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RADIATION RESISTANT MINERAL OILS

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The present invention relates to the preparation of radiation resistant mineral oils. More particularly the invention relates to novel compositions of matter involving white mineral oils or lubricating oils which have added to them certain materials that tend to minimize deterioration of such oils when subjected to gamma radiation.

Oils in general deteriorate when subjected to intense gamma radiation. White mineral oils in particular are subject to such damage which limits their usefulness in radiation-proof windows and the like. There are many situations in present technology where mineral oils such as white oils or lubricating oils are used in close association with varying degrees of intensity of gamma radiation; for example, oils are required in nuclear power plants, in turbines, control rod mechanisms, food sterilization by radiation, space ship lubrication and the like. The mechanisms employed in connection with or in the presence of intense gamma radiation require lubrication but heretofore it has been a problem to devise an oil which will withstand the radiation and will not become rancid and break down under such radiation.

It has now been discovered that such oils can be protected to the extent that their deterioration by gamma radiation is minimized. To produce mineral oil compositions which stand up well in the presence of gamma radiation requires the use of protective additives. If there is added to the oils one or more liquid scintillation phosphors either alone or admixed with a compound capable of absorbing ultraviolet light, this can be achieved. Ordinary white mineral oil shows radiation damage when subjected to even low doses of gamma radiation, i.e. of the order of less than 10^4 roentgens and becomes seriously deteriorated at 10^6 roentgens. Ordinary highly refined mineral lubricating oils tend to break down between 10^6 and 10^7 roentgens. White mineral oils treated in accordance with the present invention are able to withstand 2.3×10^5 roentgens at 10^4 roentgens per hour without being substantially changed in any detectable respect, and highly refined lubricating oils are improved in proportion to their original resistance.

Liquid scintillation phosphors are employed in producing the compositions of the present invention. These compounds are described in considerable detail in "Nucleonics," December 1955, pp. 38–41, see particularly the tables appearing on pps. 40 and 41. As stated in the article, the liquid scintillation phosphors are selected from the group consisting of aromatic hydrocarbons, furans, pyrroles, oxazoles, 1,3,4-oxadiazoles, pyridines, indoles, and benzoxazoles. These compounds may have substituent groups attached to them, such as methyl, methoxyl, fluoro, and chloro. The specific compounds therein disclosed are incorporated into this description by express reference and are made a part hereof.

The mineral oils to which the phosphors are added are those mineral oils which are customarily employed as white oils for "look" windows in nuclear reactor installations or in "hot cell" installations operating in the presence of radioactive materials and for lubricating oils of the general type employed for lubricating conveyors, nuclear control rods, and the various types of machinery in which friction must be controlled and which are subject to radioactive radiation as heretofore set forth.

In general, the lubricating oils are highly refined and are one of three types.

(1) Oleum treated naphthenic or paraffinic lubricating oils, for example, white mineral oils of the USP and National Formulary grades, or technical white oils meeting less exacting specifications.
(2) Phenol extracted lubricating oils such as turbine oils, motor oils and other lubricants from which the major portion of aromatic compounds have been removed.
(3) The hydrogenated and therefore fully saturated lubricating oils such as "super-refined" semi-white oils used in aviation jet engines.

In general, between about 75 p.p.m. and about 1,000 p.p.m. (0.1%) of a liquid scintillation phosphor or a mixture of scintillation phosphors is sufficient to minimize the deterioration of the oil due to gamma radiation. However, if desired, greater quantities of phosphors may be employed; for example, up to about 0.5% by weight, but effective concentrations are generally attained without using as much as 0.5% of the phosphors.

Additionally, an ultraviolet compound capable of absorbing ultraviolet light may also be added to the mineral oil composition. A primary solute (liquid scintillation phosphor) is believed to draw off excitation energy from the mineral oil component which the latter receives by reason of its absorption of the gamma radiation and conversion of the energy to the longer wave length ultraviolet radiation. The function of an ultraviolet light absorber is merely that a fluoroescent material is maintained in the solution in order to get a more favorable wave length (such as visible or infra-red radiation) so that the energy of the gamma radiation is dissipated in the form of low energy photons and is therefore unable to seriously break down or deteriorate the structure of the oil molecules. The phosphor serves to convert ionizing radiation of either the beta or gamma form to ultraviolet light. The presence of the ultraviolet light absorber, although it contributes little to this primary system, does effectively remove the secondary effects of the ultraviolet and hence, although it is not necessary, the presence of an ultraviolet light absorber is in most instances a desirable addition to the composition. The above discussion is, of course, theoretical and there is no intention of limiting the invention to that theory.

