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HIGH TEMPERATURE DYE-THICKENED GREASE COMPOSITION

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This invention relates to lubricating grease compositions. More especially it relates to improved grease compositions especially useful at elevated operating temperatures.

As lubricants are required to perform at higher and higher temperatures because of increased speeds of engines and machines, the advent of jet propulsion and atomic energy as sources of power, etc., it has become increasingly difficult to provide greases fulfilling the requirements of such lubricants. In attempting to provide suitable greases, the art has progressed from the use of petroleum lubricant vehicles thickened with metal soaps of long chain fatty acids to more thermally stable synthetic lubricating oils such as the aliphatic diesters, silicone polymers, etc. thickened with such soaps or inorganic materials, such as silica gels or clays. The progress of thickener research has not in general kept pace with the development of lubricant vehicles. At operating temperatures as high as 400–450° F., there are few greases available which will retain their consistency and lubricity for any substantial period of time.

One of the prominent advances in the art of high temperature grease lubrication has comprised the provision of greases gelled with dyes or pigments, namely, indogen compounds, phthalocyanine compounds, anthraquinones, azines, and especially indanthrene compounds. The art of preparing greases from these particular classes of materials has not been developed. Consequently, the greases comprising such dyes normally require excessive amounts of the gelling agent to produce the grease structure.

It is an object of the present invention to provide improved grease compositions. It is another object of the present invention to provide grease compositions especially useful at high operating temperatures. It is a particular object of the present invention to provide dye gelled greases having a reduced dye requirement for a given grease consistency. It is a special object of the present invention to reduce the high cost of dye gelled greases. Other objects will become apparent during the following description of the invention.

Now, in accordance with the present invention, it has been found that the consistency of greases gelled with compounds of the group consisting of indanthrene dyes, indogen dyes, n-acyl-9,10-dihydroxy-1,4-diamino anthracenes, n-acyl-9,10-dihydroxy-1,2-diamino anthracenes, n-acyldiaminoanthraquinones and n-acylaminophenols may be materially increased by the incorporation of substantial amounts (1.5–20% by weight of the grease) of an aliphatic hydrocarbyl amine, preferably an alkane diamine having less than 10 carbon atoms per molecule. Another unexpected feature of this invention comprises the fact that the presence of this substantial proportion of amine in greases of this particular type unexpectedly improve the bearing life of bearings being lubricated with the compositions. This is especially noticeable at temperatures in excess of 300° F.

The chief benefit derived from the present invention comprises a drastic reduction in the cost of the subject greases. This is material since the principal gelling agent, namely, the dyes and the amino phenol compounds listed above, are extremely expensive materials while the amines are far less costly. For example, the indanthrene dyes at the present time cost in the order of

$11.00 a pound while the amines are currently priced at 60–70 cents a pound. Consequently, any reduction in the dye content of the grease by a corresponding addition of the amine results in an approximate twenty-fold saving in grease thickener cost. However, not only is this cost reduction a principal factor but also the unexpected improvement in bearing life caused by the presence of the large quantities of amines present constitutes an impressive improvement in lubricating greases of this particular class.

While the proportion of amine normally utilized for increasing the consistency of the subject grease compositions is between 1.5 and about 20% by weight thereof, another measure of the suitable proportions may be expressed in terms of equivalents of dye per hundred grams of grease. The maximum effect is obtained if between about 0.02 and 0.1 equivalents of amine per hundred grams of grease is utilized, although substantial increases in consistency and in bearing life are obtained when the proportion of amine is between about 0.005 and 0.2 equivalents per one hundred grams of grease.

Suitable aliphatic diamines include the following:

A. Acyclic diamines:
- 1,3-diamino-2-ethylpropane
- 1,4-diamino-2-propylbutane
- 1,5-diamino-3-methylpentane
- 1,5-diamino-3-butylpentane
- 1,6-diamino-4-ethylhexane
- 1,2-diamino ethane
- 1,3-diamino propane
- 1,4-diamino butane
- 1,5-diamino pentane
- 1,6-diamino hexane
- 1,7-diamino heptane
- 1,8-diamino octane
- 1,9-diamino nonane
- 1,10-diamino decane
- 1,1-diamino ethane
- 1,2-diamino propane
- 1,3-diamino butane
- 1,4-diamino pentane
- 1,4-diamino hexane
- 1,4-diamino heptane
- 1,4-diamino octane
- 2,6-diamino nonane
- 3,6-diamino decane

