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GAMMA RADIATION DAMAGE STUDIES OF ORGANIC PROTECTIVE COATINGS AND GASKETS

J. C. Bresee
C. D. Watson
J. S. Watson

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CHEMICAL TECHNOLOGY DIVISION

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J. C. Bresee, C. D. Watson and J. S. Watson

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ABSTRACT

Studies have been carried out on the effect of gamma irradiation on mounted and unmounted protective coatings and various gasket materials. Qualitative results of screening studies and quantitative results of decontamination tests and physical property measurements are reported.

FOREWORD

This report* presents radiation stability data on many industrial materials tested on a laboratory scale to aid in the selection of materials for the construction and operation of radiochemical processing plants at Oak Ridge National Laboratory.

These materials were acquired (1) by accepting samples from some vendors who solicited Oak Ridge National Laboratory, and (2) by a non-exhaustive scanning of industrial publications and inquiring of those vendors whose products appeared to be of interest. The limited scope of the testing program did not justify ascertaining and contacting all possible sources of acceptable materials. Doubtless, there are many useful materials which were not tested. Accordingly, this report does not present a comprehensive comparison of all materials in the general groups tested.

It is not the purpose or intent of this report to endorse or condemn any of the products so tested or to implicate in any way a manufacturer or distributor of such products, but rather to present data compiled during the course of laboratory operations which may be of interest to others working on similar problems.

Materials that apparently exhibited poor radiation stability in these tests need not be considered inferior products, because slight variations in composition (such as the nature or content of plasticizers, binders, fillers, pigments, etc.) may in many cases affect radiation stability properties quite drastically. Although a detailed study of varying composition was not made, it was evident that in many cases a poorly rated product could easily be made to test higher by a slight change in raw materials or processing procedure.

The tests presented in this report are empirical tests which have been developed only for immediate comparison purposes. Standard methods have not been established for radiation stability, chemical resistance, or decontamination tests, and because of the variety and number of samples involved there is reason to believe that a few products may have received incorrect ratings.

The authors believe, however, that this report presents data adequate for empirical purposes and that it contributes heretofore unpublished data that may be of general interest to users of radiochemical facilities.

The tests presented herein fulfill Oak Ridge National Laboratory's past needs. Work of this type is continuing at many industrial laboratories.

The Authors

*Some of this information is being published in the September, 1956, issue of Nucleonics.

1.0 SUMMARY

Studies were carried out on the effect of gamma irradiation on a series of organic protective coatings and gasket materials. The tests were designed to simulate the exposure of various materials of construction to penetrating radiation in high level radiochemical processing plants. A cobalt-60 source was used and the range of total accumulated gamma exposure investigated was 10^6 to 10^9 roentgens (R, γ) in air.

Mounted coatings with the following polymer bases were studied: furane, vinyl, epoxy, phenolic, polyester, silicone-alkyd, neoprene, and styrene. Two types of coatings, one each of the furane-based and epoxy-based coatings, showed excellent radiation stability, chemical resistance, and decontaminability.

All unmounted coatings, vinyl and polyethylene based, failed either due to drastic embrittlement or polymer degradation as evidenced by surface tackiness. Tests of asphalt and tar radiation stability showed that both could be used for coating earthen basins for containing radiochemical wastes provided (1) the coating exposure did not exceed 10^9 R, γ, (2) the wastes are neutralized, and (3) the temperature of the wastes does not exceed 200°F.

Non-halogenated polymers were much more radiation resistant gasket materials than were halogenated polymers. Both telfon and Kel-F evolved corrosive gases and were completely degraded by irradiation to 10^8 R, γ, while polyethylene and polystyrene were resistant to 10^9 R, γ.

2.0 INTRODUCTION

The effect of gamma radiation on materials useful in radiochemical processing has been investigated. A cobalt-60 gamma source was used in the investigation, and the materials studied were a series of organic protective coatings and gasket materials.

During the chemical processing of spent nuclear reactor fuels, materials of construction are often subjected to intense irradiation. The primary source of the radiation is the fission product content of the fuels, and the penetrating radiation consists of gamma rays and energetic beta particles (so-called "hard betas"). Under unusual circumstances, process equipment might also be exposed to fast and thermal neutrons.

The economics of a nuclear power economy demand that power cycles be run with as high a fuel "burn-up" and as low a fuel element cooling time as is technically feasible. Both factors would result in an increasing concentration of radioactive fission products in chemical process streams. The

effect of high energy radiation on materials of construction, often merely a laboratory curiosity in the past, has become more and more important to design engineers.

