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POLYAZOPHENOLS AND POLYAZOPHENOL GREASES

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This invention relates to new compositions of matter, namely polyazophenols and to new grease compositions containing the same and particularly grease compositions capable of functioning at temperatures above 300° F.

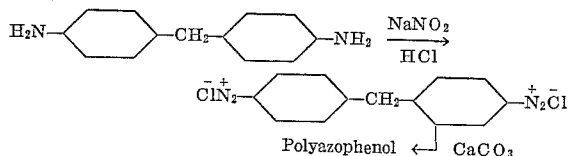
In recent years, a demand has been created for greases providing excellent lubrication at temperatures in excess of 300° F. (149° C.). A variety of oils of lubricating viscosity have been developed to meet this demand, such oils including hindered esters, hydrogenated polyolefins and polysiloxanes (generally referred to as "silicones"). Few thickening agents stable at such operating temperatures have been developed.

It is an object of the present invention, therefore, to provide greases capable of withstanding severe operating conditions. It is a particular object to provide greases effective for relatively high temperature use, such as 300° F. and higher. Another object is to provide greases stable during extended storage periods, that is, substantially free of a separation of oil therefrom ("bleeding") during such storage. A further object is to provide new compositions of matter which can serve as grease thickening agents. Other objects will be apparent from the following description.

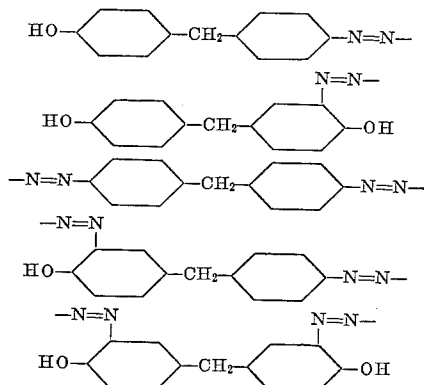
In accordance with the present invention, there are provided new compositions of matter comprising polyazophenols.

In accordance with this invention, there are also provided grease compositions comprising an oil of lubricating viscosity and a grease-forming quantity of a polyazophenol.

The polyazophenols are prepared by diazotization of an aromatic polyamine to form an intermediate diazonium compound which is treated with a weak base such that the intermediate is converted to the polyazophenol. This is illustrated below by using 4,4'-dianilinomethane as the aromatic diamine:



Since the structure of the polyazophenols is not known, they are best described as reaction products of the aromatic polyamines from which they are prepared. Among the possible groups most probably present in a polyazophenol formed from 4,4'-dianilinomethane are the following:



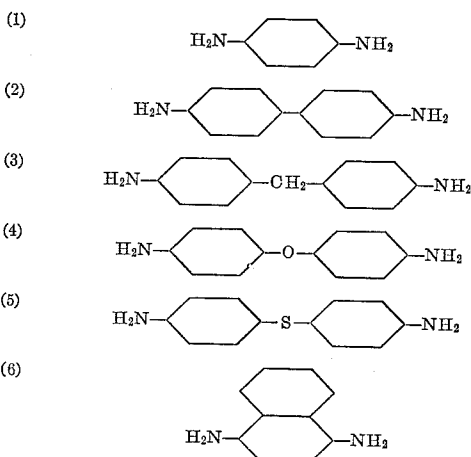
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As indicated above, the preparation of the polyazophenols involves diazotization of an aromatic polyamine. Conventional diazotization conditions and reactants are employed. For example, sodium nitrite and hydrogen chloride can be used. Similarly, temperatures of the order of less than about 5° C. are employed. The corresponding intermediate diazonium compound formed from the polyamine is treated with a weak base, particularly calcium carbonate, which promotes slow hydrolysis of the intermediate compound to the polyazophenol. Excess base is employed, preferably at least 5-20 percent by weight in excess of stoichiometrical requirements. Treatment with a base is at a temperature from about 0° C. to about 100° C., preferably 25-50° C., for a time interval of several hours, followed by a somewhat higher temperature within the range, as about 70-85° C., for a shorter period of time. Completion of reaction is indicated by testing a sample of the reaction mixture with an alkaline solution of beta-naphthol or like reagent. When no further coupling with the naphthol occurs, reaction is complete. Treatment with a base is generally carried out at atmospheric pressure.

