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LUBRICANTS IN NUCLEAR TECHNOLOGY: A BRIEF REVIEW

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BHABHA ATOMIC RESEARCH CENTRE
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ABSTRACT

The report summarises the current status of the development and the use of lubricant for variety of purposes in nuclear technology.

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The radiation resistant lubricants and hydraulic fluids which are important in nuclear reactors[1,2,3,4,5,6], aerospace technology[7,8,9], and modern military applications have been the subject of numerous reviews in the past. They are also essential in fuel processing plants and waste processing plants where handling equipments are exposed to intense radiation for prolonged periods. The present report summarises the current status of the field.

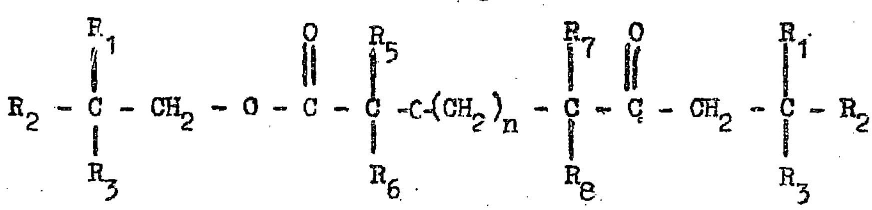
In nuclear reactors some of the vital parts which operate in radiation field are control drive mechanisms, coolant pumps, valves, fuelling machines and other auxiliary equipment for handling spent fuel elements. A comparative estimate of the doses received by these parts in reactors of different concepts are given in Table I[10]. It is obvious that a suitable lubricant should be capable of withstanding a dose in excess of 10^8 rads. Under these conditions conventional lubricants show enhanced viscosity index (Table II)[10] and consequently impaired performance. The lubricant requirement for control rod mechanism of a typical reactor (strictly valid for CO_2 cooled graphite moderated) is given in Table III[10].

1. DEVELOPMENT OF RADIATION RESISTANT LUBRICANTS

Essentially a lubricant consists of a base oil (natural or synthetic), a thickener, an antioxidant, an antiwear agent and sometimes a fire resistant agent. The base oil constitutes 75 to 100% of most organic lubricants and as such the radiation resistance is predominantly determined by its chemical nature. In general, the aromatic content is known to render it more resistant. One of the most promising synthetic fluids are polyphenyl ethers. Bis (p-phenoxyphenyl) and bis (p-tert-butyl phenoxy) phenyl ethers show reasonably good viscosity/temperature characteristics at elevated temperatures of 430°C to 480°C (even at 540°C for a few hours) and retain their integrity at doses in excess of 10^9 rads.

Recently Hollinghurst[11] has developed an equally resistant fluid with partially hydrogenated terphenyl blends for irradiation doses of 10^9 rads. The proposed components are a hydrocarbon mineral oil, 1 - 20 wt% unhydrogenated polyphenyls and 1 - 30 wt% polystyrene, polyalkyl styrene, an alkyl or aryl selenide or aryldisulphide. The degree of hydrogenation of terphenyl is such that the total polyphenyl components present is at least 30% of the theoretical amount for complete hydrogenation.

Yet another fluid capable of withstanding a dose of 10^9 rads seems to have been developed by Das Gupta and Slobodian[12]. It is produced by copolymerising commercially available long chain hydrocarbon lubricants having 12 - 26 carbon atoms with 10-50 wt% styrene by exposing to 10^7 rads. Mc Cabe[13] has suggested the use of certain types of hindered esters of carboxylic acid having the general formula:



in which R_1 and R_3 are alkyl groups containing not more than 3 carbon atoms in each, R_2 is an acyclic alkyl group containing from 2 - 8 carbon atoms and may contain a single branch of not more than 2 carbon atoms, R_5, R_6, R_7 and R_8 are alkyl groups containg 2 - 4 carbon atoms each and n is an integer varying from 2 - 6.

Some of the additives[14] tried to improve the radiation resistance of base oil are iodonaphthalene[a], (phenyldibutyl dithiophosphate, mercaptobenzothiazole, dihexacosyl polysulphide, and hexadecanethiol)[b], scintillation phosphors[c] (aromatic hydrocarbons, furans, pyrroles, oxazoles, 1,3,4 oxadiazoles, pyridines, indoles and benzoxazoles) and asphaltenes[d].

