United States Patent Office 3,244,626 Patented Apr. 5, 1966

3,244,626

RADIATION RESISTANT LUBRICATING GREASE

Joseph F. Lyons, Poughkeepsie, and Norman R. Odell, Wappingers Falls, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Jan. 15, 1962, Ser. No. 168,569
7 Claims. (Cl. 252—29)

This invention relates to the lubrication of machines which are exposed to nuclear radiation and to improved lubricating compositions for such purpose. More particularly, it relates to lubricating greases containing finely divided graphite of a particular type as the thickening agent therein.

Lubricating greases exposed to nuclear radiation undergo chemical and physical changes which result in a deterioration of their lubricating properties, involving both viscosity changes in the oil base and a breakdown of the grease structure. Greases thickened with finely divided solids are particularly subject to the latter type of deterioration, due to the effect of nuclear radiaton upon the surface energies of the solid particles.

In accordance with this invention, greases which are especially suitable for lubrication in the presence of nuclear radiation are obtained by employing finely divided graphite of a particular type, characterized by an irregular intercrystalline arrangement, as the thickening agent. The graphites employed for this purpose have a particle size below about 0.5 micron, in their largest dimension, and an abnormally high surface area in the range from about 500 to 900 square meters per gram, due to the irregular surface and porous structure of the particles. The preferred material of this type has a surface area in the range from about 600 to about 800 square meters per gram, as measured by the conventional nitrogen adsorption method. These greases undergo only a relatively small amount of change in consistency and other lubricating properties as compared with other solids thickened greases of the prior art when they are subjected to nuclear radiation.

The discovery of the grease forming properties of these graphites was entirely unexpected, since graphites have been regarded as unsuitable for use as grease thickening agents because of their non-polar character, and little or no grease forming effect has been found with the finely divided graphites employed heretofore as fillers and lubricant improvers in lubricating compositions, even when employed in the compositions in high proportions. It is believed that the different grease forming properties of the graphites which we employ are due to a combined effect of their small particles size and the irregularity of the particle surface which gives rise to heterogeneous surface energies apparently compensating sufficiently for the lack of polarity of the material.

The lubricating greases of this invention comprise essentially a lubricating oil as the major component thickened to a grease consistency with a finely divided graphite of the character described above. The graphite will usually be present in an amount from about 15 to about 45 percent by weight, and preferably from about 20 to about 40 percent by weight, based on the weight of the composition.

The lubricating oils employed in these greases are preferably hydrocarbon oils, particularly mineral lubricating oils having Saybolt Universal viscosities in the range from about 75 seconds at 100° F. to about 225 seconds at 210° F., high molecular weight aromatic compounds, and hydrocarbon polymers in the lubricating oil viscosity range. The preferred mineral oils are distillate oils having viscosities in the range from about 300 seconds at 100° F. to about 100 seconds at 210° F., which may be obtained by blending lighter and heavier oils in the

lubricating oil viscosity range and which may be either paraffnic or naphthenic in character. Particularly preferred lubricating oils are those of predominantly aromatic character, represented by VGC constants of at least about 0.870, and preferably in the range from about 0.900 to 1.100. The VGC is an arbitrary constant calculated from the Saybolt Universal viscosity and the specific gravity of the oil, and decreases with paraffinicity (Hill and Coats, Ind. Eng. Chem., v. 20, p. 641–4 (1928). Alkylated naphthalene and biphenyl compounds, including alkylated and halogenated naphthalene and biphenyl compounds are especially suitable materials of this character.

Synthetic lubricating oils of various types containing elements in addition to carbon and hydrogen, may also be employed to form lubricating greases in accordance with this invention, although the greases thus obtained are less resistant to radiation and therefore less desirable for use in the presence of substantial amounts of radiation than greases prepared from hydrocarbon oils as described above. Suitable synthetic oils include particularly di- and polyesters, di- and polyethers and the sulfur analogs thereof, having viscosities within the lubricating oil viscosity range. Examples of suitable diesters include di-2-ethylhexyl sebacate, di(secondary amyl) sebacate, di-2-ethylhexyl azelate, di-iso-octyl adipate, etc. Particularly suitable polyesters are those described in U.S. 2,628,974, obtained by reacting an aliphatic dicarboxylic acid with a glycol and a monofunctional aliphatic alcohol or acid. Another very suitable class of synthetic oils comprises silicone oils, such as, for example dimethylsilicone polymer, diphenylsilicone polymer, methylphenylsilicone polymer, methylethylsilicone polymer, methylchlorophenylsilicone polymer, etc. These synthetic oils are also thickened to a grease consistency by graphite of the character employed in accordance with our invention, and the greases thus obtained are unexpectedly superior in general to greases obtained from these synthetic oils by employing conventional solid thickeners.