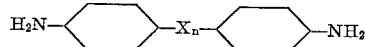
Aromatic polyamines are used in forming the polyazophenols. Each amino group of the polyamine should be diazotizable. The amines can be otherwise unsubstituted or substituted. In the latter event, at least one position ortho to an amino group should be unsubstituted and not sterically hindered. Thus, ortho diamines and related polyamines are not used. Typical substituents include chlorine, bromine, alkyl, cycloalkyl, aryl, aryloxy, alkoxy and cycloalkyloxy. Preferred herein for the formation of grease thickening agents are aromatic diamines represented by the general formula:



wherein the amino groups are attached to different carbon atoms of an aromatic hydrocarbon radical, Ar, and are in para relationship. Typical diamines are the following



Diamines identified as (2) through (5), above, can be represented by the general formula



wherein X is selected from the group consisting of oxygen, sulfur and (CH₂)_m and n is selected from 0 and 1 and m is at least 1.

Particularly preferred herein, in order, for the formation of polyazophenols are (4), (2) and (3), above.

In the grease compositions of this invention, the polyazophenols are present in concentrations ranging from about 5 to about 50 percent by weight. Preferably, con-

centrations of the approximate range 10 to 20 percent by weight, are used.

It is to be understood that two or more of the polyazophenols can be used together in a grease composition.

It has also been found that an auxiliary thickening material can be used with one or more polyazophenols in the new grease compositions. The auxiliary thickener can be used in concentrations varying from 1 to 50, and preferably 10 to 25, percent by weight of the polyazophenol. Expressed otherwise, from 0.25 to 25, and preferably 0.5 to 12.5 percent by weight of the grease composition can comprise auxiliary thickener.

The auxiliary thickener can be: a pigment such as a perylimide, anthanthrone, naphthalic imidazole, oxazole, and the like; coated silicas, silica aerogels; organophilic clays; substituted ureas; pryomellitdiimides, and ammeline.

Preferred auxiliary thickeners are essentially hydrophobic clays. Such thickening agents can be prepared from clays which are initially hydrophilic in character, but which have been converted into a hydrophobic condition by the introduction of long chain hydrocarbon radicals into the surface of the clay particles, prior to their use as a component of a grease composition, as, for example, by being subjected to a preliminary treatment with an organic cationic surface active agent, such as an onium compound. Typical onium compounds are tetra alkyl ammonium chlorides, such as dimethyl dioctadecyl ammonium chloride, dimethyl dibenzyl ammonium chloride and mixtures thereof. This method of conversion, being well known to those skilled in the art, is believed to require no further discussion, and does not form a part of the present invention. More specifically, the clays which are useful as starting materials in forming the thickening agents to be employed in the grease compositions, can comprise the naturally occurring chemically unmodified clays. These clays are crystalline complex silicates, the exact composition of which is not subject to precise description, since they vary widely from one natural source to another. These clays can be described as complex inorganic silicates such as aluminum silicates, magnesium silicates, barium silicates, and the like, containing, in addition to the silicate lattice, varying amounts of cation-exchangeable groups such as sodium. Hydrophilic clays which are particularly useful for conversion to desired thickening agents include montmorillonite clays, such as bentonite, attapulgite, hectorite, illite, saponite, sepiolite, biotite, vermiculite, zeolite clays, and the like. The clays can be treated with quaternary ammonium halides to bind the quaternary ammonium portion thereof to the clay. One typical auxiliary thickener is a sodium montmorillonite clay which has been treated with dimethyl dibenzyl quaternary ammonium chloride, and then washed with water to remove sodium chloride therefrom.

Oils used in the greases of this invention can be mineral or synthetic oils of lubricating viscosity. When high temperature stability is not a requirement of the finished grease, mineral lubricating oils can be used. Suitable mineral oils have a viscosity (S.U.V.) of at least 40 seconds at 100° F., and particularly those within the range of about 60 seconds to about 6000 seconds at 100° F.

