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The deterioration of mechanical properties of chloroprene rubber in various conditions

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The changes of mechanical properties of chloroprene rubber, used as a jacket material for electric cables in nuclear power generating stations, were investigated under various deterioration environments. The heat resistant properties of the rubber material were measured at various temperatures using a stress relaxation method. From the view point of stress–strain behaviour and chemorheology, the addition of antioxidant and/or antirad reagent to the rubber improves the resistance to heat and/or radiation, respectively. The effects of dose-rate and surrounding atmosphere on the mechanical properties of rubber under radiation were also studied. The radiation damage of rubber was accelerated remarkably under a pressure of 90 atm of air. A vibration fatigue test under heat and radiation was also performed.

1. Introduction

The use of polymer materials in the nuclear industry is limited due to their relatively low radiation stability compared with inorganic materials. Rubber is occasionally used as a heavy-duty material under the environments of heat, irradiation, etc. Some parts of electric cables insulated with rubbers cannot be easily replaced by other types of materials because of their good electrical and thermal properties. Consequently, it is required that such rubbers should be sufficiently durable that they last the life-time of 40 years of nuclear reactors.

Chloroprene (neoprene) rubber is used as a jacket material for electrical cables in nuclear power generating stations. The tensile strength and elongation-at-break decrease to between 10 and 50% of their initial values after irradiation of 20 Mrad at room temperature [1]. Several types of synthetic rubber were evaluated by chemical stress relaxation measurements at 100° C [2], in which it was reported that neoprene W-type had better heat resistivity than GN-type. In this paper, a neoprene W-type sample is used to investigate the deterioration mechanism in a heat and/or radiation environment by a chemical stress relaxation measurement and a vibration fatigue test. The stress–strain behaviours of the irradiated samples were also measured, in order to get information on the change of mechanical properties resulting from radiation damage.

2. Experimental procedure

2.1. Material

A moulded film of neoprene (W-type), of thickness 2 mm, was studied. The sample has the same ingredient composition, which is shown in Table I, that is used for the insulation of cables in nuclear power generating stations. The sample numbers indicate the different additives such as antirads and antioxidants.

2.2. Irradiation

The samples were irradiated in air by Co-60 γ-radiation at room temperature. The dose rates of 0.1 and 1 Mrad h^{-1} were measured by commercial cobalt glass dosimeters.

2.3. Chemical stress relaxation measurement

Both continuous and intermittent stress relaxation measurements (at 10% strain) were performed at a constant temperature (± 2° C) in the range from room temperature to 150° C. In the continuous

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TABLE I Composition of samples

Composition	Sample number				
	500	501	503	506	507
Polychloroprene	100	100	100	100	100
ZnO	5	5	5	5	5
MgO	4	4	4	4	4
2-Melcaptoimidazoline	0.5	0.5	0.5	0.5	0.5
Stearic acid	0.5	0.5	0.5	0.5	0.5
Hard clay	50	50	50	50	50
Carbon black	30	30	30	30	30
Aromatic oil (contains benzene ring)	–	5	–	–	–
Paraffine oil	–	–	5	–	–
Derivative of diphenylamin (DDA)	–	–	–	2	–
Tetramethyuram disulfide	–	–	–	–	2

stress relaxation the effect of chain scission alone is observed, and the intermittent stress relaxation reflects the combined effect of chain scission and cross-linking [2].

2.4. Vibration fatigue test

Each sample of 20 mm width and 2 mm thickness was held in a pair of jaws. The initial distance apart of the jaws was 50 mm and one jaw was connected to a load cell and the other was linked to a driving mechanism.

The periodic (10 Hz) stress force (of magnitude 2.5 kg cm^{-2}) was consistently loaded on the sample of neoprene under an irradiation dose-rate of 3×10^5 rad h^{-1} in air at various temperatures.

