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COMPLETE SPECIFICATION

Improvements in or relating to Lubricants Resistant to Atomic Radiation

We, ESSO RESEARCH AND ENGINEERING COMPANY, formerly known as Standard Oil Development Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improved lubricants which are resistant to the destructive effects of atomic radiation. More particularly, the invention is concerned with improved lubricating oils and greases which are more stable and which retain their lubricating effect for a longer period of time than conventional lubricants under the influence of neutron and gamma radiation. In brief compass, the invention pertains to lubricants containing substantial proportions of materials having high gamma ray absorption coefficients and large capture cross-sections for thermal, i.e. slow, neutrons.

Present developments in the use of atomic energy indicate that nuclear reactors are being designed at a rapidly increasing rate for use as power plants for ships, aircraft and other carriers as well as for the generation of steam and electric power. Such atomic power plants have many moving parts which require lubrication, the lubricant being exposed to neutron and/or gamma radiation.

For example, the nuclear reactor itself is equipped with a large number of lubricated hydraulic lifters and control valves which are directly exposed to neutron as well as gamma radiation. The heat transfer fluid, usually a liquid metal, used to control the reactor temperature becomes radioactive in the atomic pile. The gamma radiation emitted by this fluid penetrates its piping and various other plant equipment and reaches lubricants used in various parts of the plant, particularly in relatively compact units as they are required in submarines or aircraft. A successful application of the nuclear reactor to this type of power generation and transmission requires, therefore, lubricants which retain their lubricating effect under the influence of neutron and gamma radiation.

Conventional lubricants rapidly fail under these conditions. It is well known in the art that organic matter undergoes severe decomposition by destructive dehydrogenation, charring, and carbonization, when subjected to neutron irradiation. Gamma radiation strongly promotes such reactions as cracking, polymerization, desulfurization, decarboxylation, alkylation, and dehydrogenation, which may take place in conventional mineral oils and most synthetic lubricating oils resulting in a rapid reduction or even complete destruction of the lubricating effect of the lubricant used. The present invention greatly alleviates this difficulty and allows lubrication of frictional surfaces in the proximity of a source of atomic radiation which would ordinarily be capable of decomposing conventional lubricants.

The term frictional surfaces, as used herein, refers to two surfaces that are substantially in contact and moving in relation to each other, that may be lubricated to decrease the frictional forces between the frictional surfaces. For example frictional surfaces may be the moving surfaces of moving parts of machinery such as bearings, gear wheels, driving chains, levers, sliders and guides.

Materials which may be used in accordance with the invention as moderators to reduce the damaging effect of gamma radiation must be capable of decreasing the energy content of the gamma rays by providing a high frequency of collisions between gamma rays and electrons. Such collisions result in a finite proportion of the gamma ray energy being absorbed by the electron and in a corresponding reduction of the effect of gamma radiation on the environment of the moderator. This energy absorption is a function of the so-called "gamma ray absorption coefficient" of the moderator, which in turn is determined by the molecular weight and density of the material. The gamma ray absorption coefficient of a moderator is the greater the higher its molecular weight and/or the greater its density. Also, certain morphological aspects affect the gamma ray absorption coefficient and with it the utility of a material as moderator. For example, materials having a hexagonal close-packed or laminar structure, such as lead or graphite, are particularly suitable for use in the present invention.

The term gamma ray absorption coefficient, as used herein, is defined by the term μ/ρ where ρ is the density and μ is defined by the equation $a = a_o e^{-\mu d}$ where a is the intensity after the gamma rays have passed through the absorbent material, a_o is the initial intensity of the gamma rays, d is the thickness of the material measured in centimetres and where the initial energy of the gamma rays is 4 m.e.v.

The lubricant composition of the present invention comprises a lubricating oil having incorporated therein a sufficient proportion of an element or compound having a gamma ray absorption coefficient of at least 3 and a sufficient proportion of an element or compound having a capture cross section for thermal neutrons of at least 2,500 barns to stabilize the said oil against atomic radiation.

The elements and compounds incorporated in the lubricant are referred to herein as moderators. The most outstanding examples of moderators having a gamma ray absorption coefficient of at least 3 are heavy metals, such as titanium, molybdenum, mercury, lead, bismuth, thorium, and platinum. These moderators may be added to conventional lubricants in powdered form i.e. finely divided, as metals, metal oxides or metal sulfides or in the form of compounds soluble in the base oil of the lubricant, for example as naphthenates, stearates, sulfonates, chelates, organic thiophosphorus acid salts, or phosphides. Other suitable moderators having a gamma ray absorption coefficient of at least 3 include powdered graphite and various other powdered minerals which exhibit laminar structure, such as mica, asbestos, and talc. The moderators may be present in the lubricants in proportions of 2—30 wt. %, and preferably 5—20 wt. %.

