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LUBRICATING GREASES FOR NUCLEAR POWER PLANTS EQUIPMENT

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Abstract: *Among the many other organic products, lubricants used in nuclear power equipment are subject to irradiation which induces the degradation of their physic-chemical and tribological properties. The lubricating greases used in bearings, electric motors, in gear-boxes or slideways or on pivotal forming parts of the equipment essential to the safe and efficient operation of a nuclear power plant are regarded as important materials of the power station. In the lubricating places subject to radiation the life of the lubricating grease will be reduced due to the deterioration of the three main components of the lubricant: the oil, the thickener and the additives. The resistance to radiation of the lubricating greases is in accordance with their chemical nature. The exposure to radiation accelerates the oxidation of lubricants. Irradiation may affect some of the important properties of the lubricant, such as the viscosity, consistency, acidity oxidation stability. Continued and long time exposure to radiation turns almost all liquid or semisolid organic lubricants into hard, brittle solids. The radiation effects on lubricants depend upon the amount of absorbed energy, the composition of the product and the environmental conditions such as pressure, temperature and gaseous composition of the atmosphere. The general effects of the radiation on lubricants are: a change in the physical properties, an increase of viscosity and the products get dark and acquire an acrid odour, the hydrogen content decreases and the density increases; also, gases release or polymerization to a solid state may occur. Our paper emphasizes the effect of gamma radiations, with 10^6 to 10^9 rad dose rate, on lubricating greases The grease formulations and tests developed by us purposely for nuclear power plants and also the criteria for selection of lubricants to use in nuclear reactors are presented.*

Key words: *Lubricating greases, radiation resistance, oil, additive, thickeners.*

1. INTRODUCTION

Lubricants must provide adequate lubrication of different nuclear reactor systems such as: control road mechanisms, fuel handling devices, primary coolant pumps, auxiliary motors, turbines, etc. These components are subject to different levels of irradiation.

The selection of lubricants for nuclear power plants is a complicated decision involving many parameters such as tribological properties, radiation resistance, corrosion resistance availability, cost, etc. It is important that oils and greases be evaluated for their resistance to irradiation if they are to be used in a high-radiation environment. Like many others organic components such as plastics and polymeric insulating materials the structure of lubricating greases can be destroyed in radiation environment.

2. THE EFFECT OF RADIATION ON LUBRICATING GREASES

Lubricating greases are non Newtonian products obtained by dispersing of thickening agent in a liquid lubricant. Greases contain several components of different types which may be conveniently classified into three groups (fig. 1, 2):
1. The lubricating fluid: This is normally the major part of the grease, examples being mineral oil, polyalphaolefins, esters, silicones, poly phenylethers, etc.
2. The thickener: This component is largely responsible for the rheological properties of the

grease, conferring consistency and structure to the product, examples being soaps, modified clays, silica, pigments, polyurea, etc.

3. Additives: These components improve some characteristics of the base grease and confer other additional properties. Lubricating grease additives are specific products.

The optimum additives combination should meet the requirements regarding: oxidation stability, load carrying capacity (EP), wear reduction (AW), corrosion protection.

