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# RADIATION-RESISTANT LUBRICANT COMPOSITION

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This invention relates to the stabilization of non-asphaltogenic organic compounds. More particularly, it is related to the stabilization of such compounds against deterioration due to ionizing radiation.

With the advent of a nuclear power industry, problems of lubrication and power transmission within the radiation zone have arisen due to the adverse effect of radiation upon most previously known lubricating compositions, which are either normally liquid lubricants or greases. Lubricants which are usually regarded as highly stable, such as the silicones, assume a rubbery consistency due to resinification in the presence of ionizing radiation. On the other hand, many grease compositions either become resinous in character or liquefy due to destruction of the grease-forming matrix of the gelling agent. The maintenance of a predictable viscosity and consistency is required not only in sites of lubrication but also where relatively thin oleaginous substances are utilized in the operation of hydraulic systems or for heat transfer media.

It is an object of the present invention to provide compositions having improved resistance to alteration by ionizing radiation. It is a particular object of the invention to provide compositions suitable for use in the operation of equipment emitting ionizing radiation. It is a further object of the invention to provide lubricating oils and greases as well as hydraulic fluids and heat transfer media suitable for this purpose.

Now, in accordance with the present invention, non-asphaltogenic organic compounds suitable for lubricating purposes and/or power or heat transfer are stabilized against deterioration due to ionizing radiation by modification of the compounds with a stabilizing minor proportion of asphaltenes.

Where throughout the specification the term "lubricant" or similar phrase is employed without being more specific, it will be understood that reference is being made not only to lubricating oils and greases but also to other normally fluid substances useful for the operation of hydraulic equipment as a hydraulic fluid or in a heat transfer system as a heat transfer media.

The term "asphaltenes" is defined in Abraham, "Asphalts and Allied Substances" on pages 1165–6, fifth edition 1945, as being the non-mineral constituents remaining insoluble in petroleum naphtha at 65–75° F., thus differentiating them from the maltenes (petrolenes) which dissolve in the same medium and under the same conditions. A further limitation comprises the proportion of petroleum naphtha employed for the purpose of causing separation. According to the standardized method, 50 volumes of petroleum naphtha are employed, the test temperature normally being ambient room temperature (65–75° F.). While this standard procedure defines the term, it will be understood that the asphaltic fraction insoluble at room temperature in any aliphatic hydrocarbon having 5–12 carbon atoms per molecule may be regarded as "asphaltene" for the purpose of the invention.

Asphaltenes may be isolated from other asphaltic constituents by preferential precipitation. For example, asphalts may be introduced into an aliphatic hydrocarbon precipitant ($C_{5-12}$ alkanes) by several alternative methods, dependent upon their physical characteristics. For example, hard asphalts (especially cracked or blown) having penetrations at 77° F. less than about 10 are preferably introduced by first dissolving them in a minimum amount of an aromatic hydrocarbon solvent. In order to minimize the effect of the aromatic solvent upon the precipitation of the asphaltene, it is preferred that the proportion of solvent be restricted to between about 0.5 and 2 volumes for each volume of the asphaltic residue. The aromatic solvent is preferably one predominating in aromatic hydrocarbons having less than 10 carbon atoms per molecule, of which benzene, toluene and xylene are suitable members.



Softer asphalts may be dispersed for the present purpose by refluxing in the presence of a limited proportion of the precipitating aliphatic hydrocarbon, although the aromatic solvent may be used in addition to or in place of the aliphatic medium. The maltene solution and precipitated particles are separated by any suitable means, including filtration, centrifuging, sedimentation, decanting or similar treatment. Following separation of the asphaltene particles, they may then be dissolved in an aromatic volatile solvent such as xylene or the like for use in the modification of microgel grease compositions. They may be added to such compositions under a variety of circumstances, such as by addition to an aqueous gel of the gelling agent or by dispersal in the lubricating oil prior to or subsequent to incorporation of the gelling agent in the oil. Preferably, asphaltenes are incorporated in the oil subsequent to addition of the colloidal gelling agent thereto and removal of any volatile solvents initially introduced together with the gelling agent.

The asphaltenes may be oxidized either prior to or subsequent to their separation from other asphaltic components such as maltenes and the like. Oxidation may be carried out by means well known in the asphalt art. For the most part, such operations are conducted by simply blowing the asphaltic body with air at an elevated temperature (350–575° F.) for an extended period of between about 0.5–24 hours. The oxidation may be carried out in the presence of oxidizing catalysts if desired, such as phosphoric acid, phosphorus pentoxide, ferric chloride, Friedel-Crafts catalyst, and the like although this is not an essential feature of this invention.