Synthetic vehicles can be used, instead of mineral oils, or in combination therewith. Typical synthetic vehicles are: polypropylene, polypropylene glycol, trimethylol propane esters, neopentyl and pentaerythritol esters, di(2-ethyl hexyl) sebacate, di(2-ethyl hexyl) adipate, dibutyl phthalate, polyethylene glycol di(2-ethyl hexoate), fluoro-carbons, silicate esters, silanes, esters of phosphorus-containing acids, liquid ureas, ferrocene derivatives, hydrogenated mineral oils, chain type polyphenyls, siloxanes and silicones (polysiloxanes), alkyl-substituted diphenyl ethers typified by a butyl-substituted bis-(p-phenoxy phenyl) ether, and phenoxy phenyl ethers.

Other hydrocarbon oils include synthetic hydrocarbon

polymers having improved viscosity indices, which polymers are prepared by polymerizing an olefin, or mixture of olefins, having from 5 to 18 carbon atoms per molecule in the presence of an aliphatic halide and a Ziegler-type catalyst. Such synthetic hydrocarbon oils are described by Armstrong et al. in application U.S. Ser. No. 314,575, filed Sept. 26, 1963, and now abandoned.

It is to be understood, however, that the compositions contemplated herein can also contain other characterizing materials. For example, antioxidants such as phenyl alpha-naphthylamine (PAN), corrosion inhibitors, extreme pressure agents, viscosity index agents and fillers, can be used. Among such materials are colloidal silica, calcium acetate, calcium carbonate and molybdenum disulfide. Such characterizing materials do not detract from the lubricating value of the compositions of this invention, nor do they detract from the beneficial character of the polyazophenol compounds; rather, the characterizing materials serve to impart their customary properties to the particular compositions in which they are incorporated.

The greases of this invention can be prepared in accordance with conventional grease manufacturing procedures, as by any mixing technique wherein solid particles are wetted by a fluid. Typical equipment for such use includes a colloid mill, 3-roll ink mill, Manton-Gaulin homogenizer and the like.

The polyazophenols and greases of this invention are illustrated in the several following examples, wherein all parts are by weight unless otherwise indicated.

Example 1

A polyazophenol was prepared from 4,4-dianilinomethane according to the following procedure.

The 4,4'-dianilinomethane (39.6 g.) was dissolved in a mixture of concentrated HCl (100 g.) and water (600 cc.) and was cooled to -5° C. A solution of NaNO₂ (28 g.) in water (50 cc.) was added over a 15 minute period at about 0° C. CaCO₃ (36 g.) was then added in small portions at 0° C. The solution was a clear, pale yellow until neutralized with excess calcium carbonate after which it became hazy. The cooling bath was removed and stirring continued. After about 10 minutes the mixture was a hazy yellow at 4° C., then a clear crimson color after 1 hour (12° C.). After three days a dark brown suspension was formed (25° C.). This was heated at 70° C. for 2 hours, then acidified with HCl. A finely divided purple-brown solid was filtered off, washed well with cold water, then with methanol and air dried to a fluffy, brown amorphous powder. Yield was 39.3 g. The melting point was above about 250° C. Analysis showed 7.8% nitrogen. The polymer was insoluble in water, methanol, acetone and benzene.

Greases were prepared from a variety of fluids using the polyazophenol described in Example 1 as thickener, as illustrated by the following examples:

Example 2

Eleven parts of a silicone fluid (7046 of Dow Corning) was mixed with two parts of the polyazophenol (Example 1) and was milled on a hot plate at 93° C. The resulting grease, containing 15% thickener, had an ASTM penetration of 375.

Example 3

Nineteen parts of a silicone fluid (SF-1029 of General Electric) was mixed with 3.7 parts of the polyazophenol (Example 1) and was milled to a greaselike consistency as in Example 2. This grease, containing 16% thickener, had an ASTM penetration of 325.

Example 4

Fourteen parts of a silicone fluid prepared by alkylating a methyl hydrogen silicone (1107 of Dow Corning) with hexene-1 was thickened to a grease consistency with three parts of the polyazophenol (Example 1). This

grease, containing 18% thickener, had an ASTM penetration of 288.

Example 5

Fourteen parts of a hydrogenated polyolefin fluid having a viscosity of 150 SUS at 38° C. was thickened with three parts of the polymer (Example 1) as above. This grease, containing 18% thickener, had an ASTM penetration of 286, and a dropping point of 217° C.