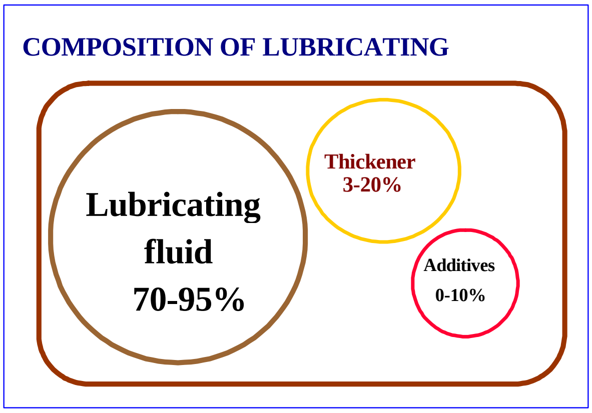

Figure 1. Composition of lubricating greases

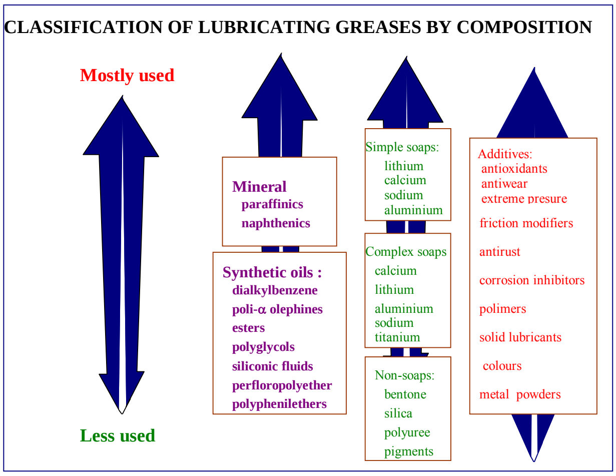

Figure 2. Classification of greases by composition

2.1 Effect of radiation on base oil

Radiation resistance is defined as the ability of a lubricant to maintain its principal physic-chemical properties unchanged under the action of ionizing radiation [5]. Physical and chemical characteristics of base oil can be appreciably affected by radiations. This depends on both the nature of the oils and the total dose of irradiation. The changes of oil subject to radiation can be evaluated by examination of four processes: viscosity changes, density changes, oxidation reactions and changes in colour.

Changes of base oil viscosity can occur as an effect of polymerization processes (increases of viscosity) or of chain breaking reactions (which cause viscosity to decrease). These alterations in base oil viscosity are thought to have the most significant effect when the order of change reaches 2 to 4 times the initial value [1]. At this level the lubricated bearing must work with an unsuitable lubricant and this can cause an increased operating temperature and hence accelerated degradation of the grease. If the result of irradiation process is to break-down with a fluid forming insufficient film thickness for adequate lubrication it is cased rapid lubrication failure.

Changes of fluid density are the result of chemical degradations accompanied by release of gases, while the effect of oxidation of the oil is an increase in viscosity and generating sludge. The formed sludge will accelerate further oxidation, generate products having acidic nature and reduce the service life of the lubricant.

The most readily detectable modifications of lubricants in service under radiations are colour changes. There is much information related to studies of radiation effects on lubricating oils, but very few related to radiation effects on individual groups of hydrocarbons as components in these oils. [3]. For a given gamma radiation dose the degree or degradation observed depends on the type of chemical bonding present. The least resistant to radiations from among chemical bonds is the covalent bond, as expected [4]. Organic compounds and some inorganic compounds exhibit this type of bonds. An important variation in strength of covalent bonds is present in compounds of different types and therefore a wide variation in their radiation resistance. Ring type structure of aromatic hydrocarbons is more resistant to radiation damage than all others types of hydrocarbons [4].

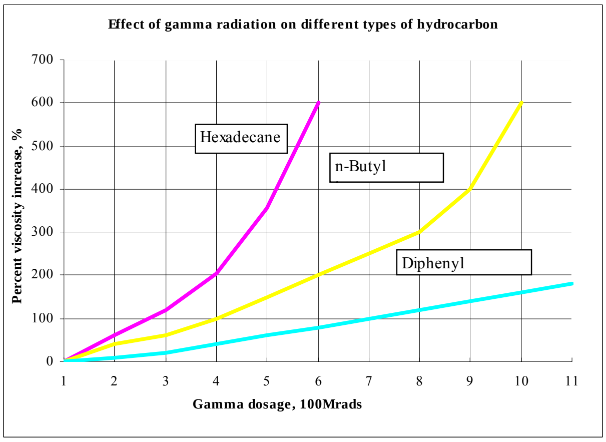

Figure 3. Effect of γ radiation on different types of hydrocarbons

The figure above illustrates that aromatic hydrocarbons (n-butyl benzene) are more resistant to irradiation than aliphatic compounds (hexadecane) are. Polyphenyls are the most resistant of all [4, 5]. In aromatic hydrocarbons "π" electrons of aromatic ring moving to higher energy levels return then to normal orbits energy without causing destruction of the molecule. Oils containing aromatic hydrocarbons have larger action against radiation due to a partial transfer of energy from radiation on benzene cycles.