The average gamma energy emitted by cobalt-60 is 1.2 Mev. The radiation source used in this investigation provided an intensity of $1.2\text{-}3.6 \times 10^4$ R, γ (in air) per minute, and the range of total accumulated irradiation of the test specimen was from 10^6 R, γ to 10^9 R, γ.

3.0 MECHANISM OF GAMMA RADIATION DAMAGE

The effect of gamma radiation on organic coatings (and on organic materials in general) is due to ionization of atoms in the molecular structure. When gamma radiation in the energy range 0.1 to 10 Mev interacts with atoms of low atomic number, such as hydrogen, carbon, nitrogen, fluorine, and chlorine, the radiation damage results primarily from the Compton effect. Gamma-ray photons collide elastically with electrons, and the recoil electron produced causes excitation and ionization as it travels through the material being irradiated.

Energy absorbed from the electron (or beta particle) by an atom is quickly distributed throughout the various degrees of freedom of the organic molecule, but, during the process of distribution, sufficient vibrational energy may be present at one time in one portion of the structure to rupture a covalent bond. Obviously, the probability of a bond rupture is a function of the binding energy of the bond. If the molecule is able to distribute the concentration of energy at the point of ionization without bond rupture, the sole effect of the γ-electron interaction would be an increase in the average "temperature" in the vicinity of the collision.

If a covalent bond is broken in a polymer molecule, several effects are possible and probably occur simultaneously throughout the coating or plastic. If the break occurs in the main polymer chain near the end of a chain, the smaller fragment may be small enough to diffuse through the material to a surface or to an imperfection and form a gas molecule at that point. The same effect would probably occur if the break occurs between the main chain and a small side chain, group, or atom.

In either case, the point of break on the chain would be a reactive center, whether the rupture left it ionic, a free radical, or an unsaturated covalent bond. If the reactive center occurs near the center of a polymer chain, there is a possibility of a reaction between that center and the end of the main chain or side chain of a neighboring polymer molecule. A relatively few such "cross links" can change the properties of a linear (or thermoplastic) polymer significantly, resulting eventually in a rigid structure similar to a thermosetting resin.

If a break in a main polymer chain takes place near the center, neither fragment would diffuse from the vicinity of the break and either fragment may recombine with the reactive end of another chain, but the overall result of a series of such breaks would be a significant decrease in the viscosity of the polymer. (Breaks in a few very long chains in a polymer decrease the weight average molecular weight greatly, and the weight average molecular weight determines the viscosity of a polymer).

The discussion thus far has been confined to the effect of γ radiation on the polymer structure of organic coatings and other plastics. Two other important constituents of most coatings and plastics are the pigment or filler and the plasticizer.

The pigment or filler is usually inorganic, and experiments have shown that the effect of gamma irradiation on inorganic materials is much less important than the effect on organic materials. In general, the only changes in inorganic material due to gamma irradiation are changes in color (the darkening of ordinary glass by γ's is a striking example of this effect) and an increase in temperature. There may be increased thermal effects in the vicinity of an inorganic particle of filler or pigment, due to the greater attenuation of gamma rays passing through heavier inorganic material. In addition, "pair production" (the formation of a positron and an electron from an energetic gamma photon passing near an atom of high atomic number) may also damage organic material near a pigment or filler particle.

On the other hand, it is obvious that an increase in the percentage of material relatively unaffected by gamma irradiation in a specimen may decrease the total damage per unit volume of the specimen and result in a slower change in properties than if the pigment or filler were not present. The influence of an inorganic material on the radiation damage resistance of an organic coating or plastic is a complicated function of the density of the material, the degree of dispersion, the proportion of inorganic material to organic, and the bond (if any) existing between the two; consequently, it is very difficult to predict the advantage or disadvantage of an inorganic filler or pigment without considering each case separately and carrying out evaluation experiments.

The plasticizer in an organic coating or plastic is usually a low-molecular-weight organic compound. Changes in its molecular weight due to gamma irradiation would have little effect on the viscosity (or weight average molecular weight) of the mixture unless the plasticizer molecule entered into a cross-linking reaction with the long-chain polymer molecules. Such a possibility does exist, particularly in cases where the plasticizer is a mixture of low-molecular-weight polymer molecules.

