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Adhesion Between Polymers and Evaporated Gold and Nickel Films

Yoshinori Yamada,
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*Lewis Research Center
Cleveland, Ohio*

NASA

National Aeronautics
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Summary

To obtain information on the adhesion between metal films and polymeric solids, the adhesion force was measured by means of a tensile pull test. It was found that the adhesion strengths between polymeric solids and gold films evaporated on polymer substrates were $(1.11 \pm 0.53) \times 10^6$ N/m² on PTFE, about 5.49×10^6 N/m² on UHMWPE, and 6.54×10^6 N/m² on 6/6 nylon. The adhesion strengths for nickel films evaporated on PTFE, UHMWPE, and 6/6 nylon were found to be a factor of 1.7 higher than those for the gold-coated PTFE, UHMWPE, and 6/6 nylon.

To confirm quantitatively the effect of electron irradiation on the adhesion strength between a PTFE solid and metal films, a tensile pull test was performed on the irradiated PTFE specimens, which were prepared by evaporating nickel or gold on PTFE surfaces irradiated by 2-keV electrons for various times. After irradiation, the adhesion strength increased to $(4.92 \pm 0.92) \times 10^6$ N/m² for nickel-coated PTFE and $(1.82 \pm 0.48) \times 10^6$ N/m² for gold-coated PTFE. The improvement in adhesion for nickel is higher than that for gold.

Introduction

The adhesion between metals and polymers has been studied, and adhesion mechanisms have been proposed by several authors (refs. 1 and 2). Van der Waals interaction at the interface may be one of the important factors responsible for the adhesion phenomenon. Wheeler and Pepper suggest that chemical interaction might be important, as well, on the basis of the results observed by XPS (refs. 3 and 4). They found qualitatively that the adhesion property was improved and that crosslinks might be formed in the surface region by X-ray irradiation of PTFE.

The adhesion between films and bulk substrates can be measured by various methods (ref. 5). Although adhesion properties can be easily and quickly determined using a tape peel test, quantitative determination of adhesion properties should be made using a tensile pull test. To understand the adhesion mechanism between metals and

polymeric solids and the effect of irradiation on the adhesion, it is important to obtain quantitative information on the adhesion strengths between metals and polymeric solids.

The purposes of the present work are (1) to determine quantitatively the adhesion strengths between PTFE, UHMWPE, and 6/6 nylon solids and gold and nickel films and (2) to observe the effect of electron irradiation on the adhesion strength between irradiated PTFE and gold and nickel.

Experimental

Samples and Preparation of Test Specimens

Three commercial grade polymeric solids, polytetrafluoroethylene (PTFE), ultra-high molecular weight polyethylene (UHMWPE), and 6/6 nylon, were used for the measurements. Test specimens, which were prepared by cutting from rods, were 1 cm in diameter and about 1.5 cm long. A surface layer was removed from one end surface of the cylindrical test pieces with a clean scalpel. The surfaces prepared by removing the surface layer had some knife marks and were not smooth. To obtain smooth surfaces, the polymer surfaces were rubbed on a clean paper.

Gold or nickel was evaporated on the polymer substrates in a vacuum chamber for 5 min at a pressure of about 5×10^{-7} torr. The thickness of coated metal film was estimated to be about 60 μ m by SEM micrographs. In order to observe the effect of electron irradiation on the adhesion between metal films and PTFE, PTFE surfaces were irradiated in the evaporation chamber by 2 keV electrons for various times at about 5×10^{-8} torr before gold or nickel was evaporated on the PTFE surfaces. The electron beam was rastered over the entire surface of the specimen. Electron beam current density was measured to be 6 μ A/cm² by a Faraday cup with 1.6-mm-diameter hole.

Measurement of Adhesion Strength

After the evaporation, the test pieces were taken out the chamber, and a stud consisting of a glass plate

cemented to a metal rod was fixed on the metal film with epoxy resin adhesive.¹ The test pieces were cured at room temperature for about 18 hr. The tensile pull test was performed in a commercial tensile testing apparatus. A diagram of the specimen mounting is shown schematically in figure 1. The speed of the crosshead was 0.2 mm/sec.