Effect of radiation on thickeners

The effect of radiations on thickeners, no matter what their nature- either soap or inorganic type, is a decrease in their consistency and the result is the decline of their efficiency in lubrication. Frequently, the degradation of thickener is oil separation as a result of broken bounds between fluid and thickener, therefore through the destruction of specific greases structure.

Effect of radiation on additives

Due to the variety of nature and functionality of the additives it is not possible to make a generalisation about the radiations effect on additives [1].

Using FTIR analysis it was established that when the greases are subject to radiations antioxidants additives are consumed more quickly than the grease works in the same operating conditions without radiations. On the other hand, it is known that EP/AW additives are sensitive to irradiation, producing high level of sludge residues [1]. That's why it is preferable that greases used in radiation environment should not contain EP/AW.

Effect of radiation on fully formulated lubricating greases

As we showed each of the component discussed above should be affected by irradiation.

The damage or the changes of the specific properties of the greases, even those of a single component induce the degradation of the whole product. It is estimated that up to a certain radiation dose the effects of irradiation on the main components- lubricant fluid and the thickeners- should be compensated. In these situations damages could not be noticed of the whole product if using direct methods, but other sophisticate analyses such as dialysis separation, IR spectroscopy, or thermal methods are suitable to trace out the changes occurred. The following aspects can describe the behaviour of the lubricating greases under irradiation conditions:

- Penetration changes
- Dropping points changes
- Increase of evaporation loss
- Gases release
- Increase of acidity, or decrease of alkalinity.

Degradation tendency of lubricating greases formulated with low irradiation stability components is often hidden by the compensation of the softening occurrence as a result of incipient polymerization process. Further the polymerization of hydrocarbons will be more important and the product becomes hard and rubberized or brittle solids. In these conditions determination of penetration of the products with high irradiation level failed to be achieved.

Under irradiations conditions conventional greases made of mineral oil and calcium, sodium, aluminium or lithium soaps as thickeners, are destroyed before the increase of oil viscosity as a result of polymerisation processes occurring through. At high level of radiation this kind of lubricants initially become fluids and subsequently solids [2]. The softening of these greases appears at 10-100 Mrad irradiation dose, so that at 300-700 Mrad dose they become fluids. That's why it is recommended to use conventional greases only for lubrication of equipment working under the radiation dose less 10^7rad. Moreover it is not recommended to use soaps made greases in CO_2 atmosphere. The progress in synthesis of the synthetic lubricants leads to getting a remarkable behaviour of the non-soap greases under high radiations level [1, 4].

The great majority of lubricating greases with high radiation resistance are made with dialkil-benzene, polyglycols, perfluorpolyethers, silicon fluids, and polyphenilethers and non-soap thickeners [3].