It is more probable that gamma irradiation would affect a coating or plastic (through its effect on the plasticizer) by degradation of the plasticizer molecules, migration of the resulting low-molecular-weight molecules to a surface or imperfection, and formation of a gas. The net result would

be desolvation of the polymer molecules. Desolvation brings about an increase in the attractive forces between such molecules (an increase in "crystallization") and an increase in the rigidity of the structure. Desolvation might also result from an increasingly cross-linked structure shrinking and "squeezing-out" liquid plasticizer from the polymer matrix, thus segregating the plasticizer in droplets throughout the specimen.

From the previous discussion of the possible effects of gamma irradiation on the polymer, filler or pigment, and plasticizer in a coating or plastic, it may be seen that either a decrease or increase in the rigidity of an irradiated specimen might be expected. Indeed, since many of the effects may be in competition, a temporary decrease followed by an increase might occur. In addition, other effects such as blistering (from separation of liquid or gas phases within the polymer), cracking (from shrinkage of the polymer framework), and peeling (from failure of the bond between a coating and the coated surface) might take place as the result of gamma irradiation.

The acceptability of an organic coating or plastic after undergoing radiation-induced changes in its properties depends upon the requirements of its use. For example, an organic coating which becomes quite rigid without cracking, blistering, or peeling during gamma irradiation might be quite satisfactory when applied to a rigid surface such as concrete. The same coating would be useless on a flexible surface. Obviously, flexibility is absolutely essential to a strip-coating, but the maintenance of an unbroken, chemically-resistant surface is the most important requirement of a coating which is decontaminated chemically.

In the following sections, studies of radiation damage to organic coatings and gasket materials will be reported. The results of the tests will be presented, and limitations imposed by radiation damage on the use of the material will be discussed.

4.0 PROTECTIVE COATINGS

The most important uses of protective coatings in radiochemical processing are (1) to prevent corrosion of auxiliary process equipment (equipment not normally in contact with main process streams) and (2) to improve the decontaminability of auxiliary equipment, the outside surface of main process equipment, and other surfaces such as the walls and floors of high-activity cells.

Coatings can be applied to surfaces in a number of different ways. They can be painted on a surface and hardened by evaporation of a volatile solvent. In addition, many paints are hardened by chemically-catalyzed crosslinking or by high temperature crosslinking (baking). Coatings can also be applied at high temperatures in a molten condition and hardened

merely by cooling. Finally, coatings can be applied in the form of a hardened sheet and locked to a surface either by an adhesive or a fastener. In the case of concrete coating, the inside of a concrete form can be lined with a "T-locked" plastic sheet and the wall poured onto the coating.

Samples of coatings which are applied in the various ways listed above have been irradiated with the cobalt-60 gamma source. For the sake of convenience, several types of coatings which in actual use would be subjected to radiation while mounted on a surface were irradiated in an unmounted sheet form. These coatings included strip-coats, a flame-sprayed polyethylene coating, and samples of "T-locked" plastic sheet. All other coatings were applied to either panels (aluminum, steel, or concrete) or steel immersion rods.

For the case of the three types of coatings irradiated in sheet form, the strength of the bond between the coating and a surface is quite weak (for strip-coats, deliberately so), and changes in the bond due to irradiation would be less important than changes in the physical properties of the coating. The most important requirement of strip-coats (coatings which permit decontamination of a surface by "stripping" the coating from the surface) for radiation resistance is that the sheet form of the coating remain strong and flexible. Irradiation of the sheet form of many coatings allowed a screening of those coatings whose physical changes precluded their use when applied to a surface. It was planned to irradiate in a mounted form any coatings which did not "fail" when irradiated in sheet form.

Throughout the discussion of the radiation stability of protective coatings, the question of whether or not a coating has "failed" will be raised. As was mentioned in the previous section, the acceptability or failure of a coating depends upon the requirements of its use. In the same way, the types of tests which were used to study the effect of gamma irradiation on protective coatings varied with the projected use of the coating.

4.1 Types of Tests

The tests performed on protective coatings consisted of qualitative and quantitative tests of specimens unirradiated and gamma irradiated to various levels of total accumulated irradiation. The qualitative tests were visual observations of changes due to radiation in both mounted and unmounted specimens. The quantitative tests consisted of chemical resistance tests and chemical decontamination tests.

Most specimens were irradiated in water-tight containers with air in contact with the irradiated surfaces. However, on two occasions the containers developed leaks and the specimens were in contact with water during part of the test period. In addition, one series of experiments was performed with coatings mounted on steel panels and covered with distilled water.

