 3 to 24 carbon atoms each.

7. An improved lubricant consisting essentially of a dispersion of a grease-forming silica gel in a major amount of a mineral oil bright stock and methylene bis(salicylic acid), the silica being present in an amount between about 2% and about 20% by weight of the grease composition and the acid being present in an

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amount between about 1% and about 10% by weight of the composition.

8. An improved lubricant consisting essentially of a dispersion of a grease-forming silica gel in a major amount of a mineral oil bright stock and zinc di(isopropylsalicylate), the silica being present in an amount between about 2% and about 20% by weight of the grease composition and the salicylate being present in an amount between about 1% and about 10% by weight of the composition.

9. A composition according to claim 8 containing in addition between about 1% and about 10% by weight of a mononuclear hydroxy benzoic acid.

10. An improved lubricant consisting essentially of a dispersion of a grease-forming silica gel in a major amount of a mineral oil bright stock and the calcium salt of C₁₄₋₁₈ salicylic acids, the silica being present in an amount between about 2% and about 20% by weight of the grease composition and the salt being present in an amount between about 1% and about 10% by weight of the composition.

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