It is preferred that the moderator having a capture cross-section for thermal neutrons of at least 2,500 barns should, after neutron bombardment, revert to form stable non-radioactive isotopes of at least the same minimum capture cross-section by releasing the absorbed energy in the form of harmless electromagnetic radiation. Data on neutron cross-sections of most elements and the stability of their isotopes are now available in the literature permitting the selection of materials suitable for the purposes of the present invention. Typical representatives of this class of materials are the elements cadmium, samarium and gadolinium. The pertinent characteristics of these elements are summarized in the table below.

Element	Thermal Neutron Capture Cross-Section of Element (Barns)	Principal Isotopes for Neutron Absorption	Thermal Neutron Capture Cross-Section for Principal Isotope (Barns)
Gadolinium 156.9 Atomic Wt.	36,000	$_{Gd}155$ $_{Gd}157$	50,000 180,000
Samarium 150.43 Atomic Wt.	8,000	$_{Sm}149$	46,000
Cadmium 112.41 Atomic Wt.	2,900	$_{Cd}113$	24,000

Moderators of this class may be added to lubricants in the form of the finely divided metals, their oxides, sulfides, phosphides, and phosphorus acid salts, or as compounds soluble in the base oil of the lubricant, such as the naphthenates, petroleum sulfonates, fatty acid soaps, e.g. stearates and oleates (complexes of the type which may be employed in greases) of such soaps with the metal salts of low molecular weight carboxylic acids; chelates and porphyrin derivatives of such metals.

The degree of protection afforded by such a moderator is, of course, a function of its concentration in the lubricant as well as its specific capture cross-section. This is illustrated by the following tabulation of the neutron absorption by the preferred moderators of the invention at varying concentrations in a lubricant film of 0.05 cm. thickness.

Additive	Capture Cross-Section (Barns)	Concentration Weight Percent	Percent Neutron Absorption
Gadolinium	36,000	50	100.0
		10	99.6
		1	42.5
Samarium	8,000	50	99.8
		10	70.8
		1	11.6
Cadmium	2,900	50	95.4
		10	45.9

As indicated by the above table, effective concentrations of the moderator having a capture cross-section for thermal neutrons of at least 2,500 may vary between about 1 and 50 wt. % of the lubricant, depending somewhat on the specific moderator used. Concentrations of about 10—40 wt. % of such moderator are usually preferred.

When oil-insoluble moderators are used, these materials should be employed in finely divided form. Particle sizes of less than 100 microns are suitable, sizes of about 50—75 microns being preferred.

The lubricating oil base of the lubricants of the invention may be of either mineral or synthetic origin. These oils should have a viscosity of about 2 centistokes at 210°F. to about 60 centistokes at 210°F. While all types of mineral oils of lubricating grade have utility for the purposes of the invention, those obtained from predominantly naphthenic stocks are more desirable, acid treated naphthenic type mineral lubricating oils being preferred. Of the synthetic oils, non-ester types are preferred. Suitable synthetic oils include Fischer-Tropsch synthesis products, hydrocarbon polymers, formals, acetals, glycols, ethers, glycol and polyglycol ethers, carbonates, silicanes, silicones, silicates, fluoro- and perfluorocarbons, of lubricating grade, all of which are well known in the art.

Greases in accordance with the invention may be prepared from the above-mentioned lubricating oils by adding a moderator of each type according to the invention and incorporating a conventional grease thickener in grease-making proportions of, say about 3—50 wt. %, preferably 10—30 wt. %, based on total lubricant. The oil base may form 20—95 wt. % of the composition or finished grease. Quite generally, non-soap type grease thickeners are preferred because of their greater stability toward gamma radiation. Essentially inorganic thickeners, such as carbon black, finely divided silica, silica gel, various metal silicates, including calcium silicate, bentonites, Bentones, Attapulgus clays, and various gel-forming amphoteric metal oxides including Al_2O_3, Fe_2O_3, Bi_2O_3, and SnO_2, are most desirable. Some examples of Bentones are given in J. Phys. Chem. *45*, 65—81 (1941).