Visual observations were made, in the case of mounted specimens, of changes in surface hardness or tackiness, changes in color, and other phenomena such as cracks, blisters, and scaling or flaking. Specimens were studied with the aid of a microscope, and records were made photographically and photomicrographically. In the case of unmounted specimens, simple flex tests were combined with an examination of the condition of the surface.

Standard chemical resistance tests were run on irradiated and unirradiated specimens. Cold-rolled steel immersion rods (diameter 3/8 inch, length 6 inches) with one rounded end were coated with the paint to be tested and were irradiated to various levels of accumulated irradiation. Those specimens which did not "fail" (from visual observations) were immersed in several chemical reagents after an accumulated dosage of approximately 10^9 R, γ (in air). The reagents used were 3 molar nitric, sulfuric, and hydrochloric acids, 3 molar sodium hydroxide, and an organic solvent (methyl isobutyl ketone). The tests were continued until failure or for a total of nine days, and the results with irradiated specimens were compared with those for unirradiated specimens.

A second phase of the chemical resistance studies occurred in the process of preparing specimens for decontamination tests. Protective coatings were applied to aluminum, steel, and concrete panels and were irradiated to various levels of total accumulated irradiation. The test panels were then contaminated with 0.1 ml fission products in 6 molar HNO_3. Many specimens that satisfactorily resisted 3 molar HNO_3 during immersion tests were attacked by the contaminating acid, so several decontamination studies were rerun with 3 molar contaminating acid.

The chemical decontamination procedure consisted of scrubbing those specimens which withstood the contaminating acid with water, 3 M HNO_3, and in most cases concentrated citric acid. After each wash the surfaces of the specimens were monitored and a decontamination factor (DF) was calculated. The process of contamination and decontamination was repeated three times or until the coating failed.

From the above discussion, it may be seen that tests were performed in series, and essentially only those coatings which "passed" the previous tests were subjected to later ones. Consequently, only a few of the total number of coatings studied were carried through the decontamination tests.

In many cases, mounted coatings were irradiated on two or three different types of surfaces - aluminum, steel, and concrete. The series of tests was necessary since, as will be discussed later, the stability of an irradiated coating was strongly influenced by the surface to which the coating was applied. Similar tests were performed for each type of coated panel.

4.2 Tabulation of Results

The results of the radiation stability studies of protective coatings are shown in Tables I through IV and Figures 1 through 7.

4.2.1 Mounted Coatings

In Table I are presented the results of screening studies of mounted protective coatings. The bar graph included in the table shows the gamma dosage at which the coating failed or the maximum dosage applied to the coating without failure.

The influence of the surface to which the coating was applied on the stability of the coating may be seen by comparing the performance of a single coating type on several surfaces. The differences are often striking. For example, the vinyl coating Amercoat-33 which failed on an aluminum panel after 2.4×10^8 R, γ did not fail on a concrete panel until 1.22×10^9 R, γ, over five times the gamma dosage.

In most cases the greater stability of coatings on concrete may be attributed to: (1) the greater chemical resistance of concrete to attack by gaseous and liquid decomposition products from the coating, and (2) the absorption of these products in the porous concrete structure. In the case of vinyl coatings, the chemical attack would be from halide acids, and the results of this attack may be seen clearly in photographs and photomicrographs of irradiated coatings on metal surfaces. [See Figures 1, 2, 3, 5, and 6 (Panels 1, 2, 4, 5, 6, and 8)].

Of the 23 mounted coatings tested, only four polymer-base types did not fail at the maximum dosages used. These were the furanes, the epoxys, the silicone-alkyds, and one modified phenolic specimen. (Coatings number 1, 6, 7, 9, 11, 14, 15, and 21). Eight coatings which exhibited radiation stability, plus three examples of low-irradiated vinyl coatings and one neoprene base coating, were tested for chemical stability and decontaminability after irradiation.

In Table II it may be seen that six of the irradiated coatings were not resistant to the organic solvent hexone. In addition, several lacking solvent resistance also did not resist either acids or a base. All resistance ratings for coatings after irradiation were the same as those before irradiation, with four exceptions. Amphesive-801 lost its resistance to caustic and hexone due to irradiation and Epon-1001 lost its resistance to hexone. On the other hand, Epon-395 became resistant to sulfuric and hydrochloric acid as the result of gamma irradiation.

Two coatings, the vinyl-base Amercoat-33 and Corrosite-22, showed good decontaminability but failed at higher gamma dosages (2.4×10^8 R, γ). The silicone-alkyd coating was difficult to decontaminate on concrete and failed on a steel panel surface during contamination.