3. Results

3.1. Chemical stress relaxation

Fig. 1 shows the chemical stress relaxation curves of sample No. 500, the reference sample without additives, at various temperatures. In the usual continuous stress relaxation measurements, the

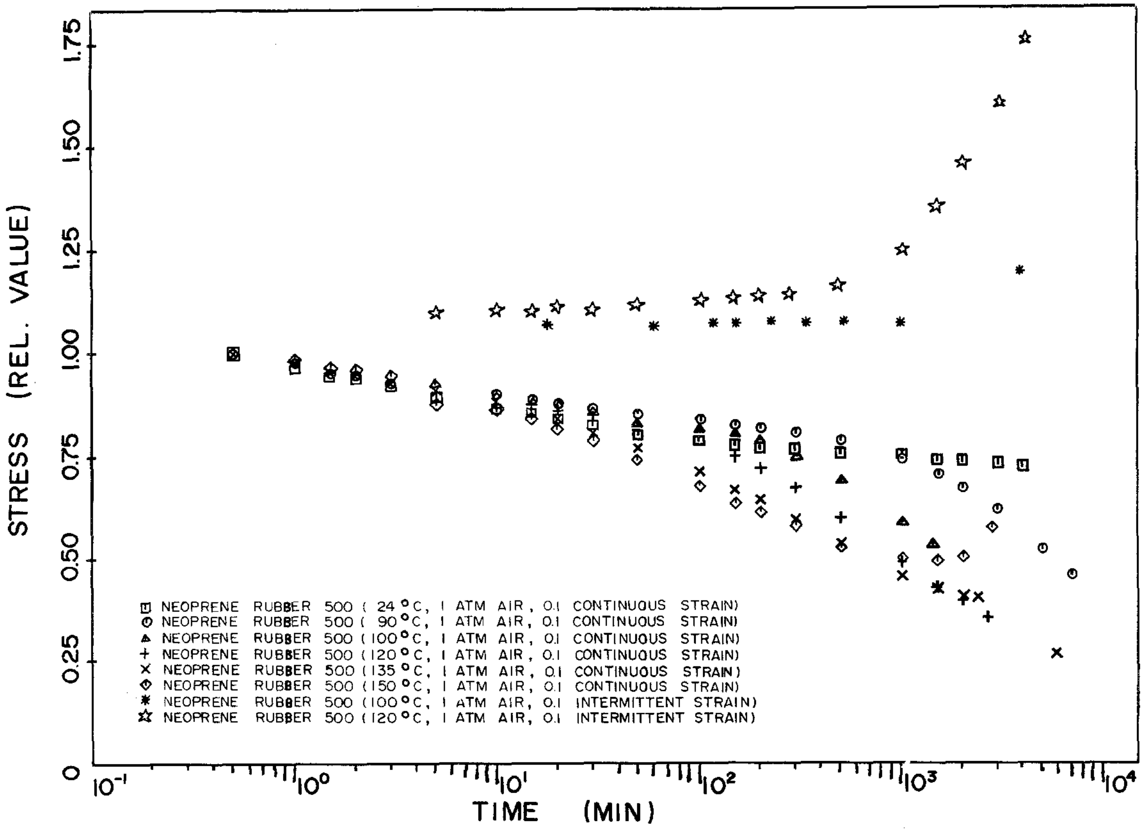

Figure 1 Stress relaxation curve at various temperatures for chloroprene rubber without additives.

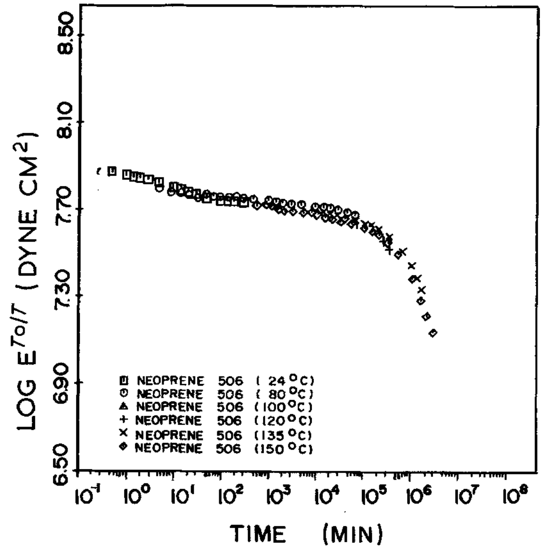

Figure 2 Master curve of the stress relaxation of chloroprene rubber. (Sample No. 506).