B. Alicyclic diamines:
- 1,2-diaminocyclohexane
- 1,4-diaminocyclohexane
- 1-(aminomethyl)-2-aminocyclohexane
- 1,4-(aminoethyl)cyclohexane
- 2,2-diamino-1-cyclohexylpropane

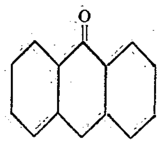
The amines are preferably incorporated by homogenizing them with the finished grease containing the principal thickening agent and the lubricating oil. However, the amines may be incorporated with the thickener at the time the grease is originally prepared or may be dispersed in lubricating oil prior to addition of the principal thickening component.

The most effective dye for use in high temperature greases has been found to be the parent compound of the series, namely, indanthrene itself, but other indanthrene compounds may be employed. It is best to utilize the indanthrene compounds in their non-metallic form, that is, without neutralization of the carbonyl groups in said compounds with such ions as sodium or potassium, calcium, etc. While it is possible to employ the partially or fully neutralized indanthrene compounds as grease thickening agents, greases having maximum lubricating life at elevated temperatures are those in which the carbonyl group are free of any metallic substituents.

Typical indanthrene compounds suitable for the present purpose include the following:

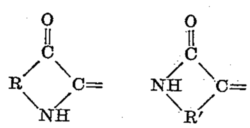
Indanthrene	Violanthrone
Flavanthrone	3,3'-dichloroindanthrene
Pyranthrone	3-chloroindanthrene

The indanthrene dyes, which are used as the gelling agents in the subject greases, contain two units of the following essential typical grouping per molecule:



The tricyclic radical, it will be noted, has at least one carbonyl radical on the middle ring of the group. Some specific members of the indanthrene series, such as indanthrone, have two such carbonyl radicals attached to the middle ring. Others, such as flavanthrene, contain the single essential carbonyl radical, the tricyclic group being linked to a second such group by means of nitrogen linkages, or (as in the case of pyranthrone) through unsaturated hydrocarbon linkages. Thus, the two tricyclic nuclei may be linked by two —N= groups (as in flavanthrene); by two —NH—groups (as in indanthrene blue); by two =CH— groups (as in pyranthrone); or by intervening condensed ring systems (as in violanthrone). Another characteristic of the indanthrene dyes is that nitrogen is not a nuclear element present in the rings making up the essential tricyclic nuclei.

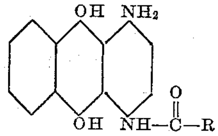
Another class of dye materials which may be utilized in high temperature greases prepared by the process of this invention include indogen compounds having the general structure:



In the above formulae, R and R' represent aryl ro alkylaryl radicals which are linked to the adjoining members of the heterocyclic rings by bonds disposed in ortho relation. These radicals may be the same or different and may be mono- or polycyclic, e.g., phenylene, bipheylene, naphthylene, etc. These aryl or alkaryl radicals may be substituted radicals, containing various substitents such as hydroxy, carboxy, halo, nitro, etc. Examples of such compounds are indigo, iso-indigo, 3-keto-indoline, isatide, isatin, etc. It should be understood that these specific examples are enumerated for purposes of illustration and not of limitation.

A third class of dye or pigment materials which may be employed in the production of high temperature greases by the process of this invention comprise phthalocyanines, which include not only metal free phthalocyanine but metal phahalocyanines such as zinc, nickel, aluminum, and particularly copper phthalocyanine. Chlorinated phthalocyanines and chlorinated metal phthalocyanines may also be employed. Of course, mixtures of dyes from one or more of these three main groups may be utilized in grease formation.

Another class of grease-forming dyes may be grouped under the following generic formula:



In the formula, R represents an alkyl group containing from about 3 to 24 carbon atoms.

Although the acyl derivatives of the 9,10-dihydroxy-1,4-diamino anthracene within the range set out above have both oxidation inhibiting properties and thickening power, when it is desired to use the materials of invention primarily as a thickening agent, the acyl derivatives wherein R contains from 12 to 22 carbon atoms are preferable. When oxidation inhibition is the primary function desired, R should contain from about 3 to about 16 carbon atoms. A useful combination comprises a dye of the shorter chain oxidation inhibiting type together with another dye primarily useful as the main gelling agent.