Example 6

Twenty-three parts of a silicone fluid (SF-1029 of General Electric) was mixed with three parts of the polyazophenol (Example 1) and one part of a hectorite which does not decompose at temperatures up to about 316° C. The resulting dry mass was wet with about two parts of acetone and was milled on a hot plate while heating to about 150° C. The resulting grease contained about 15% total thickener of which 25% was the experimental clay. It had an ASTM penetration of 308, and a dropping point greater than 260° C.

The greases of Examples 2 to 5 inclusive showed a tendency to bleed after standing several days. The grease of Example 6, in which the mixture of polymer and hectorite clay was used as thickener, showed no bleeding at room temperature after two months.

Example 7

Oxydianiline (20 grams, 0.1 mole) was dissolved in a mixture of concentrated hydrochloric acid (50 grams, 0.5 mole) and water (550 ml.). The resulting dark, red-brown solution was cooled to 0° C. A solution of sodium nitrite (14 grams, 0.2 mole) in water (50 ml.), was added dropwise with stirring to the red-brown solution at 0-2° C. during a 40 minute interval. After a further 30 minute interval at 0° C., calcium carbonate (35 grams) suspended in water (100 ml.) was added. The resulting mixture was a light buff suspension, which was stirred at 0° C. for 2 hours and then at 25° C. for 60 hours. The dark brown suspension which formed, with some dark residue on the walls of the reaction vessel used, was heated to 75° C. The temperature was so maintained for 2 hours. This suspension was acidified with hydrochloric acid; a dark brown suspension formed and there no longer was any residue on the vessel walls. The dark brown suspension was filtered while hot and material held on the filter was washed successively with hot water, cold methanol and cold acetone. It was then air-dried. The product, a polyazophenol, was a light-brown powder. The yield was 19.6 grams. The product had a melting point of greater than 250° C., and the following analysis: nitrogen, 6.8 percent; carbon, 72.6 percent; and hydrogen, 3.9 percent.

A crude diamine was used in this preparation. It was predominantly oxydianiline.

Example 8

Two parts by weight of the polyazophenol formed in Example 7 were mixed with 16 parts by weight of a silicone fluid (Dow Corning XF-7046), and the resulting mixture was milled on a hot plate while it was heated to about 150° C. On cooling, the resulting grease had a smooth, buttery consistency. The ASTM penetration was 240. The grease showed no bleeding at room temperature (20-25° C.) after two weeks.

Example 9

The procedure described in Example 7 was followed with the following quantities:

Oxydianiline	30.
Concentrated HCl	80 in 800 cc. H ₂ O.
Sodium nitrite	21 in 100 cc. H ₂ O.
Calcium carbonate	34.5.

The yield of polyazophenol was 29.8 parts.

Example 10

Three parts by weight of the polyazophenol prepared in Example 9, were mixed with 33.5 parts of a silicone fluid (Dow Corning XF-7046), and the resulting mixture was milled to a grease consistency. The grease which formed had an ASTM penetration of 296.

Example 11

Benzidine dihydrochloride (29 grams, 0.1 mole, equivalent to 18.4 grams of benzidine) was suspended in water (600 ml.) and concentrated hydrochloric acid (30 grams). The resulting suspension was cooled to 0° C. A solution of sodium nitrite (14 grams, 0.2 mole) in water (50 ml.) was added dropwise to the suspension during a 10 minute interval. A clear, orange-yellow solution was formed. This was stirred for an additional 15 minute interval at 0° C.

A slurry of calcium carbonate (18 grams, 0.18 mole; 20 percent excess) in water (100 ml.) at 0° C., was added to the solution. A hazy, yellow-green suspension was formed and this soon turned yellow-orange in color. After a further 30 minute interval at 0° C., the yellow-orange suspension was stirred at 25° C. for 70 hours. A dark brown suspension, and some dark residue, was formed. The resulting product was heated to 70° C. and was so maintained for 4 hours. It was then acidified with HCl and was filtered while hot. The filtrate was water-white. The material held on the filter was washed well with hot water, then with acetone and air-dried to give a very bulky, light brown powder. This polyazophenol product had a melting point greater than 250° C. The yield was 18.3 grams.