Asphaltenes may be prepared by blowing a naturally occurring asphaltic material whereby maltenes are converted to asphaltenes and in the course of blowing asphaltenes are apparently further polymerized. Asphaltenes have a structure of such complexity that it has not been fully described. However, in addition to the definition given above, analyses of typical asphaltenes provide further information. Table I gives an elemental analysis of typical asphaltenes:

TABLE I

*Asphaltene Analysis*

| Feed | Asphaltene Yield | Elemental Analysis, percent wt. | | | | | Mol. Wt. |
|---|---|---|---|---|---|---|---|
| | | C | H | N | S | O | |
| California Crude, Flasher Pitch | 25.1 | 85.02 | 8.50 | 2.26 | 2.25 | 1.58 | 2,120 |
| California Crude, Straight-Run Residue | 10.4 | 85.14 | 8.63 | 2.3 | 1.9 | 1.46 | 2,050 |

It has been determined that asphaltenes are polycyclic, contain hetero atoms, particularly nitrogen, sulfur and oxygen, and usually contain between 1 and 13 hetero atoms, usually 4–10, per asphaltene molecule, on the average. The metallic content of asphaltenes is in the order of 0.1–0.3%, the major constituents being iron, vanadium, sodium and nickel. About ¼ of the nitrogen atoms are weakly basic and only about 1% of the nitrogen atoms

are strongly basic. Approximately ⅓ of the sulfur groups exist as aliphatic or alicyclic sulfides, 1% as disulfides and 57% of the sulfur as thiophenes or polythiophenes. In the average asphaltene molecule, there are believed to be about 150 carbon atoms, 18 hydroxyl groups, 3.4 nitrogen atoms, 1.5 sulfur atoms and 2.1 oxygen atoms, although this analysis will depend upon the molecular weight selected as being nearest actuality. Moreover, there are understood to be about 10 methyl radicals in the average asphaltene molecule. The molecular weights of asphaltenes vary widely dependent upon the method by which the molecular weight determination is made. Table II shows that these vary all the way from about 2000 to 100,000 depending upon the method.

TABLE II

| Solvent | Particle Weight Derived From— | | | |
|---|---|---|---|---|
| | Freezing Point Depression | Vapor Pressure Depression | Osmotic Pressure | Films Spread on Water |
| Benzene | 2,000–4,000 | 12,000 | 82,000 | 50,000–100,000 |
| Carbon Disulfide | | 13,000–22,000 | | |
| Nitrobenzene | 800 | | | |
| Camphor | 600 | | | |

Asphaltenes may be utilized in amounts varying from about 0.1% to about 10%, based on the total composition for the purpose of stabilizing non-asphaltogenic organic lubricants. Preferably, however, amounts in the order of between about 0.25% and about 5% are found to be most suitable. The proportion will vary with the intensity of radiation expected and the relative stability of the lubricant being so modified. In many cases there is no objection to adding whole asphalt of the lubricating composition, especially if the asphalt contains more than about 25% by weight of asphaltenes.

By the term "non-asphaltogenic" lubricants will be understood to mean any lubricants which do not contain normally occurring or added asphaltic constituents in amounts sufficient to inhibit radiation damage, that is, less than about 0.1% by weight. The lubricating materials which may be modified in accordance with the present invention include particularly liquid lubricants and plastic lubricants referred to usually as greases. They comprise lubricating oils which may be mineral lubricants, especially petroleum lubricating oils as well as synthetic lubricants, including esters, ethers, silicone fluids, and other well known materials. Specific lubricants include mineral oil bright stocks, methyl phenyl silicone fluids, dimethyl silicone fluids, polyphenyl ethers, diesters of aliphatic dicarboxylic acid with monohydric alcohols, such as bis(2-ethylhexyl)sebacate, polyesters, such as pentaerythritol esters of $C_{6-14}$ aliphatic monohydric alcohols, complex esters formed between polybasic aliphatic acids and polyhydric alcohols, esters of polyalkylol alkanes, and other materials well known for their lubricating properties.

While grease compositions containing asphaltenes are not intended to be restricted to lubrication in the presence of radiation, this constitutes one of the environments in which the properties of these greases show up to greatest advantage. For this purpose, residual lubricating oils commonly known as bright stocks are preferred. 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 dewaxed and deasphalted (if an asphaltic crude is employed). Following this, the raffinate is treated with a solvent for the purpose of reducing or removing the aromatic fractions. 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 should have the following ranges of properties:

TABLE III

*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 >100, preferably >115.
Flash, °F. >475, preferably >500.
Fire, °F. >550, preferably >600.
Pour Point, (° F.) +25 maximum, 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 IV

*Examples of Typical Bright Stocks*

| | SUS | | Viscosity Index | Ring Analysis | | | Ratio of Paraffines to Naphthenes | Average Mol Weight | Average Rings per Mol |
|---|---|---|---|---|---|---|---|---|---|
| | 100 | 210 | | Aromatic | Naphthenes | Paraffines | | | |
| 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 |
| Coastal Bright Stock | 1,251 | 85 | 63 | 4 | 35 | 61 | 1.74 | 515 | 3.4 |

TABLE V

*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 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 that 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.

The fluids useful in the operation of equipment within radiation zones may be thickened or gelled to a grease consistency by the presence of a wide variety of colloidal materials including the conventional soaps, such as alkali metal or alkaline earth metal as well as polyvalent metal soaps of fatty acids or hydroxy fatty acids. However, it is preferred that non-soap gelling agents be utilized such as silica aerogels, finely divided silica prepared by burning silanes, clays, ammonium clays, such as trimethyl-stearyl-ammonium bentonites and, especially, high temperature gelling agents, such as indanthrene dyes, indogens, and polymer coated clays, such as clays coated with phenol-formaldehyde resins, aniline-formaldehyde resins and the like. Graphite may be employed for this purpose as well. The proportion of gelling agents will depend upon the consistency of the greases desired and upon the temperatures to which the grease compositions will be subjected. Normally, this will be between 2 and 40% by weight of the total grease composition. Methods of preparing such greases are known in the art.