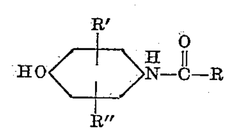
The acyl derivatives of the invention are prepared by heating the 9,10-dihydroxy-1,4-diamino-anthracene with the organic acid at reaction temperatures of about 100 to 250° C. Boric acid may be used as a catalyst for the reaction. The product may be purified by slurrying with water containing small amounts of caustic.

Suitable species of such dyes include the following:

1-N-stearoyl-1,4-diamino-9,10-dihydroxyanthracene
1-N-stearoyl-1,4-diamino-9,10-dihydroxyanthracene
1-N-dodecoyl-1,4-diamino-9,10-dihydroxyanthracene
1-N-octoyl-1,4-diamino-9,10-dihydroxyanthracene
1-N-propoyl-1,4-diamino-9,10-dihydroxyanthracene
1-N-heptoyl-1,2-diamino-9,10-dihydroxyanthracene
1-N-st earoyl-1,2-diamino-9,10-dihydroxyanthracene
1-N-decoyl-1,2-diamino-9,10-dihydroxyanthracene

The corresponding 1,4-diamino-anthraquinones may be utilized as well.

The N-a cyl amino phenols useful to form then on-soap grease compositions of this invention have the following general formula:



wherein R is an alkyl group containing from 14 to 22 carbon atoms, preferably an alkyl group which is non-benzenoid in nature, and wherein R' and R'' are hydrogen atoms or alkyl groups containing from 1 to 20 carbon atoms.

The preferred embodiment of this invention contemplates the use of compounds, according to the formula above, wherein R' and R'' are hydrogen atoms and wherein R is a straight chain aliphatic group containing from 14 to 22 carbon atoms. Exemplary of these preferred compounds are N-palmitoyl p-amino phenol, N-stearoyl p-amino phenol, and N-arachidoyl p-amino phenol, N-behenoyl p-amino phenol with the N-stearoyl or N-palmitoyl p-amino phenol or mixtures of each being especially preferred.

The alkylated acyl p-amino phenols exemplified by the formula above when R' and R'' are alkyl groups containing from 1 to 20 and preferably from 4 to 15 carbon atoms, are also operable as lubricating oil thickeners. Compounds such as N-n-valeryl-4-amino-3-pentadecyl phenol, (N-n-pentanoyl-4-amino-3-pentadecyl phenol), N-n-propanoyl-4-amino-2,6-di-tert.-butyl phenol, N-n-hexyl-4-amino-2-hexyl phenol, are examples of the alkylated acyl p-amino phenols which are operable.

The lubricating oil chosen to form the greases of invention may be widely varied. The oil chosen to prepare the grease composition should be capable of performing the lubricating function if it could be used as a liquid. Mineral lubricating oils having a viscosity within the range of from about 35 to about 200 SUS at 210° F. may be used for most applications. The mineral oil may be of a paraffinic or of a naphthenic nature depending upon the crude source, and any of the various distillates refined by the various refinery techniques are operable.

Synthetic lubricating oils may also be utilized in preparing the lubricating greases of this invention. Synthetic lubricating oils having a viscosity within the range stated above are operable. These oils include esters of monobasic acids, such as the C_8 Oxo alcohol ester of C_8 Oxo acid, esters of C_{13} Oxo alcohol and octanoic acid, etc.; esters of dibasic acids, such as di-2-ethylhexyl sebacate, di-nonyl-adipate, etc., esters of glycols, e.g., the C_{13} Oxo acid diester of tetraethylene glycol, etc., complex esters, such as the complex ester formed by reacting one mol of sebacic acid with two mols of tetraethylene glycol and two mols of 2-ethyl hexanoic acid; other types include complex esters formed by reacting one mol of tetraethylene glycol with two mols of sebacic acid and two mols of 2-ethyl hexanol, complex esters formed by reacting together one mol of azelaic acid, one mol of tetraethylene glycol, one mol of C_8 Oxo acid, and the like. A recently developed class, namely diaryl dialkyl silanes, (e.g., diphenyl didodecyl silane) may be employed. Esters of phosphoric acid may be used, such as the ester formed by contacting three mols of the monomethyl ether of ethylene glycol with one mol of phosphorus oxychloride. Halocarbon oils, such as the polymers of chlorotrifluourethylene may be employed as well as alkyl silicon compounds, such as methyl polysiloxanes, ethyl polysiloxanes, methyl-phenyl polysiloxanes, ethyl-phenyl polysiloxanes, chlorophenyl silicones, and the like. Sulfite esters, such as those formed by reacting one mol of sulfur oxychloride with two mols of the methyl ether of ethylene glycol and the like also are useful, as are carbonates such as those formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol, mercaptals such as those formed by reacting 2-ethylhexyl mercaptan with formaldehyde, formals such as those formed by reacting C_{13} Oxo alcohol with formadehyde, polyglycols, such as those formed by condensing butyl alcohol with up to fifty units of propylene oxide, or mixtures of any of the above synthetic oils in any proportions.

