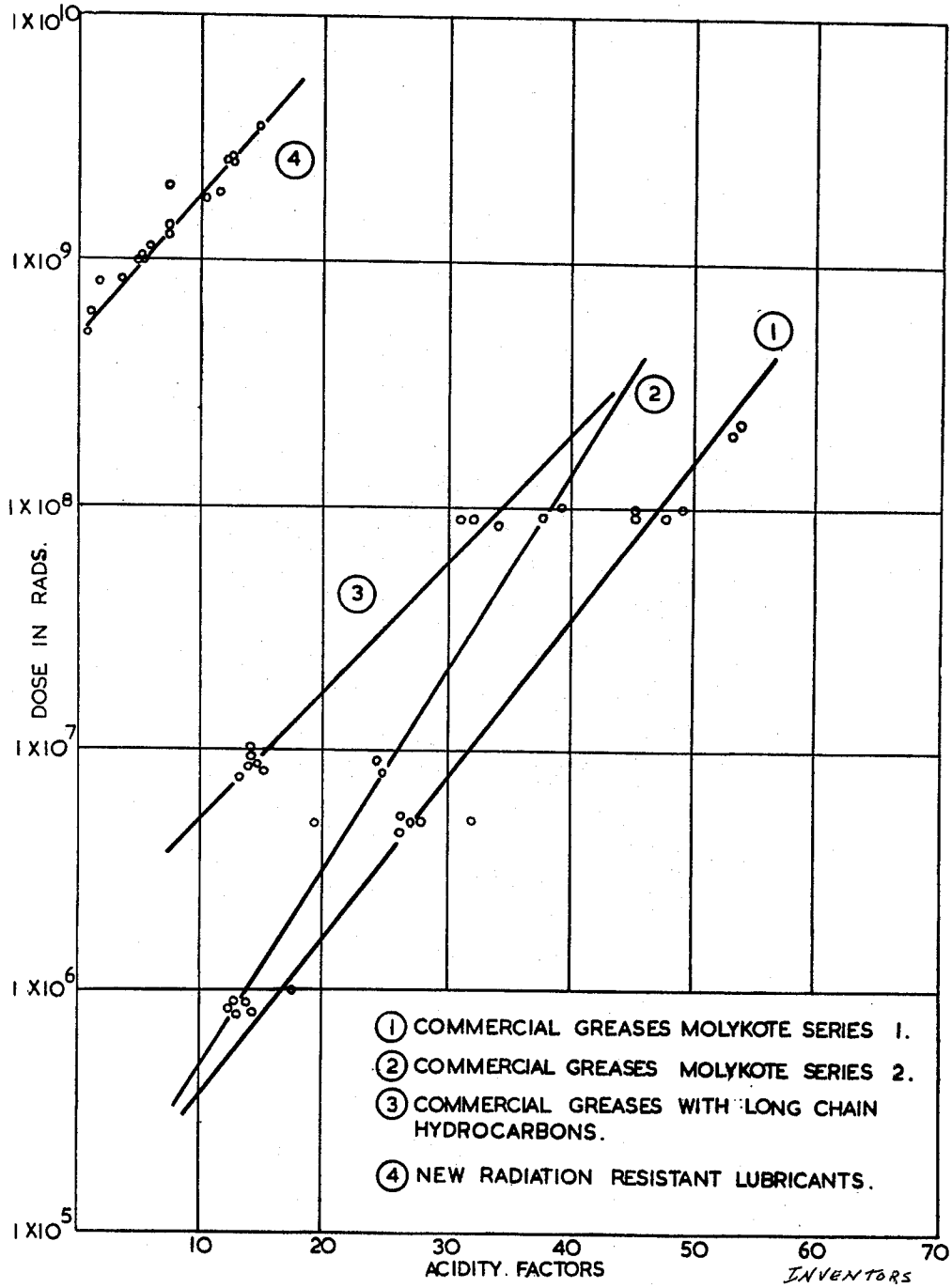
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RADIATION RESISTANT LUBRICANTS

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RADIATION RESISTANT LUBRICANTS

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This invention relates to lubricating oils and greases for use in areas where they are subjected to large doses of high energy radiation of the order of 10^9 rads and greater and which can maintain their lubricating properties with little or no deterioration.

When greases and oils are exposed to radiation, changes occur which result in a loss of their lubricating properties. Changes in molecular structure take place, gases are evolved, oxidation products are formed and there is an increase in acidity.