Two types of coatings, one each of the furane-base and epoxy-base coating (Nos. 1 and 14), showed excellent chemical resistance and decontaminability. It is interesting to note that the other two coatings of similar polymer base (Nos. 11 and 15) both lacked solvent resistance after irradiation.

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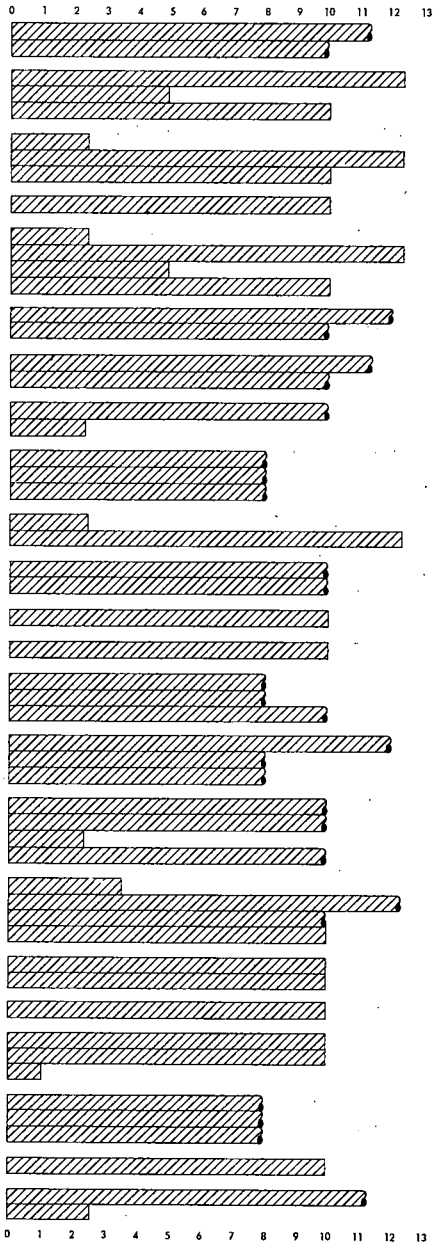
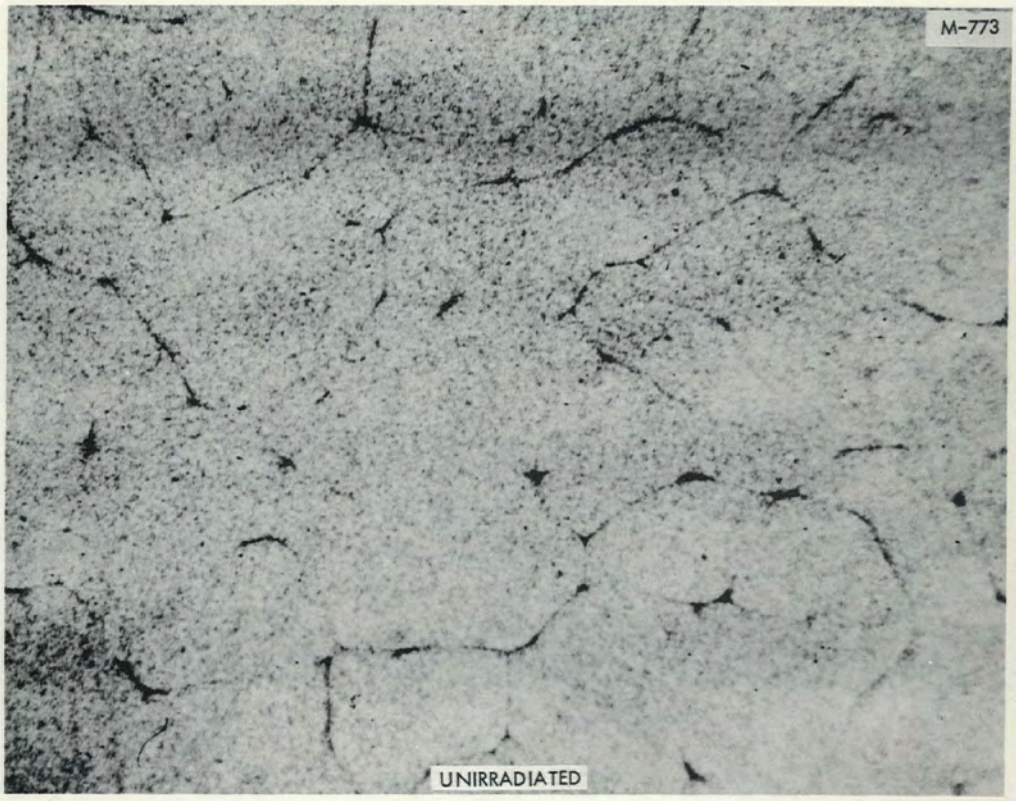
TABLE I