Results and Discussions

Adhesion Strength Between Polymeric Solids and Metal Films

Typical examples of tensile pull test measurements are shown in figure 2. It can be confirmed visually that metal films are almost completely removed from the polymer substrates after the tensile pull test. The adhesion force necessary to pull the metal film from the polymer substrate is shown in figure 3 as a function of stud area.

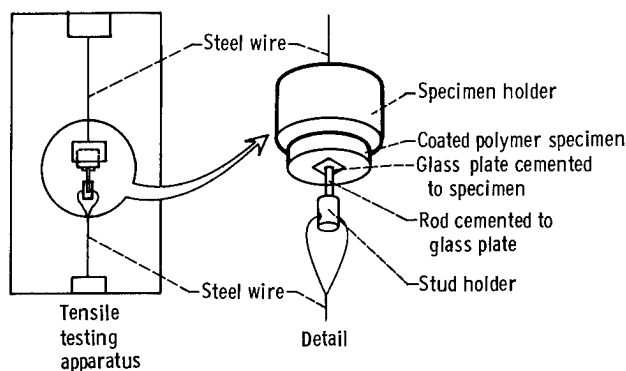


Figure 1.—Schematic diagram of mounting a specimen in tensile testing apparatus.

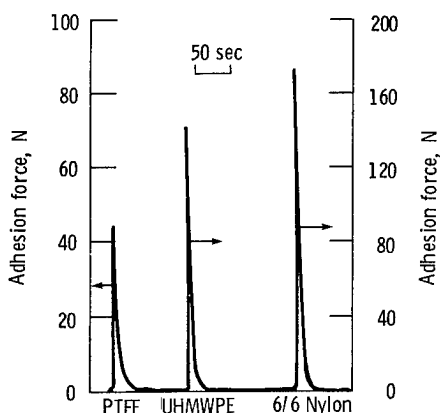


Figure 2.—Typical records of adhesion force measurements for three nickel-coated, unirradiated polymers.

¹Room temperature cure epoxy; QUAD 101-921-B (Quad Group Co.). The epoxy adhesive used in the present work can be cured at room temperature and is specially formulated to eliminate shrinkage which may occur during cure.

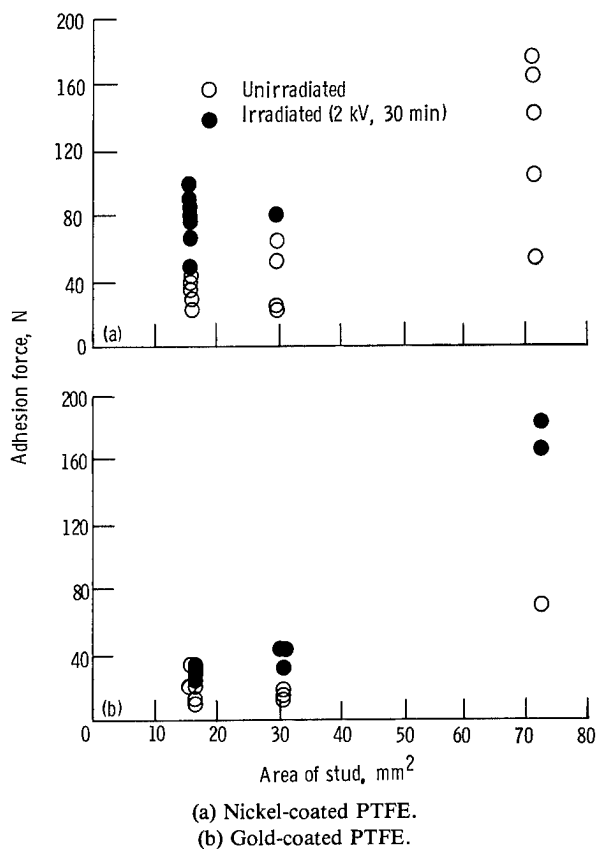


Figure 3.—Adhesion force as function of stud area.

As shown in the figure, the adhesion force is approximately proportional to the stud area. However, the scatter of data points for the large stud area is greater than that for the small stud area. All the results shown later were obtained using a stud having a 16-mm² area.