It is known that aromatic and substituted aromatic compounds have greater radiation stability than aliphatic and alicyclic hydrocarbons of comparable molecular weight. It has been assumed that this stability is connected with the strongly resonating nature of the aromatic structure which allows for a rapid energy dissipation in the molecule thus reducing the degree of degradation and probability of bond rupture. If lubricants are to be rendered relatively insensitive to radiation it is thought necessary that their molecules should contain groupings which would stabilize them.

Greases differ from most lubricating oils in that thickening agents are present. Experimenters have found that with low doses of radiation, lubricating greases in which soaps were added as gelling agents, become fluids. This is thought to be due to the breakdown of the soap-gel structure. With sodium soap greases others have observed softening initially, followed by hardening of the products at higher doses. The softening has been explained as being due to the formation of sodium carbonate resulting in an oil insoluble residue. On further irradiation the base fluid underwent cross-linking resulting in the observed hardening.

In the present invention new lubricants for high radiation have been developed and a description of the invention now follows in which comparisons will be made between the properties of the new lubricants exposed to high radiation doses and conventional lubricants which have not been irradiated. A comparison of the effects of radiation on the new and conventional lubricants is also made.

In following the teaching of the invention, a conventional commercial grease or oil (base lubricant) containing long chain hydrocarbons or substituted hydrocarbons is mixed with varying proportions of a monomer such as styrene. Long chain hydrocarbons are organic molecules of the paraffin type such as Vaseline, SAE 30 and 40. Substituted hydrocarbons, for the purpose of the present application, are grease compositions in which additives such as silicones, aromatic compounds, soaps and other gelling agents have been added as blenders. The molecule of styrene includes a benzene ring and a vinyl double bond but it is believed that any monomer of similar molecular structure with one or more benzene rings and an available vinyl double bond may be substituted. The percentage of styrene by weight added to the base lubricant should preferably be about 10% although the range of about 10% to about 33% has been found satisfactory, and any percentage of styrene will produce improvements. Addition of styrene above 33% tends to make the final product excessively viscous. Quantities of more than about 50 percent styrene lead to less attractive properties because of the excess quantities of polystyrene which will be formed. The mixture of base lubricant and styrene is placed in a radiation field

and is irradiated to a dose of about 1×10^7 rads with periodic shaking. An improved substance results. The composition formed during the irradiation is different from the base lubricant in having a changed molecular structure but no significant changes in physical properties are observed. Infrared spectroscopic investigation shows that copolymers of the hydrocarbons in the base lubricant with styrene have formed with no evidence of oxidation or production of acids. A small amount of finely divided molybdenum disulphide (such as Molykote Z) may be added as a solid lubricant to prevent metal to metal contact and to provide a low coefficient of friction under high loading conditions; this substance does not react with the lubricant. For the preparation of the new lubricants, it is imperative that the reaction which takes place when the mixture of the base lubricant and styrene are irradiated, occurs, before the substance is put to use as a lubricant. The mixture itself cannot be used since it would be unstable and there would furthermore be a loss of styrene due to evaporation.

A series of new compositions formed by the foregoing process were then tested for their radiation resistant properties by comparison with the base grease or oil from which they were formed. The irradiation of all lubricant samples was carried out in the Atomic Energy of Canada Limited "Gammacell 220" in which the radiation field was of the order of 10^6 rads per hour. Samples were kept in open aluminium boats or in loosely stoppered bottles so that deterioration due to various causes such as radiolysis, oxidation and cracking could take place. Infrared spectroscopic techniques were used for studying molecular changes and determining progressive deterioration, by quantitatively measuring the acidity produced. Stearic acid was used as the standard and unirradiated control samples of all greases and oils were used for comparison.

The brand-named lubricants were as follows: Graham Drive Traction Blue, Retinax–A, Darina No. 2, Marfak H.D. 2, SKF Ball Grease, Molykote Series.

Table I shows the effects of radiation on a series of lubricating oils and greases. It is seen that conventional lubricants undergo definite deterioration with doses below about 10^7 rads.

The effects of radiation on the newly produced lubricant samples can be seen from Table II. All samples show negligible deterioration even with doses up to 10^9 rads. They can withstand on the order of 250 times as great a dose before showing the same extent of breakdown as the base lubricant.