SCREENING STUDIES OF MOUNTED PROTECTIVE COATINGS

COATING[1]	POLYMER BASE	SURFACE OF APPLICATION	VISUAL OBSERVATIONS AT END OF IRRADIATION
1. ALKALOY-550	FURANE	CONCRETE PANEL STEEL IMMERSION ROD	NO VISIBLE CHANGE NO BLISTERING OR CHECKING
2. AMERCOAT-23	VINYL CHLORIDE	CONCRETE PANEL STEEL PANEL STEEL PANEL – WET	BLISTERED, SOME CRACKS BLISTERED (SEE FIG. 1) ONE LARGE BLISTER ON PANEL SURFACE (SEE FIG. 6)
3. AMERCOAT-33	VINYL CHLORIDE	ALUMINUM PANEL CONCRETE PANEL STEEL PANEL – WET	BLISTERED (SEE FIG. 2) BLISTERED, SOME CRACKS MANY PINPOINT BLISTERS (SEE FIG. 6)
4. AMERCOAT-44	VINYL	STEEL PANEL – WET	MANY PINPOINT BLISTERS (SEE FIG. 6)
5. AMERCOAT-55	VINYL	ALUMINUM PANEL CONCRETE PANEL STEEL PANEL STEEL PANEL – WET	BLISTERED (SEE FIG. 3) SMALL BLISTERS BLISTERED BLISTERED
6. AMERCOAT-1574-SE	EPOXY	CONCRETE PANEL STEEL PANEL – WET	TACKY, SOME BRITTLENESS, SPLOTCHY DISCOLORATION COLOR STREAKED, SOME HARDENING (SEE FIG. 6)
7. AMPHESIVE-801	MODIFIED PHENOLIC	CONCRETE PANEL STEEL IMMERSION ROD	NO VISIBLE CHANGE DRASTICALLY EMBRITTLED
8. AMPREG-E	POLYESTER RESIN	CONCRETE PANEL STEEL IMMERSION ROD – WET	LAYER OF CRYSTALS ON SURFACE OF COATING (SEE FIG. 4)
9. BARRETT SILICONE	SILICONE-ALKYD	CONCRETE PANEL STEEL IMMERSION ROD STEEL PANEL	
10. CORROSITE-22	VINYL	ALUMINUM PANEL CONCRETE PANEL	BLISTERED (SEE FIG. 5) BLISTERED, CRACKED
11. DURALON-36	FURANE	CONCRETE PANEL STEEL IMMERSION ROD	DARK ORANGE SPOTS, (BORDERLINE CASE) BRITTLE
12. DUPONT WHITE	VINYL CHLORIDE	STEEL PANEL – WET	ENTIRE SURFACE BADLY BLISTERED
13. DYNA-CLAD	VINYL CHLORIDE	STEEL PANEL – WET	ENTIRE SURFACE BADLY BLISTERED
14. EPON-395	EPOXY	STEEL IMMERSION ROD STEEL PANEL STEEL PANEL – WET	COLOR CHANGE FROM GRAY TO GREEN, HARDENED
15. EPON-1001	EPOXY	CONCRETE PANEL STEEL IMMERSION ROD STEEL PANEL	TACKY, SOME BRITTLENESS, SPLOTCHY DISCOLORATION
16. NEOBON	NEOPRENE	CONCRETE PANEL STEEL IMMERSION ROD STEEL IMMERSION ROD – WET STEEL PANEL	HARDENED BUT NO CRACKS OR BLISTERS HARDENED ON TIP OF ROD SOME CRYSTALLIZATION BELOW SURFACE, MUCH HARDER SURFACE
17. NUKEMITE-40	VINYL	ALUMINUM PANEL CONCRETE PANEL STEEL IMMERSION ROD STEEL PANEL – WET	BLISTERED SURFACE SOFT, ROUGHENED FEW SMALL BLISTERS, COLOR MUCH DARKENED (SEE FIG. 6)
18. PHENOLINE-3	PHENOLIC	CONCRETE PANEL STEEL IMMERSION ROD	VISIBLE CRACKS VISIBLE CRACKS
19. POLYCLAD SEALCOAT	VINYL CHLORIDE	STEEL PANEL – WET	SURFACE BADLY WRINKLED (SEE FIG. 6)
20. PRUFCOAT	STYRENE	CONCRETE PANEL STEEL IMMERSION ROD STEEL PANEL – WET	HARD, BRITTLE CRATERS, NO BLISTERS, DARKENED LAYER UNDER SURFACE CHECKED, CRACKED, BLISTERED PAINT CRACKED FROM PANEL (SEE FIG. 6)
21. SOLAR SILICONE ALKYD	SILICONE-ALKYD	CONCRETE PANEL STEEL IMMERSION ROD STEEL PANEL	
22. UCILON	VINYL CHLORIDE	STEEL PANEL – WET	SURFACE BLISTERED (SEE FIG. 6)
23. ZEROX-110	STYRENE-BUTADIENE	CONCRETE PANEL STEEL IMMERSION ROD – WET	EXTREME CHECKING, COLOR DARKENED