In the case of PTFE, the tensile pull test was performed about 10 times for each coating/substrate combination. A few measurements in which very low adhesion strength was observed were omitted because examination showed that the epoxy had failed or the glass plate was not perpendicular to the metal rod. The results are shown in table I and figure 4. The adhesion strength obtained shows scatter, which may be caused mainly by the difference in polymer surface roughness and the inhomogeneous formation of bonding at the interface between polymer surfaces and metal films. The adhesion measurements and their standard deviations are summarized in table I. The standard deviation of adhesion strength is about 0.5×10^6 N/m², and the ratio of standard deviation to the average adhesion strength becomes smaller with increasing the adhesion strength, ranging from 48 to 19 percent. Not enough measurements were taken to calculate standard deviations for UHMWPE and 6/6 nylon. Twenty percent may be a reasonable estimate when considering the results for PTFE. This estimate is used subsequently whenever an error estimate is desired for these two polymer substrates.

TABLE I.—ADHESION STRENGTH OF THREE KINDS OF POLYMER SUBSTRATES

Polymer	Metal	Irradiation	Average of adhesion strength, A , N/m^2	Standard deviation, s , N/m^2	Ratio, s/A , percent
PTFE	Gold	Unirradiated	1.11×10^6	0.53×10^6	48
	Gold	Irradiate	1.182	.48	26
	Nickel	Unirradiated	1.92	.51	28
	Nickel	Irradiate	4.92	.92	19
UHMWPE	Gold	Unirradiated	5.49×10^6		
	Nickel	Unirradiated	9.12		
6/6 Nylon	Gold	Unirradiated	6.54×10^6		
	Nickel	Irradiate	10.84		

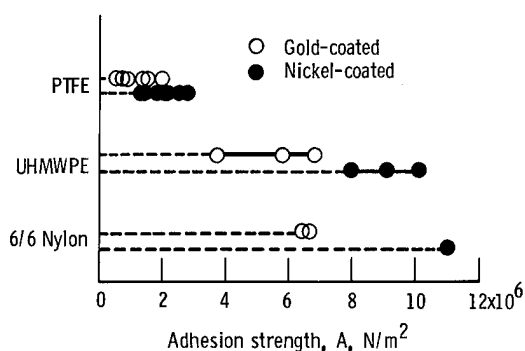


Figure 4.—Adhesion strength of three polymer substrates.

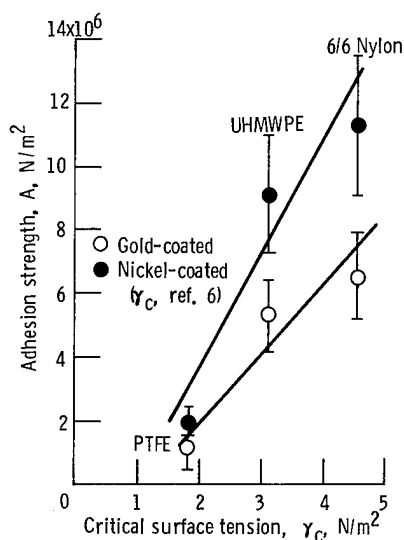


Figure 5.—Correlation between adhesion strength and critical surface tension of polymers.

The adhesion strengths for three polymer substrates are shown in figure 4. Adhesion strengths for gold-coated polymers are determined to be $(1.11 \pm 0.53) \times 10^6$, 5.49×10^6 , and 6.54×10^6 N/m^2 for PTFE, UHMWPE, and 6/6 nylon, respectively. Adhesion strengths for nickel-coated PTFE, UHMWPE, and 6/6 nylon are a factor of 1.7 higher than those for gold-coated PTFE, UHMWPE, and 6/6 nylon.

Table I and figure 4, show that both metals adhere better to UHMWPE and 6/6 nylon than to PTFE and that nickel adheres better than gold does to all the polymers, although the scatter in the result makes the latter result less certain. Figure 5 shows the relationship between the adhesion strength and Zisman's critical surface tension (ref. 6). Bars drawn in the figure indicate the range of the standard deviation. Good correlation between them, which is found for nickel-coated and gold-coated polymers, suggests that the Van der Waals force may be responsible for the increase in adhesion as the polymer is changed from PTFE to UHMWPE to 6/6 nylon. As just described, it was confirmed that nickel adheres to polymers better than gold does. If the Van der Waals force is the main factor in the increased adhesion of nickel and the adhesion strength correlates with the

adhesive energy at the interface, the difference of adhesion strength between a nickel-coated polymer and a gold-coated polymer would be reduced primarily to the difference between the dispersion constants, which are included in the formula for the Van der Waals force.