Example 12

Three parts by weight of the polyazophenol formed in Example 11 were mixed with 15 parts by weight of a silicone fluid (Dow Corning XF-7046), and the resulting mixture was milled to a grease consistency. The grease had an ASTM consistency of 264 and a dropping point in excess of 260° C.

Example 13

Thiodianiline (10.8 grams, 0.05 mole) was suspended in water (400 ml.) and concentrated hydrochloric acid (25 grams, 0.25 mole) was added to the suspension. The latter was tetrazotized at 2-4° C. with sodium nitrite (7.0 grams, 0.1 mole) in water (50 ml.). A clear orange solution was formed. This solution was stirred for an additional 10 minute interval at 3° C. Calcium carbonate (10 grams; 50 percent excess) was added in bulk to the solution. A yellow suspension was formed; this suspension was stirred at 0-3° C. During the initial 30 minute interval, some light foaming occurred. After 2 hours, a light buff colored suspension was formed. After a total of 5 hours, the temperature was raised to 25° C. and was so maintained for 50 hours. The resulting reaction mixture was heated to 70° C. and was held at 70° C. for 3 hours. It was then acidified with hydrochloric acid and was filtered while hot. The material held on the filter was washed well with hot water, then with acetone and was air-dried. The product, a polyazophenol, was a very bulky, orange-brown powder. It had a melting point in excess of 250° C. and the following analysis: nitrogen, 7.0 percent; carbon, 64.1 percent; hydrogen, 4.4 percent; and sulfur, 14.0 percent. Yield was 10.8 grams.

Example 14

Two parts by weight of the polyazophenol of Example 13 and 10 parts of silicone fluid (Dow Corning 200) were mixed and were milled to a grease consistency. The grease had an ASTM penetration of 314.

None of the greases of Examples 8, 10, 12 and 14, above, exhibited any tendency to bleed during storage.

The new greases can be used for a wide range of industrial applications, including lubrication of automotive and aircraft equipment.

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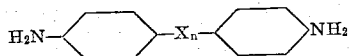
Although the present invention has been described with preferred embodiments, it is to be understood that modifications, and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

We claim:

1. A grease comprising an oil of lubricating viscosity and a grease-forming quantity of a polyazophenol formed by diazotization of an aromatic polyamine represented by the general formulas



wherein Ar is an aromatic hydrocarbon radical, and



wherein X is selected from the group consisting of oxygen, sulfur, and $(\text{CH}_2)_m$ and n is selected from the group consisting of 0 and 1 and m is at least 1 in which the amino groups are other than in ortho relationship to form a corresponding diazonium compound and treating the diazonium compound with a base which promotes slow hydrolysis of the diazonium compound to the polyazophenol.

2. A grease defined by claim 1 wherein the base is calcium carbonate.

3. A grease defined by claim 1 wherein the polyamine is oxydianiline.

4. A grease defined by claim 1 wherein the oil is a polysiloxane.

5. A grease defined by claim 1 wherein the oil is a hydrogenated polyolefin fluid.

6. A grease defined by claim 1 wherein the grease-forming quantity is from about 5 to about 50 percent by weight.

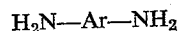
7. A grease defined by claim 1 containing from about

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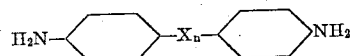
0.05 to about 25 percent by weight of an inorganic grease-thickening agent.

8. A grease defined by claim 7 wherein the inorganic grease-thickening agent is a clay.

9. A polyazophenol formed by diazotization of an aromatic polyamine represented by the general formulas



wherein Ar is an aromatic hydrocarbon radical, and



wherein X is selected from the group consisting of oxygen, sulfur, and $(\text{CH}_2)_m$ and n is selected from the group consisting of 0 and 1 and m is at least 1 in which the amino groups are other than in ortho relationship to form a corresponding diazonium compound and treating the diazonium compound with a base which promotes slow hydrolysis of the diazonium compound to the polyazophenol.

10. A polyazophenol defined by claim 9 wherein the base is calcium carbonate.

11. A polyazophenol defined by claim 9 wherein the polyamine is oxydianiline.

12. A polyazophenol defined by claim 9 wherein the diazonium compound is treated at a temperature between about 0°C . and about 100°C .

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