The equipment in which the compositions of the invention are to be utilized includes nuclear reactors and power generators as well as research equipment, such as Van de Graaff accelerators and other accelerators of similar nature wherein ionizing radiation is emitted by the equipment. Moreover, the radiation resistant lubricants of the invention may be employed in the operation of equipment within the radiation zone of spent fuel elements, or in storage locations where products which emit radiation particles are stored. Of course, the lubricants may be utilized in equipment, such as nuclear powered aircraft, wherein the nuclear power plant is supplemented by auixiliary power equipment, such as gas turbine engines or jet engines as well as internal combustion engines. The same requirements for radiation resistance exists under such circumstances as when the lubricant is employed in the direct operation of equipment forming a component part of a nuclear power plant or other radiation emitting piece of equipment. The fluids may be utilized in conjunction with shields since they may be contained in hollow walls or other tanks forming a shield between the radiation emitting source and surrounding space. Under these circumstances the compositions forming part of the shielding material may be utilized first for this purpose and later circulated for use as a hydraulic fluid, heat transfer medium or as a lubricant.

The presence of asphaltenes in the non-asphaltogenic lubricant minimizes alterations in the physical and chemical properties of the lubricant during its exposure to radiation. This protective function of asphaltenes is greatly increased when the latter are subjected to oxidation prior to their incorporation in the lubricant.

Following are examples of compositions typical of those considered within the present invention:

EXAMPLE I

| | Percent |
|---|---|
| Bright stock mineral oil | 99 |
| Asphaltenes | 1 |

EXAMPLE II

| | Percent |
|---|---|
| Bright stock mineral oil | 99.5 |
| Air blown asphaltenes, 250° F. softening point | 0.5 |



EXAMPLE III

| | Percent |
|---|---|
| Methyl phenyl silicone oil (Dow Corning Fluid 710) | 99.5 |
| Asphaltenes from West Coast Crude | 0.5 |

EXAMPLE IV

| | Percent |
|---|---|
| Bis-(2-ethylhexyl)sebacate | 98 |
| Air-blown asphaltenes from West Coast Long Residue | 2 |

EXAMPLE V

A bright stock mineral oil modified with 0.75% by weight of West Coast asphaltenes was exposed to the radiation emitted by a Van de Graaff accelerator until it had adsorbed $2\times10^8$ rads of radiation. The viscosity of the composition before exposure was 4611 SSU and after irradiation was 6032, or an increase of 31%. When the bright stock was irradiated without being modified with asphaltenes, the viscosity increase after the same dosage was 48%.

EXAMPLE VI

Methylphenyl silicone oil modified with 0.5% West Coast asphaltenes was irradiated to the same dosage and increased in viscosity during this period from 1268 to 1907 SSU at 100° F., or a percentage increase of 50%. When the methylphenyl silicone oil was irradiated for the same dosage in the absence of asphaltenes it increased 78% in viscosity.

EXAMPLE VII

A radiation-stable lubricant can be prepared by dewaxing and deasphalting a short residue to obtain a bright stock lubricating oil, precipitating asphaltenes from the asphalt removed thereby and recycling them to the bright stock in an amount of 0.1–10% by weight.

We claim as our invention:

1. A radiation-resistant lubricant composition consisting essentially of a major proportion of a lubricating oil, said oil being one which inherently contains less than about 0.1 percent by weight of asphaltic constituents, and is an oil of the group consisting of petroleum lubricating oils and silicones and 0.1–10 percent by weight, sufficient to improve resistance of the oil to damage by ionizing radiation, of added asphaltenes.

2. A lubricant composition according to claim 1 wherein the oil is a petroleum oil.

3. A radiation-resistant lubricant composition consisting essentially of a major proportion of a lubricating oil, said oil being one which inherently contains less than about 0.1 percent by weight of asphaltic constituents, and is an oil of the group consisting of petroleum lubricating oils and silicones and 0.1–10 percent by weight, sufficient to improve resistance of the oil to damage by radiation, of oxidized asphaltenes, said asphaltenes having been oxidized for 0.5–24 hours at 350–575° F.

4. A radiation-resistant lubricant composition consisting essentially of a major proportion of a lubricating oil, said oil being one which inherently contains less than about 0.1 percent by weight of asphaltic constituents, and is an oil of the group consisting of petroleum lubricating oils and silicones and 0.1–10 percent by weight, sufficient to improve resistance of the oil to damage by radiation, of airblown asphaltenes, said asphaltenes having been airblown for 0.5–24 hours at 350–575° F.

5. A radiation-resistant lubricant composition comprising a major proportion of a methylphenyl silicone oil and 0.1–10% by weight, sufficient to improve resistance of the oil to damage by radiation, of added asphaltenes.

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