The conventional lubricant bases were also tested with the addition of polystyrene to determine that it was not merely a mixture of the base with polystyrene which was responsible for the improvement. The lubricants with polystyrene incorporated showed some improvement over the base but considerable thickening and hardening was observed with high radiation doses, the improvement depending upon the percentage of polystyrene added. All such mixtures showed over 50% deterioration before a dose of 4×10^8 rads was delivered.

In the accompanying drawing, the figure summarizes the findings of Tables I and II and is a graph of radiation dose against relative acidity formed for three conventional types and for the new lubricants.

The lubricants of the invention were put to further tests to determine their properties and suitability. Standard qualification tests were also made upon certain samples of the new lubricants exposed to 1×10^9 rads. These were compared with unirradiated base lubricant samples.

(*1*) *Homogeneity and viscosity.*—There was no marked change in appearance after irradiation. The samples were smooth, homogeneous, free from lumps and other undesirable characteristics. The composition and consistency were uniform and there was no sedimentation. The viscosity indices of the new grease compositions irradiated to

a dose of 1×10^9 rads were high and remained the same as those of the original base greases used.

(2) *Evaporation loss tests.*—According to ASTM Specification D972–51T a lubricant should not lose more than 5% of its weight in 22 hours under the conditions of the experiment. The results shown in Table III were obtained. The improvement in the Graham Drive Traction Blue is most marked.

(3) *Gear wear tests.*—The Navy Gear Wear test C.G.S.B. schedule 3 GP–O method 80–4 was used and the results are expressed as weight losses in milligrams per 1000 cycles. The tolerance losses should not be greater than 5 milligrams per 1000 cycles and 10 milligrams per 1000 cycles for the five pound and ten pound loads respectively. From Table IV it is clear that in the samples tested the losses obtained were well within the tolerances and that even after being subjected to high radiation doses there were not significant differences between these new lubricants and the unirradiated base controls.

(4) *Dropping point.*—This is the temperature at which a grease passes from a semi-solid to a liquid state under the conditions of the test. Following the ASTM D566–42 method the new lubricant compositions were compared with the unirradiated bases. The results are presented in Table V. The dropping points of the irradiated samples were not found to be significantly different from the control samples.

(5) Copper corrosion tests were conducted to obtain an indication of the corrosive effect of the lubricants on metal parts in general within which they might come in contact. No corrosion or staining of copper was observed with any of the irradiated samples or controls. Both the control and the irradiated samples of this grease produced some stains on the copper strips used but not enough to make them unsuitable for use as lubricating oil. This effect was not enhanced in any way because of the irradiation. It is concluded, therefore, that large doses of radiation do not tend to produce any corrosive agents in the new lubricant compositions in addition to those originally present in the base.

Mechanism of production of the lubricants of the invention

In the new compositions the irradiation induced reactions can be divided into three stages. The first consists of reactions whereby the radiation resistant lubricants are formed. Doses of about 10^7 rads are required to complete this stage. It is believed that the reaction proceeds through a free radical mechanism. This reaction results in the addition of one or more polystyrene groups to the long chain molecules of the lubricant hydrocarbon base. Polystyrene can be made to form as well if excess styrene is added, but under the conditions discussed above for the separation of radiation resistant greases this reaction is of no consequence. In the second stage the radiation has little effect on the new lubricants. The copolymers formed in the first stage are stable over a wide range of radiation exposure and doses of up to 10^9 rads make no significant changes in molecular structure as observed using infrared spectroscopic techniques. When subjected to doses in excess of 1×10^9, a third stage is reached where a new series of reactions is initiated. The rate of these reactions is extremely slow, when compared to the reactions in the formation stage. Spectroscopic studies indicate that compounds of low molecular weight are formed, gases such as methane are evolved and unsaturated hydrocarbons, carbon dioxide and carbon monoxide are produced. The grease itself developed double bonds the majority of which were of the vinylene type. Vinyl and vinylidene double bonds, carboxyl and hydroxyl groups were also present.

It is seen, therefore, that base lubricants to which styrene (or a similar compound having an aromatic ring and vinyl linkage) has been added are highly radiation resistant in comparison to those in which polystyrene is merely introduced as an additive. Those containing the polystyrene additive were superior to control samples, but this is believed to be due to the presence of the benzene rings in the polystyrene which rapidly dissipate the absorbed energy. By virtue of the mechanism of formation of the new lubricants it would be expected that they can be produced by the introduction of a free radical inducing agent as an initiator into the mixture of the base lubricant and styrene-like monomer, without the use of irradiation for the first stage mentioned above.