Additives of various types which do not undesirably affect the novel and advantageous properties of these greases may be employed, such as, for example, oxidation inhibitors, corrosion inhibitors, tackiness agents, extreme pressure agents, etc., of various types. Very advantageously, the compositions may contain about 0.1 to about 5 percent by weight of an oxidation inhibitor of the amine type, such as diphenylamine, alphanaphthylamine, betanaphthylamine or paraphenylenediamine. Another very suitable class of compounds having oxidation inhibiting and other advantages for use in these greases are dihydroquinoline polymers, particularly 2,2,4-trimethyldihydroquinoline trimer. Also, additional thickening agents may be employed in minor amounts, such as other finely divided solids of various types and metal soaps of high molecular weight fatty acids such as are conventionally employed in lubricating greases.

Graphites having the irregular crystalline structure required for use in accordance with this invention may be obtained by the high temperature graphitization of carbons resulting from the coking of hydrocarbonaceous materials, containing a small amount of carbide forming metal. A very suitable material of this character is petroleum coke, containing about 0.5–2 percent of inorganic ash comprising metals present in the original oil. The coke is prepared for graphitization by heating at about 1000–1800° C. for a sufficient period to reduce its volatile content below about 0.5 percent, and grinding, suitably to about rice sized particles. Graphitization may be carried out by the well known Acheson process, wherein the coke is heated in an electric furnace at a temperature above 2000° C., most suitably at 2300–2400° C., for at least about 24 hours. The crystalline structure of graphites obtained in this manner is different

from that of other graphites in general, including both natural graphites and graphites prepared from carbonaceous materials of a different type such as carbon blacks, these other graphites forming particles having smooth surfaces due to their regular crystalline arrangement.

The graphite which may be obtained as described above is reduced to a suitably small particle size by any convenient method, such as by milling an aqueous slurry of the graphite particles in a ball mill or colloid mill or by slurry pulverization as described by Eastman et al. in U.S. 2,735,787. The reduction can be carried out very advantageously by the Acheson deflocculating process, involving wetting the graphite particles with water containing a small amount of a deflocculating agent such as tannin, dextrin, dextrin with ammonia, etc., and working the mass thoroughly before milling. The graphite thus obtained may be purified by addition of an electrolyte to cause reflocculation of the graphite particles and water washing, followed by separation of the water and drying of the particles. If necessary, the dried particles may be remilled to break up the aggregates and the particles of the desired size separated, as by centrifuging. The process is carried out to obtain a material having a particle size in the range from 0.5 to 0.01 microns, and preferably from about 0.3 to 0.03 microns, for use in accordance with this invention.

If desired, the graphite particles obtained as described above can be further treated to reduce their ash content by treating with hydrofluoric acid, followed by water washing.

The grease preparation may be carried out by merely mixing together the thickener and any additives employed with the lubricating oil, employing any means suitable for accomplishing a thorough dispersion of the thickener and additives in the lubricating oil base, such as by milling in a colloid mill or in a paint mill. The mixing may be carried out at ordinary temperatures or at elevated temperatures such as up to about 300° F. or higher, if desired, in order to dissolve any difficultly soluble additives employed.

The following examples describe grease compositions which are representative of the grease compositions of our invention.

Example I

A lubricating grease having the following composition in percent by weight:

Graphite	22.9
Mineral lubricating oil	77.1

The mineral lubricating oil employed is a refined naphthenic distillate oil having a Saybolt Universal viscosity at 100° F. of 313 and a VGC of 0.875.