Benjamin and Weaver (ref. 7) calculated approximately the interfacial energy for metal films on a glass substrate. A summary of their calculations is reviewed in appendix A. According to the calculations described therein, and summarized in table II, the ratio of the dispersion constant for the nickel-coated system $C(Ni)$ to that for the gold-coated system $C(Au)$ is estimated to be 1.2, which is consistent with stronger nickel adhesion. On the other hand, the ratios of the adhesion strength for the nickel-coated polymer $F(Ni)$ to those for the gold-coated polymer $F(Au)$ obtained in the present experiment are 1.7 ± 0.9 , 1.7 ± 0.5 , and 1.7 ± 0.5 for PTFE, UHMWPE, and 6/6 nylon, respectively. To

TABLE II.—ESTIMATION OF DISPERSION CONSTANT

	PTFE	UHMWPE	6/6 Nylon	Nickel	Gold
Density, ^a ρ , g/cm ³	2.16	0.919	1.15		
Refractive index, ^b n	1.35	1.49	1.53		
Ionization potential, ^c I , erg	1.66×10^{-10}	0.82×10^{-10}	1.09×10^{-10}	^d 12.21×10^{-10}	^d 14.75×10^{-10}
Polarizability, ^e α , cm ³	4.27×10^{-24}	3.91×10^{-24}	25.8×10^{-24}	1.87×10^{-24}	1.28×10^{-24}
Dispersion constant, $C(Ni)$, erg-cm ³	1.36×10^{-58}	1.17×10^{-58}	7.94×10^{-58}		
Dispersion constant, $C(Au)$, erg-cm ³	1.11×10^{-58}	0.94×10^{-58}	6.45×10^{-58}		
$C(Ni)/C(Au)$	1.23	1.24	1.23		

^aDensity of polymers with 50-percent crystallinity and calculated from the densities of crystalline and amorphous.

^bRef. 10

^cIonization potentials for polymers were calculated from the ionization potentials of elements composing polymers.

^dRef. 11.

^ePolarizations for polymers were calculated from refractive index using the Clausius-Mosotti equation.

calculate precisely the interfacial energy, the difference of equilibrium distance r between the nickel-coated and gold-coated systems should be accounted for. If the reasonable values for r in these systems were estimated, better agreement between experiment and calculation might be obtained. Unfortunately, reasonable values of r cannot be estimated for lack of knowing the morphology of the polymer solids.

Effect of Electron Irradiation on the Adhesion

The adhesion between metals and PTFE can be improved by electron or X-ray irradiation of PTFE surfaces (ref. 3). To confirm quantitatively the effect of irradiation on the adhesion, the tensile pull test was performed on the specimens irradiated. These specimens were prepared by evaporating nickel or gold on the PTFE

surfaces irradiated by specimens electron beam for various times. In figure 6, the adhesion strength is shown as a function of irradiation time. It is found that the adhesion strength increases with increasing irradiation time. The adhesion strengths before irradiation and after 30 minutes of irradiation are presented in figure 7 to show clearly the effect of irradiation on adhesion. In figure 7, the adhesion strengths for uncoated and unirradiated PTFE are shown as references. The adhesion strengths for nickel-coated and gold-coated PTFE increase to $(4.92 \pm 0.92) \times 10^6$ N/m² and $(1.92 \pm 0.51) \times 10^6$ N/m², respectively. The ratios of adhesion strengths after irradiation to those before irradiation were estimated to be 1.6 ± 0.9 and 2.6 ± 0.9 for gold-coated and nickel-coated PTFE, respectively. The magnitude of improvement for nickel-coated PTFE is marginally higher than that for gold-coated PTFE.