Other notable studies reported in literature are by Schulze et al.[15], Bethlendy et al.[16], Heinz[17], Irving et al.[18] and Zaslavasky et al.[19]

2. RADIATION RESISTANT GREASES

The most important ingredients in grease are the base oil and the gelling agent. Use of aromatic compounds with their superior resistance to radiolysis can be used in both portions of the grease e.g. alkyl biphenyl oil gelled with sodium n-octa decyl tetraphthalamate available commercially as NRRG 159 (Standard Oil Co.). Inorganic gelling agents such as graphite or silica in alkyl benzene (NRRG - 300) or silica thickened mineral oil (APL 700,701 Shell Oil Co.) appear to be suitable. Other additives suggested were bentonite, silica, urea derivatives, soap, clay or carbon black.

Furuya[20] irradiated silicone grease, APL-700 and NRRG - 235 to dose of 2 x 10^8 rads and observed that only the last two are stable under these conditions. Silicone grease starts losing its integrity beyond a dose of 3 x 10^6 rads.

With respect to radiation stability lubricants, in general, can be classified as follows:-

a) $< 10^6$ rads - no unusual problem from radiation

b) $10^6 - 10^7$ rads - methyl silicones, aliphatic diesters and phosphate esters become affected and polymers in solution degrade

c) $10^7 - 10^8$ rads - radiation effects on physical properties of diesters and certain mineral oils marginal. Oxidation stability and thermal stability are adversely affected for all fluids.

d) $10^8 - 10^9$ rads - Oxidation and thermal stability of most lubricants are seriously impaired. Major changes occur in most physical properties. Aliphatic ethers, aromatic esters and certain mineral oils may be used.

e) $10^9 - 10^{10}$ rads - polyphenyls, polyphenyl ethers or alkyl aromatics are recommended.

f) $> 10^{10}$ rads - laminar solids should be used.

Since irradiations under dynamic and static conditions could give different results, Jacobson et al.[21] designed a capsule for inpile dynamic evaluation test in NASA Plum Brook reactor facility to measure friction coefficient during radiation exposure at a neutron flux 5 x 10^{12} n/cm^2/sec.

3. DRY LUBRICANTS

In certain cases, various substitutes for conventional lubricants are employed. For example in water and heavy water moderated reactors, water lubricated stainless steel bearings are often used. Resin bonded asbestos containing graphite has also been employed whereas nylon or poly tetra fluoro ethylene bushes are other alternatives in lower radiation areas.

Molybdenised lubricating greases have been used as a dry powder or a paste for a variety of purposes. Solid lubricants like graphite, MoS_2 mixed with PbS, PbO, SnS_2, CdS, Sb_2S_5 or ZnS are used for specific purposes. Lipp and Stern[22] studied the effect of neutron irradiation on graphite $+CrCl_3$, B_2O_3, LiF, $(PNCl_2)_3$ or AgCl at 800°C and obtained best wear properties (wear coefficient remained below 0.10 from 40°C-800°C) for graphite $+CrCl_3$ upto integrated neutron flux of 10^{16} n/cm^2. Haley and Danniel[23] did not observe any significant wear life of mixture of PbS + MoS_2 + B_2O_3 and MoS_2 + graphite films upto γ dose of 1.47×10^9 rads and integrated neutron flux of 2.85×10^{16} n/cm^2.

4. EXPERIENCE OF LUBRICANTS USED IN REACTORS

The compatibility of lubricants with the material of construction is of great importance in the choice of lubricants used e.g., lubricants containing chloro or chloro-fluoro compounds can not be used on 300 series stainless steels in high temperature water systems as it leads to serious stress corrosion[24]. Also in CO_2 cooled graphite moderated reactor[10] additives containing even traces of Hg, Ba, Na, Tl, Sm, Zn, Ag, Ni etc. are not compatible with magnox fuel element cans. For Ti surface the best lubricant is benzyl iodide. For CO_2 cooled graphite moderated reactor, conventional turbine oil comprising a high viscosity index base oil containing conventional oxidation inhibitors (amine type), rust inhibitor and a defoamant was shown to be stable to 10 - 100 M rads (Table IV).[10] Certain additives were shown to extend the range of applicability to 500 - 1000 M rads. Conventional greases of the hydrocarbon type thickened with Ca, Al, Ni soaps showed softening in the region of 10 - 100 M rads. Some of the suggested greases[25] were APL 700 of NLG 1,2 consistency (capable of standing upto integrated neutron flux of 1.8×10^{18} n/cm^2), or Cosmos B-30 (ESSO Petrol Co.) and Greasrex - R4 (stable upto 1×10^8 rads - $1\text{-}2 \times 10^9$ rads).

For Dragon reactor[26], Shell product APL 701 grease was recommended. No regreasing was expected during the entire life time of reactor provided grease losses by mechanical causes could be avoided.