[1] FOR COATING MANUFACTURER, SEE TABLE VII.



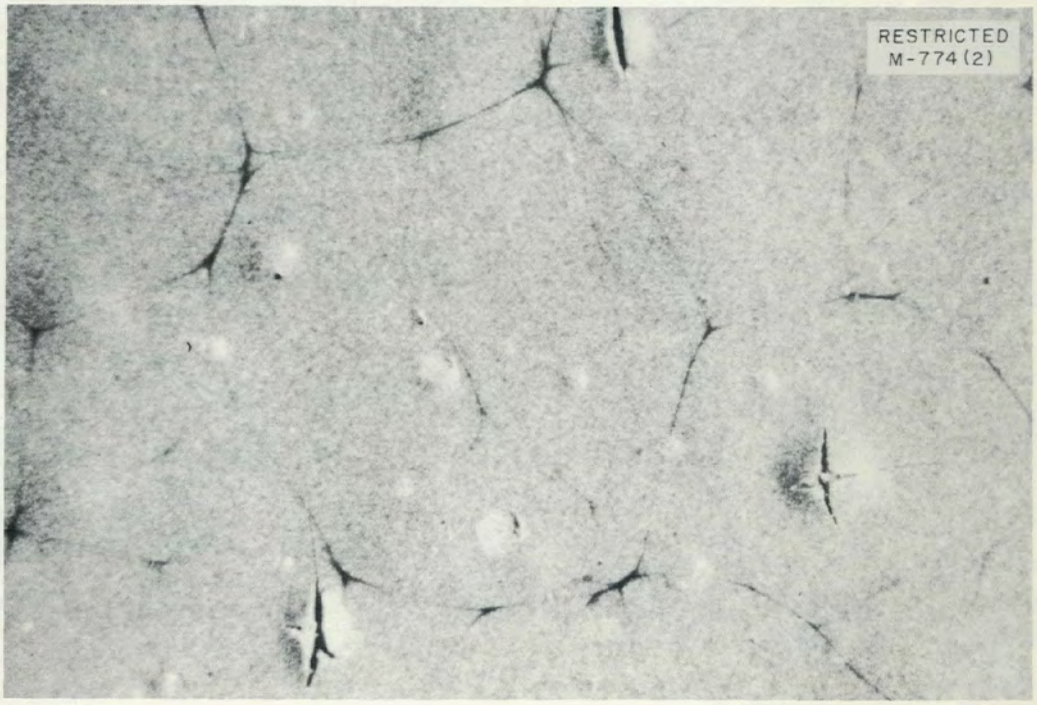
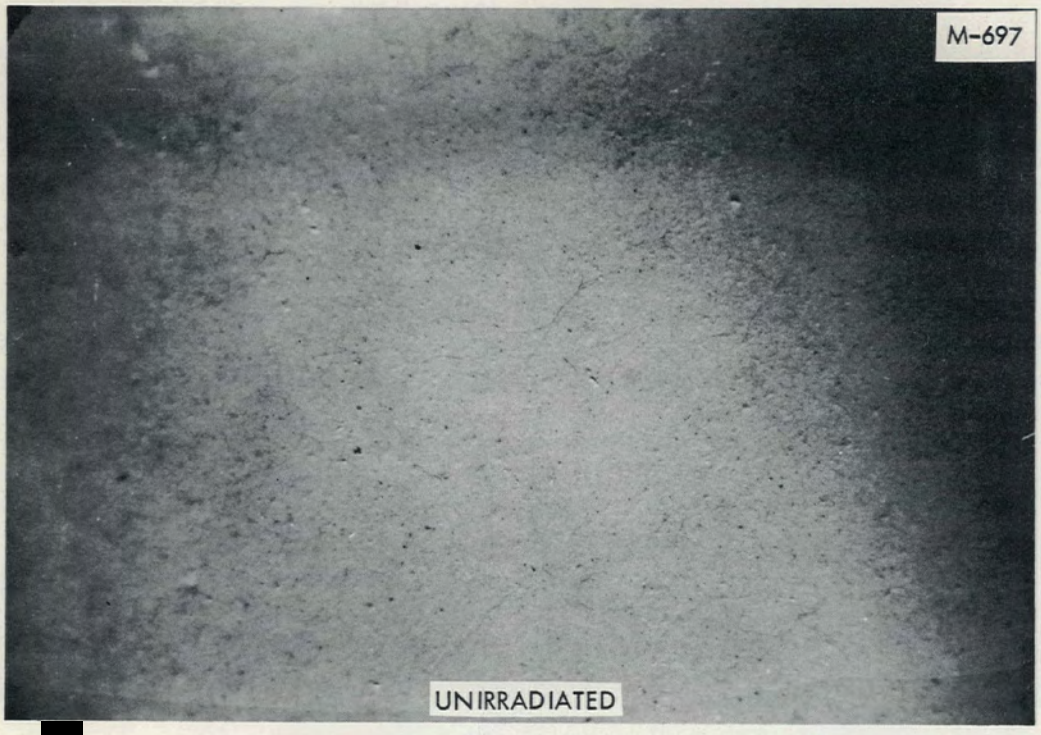