When polymeric solids are irradiated, radicals are formed and degradation and cross-linking can occur. The

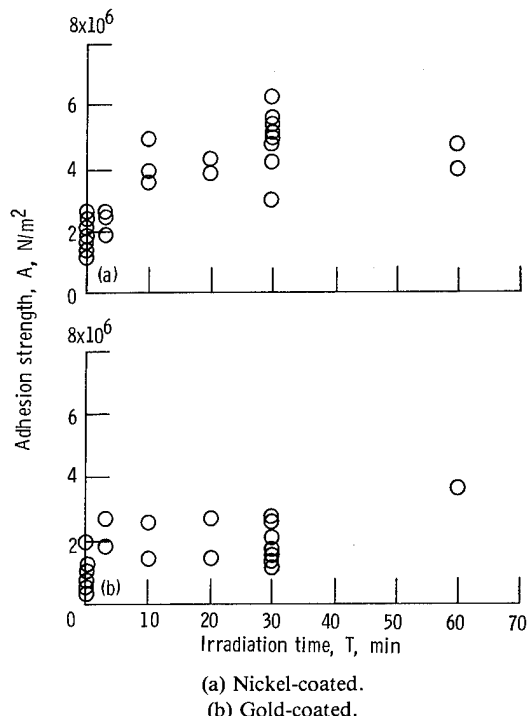


Figure 6.—Adhesion strength as function of irradiation time.

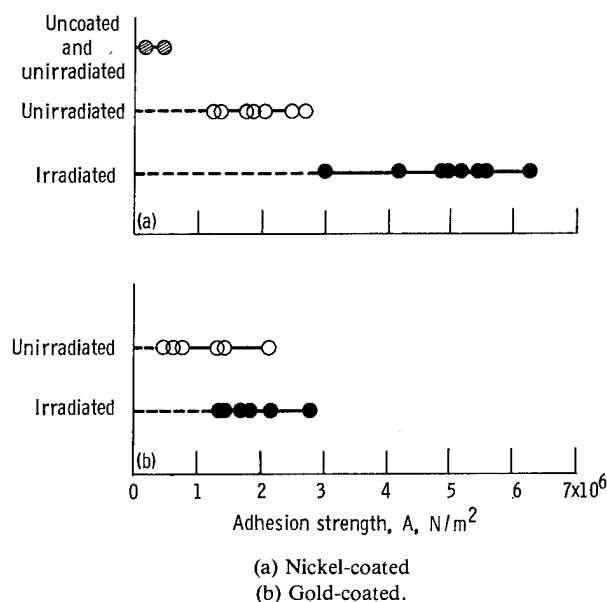


Figure 7.—Adhesion strengths for unirradiated and irradiated (2 kV, 30 min) PTFE surfaces.

extent of these effects depends primarily on the radiation dose and not on the type of radiation (ref. 8). In the early studies on radiation damage of polymers, the concentration of radicals formed by accelerated deuteron irradiation of PTFE was measured by ESR and found to saturate at a total dose of about 4×10^8 rad (ref. 9). Recently, Wheeler and Pepper (refs. 3 and 4) observed that crosslinks can be formed as a result of the radicals produced by X-ray and electron irradiation of PTFE, and they suggest that there may be nickel-carbon chemical interaction at the interface between the irradiated PTFE surface and nickel film. The dose rate used in their experiment was estimated to be about 10^7 rad/sec.

As described in appendix B, the irradiation intensity used in the study was calculated to be 3.6×10^7 rad/sec, and the total dose will be 10^9 rad after a few minutes of irradiation if all the incident intensity reaches the sample. If chemical changes similar to those produced by X-ray irradiation can be caused by electron irradiation, it is reasonable to explain the improved adhesion between irradiated PTFE and metal films on the basis of the results observed by Wheeler and Pepper.

As also suggested by Wheeler and Pepper, increased physical force, which may be due to an increase in density of the PTFE surface region, seems to be responsible for improved adhesion for gold-coated PTFE. It should also be noted that a disproportionation reaction may occur in the PTFE producing olefinic bonds that could contribute to greater Van der Waals forces. The fact that the magnitude of improved adhesion for nickel-coated PTFE seems to be higher than that of gold-coated PTFE suggests that a chemical interaction may be responsible, in part, for the adhesion of nickel-coated PTFE.

However, more information on the modifications of surface region of PTFE by electron irradiation should be necessary for the complete comprehension of the improved adhesion.

Conclusions

1. For unirradiated polymers, adhesion strengths between a gold film and polymeric solids are measured to be $(1.11 \pm 0.53) \times 10^6$, 5.49×10^6 , and 6.54×10^6 N/m² for PTFE, UHMWPE, and 6/6 nylon, respectively. The higher the surface tension of the polymer becomes, the stronger the adhesion strength becomes, which is consistent with Van der Waals forces being responsible for the increased adhesion.