The graphite is a material of the character described hereinabove having an irregular crystalline structure and composed of individual particles in the 0.05 to 0.15 micron range, and aggregates in the 0.3–0.5 micron range, and having an inorganic ash content below 0.4 percent and a surface area of 645 square meters per gram, as measured by the nitrogen adsorption method. It may be obtained from petroleum coke resulting from the distillation of a paraffinic crude, having a volatile content of about 15 percent and containing 1.2 percent of inorganic ash, consisting chiefly of silica and compounds of chromium, vanadium and iron. Conversion of the coke to graphite may be carried out by the process comprising the steps of grinding to about 20 mesh, heating at 1200° C. for 10 hours, and then further heating in an electric furnace of the resistance type at 2300–2400° C. for 35 hours. Size reduction of the graphite thus obtained may be carried out by grinding to 200 mesh, moistening with about an equal weight of water containing 6 percent by weight of tannin, and mortar mixing the slurry for 5 days. The graphite particles may be separated from the aqueous solution by diluting the mixture with additional water and adding a small amount of hydrochloric acid, sufficient to give about a 0.5 percent solution, separating the partially reflocculated particles as by centrifuging, and repeatedly washing the particles with distilled water. The mass may be dried in an oven, suitably at about 200° F., and subjected to milling, suitably in a Waring Blendor, or in a ball mill for larger size batches, to substantially break up the aggregates formed by reflocculation.

The grease preparation is suitably carried out by mixing together 49 grams of the graphite and 116.5 grams of the mineral lubricating oil and milling the mixture in a Premier Colloid Mill with two passes at 0.002 inch clearance.

A smooth black grease is obtained as described above having a penetration at 77° F. of 298 unworked, 319 worked 60 strokes (converted from a ¼ cone, ⅓ size worker). This grease has very satisfactory lubricating properties generally, including very superior extreme pressure properties as compared with carbon black thickened greases of approximately the same grade.

In contrast to this result, attempts to prepare a graphite thickened grease with finely divided graphites of the types employed heretofore in lubricating compositions were unsuccessful, a fluid product being obtained with 30 percent by weight of a finely divided graphite having a particle size below 1 micron maximum dimension and a surface area of 370 square meters per gram in the naphthene distillate oil described above.

Example II

A lubricating grease having the following composition in percent by weight:

Graphite	34.7
2,2,4-trimethyldihydroquinoline trimer	3.0
Mineral lubricating oil	62.3

The graphite employed is that described in Example I. The mineral lubricating oil is a blend of a refined residual oil having an SU viscosity at 210° F. of about 117 seconds obtained from a paraffin base crude and a refined paraffinic distillate oil having an SU viscosity at 100° F. of about 338 seconds. The grease preparation is carried out by milling a mixture of 200 grams of graphite, 15 grams of the inhibitor, 364 grams of the residual oil and 121 grams of the distillate oil in a Premier Colloid Mill with 2 passes at 0.002 inch clearance.

A black glossy grease is obtained as described above, having very superior stability and other desirable lubricating properties as shown by the following typical test results:

Penetration at 77° F.:	
Unworked	294
Worked, 60 strokes	290
Worked, 100,000 strokes	217
Dropping point, ° F.	500+
ASTM bomb oxidation test (100 hr. at 210° F.) lb. drop	5
Dynamic water resistance loss, percent	2.5
Water absorption test absorption, percent	65
Worked penetration after test	264

Example III

A lubricating grease having the following composition in percent by weight:

Graphite	30.9
Alkylated biphenyl	69.1

The graphite is the material described in Example I. The alkylated biphenyl is a commercially obtained mixture of mono-, di-, and polyamylbiphenyls. The grease preparation is carried out as described in Example I.

A smooth black glossy grease is obtained as described above having a penetration at 77° F. of 287 unworked, 313 worked 60 strokes (converted from a ¼ cone, ⅓ size worker) and very satisfactory lubricating properties generally.

The following table shows the resistance to change of the above greases when they are subjected to nuclear radiation. The test comprises statically radiating the grease samples (about 2 ounces) in sealed heavy wall Pyrex glass capsules enclosed in stainless steel cylinders, employing a cobalt-60 radiation source possessing a high specific activity of 45 Curies per gram. The samples are subjected to the gamma radiation of the cobalt-60 for 50 hours for a total dosage of 10^8 rads, and a determination made of the changes in both unworked and worked penetration. The table gives representative results obtained upon the greases of our invention and for comparison those obtained upon a carbon black thickened grease. The latter grease comprised a mineral lubricating oil of the type described in Example II, thickened with 15 percent by weight of a commercial carbon black sold under the trade name of Kosmos BB.