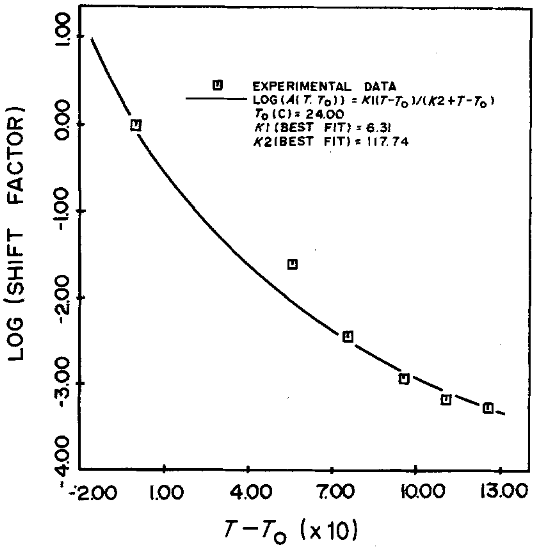

Figure 3 Relationship between the shift factor, A, and temperature $(T-T_0)$.

stress decreases more rapidly with time at elevated temperatures. In the curve obtained at 150° C, however, the stress increases over 10^3 min. The result may be interpreted to be caused by cross-linking between the chain molecules becoming more predominant compared with chain scission as the temperature increases, and this tendency becomes more marked after 10^3 min, as is obvious in the intermittent stress relaxation curves at 100 and 120° C. The strong cross-linking effect influences the curve of the continuous stress relaxation, as shown by the increase of stress after 10^3 min at higher temperatures such as 150° C.

The stress relaxation curves obtained at temperatures above 24° C can be shifted along the logarithmic time-axis until a portion of the curve is superimposed on the curve for 24° C (297 K). Fig. 2 shows a master curve which indicates fairly good superposition. This implies that the time–temperature superposition principle is valid even for chemical stress relaxation. The shift factors are computed. The relationship between the shift factors and temperature difference ($T-T_0=$ 24° C) is shown in Fig. 3. When the temperature increases, the shift factor decreases, indicating a strong deterioration at higher temperature.

Fig. 4 shows the effect of additives, processing oil (paraffinic oil) or antioxidant (DDA), on the stress relaxation at 80° C. The additives make the curve shift more stable against heat, with the antioxidant showing by far the superior effect.

3.2. Mechanical properties of the irradiated samples

In order to compare the deterioration caused by heat with that caused by irradiation, various mechanical properties of the irradiated samples were measured, for example, the modulus at 100% elongation, M_{100}, the tensile strength at break, T_b, the elongation at break, E_b, and hardness. The results are summarized in Tables II and III, respectively. The total irradiation dose is 22 Mrad for all samples. The irradiation dose rates are 0.1 and 1 Mrad h^{-1}, which are adopted to investigate the dose-rate effect. As the deterioration is attributed mainly the oxidation during the irradiation, the diffusion and/or the solubility of oxygen molecules into the sample sheet affect the degree of deterioration. The sample is irradiated under an air pressure of 90 atm with 1 Mrad h^{-1} at room temperature.

Table II also shows the effect of additives, i.e. aromatic oil as an antiradiation agent, paraffinic oil as a processing oil and DDA as an antioxidant. The reference sample (No. 500) indicates that T_b and E_b decrease after irradiation with 22 Mrad, and the lower the dose rate, the more the deterioration. On the other hand, the E_b values for the samples irradiated at 1 Mrad h^{-1} either under 1 atm or 90 atm are more or less the same, while the T_b values decrease considerably, indicating chain scission by oxidation. A similar tendency is observed in the sample with the additives, although