Sommer[27] indicated that naphthenic and aromatic and benzenic oils behaved better than silicone oil and mineral oil though silicone oil was preferred to mineral oil. In the degradation, radiation type was found to be less important than radiation intensity

Sadayuki et al[28,29] described lubricating oils used in the components of the atomic power stations and observed that turbine oil with additives, gear oil, high viscosity index oil and greases were stable upto 10^7 rads and needed replacement every year.

A recent report[30] describes and incident of infiltration of 56 gallons of main helium blower lubricating oil into the primary loop of the EBOR (Experimental beryllium oxide reactor) during valve testing operations, subsequent clean up operation, and a discussion of possible causes as well as an assessment of the damage to the plant. The clean up procedure consisted of pumping out the oil followed by flushing with chloride free solution of Turco 4324-OR detergent (Turco Products Co.) at pH 9.5, cleaning up with aqueous solution containing ammonia and hydrazine and finally treating with Standard odorless thinner and butyl alcohol (as deemulsifier) so as not to leave any solid residues behind.

5. EXPERIENCE OF LUBRICANTS USED IN PLUTONIUM PROCESSING

Lubricants used in glove boxes used for plutonium fabrication are susceptible to radiolytic decomposition and the products thus formed could be corrosive and affect the integrity of the product. Kazanjian and Brown[31] summarised the experience on lathe coolant (Texaco Regal Oil A), Dow Corning 550 silicone oil, Rykon grease and Nyes Watch Oil used in Rocky Flats. Generally lathe coolant comes in contact with Pu during cutting and machining operations and the production of even 1.2×10^{-2} mg of H_2 per cm^2 of the surface of Pu (through α- radiolysis of coolant) could lead to appreciable pitting through the formation of plutonium hydride. After the machining operation, CCl_4 is used to remove residual cutting oil and as such, a mixture of CCl_4 and coolant oil is likely to be exposed to α-rays of Pu turnings in the lathe glove box causing the production of hydrogen chloride and organic acids which are known to be potential sources of corrosion.

Dow corning 550 silicone oil was found compatible but needed frequent changes.

Rykon grease (American Oil Co.) used in large quantities on the chain conveyer system that moves plutonium through glove boxes was found to be reasonably stable and its incompatibility with Pu has not been established nor anything definite could be said about Nyes Watch Oil used on Pu during inspection.

6. EXPERIENCE OF LUBRICANTS IN HOT CELLS, ELECTRON ACCELERATORS AND OTHER IRRADIATION FACILITIES

The seizure of a bearing can put an active cell out of commission for several days since its repair means prior dismantling and decontamination[32]. Radiation resistant lubricants are more desirable. MoS_2 paste could be profitably used. Alternately the machineries are piped individually to a common pump and the capillary valves in the lines ensure constant supply at all points.

Nagamitsu and Hisashi[33] report the formation of contamination film through the radiation induced polymerisation of organic gases emanating from diffusion pump fluids. The contribution of Apiezon M and Apiezon L to the formation of film was relatively small.

Thus in view of growing application of nuclear technology in India, the demand for suitable lubricants and hydraulic fluids is bound to increase. As such there is a strong need for the development of indigenous radiation resistant fluids and lubricants to meet the requirement adequately.

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Table I

ESTIMATED LEVELS IN DIFFERENT NUCLEAR REACTOR SYSTEMS (rad/year)+

Component	CO_2-cooled graphite moderated reactor		Organic moderated reactor	Liquid metal cooled reactor	Pressurised water reactor	Boiling water reactor
	Lubricant	dose				
Control rod mechanisms	grease, oil	$10^3 - 5 \times 10^5$	10^8 max	$10^4 - 10^5$	$10^5 - 10^8$	10^6 max
Fuel handling devices	grease, oil	$10^2 - 3 \times 10^9$	-	-	2×10^7 max	-
Primary coolant pumps	oil, grease for bearings	10^3 max (gas circulators)	negligible)	10^8	$10^5 - 10^7$	≠ $10^5 - 10^7$
Auxiliary pumps	oil, grease	$10^5 - 10^8$	negligible	-	$10^4 - 3 \times 10^6$	$10^4 - 3 \times 10^6$
		Ancillary and charge chute machines				
Auxiliary motors etc.	oil, grease		-	-	$10^5 - 3 \times 10^7$	$10^5 - 10^7$
Turbine	oil	-	negligible to 25	negligible	negligible to 10	negligible to 80 ≠
Spent fuel element conveyer systems	grease	2×10^8 max (chains and bearings)	presumably 10^8	presumably 10^8	presumably 10^8	presumably 10^8

+ The radiation level may vary considerably from the estimate shown depending on variants of each basic design.

≠ The dose is likely to be considerably higher because of higher radiation field produced by the radioactive steam and impurities.