A recent development in the high temperature lubricating field and in the allied field of lubrication under conditions of ionizing radiation comprises the use of polyphenyl ethers as lubricants or as lubricant components. The maximum stability obtained if the polyphenyl ethers are unsubstituted but highly stable lubricants are also prepared when alphacumyl or tertiary-butyl substituents are employed. While ortho, meta or para linkages between phenyl radicals may be utilized, it is preferred that at least 25% of the ether linkages be in the meta position relative to each other. As the meta linkage proportion increases, the pour point of the resulting lubricating oils decreases. It is possible to have, therefore, polyphenyl ethers which are all meta linked but which may instead comprise meta linkages with varying proportions of ortho or para linkages. It is preferred that the polyphenyl ether contain from 3 to 6 phenyl radicals per molecule on the average. The combination of the subject class of thickeners with such lubricants has been found to constitute an outstandingly stable lubricating grease either under conditions of temperatures in excess of 350° F. or under conditions of ionizing radiation.

It will be understood that the addition of the amines to the subject class of greases may be utilized for the purpose of increasing the consistency of the grease on the one hand or for decreasing the major thickener requirements such as dye for a given grease consistency on the other hand. The following examples illustrate the unexpected

increase in consistency of an indanthrene blue (indanthrone) grease, 28% by weight of the grease being indanthrone, the balance of the grease being a residual petroleum lubricating oil, namely, a bright stock.

Additive	Change in W 60 Pen.[1]	Percent w. Added	Equiv. Added per 100 g.	Change in W 60 Pen.[1] per equiv./100 g.
Ethylene diamine	−71	1.5	.050	−1,420
Ethylene diamine	−105	4	.134	−790
1,6 hexane diamine	−111	2.5	.044	−2,520

[1] Worked 60 strokes penetration, measured with ½ scale cone in size "O" crucible.

According to the data given above, it will be seen that a variety of amines substantially increase the consistency of the grease when utilized in proportions between 3 and 15% based on the original grease formulation.

I claim as my invention:

1. A grease composition comprising a major amount of a lubricating oil gelled to a grease consistency with a combination of 5–35% by weight of a compound of the group consisting of indanthrene dyes, indogen dyes, N-acyl-9,10-dihydroxy-1,4-diaminoanthracenes, N-acyl-9,10-dihydroxy-1,2-diaminoanthracenes, N-acyldiaminoanthraquinones and N-acylaminophenols, and 1.5–20% by weight of saturated aliphatic hydrocarbyl diamines having 2–10 carbon atoms per molecule.

2. A grease composition comprising a major amount of a lubricating oil gelled to a grease consistency with a combination of 5–35% by weight of an indanthrene dye and 1.5–20% by weight of a diaminoalkane having 2–10 carbon atoms per molecule.

3. A grease composition comprising a major amount of a lubricating oil gelled to a grease consistency with a combination of 5–35% by weight of an indanthrene dye and 1.5–20% by weight of an alkane diamine having 5–10 carbon atoms per molecule.

4. A grease composition comprising bright stock mineral lubricating oil gelled to a grease consistency with 15–30% by weight of indanthrone and 2–7.5% by weight of 1,6-diaminohexane.

5. A grease composition according to claim 1 wherein the diamine is a saturated alicyclic hydrocarbyl diamine having 6–9 carbon atoms per molecule.

6. A grease composition comprising bright stock mineral lubricating oil gelled to a grease consistency with 15–30% by weight of indanthrone and 2–7.5% by weight of ethylene diamine.

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