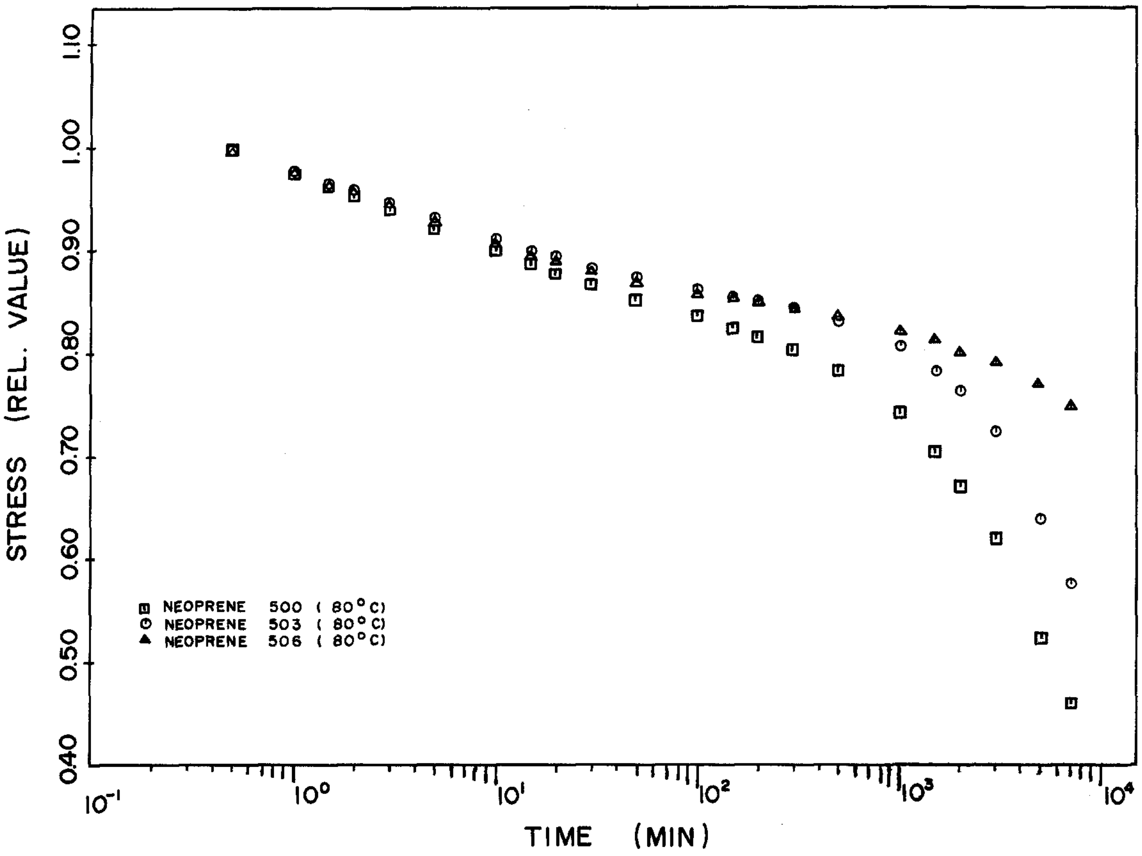

Figure 4 Effect of antioxidant on the stress relaxation curve at 90° C for chloroprene rubber.

protective effects are noticed. Table III summarizes the changes of hardness by irradiation with 22 Mrad. The samples with and without additives are hardened by irradiation under atmospheric pressure, while they are softened at 90 atm of air. EDA as an antioxidant affects the hardness to a small extent. The efficiency of additives to protect against irradiation deterioration is in the following order: DDA > aromatic oil > paraffinic oil.

3.3. Vibration fatigue test

The change of the mechanical properties of the sample with an antioxidant (No. 507) at elevated temperatures, i.e. at 150° C and 180° C, has been investigated using a vibration fatigue tester. Fig. 5 shows the relationship between the ratio of strain amplitude and the number of vibrating cycles-to-failure under the periodic (10 Hz) stress force of 2.5 kg cm^{-2}. The ratio of the strain amplitude is proportional to the apparent density of networks, ν_n, in the sample. At first, ν_n reduces gradually with increase of vibrating cycles, and then decreases rapidly above 10^5 cycles, measured at room temperature. At 150° C, ν_n decreases gradually over 10^6 cycles, while at 180° C, ν_n increases to reach a maximum at about 10^4 cycles, and finally, the sample breaks down suddenly at about 2×10^5 cycles.

4. Discussion

Generally, cross-linking and scission are caused in polymers by heat or irradiation. The ratio of cross-linking to scission is different for different polymers. It is difficult to calculate this ratio exactly from the results reported above because many additives are blended into the polymer. Since the thickness of the samples is 2 mm, the diffusion of oxygen gas might not be sufficient. However, from a practical point of view, some useful conclusions can be obtained from the results.