TABLE I

Penetration at 77° F.	Grease			
	Carbon Black Thickened	No. 1	No. 2	No. 3
Before irradiation:				
Unworked	224	279	294	287
Worked, 60 strokes	310	305	290	313
After irradiation:				
Unworked	392	317	335	313
Worked, 60 strokes	400+	332	337	313
Penetration change, percent:				
Unworked	75	13.6	14.7	9.1
Worked, 60 strokes	29.0+	8.9	16.2	0

As shown by the above table, the graphite thickened greases of our invention prepared from hydrocarbon oils undergo no more than a moderate amount of consistency change, represented by a change of generally less than 20 percent, and generally less than 15 percent for greases prepared from aromatic oils, in both unworked and worked penetrations, when they are exposed to nuclear radiation in amounts of the order of 10^8 rads. The unexpected nature of this result is shown by the large amount of breakdown of the grease structure, indicated by an increase of 75 percent in unworked penetration, of a carbon black thickened grease exposed to this same amount of nuclear radiation.

Example IV

As an example of a lubricating grease of a different type also contemplated by our invention, a grease having the following composition in percent by weight:

Graphite	30
Silicone oil	70

The graphite is the material described in Example I. The silicone oil is a material obtained commercially from the General Electric Company under the trade name of "Versilube F–50," having a viscosity of 40–60 centiscopes at 100° F. and a specific gravity of 20° C./4 of 1.03. The grease preparation is carried out as described in Example I except that the mixture may be passed through a Manton-Gaulin homogenizer for 15 minutes at 0.040 inch clearance.

A grease is obtained as described above having a penetration at 77° F. of 320 unworked, 324 worked 60 strokes (converted from a ¼ cone, ⅓ size worker). In spite of a somewhat pasty texture, it has very satisfactory properties for use as a high temperature grease, including good stability, a dropping point above 500° F. and good water resistance and oxidation resistance properties.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency by about 20–40 percent by weight of finely divided graphite having a particle size from about 0.5 to 0.01 micron and a surface area by the nitrogen adsorption method from about 500 to about 900 square meters per gram, said lubricating oil being selected from the class consisting of mineral oils, alkylated naphthalenes, alkylated biphenyl compounds and silicone oils.

2. A lubricating grease according to claim 1 wherein the said graphite has a particle size from about 0.3 to about 0.03 micron and a surface area in the range from about 600 to about 800 square meters per gram.

3. A lubricating grease according to claim 1 wherein said lubricating oil is an aromatic oil having a VGC of at least 0.870.

4. A lubricating grease according to claim 1 wherein said lubricating oil is a silicone oil.

5. An improved method for the lubrication of a system subjected to nuclear radiation including substantial gamma radiation, which comprises lubricating said system with a lubricant composition consisting essentially of a lubricating oil selected from the class consisting of mineral oils, alkylated naphthalenes, alkylated biphenyl compounds and silicone oils thickened to a grease consistency by about 20–40 percent by weight of a finely divided graphite having a particle size from 0.5 to 0.01 micron and a surface area by the nitrogen adsorption method from about 500 to about 900 square meters per gram.

6. The method of claim 5 wherein the said lubricating oil is an alkylated biphenyl compound.

7. The method of claim 5 wherein the said graphite has a particle size from about 0.3 to about 0.03 micron and a surface area from about 600 to about 900 square meters per gram.

References Cited by the Examiner

UNITED STATES PATENTS

2,449,689	9/1948	Carnell	252—29 X
2,948,679	8/1960	Rees et al.	252—29 X
2,967,827	1/1961	Bolt et al.	252—28
3,046,223	7/1962	Morris	252—29 X

FOREIGN PATENTS

117,911	1/1958	Russia.

OTHER REFERENCES

"Dag Dispersions for Industry," 1954, Catalog No. 460, Acheson Colloid Co., Port Huron, Michigan, 8 pages.

"Lubrication Problems at Nuclear Power Stations," by Copper et al., in Scientific Lubrication, vol. 9, No. 8, August 1957, pp. 31, 32, 34, 35–39.

"Radiation Resistant Greases," by Bolt et al., AECU–3148, June 30, 1956, 42 pages.

"Scientific Lubrication," vol. 9, No. 4, April 1957, pp. 28–30.

References Cited by the Applicant

Boner, "Manufacture and Application of Lubricating Greases," Reinhold Publishing Corp., 1954, page 271.

DANIEL E. WYMAN, *Primary Examiner.*

JOSEPH R. LIBERMAN, *Examiner.*

I. VAUGHN, *Assistant Examiner.*