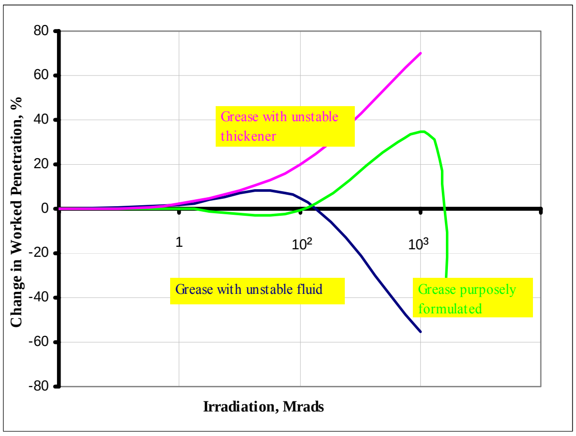

Figure 4. Effect of radiation on fully formulated greases of various stability

3. CRITERIA FOR SELECTION OF LUBRICANTS TO USE IN NUCLEAR POWER PLANTS

Nuclear power plants work continuously for long periods. Consequently, lubricant should provide long reactor regulation and safe operation. Shutdown due to lubricant change, repairs, cleaning and replacement parts that require long time lubrication should be avoided, if possible. In nuclear power plants, besides the normal technical requirements that must fulfil lubricating grease, many problems arise due to radiation. For these reasons appropriate lubricant selection is a problem of great importance for solving that; there should be a collaboration between constructor, designer, chemist and specialist in lubrication problems.

The main factors to be taken into consideration when choosing which lubricant is used in nuclear power plants are:

- Type of Reactor Construction
- Dose of Radiation
- Operating Temperature
- Working Environment
- Compatibility with the Reactor Material
- The Replacement of Lubricant
- Type of Radiation that interacts

3.1 Type of Reactor Construction

Depending on the construction of the reactor there are some requirements to be met by the lubricant as for radiation doses in the concerned areas as well as prevention of cooling agent from pollution.
Table 4 presents estimates of radiation levels for various systems of nuclear reactors in the working areas where machinery and mechanisms are exposed [1].

Table 1. Estimate of radiation levels for different reactor systems, rad/year

Component	Reactor type			
	Organic moderated	Pressurized water	Liquid metal cooled	Boiling Water
Control Rod	max.10^8	10^5-10^8	10^4-10^5	max. 10^6
Mechanism for fuel handling	-	max.$2x10^7$	-	-
Primary coolant pumps	negligible	10^6-10^7	10^8	10^6-10^7
Auxiliary pumps	negligible	10^4-$3x10^6$	-	10^4-10^6
Auxiliary motors	-	10^5-$3x10^7$	-	-
Turbines	max.25	max.10	neglig.	max.80

Lubricating greases with good water stability and suitable for extreme pressures and high temperatures conditions are recommended for water-cooled reactors.
For nuclear power plants with cooling gas there are special lubricant requirements regarding stability at high temperatures, radiation and evaporation losses that shall be as low as possible so that to prevent the cooling circuit from pollution.

Dose of Radiation

In most cases it is very difficult to make a correct assessment of total dose radiation of critical areas. Therefore always take a safety factor in setting the radiation dose to which grease is to be tested.
Generally, the lubricant stability against radiation action refers to the variation in viscosity and the consistency, stability of aging and maintaining the lubricity characteristics in real operation.

Operating Temperature

For security reasons, even if operating conditions are moderate in some cases, lubricants are preferred with good behaviour at high temperatures.

Working Environment

The environmental work with CO2, helium, light water, heavy water has a great influence on the lubricant. In some cases the atmosphere of inert gases, extremely dry and devoid of oxygen generated special lubrication conditions.

Compatibility with the Reactor Material

Compatibility with materials the reactor is built of is very important in choosing the lubricant. Often special alloys, such as unusual zircon/aluminium or aluminium/magnesium are used on which grease is tested in order to check its corrosion resistance.

The Replacement of Lubricant

Because unforeseen shutdown should be avoided in as much possible, in the case of very long exchange intervals, lubricant shall be tested to total radiation doses that exceed the product stability limit.

Type of Radiation that interacts

Greases used in nuclear power plants are prevailingly subject to gamma radiation action. This type of radiations doesn’t lead to remaining radioactivity. Handling, relubrication or lubricant change may be made without the usual special security measures.

In situations that greases are subject to the action of fast neutrons, they become radioactive themselves, especially when they contain heavy metals or elements easily activated such as chlorine, sodium, phosphorus or sulphur.

Once become radioactive, a lubricant cannot be changed without special measures. Handling of radioactive substances that exceed the limit shall be fixed by certain rules that require special action to take.