The chemical stress relaxation shows that the probability of cross-linking in the chloroprene rubber is higher than the probability of scission by heat as shown in Fig. 1. The scission of chains, although not totally prevented, is definitely some-

TABLE II Mechanical properties of irradiated samples

Dose rate (Mrad h^{-1})	Pressure (atm)	Sample No. 500			Sample No. 501			Sample No. 503			Sample No. 506		
		M_{100} (kg cm^{-2})	T_b (kg cm^{-2})	E_b (%)	M_{100} (kg cm^{-2})	T_b (kg cm^{-2})	E_b (%)	M_{100} (kg cm^{-2})	T_b (kg cm^{-2})	E_b (%)	M_{100} (kg cm^{-2})	T_b (kg cm^{-2})	E_b (%)
Original		80	170	275	57	152	330	62	152	340	68	175	360
1	1	–	142	90	101	124	110	102	126	100	85	147	210
0.1	1	–	136	60	–	118	90	–	113	70	85	125	160
1	90	–	85	80	68	74	110	56	68	120	68	125	270

Total dose: 22 Mrad

TABLE III Hardness changes by irradiation

Dose rate (Mrad h^{-1})	Pressure (atm)	Sample number			
		500	501	503	506
Original		90	85	88	88
1	1	94	90	92	90
0.1	1	94	88	90	88
1	90	74	72	72	81

Total dose: 22 Mrad

what inhibited by the addition of antioxidant. The data obtained at 150° C cannot be fitted to the master curve in Fig. 3. The reason for this is thought to be that both cross-linking and another chemical reaction take place at this elevated temperature. The chain scission reaction is caused by the oxidation, since the antioxidant produces a marked shift in the stress relaxation curve to the durable side in Fig. 4, and to higher values in Tables II and III in the case of radiolysis.

From the results in Fig. 2, the shift factors are evaluated by the Williams, Landel and Ferry (WLF) equation [4]. Fig. 3 shows the relationship between the logarithm of the shift factor and the temperature difference $(T-T_0)$, where T_0 is 24° C. Experimental data from sample No. 500 are represented by the equation:

$$\log A(T, T_0) = -K_1(T-T_0)/(K_2+T-T_0), \quad (1)$$

where $A(T, T_0)$ is a shift factor at temperature T with a reference temperature, T_0, of 24° C and K_1 and K_2 are constants with values of 8.3 and 117.7, respectively.

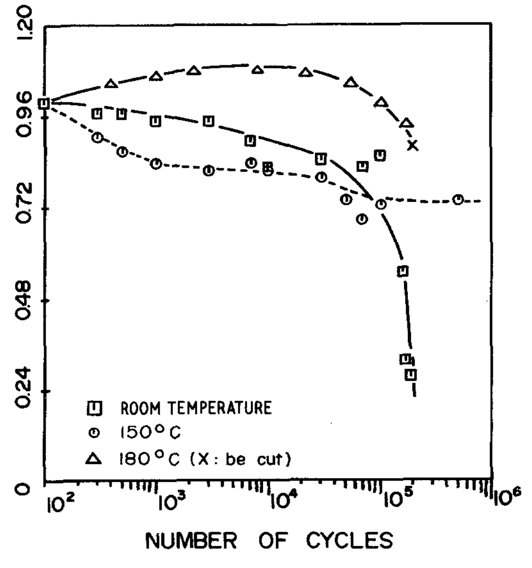

Figure 5 Vibration fatigue test of sample No. 507 at various temperatures by a constant stress force method (2.5 kg cm^{-2}).

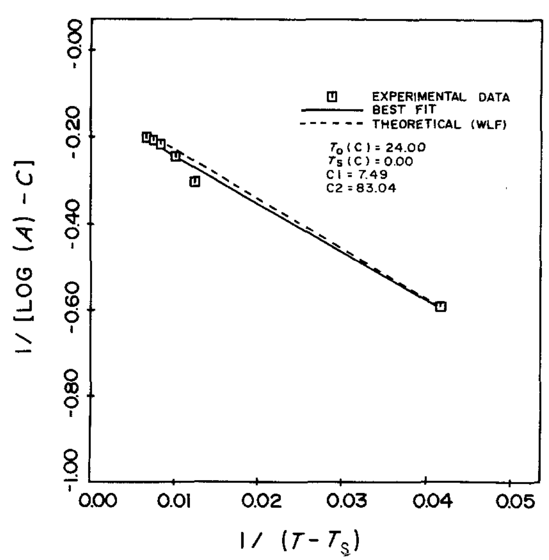

Figure 6 WLF plot for chloroprene rubber (where $C = [C_1(T_0-T_s)]/(C_2+T_0-T_s)$).