TABLE I.—EFFECT OF RADIATION ON VARIOUS COMMERCIAL GREASES AND LUBRICATING OILS

Commercial Greases or Lubricating Oils	Dose in rads	Acidity Factors
Retinax-A	8.2×10^6	13.8
Darina No. 2	8.33×10^6	14.9
Vaseline	8.50×10^6	14.3
Marfak H.D. 2	8.78×10^6	12.2
SAE 30	1.1×10^7	11.3
SAE 40	1.1×10^7	11.3

TABLE II.—EFFECT OF GAMMA RADIATION ON THE NEW COMPOSITIONS

[Base greases or lubricating oils + 10% styrene + 0.3% Molykote]

Base Grease or Lubricating Oils	Dose in rads	Acidity Factors
Retinax—A	2.2×10^9	12.9
Do	1.5×10^9	5.3
Marfak H.D. 2	1.9×10^9	10.2
Darina No. 2	1.2×10^9	13.9
SKF Ball Grease	1.1×10^9	13.1
Vaseline	2.5×10^9	10.1
Do	1.6×10^9	3.2
Shell Oil No. 30	2.5×10^9	10.3
Do	1.6×10^9	3.7
Shell Oil No. 40	2.2×10^9	10.3
Do	1.5×10^9	3.3

TABLE III.—EVAPORATION LOSS FROM THE ORIGINAL AND NEW LUBRICANT COMPOSITIONS

Samples used	Percentage evaporation loss	
	Original lubricant unirradiated	New composition irradiated to 1×10^9 rads
Retinax No. 2	1.4	3.85
SKF Ball Grease	2.3	4.19
Vaseline	0.3	1.92
Shell Oil SAE No. 40	0.6	3.07

TABLE IV.—COMPARATIVE VALUES OF GEAR WEAR TESTS

Samples used	Wt. losses in mgm./1,000 cycles with 5 lbs. load		Wt. losses in mgm./1,000 cycles with 10 lbs. load	
	Original lubricant unirradiated	New lubricant composition irradiated to 1×10^9 rads	Original lubricant unirradiated	New lubricant composition irradiated to 1×10^9 rads
Vaseline	1.1	0.7	1.9	3.7
Retinax-A	1.0	0.6	1.4	2.9
Shell Oil SAE No. 40	0.9	1.2	2.6	2.7

TABLE V.—DROPPING POINTS OF ORIGINAL AND NEW LUBRICANT COMPOSITIONS

Samples used	Dropping point in ° F.	
	Original lubricant unirradiated	New lubricant composition irradiated to 1×10^9 rads
Marfak H.D. 2	373.1	374.9
Retinax-A	364.1	308.3
Vaseline	122.0	106.7
Shell Oil SAE No. 40	Liquid	Semiliquid

We claim:

1. A lubricant for exposure to high energy radiation doses comprising a base lubricant consisting essentially of a long chain hydrocarbon copolymerized with about 10 to 50 percent styrene, said long chain hydrocarbon and said styrene being copolymerized by exposure to a dose of radiation in an amount of about 1×10^7 rads.

2. The lubricant of claim **1** wherein the amount of styrene is 10 to 33 weight percent.

3. A process for making a lubricant resistant to breakdown under large doses of high energy radiation which

comprises the steps of mixing a base lubricant comprising a long chain hydrocarbon with styrene in amounts of 10 to 50 percent by weight of said mixture and irradiating said mixture to a dose of about 1×10^7 rads.

4. The process of claim **3** wherein the amount of styrene is 10–33 weight percent.

References Cited by the Examiner

UNITED STATES PATENTS

2,967,827	1/1961	Bolt et al.	252—59 X
2,982,730	5/1961	Barry	252—59
2,989,452	6/1961	D'Alelio	204—154
2,990,350	6/1961	Natkin et al.	204—154 X
3,003,937	10/1961	Lucchesi	252—59 X
3,086,942	4/1963	Panzer	252—59 X
3,089,832	5/1963	Black	252—59 X
3,115,468	12/1963	Emrick	252—59
3,129,183	4/1964	Schneider	252—59

FOREIGN PATENTS

914,772	1/1963	Great Britain.

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