Any conventional compound having the ability of absorbing ultraviolet light may be employed. As examples of such compounds which may be used, the following are disclosed:

2-hydroxy, 4-methoxy benzophenone
2,2'-dihydroxy 4-methoxy benzophenone
2,2'-dihydroxy 4,4-dimethoxy benzophenone
4-tertiary butyl phenyl salicylate
2,4-dibenzoyl resorcinol
5-chloro 2-hydroxy benzophenone

As in the case of the liquid scintillation phosphor addition, the compounds capable of absorbing ultraviolet light are present in the compositions in about the same quantities, i.e. from about 75 p.p.m. to about 1,000 p.p.m. and may be present if desired up to about 0.5% of the composition, but here again such large amounts are unnecessary in ordinary circumstances in order to ac-

complish a minimizing of deterioration of the mineral oil due to gamma radiation.

Example

Samples of a white mineral oil of 355 SSU visc./100° F. and 80 VI were exposed to 2.3×10^5 roentgens at the rate of 10^4 roentgens/hr. alone and with the following additives.

Blend	Composition	Additive Class	Deterioration in Odor
1	No additives		Badly deteriorated—Rancid.
2	75 p.p.m. 2,2'-Dihydroxy-4-methoxy Benzophenone.	U.V.	Do.
3	75 p.p.m. 2,5-Diphenyl Oxazole.	LSP	Mild deterioration.
4	75 p.p.m. Tetra phenyl Butadiene.	LSP	Do.
5	50% #2, 50% #3	U.V.+LSP	Almost unchanged.
6	50% #2, 50% #4	U.V.+LSP	Do.
7	10 p.p.m. Ditert-butyl p-cresol.	Antioxidant	Worse than #1—Rancid.

Having now thus fully described and illustrated the character of the invention, what is desired to be secured by the Letters Patent is:

What is claimed is:

1. A gamma radiation resistant composition comprising a major proportion of mineral oil, about 75 parts per million to 0.5 wt. percent of an oil-soluble liquid scintillation phosphor capable of absorbing gamma radiation and converting said gamma radiation into ultraviolet light, when said oil is subjected to gamma irradiation, and about 75 parts per million to 0.5 wt. percent of an ultraviolet light absorber capable of absorbing said ultraviolet light emitted by said phosphor and converting said absorbed ultraviolet light into low energy photons substantially harmless to said composition.

2. A composition according to claim 1, wherein said mineral oil is a lubricating oil.

3. A gamma radiation resistant composition comprising a major proportion of mineral oil, about 75 parts per million to 0.5 wt. percent of oil soluble liquid scintillation phosphor capable of absorbing high energy gamma radiation and converting said gamma radiation into ultraviolet light, said phosphor being selected from the group consisting of aromatic hydrocarbons, furans, pyrroles, oxazoles, 1,3,4-oxadiazoles, pyrridines, indoles, and benzoxazoles, and 75 parts per million to 0.5 wt. percent of an ultraviolet light absorber capable of absorbing ultraviolet light emitted by said phosphor to thereby convert said ultraviolet light into low energy photons substantially harmless to said mineral oil.

4. A composition according to claim 3 wherein said liquid scintillation phosphor is 2,5-diphenyl oxazole.

5. A composition according to claim 3 wherein said liquid scintillation phosphor is 1,1,4,4-tetraphenyl-1,3-butadiene.

6. A composition according to claim 3 wherein said liquid scintillation phosphor is 2,5-diphenyl oxazole and said compound capable of absorbing ultraviolet light is 2,2(-dihydroxy-4-methoxy benzophenone.

7. A composition according to claim 3 wherein said liquid scintillation phosphor is tetraphenyl butadiene and said compound capable of absorbing ultraviolet light is 2,2'-dihydroxy-4-methoxy benzophenone.

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