Removal of radioactive greases can be very costly, because certain rules must be complied with safety and decontamination is rarely possible.

Storage of radioactive substances for lubrication is only possible in certain places approved for radioactive waste that should be provided with adequate radiation shield protection.

Choosing the appropriate lubricating grease for the lubrication of the machinery and mechanism in critical areas is therefore a difficult problem to solve; (which must be taken into account) the factors listed as well as experience in the world need the due consideration.

4. LUBRICATING GREASES PURPOSELY FORMULATED FOR NUCLEAR POWER PLANT EQUIPMENT

Verification in real operating conditions of the stability to irradiation and also of the tribological properties of lubricants that are used in nuclear industry is only possible in rare cases. These experiences are usually in the reactor core and in most cases after reactor shutdown, or in an accelerator. Most often static experiments are used.

Differences that were noticed in case of oils between data obtained in static versus dynamic conditions are very small, while greases experimented in dynamic conditions showed greater stability compared to those determined in static conditions. These tests are done mainly with gamma radiation in such a way that the tested product should not become radioactive.

4.1 Test Conditions

Testing our lubricating greases for nuclear power plant was achieved by comparison of their characteristics before and after irradiation, using the integrated radiation dose required for the operation. The γ irradiation of the lubricating greases samples was performed with a cobalt-60 source.

The radiation absorbed dose was measured using Frike dosimeter. The methods used the radiolytic oxidation of Fe^{2+} to Fe^{3+}. The solution used contained Fe $(NH_4)_2(SO_4)$ 10^{-3}M in H_2SO_4 0.4M. The conversion of Fe^{2+} to Fe^{3+} is measured by spectroscopy at a wavelength of 304nm. The dose was calculated using the formula:

$$D=\frac{2{,}84\cdot 10^4}{L}\cdot Do \qquad (1)$$

Where L is the length of the spectral-photometric cell, Do is the optic density.

4.2 Test Methods

The lubricating greases were determined for their features both before and after irradiation by ASTM specific tests or by Romanian standards. The test methods are listed in table 2.

Table 2. Test Methods

Characteristics	Test Methods
Dropping point	**ASTM D 2265**
Penetration, 25°C, 1/10mm	**ASTM D 217**
Colloidal stability, % oil separated	**STAS 3793**
Water resistance	**ASTM D 1264**
Corrosion test (3 hours at 100°C, steel)	**STAS 8206**

4.3 Results and disscutions

We show below the characteristics of lubricating grease purposely formulated for the fuel handling mechanism lubrication (table 3, 4):

Table 3. The characteristics of grease with inorganic thickener and mineral oil after irradiation (dose 10^4-10^6 rad)

Characteristics	Before Irradiation	After irradiation Dose, rad		
		10^4	10^5	10^6
Dropping point, °C	>260	260		
Micro penetration, 60 strokes 25°C, 1/10mm	270	276	289	308
Acidity, mg KOH/g	0.16	0.23	0.29	0.36
Water resistance	stable	stable		
Colloidal stability, % oil separated	6.3	6.4	6.7	7.1
Corrosion test (3 h at 100°C on steel)	yes	yes		

Table 4. The characteristics of grease with inorganic thickener and mineral oil after irradiation (dose 10^7-10^9 rad)

Characteristics	Before Irradiation	After irradiation Dose, rad		
		10^7	10^8	10^9
Dropping point, °C	>260	>260		
Micro penetration, 60 strokes 25°C, 1/10mm	270	316	307	230
Acidity, mg KOH/g	0.16	0.4	0.6	3
Water resistance	stable	stable		
Colloidal stability, % oil separated	6.3	7.2	5.1	8.1
Corrosion test (3 hours at 100°C on steel)	yes	yes		no

As shown in tables 3 and 4 irradiation process has no influence on the dropping point of the products. That means the lubricant obtained with our formula preserves its structure under irradiation conditions, in the range of 10^4-10^9 rad. However, the real effect of the radiation environment on greases was evaluated by their consistency. (values of micropenetration) and acidity number.