Examples of suitable organic salt-type thickeners include the hydrocarbon sulfonates of alkali metals, particularly sodium, potassium and lithium, the calcium, strontium, barium, magnesium, aluminum and certain heavy metals, such as lead; having about 8—34 carbon atoms, particularly in combination with metal salts of low molecular weight carboxylic acids having 1—5 carbon atoms per molecule. The preferred carboxylic acid soaps of the metals listed above, are those of essentially saturated fatty acids having 12—30 carbon atoms, e.g. stearic, palmitic, hydroxystearic, and hydrogenated fish oil acids, preferably in the form of complexes with the metal salts of low molecular weight saturated carboxylic acids having 1—5 carbon atoms. Other suitable organic thickeners include various amino phenol derivatives, such as N-stearoyl-p-amino phenol, and urea adducts of benzene and biphenyl.

A moderator may be a component of a grease thickening agent, for example when a metal soap and/or salt type of thickener is used, at least a portion of the metal constituent of the metal soap or salt may be a moderator of the invention. For example, cadmium stearate, or calcium stearate-cadmium acetate complexes may be used for this purpose.

Conventional methods of grease-making may be employed in preparing the greases of the invention. When using inorganic thickeners, the finely divided thickener may be dispersed in the oil base by means of homogenizers, colloid mills or similar high efficiency mixing equipment. This can be done prior to the incorporation of the moderators or in their presence. The latter method is preferred.

Soap-thickened greases may be made by saponifying suitable fats or oils containing the acids prevously described, or by neutralizing the acids as such in at least a portion of the base oil with the metal bases mentioned above. When the metal base of the thickener is different from that of the moderators the saponification is preferably carried out prior to the incorporation of the moderators. When the metal base of the thickener is the same as that of a moderator, the metal base of the moderator may be used as the saponifying or neutralizing agent. Grease-making conditions are those conventionally used including saponification temperatures of about 150°—250°F., dehydration temperatures of about 210°—300°F. and complexing or finishing temperatures of about 400°—600°F. In the case where the moderators are different from the metal base of the grease thickener, the moderators are preferably added under agitation during the cooling cycle of the grease-making process at temperatures below about 350°F. The usual finishing steps, such as homogenization and milling, may be employed.

The lubricants of the invention may contain minor proportions of conventional modifying agents, e.g. calcium sulfonate, and anti-oxidants, e.g. phenyl α-naphthylamine; corrosion inhibitors, e.g. sorbitan mono-oleate; extreme pressure agents, e.g. tricresyl phosphate, sulfurized and P_2S_5-treated materials, chlorinated hydrocarbons and esters; viscosity index improvers, e.g. polybutenes and polymethacrylates; pour point depressors, e.g. naphthalene alkylated with chlorinated paraffin wax, lauryl fumarate-vinyl acetate copolymers; tackiness and stringiness agents, e.g. polyisobutylenes.

The invention will be further illustrated by the following specific examples.

EXAMPLE I

A grease useful for the purposes of the invention may be prepared from the following components:

Component	Wt. %
Cadmium Stearate	20
Cadmium Acetate	20
Molybdenum Disulfide Powder	10
Phenyl Alpha-Naphthylamine	0.5
Formal of C_{13}-Oxo Alcohol having a Viscosity of 3.4 Centistokes at 210°F.	49.5

The grease is prepared as follows: About ⅓ of the formal is mixed with the stearic acid and heated to about 150°F. Cadmium hydroxide is added sufficient to neutralize the stearic acid. Thereafter glacial acetic acid is added and neutralized with additional cadmium hydroxide. The mixture is heated to about 220°F. until dehydration is complete. Heating is continued at a rapid rate until a temperature of about 450°F. is reached. The grease is then allowed to cool and the remaining portion of the formal is added at a temperature of about 300°F. After further cooling, the molybdenum disulfide powder and the oxidation inhibitor are added and the grease is passed through a homogenizer at a temperature of about 180°—200°F.

EXAMPLE II

A lubricating oil in accordance with the invention may be prepared by intimately mixing the components given below, at substantially room temperature or slightly elevated temperatures promoting the solution of the additives in the oil base,

Component	Wt. %
Gadolinium Naphthenate	6
Bismuth Stearate	25
Condensation Product of Salicyl Aldehyde and Propylene Diamine	1
Phenyl Alpha-Naphthylamine	0.5
Coastal Distillate of 30—40 SSU at 210°F.	67.5

EXAMPLE III

Another lubricating oil of good radiation stability is obtained by mixing the following components substantially as described in Example II.