2. Adhesion strengths between a nickel film and unirradiated polymers are higher by a factor of 1.7 than those between a gold film and unirradiated polymers. The dispersion constants for the two systems are in the ratio of 1.2 to 1.

3. Adhesion strength increases after the electron irradiation of the PTFE surface for the dose rate used in the present work. The increase is greater for nickel films than it is for gold films. This suggests a chemical interaction may be part of the cause of the increased adhesion.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

Appendix A—Estimation of Dispersion Constant

Benjamin and Weaver (ref. 7) calculated adhesion energies or binding energies between metal films and a glass substrate. The calculations described by them are now summarized.

London has given the dispersion energy between an isolated atom and infinitely large surface as

$$E = -\frac{N\pi}{6r^3}C \quad (\text{A1})$$

where N is the number of adsorbent atoms per unit volume in the substrate, r the equilibrium distance, and C the dispersion constant. The dispersion constant C is represented as

$$C = \frac{3}{2}\alpha\alpha' \frac{JJ'}{J+J'} \quad (\text{A2a})$$

where α and α' are the polarizability of the metal atom and substrate atom, respectively, and J and J' are their characteristic energies. For a first approximation ionization potential of an atom, I may be used in place of the characteristic energy. Then, equation (A2a) becomes

$$C = \frac{3}{2}\alpha\alpha' \frac{II'}{I+I'} \quad (\text{A2b})$$

The polarizability of uncharged atoms were calculated from

$$\alpha = \frac{e^2}{4\pi^2 m v_0^2} \quad (\text{A3a})$$

where v_0 is characteristic frequency and may be taken to correspond to the first ionization potential (i.e., $I = hv_0$). Equation (A3a) then becomes

$$\alpha = \frac{e^2 h^2}{4\pi^2 m I^2} \quad (\text{A3b})$$

The dispersion constant between metal atoms and elements composing polymeric solids can be calculated using equations (A2b) and (A3b). The results are listed in table II.

Appendix B—Estimation of Dose Rate

The energy loss by collision of an electron per unit length is given by the following equation (ref. 12):

$$-\frac{dT}{dx} = \frac{2\pi e^4 Z \cdot N}{m_0 v^2} \left[\ln \frac{m_0 v^2}{2I^2(1-\beta^2)} - (2\sqrt{1-\beta^2} - 1 + \beta^2) \ln 2 + \frac{1}{8} \sqrt{1 - \sqrt{1-\beta^2}} \right] \quad (\text{B1})$$

where

- T kinetic energy of an incident electron
- x pass length
- e electron charge
- m_0 electron rest mass
- v electron speed
- I average excitation potential
- Z nuclear charge
- N number of atoms per cubic cm

Using equation (B1), we can calculate the energy loss per unit path length, providing I , Z , and N are known. Experimental values of I have been obtained for some elements (ref. 13). In the case of compounds, average excitation potential can be calculated by the following equation, (ref. 14):

$$\ln \bar{I} = \frac{\sum_i N_i Z_i \ln I_i}{\sum_i N_i Z_i} \quad (\text{B2})$$

where

- N_i number of an element of kind i per cubic cm
- Z_i atomic number of an element of kind i
- I_i average excitation potential of component atoms of kind i

The value of \bar{I} for a PTFE monomer unit is calculated to be 100 eV, using values of I for fluorine and carbon atoms, 109 and 76.4 eV, respectively. The value of I for a fluorine atom can be estimated by interpolation between experimental values. N can be calculated to be 1.38×10^{22} , using the density (2.3 g/cm³) of the PTFE solid. Substituting these values into equation (B1), we can obtain 2.19×10^{-4} erg/cm as the energy loss per unit path length. The intensity of the electron beam in the present work is 3.75×10^{13} electrons/cm²-sec. Dose rate can be estimated to be about 3.6×10^7 rad/sec. Note that this is the initial dose rate. The PTFE specimen will probably charge when irradiated by electrons. This will reduce the actual electron intensity reaching the sample. Thus, 3.6×10^7 rad/sec must be considered an upper limit on the absorbed dose rate.

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