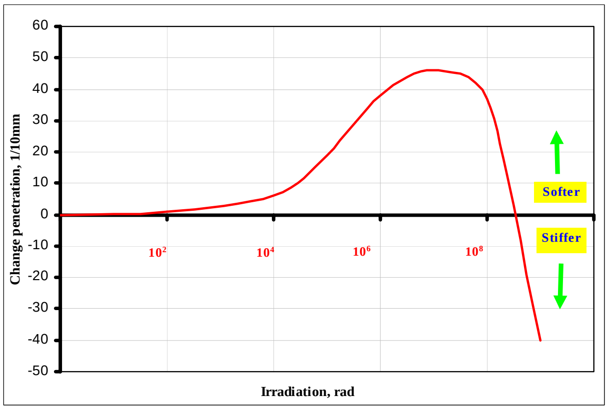

Figure 5. Effect of radiation on grease with inorganic

Till 10^5 rad irradiation dose the product maintains its penetration in the same class of consistency (NLGI 2) as fresh grease. Above this value, the softer process begins, the product belongs to NLGI 1 class of consistency (fig.5). At irradiation doses higher than 10^8 rad, the process became dramatically deteriorated. After irradiation dose of 10^9 rad the increase of oil viscosity as a result of polymerisation processes occurs, so that the grease grows stiff. On the other hand, over 10^8 rad dose, the thermal-oxidative products reactions increase significantly the acidity value of the lubricant (fig.6).

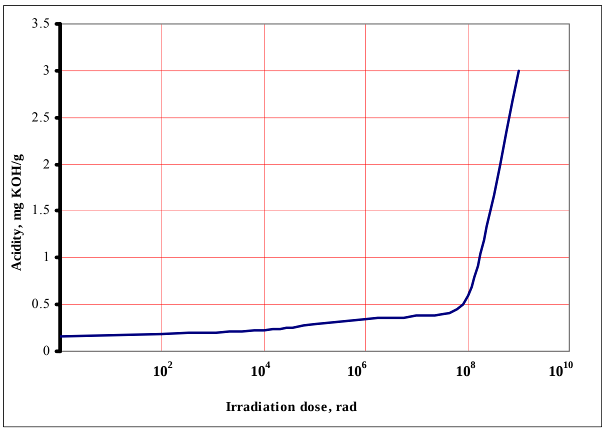

Figure 6. Effect of radiation on acidity number

As a rule, the lubricating greases that contain inorganic thickeners do not pass the water stability tests. Our grease purposely formulated for mechanism fuel handling contains inorganic thickener, presents water resistance that is not affected in test radiation conditions.

The behaviour of radiation conditions on colloidal stability of the product is not important. The small variations are the result of the penetration changes.

Tests showed that at high level of radiation dose (over 10^8 rad) corrosion could become very important.

5. CONCLUSIONS

1. The selection of lubricants for nuclear power plants is a complicated choice to make, involving many parameters such as tribological properties, radiation resistance, corrosion resistance availability, cost, etc.
2. The main factors to be taken into consideration when choosing which lubricant is used in nuclear power plants are: type of reactor construction**,** dose of radiation, operating temperature, working environment, compatibility with the reactor material, replacement of lubricant, type of radiation that interacts.
3. Each of the main components of grease may be affected by irradiation. The results of these processes is the deterioration of lubricating grease overall performance. The great majority of lubricating greases with high radiation resistance are made with dialkil-benzene, polyglycols, perfluorpolyethers, silicon fluids, and polyphenilethers and non-soap thickeners.
4. Our lubricating grease purposely formulated for mechanism fuel handling was tested by comparison of its characteristics before and after irradiation, using the integrated radiation dose within 10^4-10^9 rad. range. Tests showed that the product maintains its properties till 10^9 rad and may be used to lubricate the mechanism fuel handling.

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