Component	Parts by weight
Gadolinium Oleate	5
Mercury Naphthenate	30
Phenyl Alpha-Naphthylamine	0.5
Condensation Product of Salicyl Aldehyde and Propylene Diamine	1
Polyethylene Glycol of about 200 molecular weight	64.5

The present invention is not limited to the specific examples set forth above. The relative proportions of the lubricant constituents may be varied within the limits indicated to obtain lubricants of different characteristics.

What we claim is:

1. A lubricating composition of improved stability to atomic radiation comprising a lubricating oil having incorporated therein a sufficient proportion of an element or compound having a gamma ray absorption coefficient of at least 3 and a sufficient proportion of an element or compound having a capture cross section for thermal neutrons of at least 2,500 barns to stabilize the said oil against atomic radiation.

2. A lubricating composition as claimed in claim 1 wherein the lubricating oil is a mineral lubricating oil or a synthetic lubricating oil other than an ester.

3. A lubricating composition according to claims 1 or 2 wherein the lubricating oil has a viscosity between 2 and 60 centistokes at 210°F.

4. A lubricating composition as claimed in claim 1 wherein sufficient of a grease thickener is present to thicken the composition to the consistency of a grease.

5. A lubricating composition as claimed in

claim 4 wherein the composition comprises a mineral or synthetic lubricating oil, other than an ester, thickened with a grease thickener at least a part of which is constituted by at least one of the elements or compounds having a gamma ray absorption coefficient of at least 3 or a capture cross section for thermal neutrons of at least 2,500 barns.

6. A composition as claimed in any of claims 1 to 5 wherein the element or compound having a gamma ray absorption coefficient of at least 3 is titanium, molybdenum, mercury, lead, bismuth, thorium or platinum or a compound of such elements.

7. A composition as claimed in claim 6 wherein the compound of the element having a gamma ray absorption of at least 3 is an oxide or sulfide.

8. A composition as claimed in any of claims 1 to 7 wherein the compound having a gamma ray absorption coefficient of at least 3 or having a capture cross section for thermal neutrons of at least 2,500 barns is an oil-soluble compound.

9. A composition as claimed in any of claims 1 to 8 wherein the element or compound having a capture cross section for thermal neutrons of at least 2,500 barns is gadolinium, samarium or cadmium or a compound of such elements.

10. A composition as claimed in any of claims 1 to 9 wherein the compound having a capture cross section for thermal neutrons of at least 2,500 barns is an oxide, sulfide, phosphide, a phosphorus acid salt or a carboxylic acid salt.

11. A composition as claimed in any of claims 1 to 10 wherein the quantity of the lubricating oil is from 20 to 95% by weight of the total composition.

12. A composition as claimed in any of claims 1 to 11 wherein the quantity of the element or compound of the element having a gamma ray absorption of at least 3 is from 2 to 30% by weight of the total composition.

13. A composition as claimed in any of claims 1 to 12 wherein the quantity of the element or compound of the element having a capture cross section for thermal neutrons of at least 2,500 is from 1 to 50% by weight of the total composition.

14. A lubricant of improved stability toward atomic radiation which comprises 20% to 95% by weight of a lubricating oil having a viscosity of 2 to 60 centistokes at 210°F selected from the group consisting of mineral oils and synthetic oils, 2% to 30% by weight of a component having a gamma ray absorption coefficient of at least 3 selected from the group consisting of titanium, molybdenum, mercury, lead, bismuth, thorium and platinum, and 1% to 50% by weight of a component having a capture cross section for thermal neutrons of at least 2,500 barns selected from the group consisting of cadmium, samarium and gadolinium.

15. A lubricant of improved stability toward atomic radiation which comprises 67.5 wt. % of a mineral oil having a viscosity in the range between 30 to 40 S.S.U. at 210°F, 25 wt. % of bismuth stearate and 6 wt. % of gadolinium naphthenate.

16. A lubricant of improved stability toward atomic radiation which comprises 64.5 wt. % of polyethylene glycol having a molecular weight of about 200, 30 wt. % of mercury naphthenate and 5 wt. % of gadolinium oleate.

17. The process of lubricating equipment exposed to atomic radiation which comprises contacting frictional surfaces of said equipment with a lubricant or lubricating composition as claimed in any of the foregoing claims.

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