In general the WLF equation is expressed as follows [4], giving a best fit:

$$\log a_T = -C_1(T-T_s)/(C_2+T-T_s), \quad (2)$$

where a_T is a shift factor at the temperature T, T_s is a certain temperature 50° C higher than the glass transition temperature T_g and C_1 and C_2 are constants with values of 8.86 and 101.6, respectively.

Fig. 6 shows the relationship between the reciprocal of $\log (a_T/a_{T_0})$, where (a_T/a_{T_0}) is the ratio of the shift factor at temperature T to T_0 ($T_0 = 24°$ C), and $1/(T-T_s)$. Here T_s is equal to 0° C, since T_g for neoprene is about $-50°$ C. A solid line indicates the best fit relation to the experimental data, which yields $C_1 = 7.49$ and $C_2 = 83.04$, and the fit to the WFL equation. Equation 1, is very good (see the broken line in Fig. 6).

Fig. 7 shows the relationship between $\log a_T$ and $1/T$. The apparent activation energy is found to be 15.7 kcal mol^{-1}, obtained by the least square fit method. This value is close to the result of 18.3 kcal mol^{-1} obtained from the changes of modulus and elongation under various temperatures ranging from room temperature to 120° C [5]. It is impossible to determine if the shift factors obey either the WLF equation or the Arrhenius equation. However, the Arrhenius

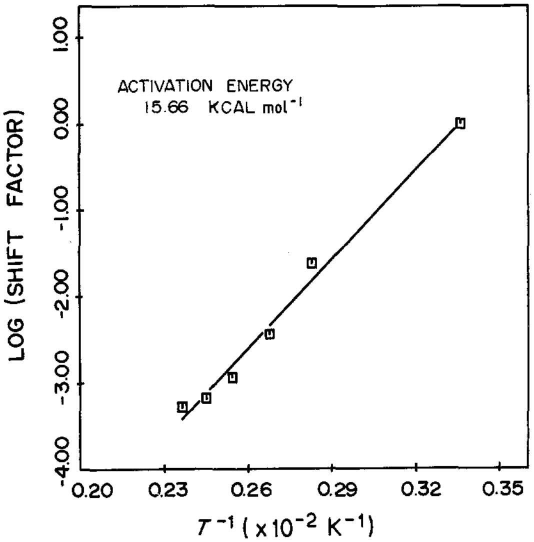

Figure 7 Relationship between the logarithm of the shift factor, log (a_T/a_0), and the reciprocal of temperature.

equation may be more applicable, since the standard deviation of the results from the line-of-best-fit is a little less.

It is generally thought that the vibration decreases the interaction between the polymer chains and the carbon which reinforces the modulus of the rubber. Irradiation exhibits the scission of the polymer chains. On the other hand, the polychloroprene chains are cross-linked by heat at elevated temperatures, as shown in the result of the intermittent stress changes. Consequently, in the vibration fatigue test under heat and radiation, the net effect of these three factors is observed.

At 180° C the cross-linking by heat is the dominant effect, in spite of the chain scission by irradiation and the decrease in the reinforcement effect of the carbon. Then the ratio of strain amplitude increases up to certain period of time at 180° C.

An anti-radiation agent, or aromatic oil, does not prevent a deterioration in the mechanical properties of the sample, if an antioxidant dose is present, as seen in Tables II and III, which implies that the chain scission takes place mainly by oxidation reaction and only partially by the direct effect of radiolysis. The oxidation under radiation may be caused by peroxide formed from the radicals and molecular oxygen in the irradiated samples.

Therefore, it is suggested that the addition of antioxidant is effective in preventing the deterioration of the mechanical properties of neoprene rubber used under irradiation in atmospheric conditions.

For example, neoprene rubber with an antioxidant can be used as a jacket material for electrical cables for use in nuclear power generating stations. Because those cables should be tested according to a qualification test such as the IEEE Standards 323 [6] and 383 [7] (1974) which requires the material to withstand irradiation of more than 76 Mrad and tests under a steam environment between temperatures of 50° C and 171° C.

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