Table II

EFFECT OF RADIATION ON CONVENTIONAL LUBRICANTS

Lubricant type	Total acid number				Change in viscosity index, points			Viscosity increase per cent		
	Nil Mrad	69 Mrad	133 Mrad	232 Mrad	69 Mrad	133 Mrad	232 Mrad	69 Mrad	133 Mrad	232 Mrad
Non-petroleum base fire-resistant hydraulic fluids:										
(a) All synthetic base type	0.2	1.0	2.5	–	21	28	–	36	80	–
(b) All synthetic base type	0.2	3.5	5.0	10.5	7	18	29	38	52	76
(c) Water base type	–	–	–	–	–	–	–	-47	-52	-43
(d) Water base type	–	–	–	–	–	–	–	-50	-40	-12
Products containing extreme-pressure additives										
(a) Marine EP turbine oil	0.05	0.2	0.45	0.55	0.5	0.9	1.5	9	17	29
(b) Automotive gear oil	2.70	2.1	2.2	–	1.0	4.0	–	3	6	–
Products containing viscosity index improvers										
(a) Aviation hydraulic fluid	0.05	0.9	1.0	–	-63	-77	–	-55	-59	–
(b) Automotive engine oil	0.55	0.6	0.65	–	-28	-31	–	-33	-33	–
(c) Automatic transmission fluid	0.15	0.15	0.15	0.20	-13	-15	-19	-25	-25	-23

Table III

SUMMARY OF UKAEA's SCHEDULE 1 GREASE REQUIREMENTS FOR CONTROL ROD MECHANISMS, SHOWING TYPICAL RESULTS FOR AN APPROVED PRODUCT

Test	UKAEA requirement	Typical results on approved product
1. Drop point (IP 132/57):-		
(a) Before irradiation	200°C min	≥ 230°C
(b) After irradiation to 5 x 10^5 rad	200°C min	≥ 230°C
2. Worked penetration (IP 50/56):		
(a) Before irradiation	220 - 320	265
(b) After irradiation to 5 x 10^5 rad	220 - 320	269
3. Loss by evaporation (ASTM D972/51T modified): CO_2 at 150°C is used in place of air for 400 hours	4% weight max.	3.4
4. Bearing rig test: 20 mm bore shielded ball bearing, 100 rev/min, CO_2 at 150°C and 200 lb/in^2 and flow of 10 litres/h, 720 hrs' duration. Grease irradiated to 5 x 10^5 rad prior to test		
(a) Bearing rotation at end of test	Free	Free
(b) Signs of fluids or solids at end of test	None	None
5. Compatibility: Sample of cleaned fuel element canning material coated with grease exposed to static CO_2 at atmospheric pressure and 500°C for 500 hrs. First hour of test with flow of CO_2 of 2 litres/min.	No signs of reaction	No reaction

Table IV

EFFECT OF RADIATION ON CONVENTIONAL HIGH QUALITY INHIBITED HYDROCARBON TURBINE/HYDRAULIC OIL

Test	Radiation dose, Mrad				
	Nil	10	100	500	1000
Specific gravity	0.889	0.888	0.889	0.893	0.898
Viscosity at 100°F cs.	89.9	91.2	101	161	297
Viscosity index	97	97	97	108	120
Color ASTM D 155-45T	2-	2-	4	7+	8+
Total acid number (IP 1/58 Method A)	0.20	0.15	0.10	0.15	0.10
Demulsification number (IP 19/55), sec	300	900	1200+	1200+	1200+
Copper corrosion test at 100°C (IP 154/59B)	1b	1b	1b	1b	1b
Turbine oil oxidation test (IP 114/56), 90 hrs at 110°C: total acid number after test	0.05	0.05	0.10	0.30	0.45
Socony Mobil B.10 oxidation test, 40 hrs at 127°C:					
(a) Total acid number after test	0.1	0.2	0.3	0.9	-
(b) Viscosity increase (compared with irradiated oil prior to oxidation test),%	1.5	2.0	3.0	2.0	-
(c) Lead loss, mg	0.7	0.5	0.8	14.3	-
(d) Sludge	Nil	Nil	Nil	Nil	-
(e) Appearance of aluminium catalyst	Clean	Clean	Clean	Clean	-
" of iron catalyst	Clean	Clean	Clean	Clean	-
" of copper catalyst	Tarnished	Tarnished	Tarnished	Tarnished	-
Load-carrying and wear characteristics, Shell four ball tests:					
(a) Seizure load, kg	150	170	190	170	-
(b) Scar diameter after 1min at 150 kg load, mm	Seized	2.66	2.9	2.49	-