Fig. 1. Effects of Gamma Irradiation on Amercoat-23 on a Steel Panel. 50X. Reduced 34%.



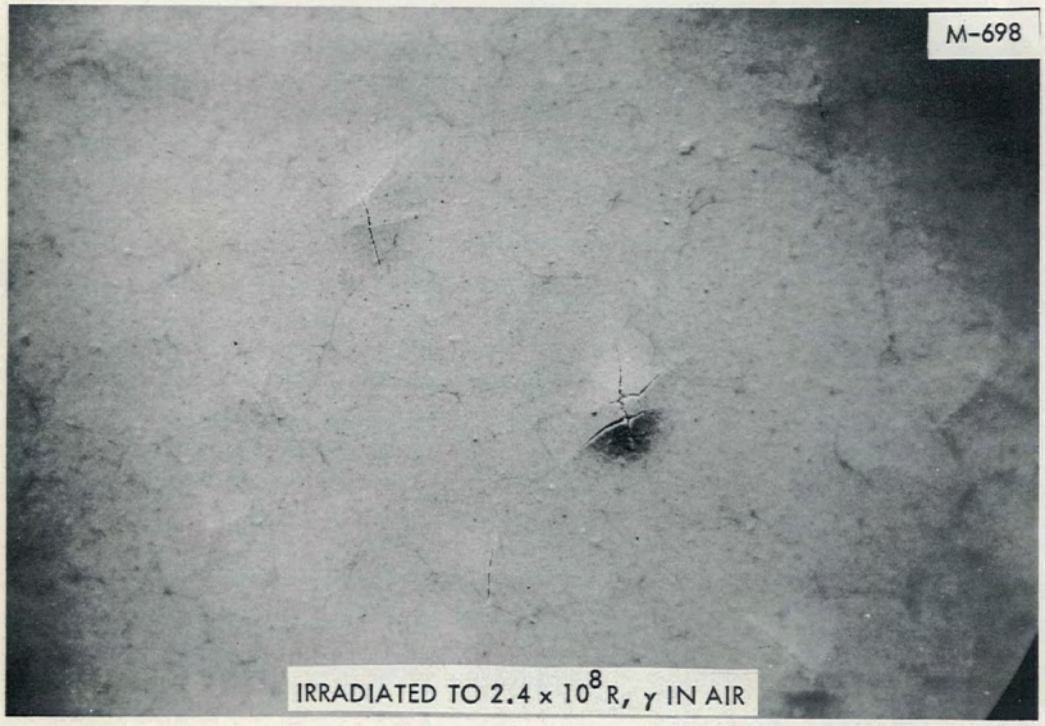


Fig. 2. Effects of Gamma Irradiation on Amercrat-33 on an Aluminum Panel. 50X. Reduced 15%.

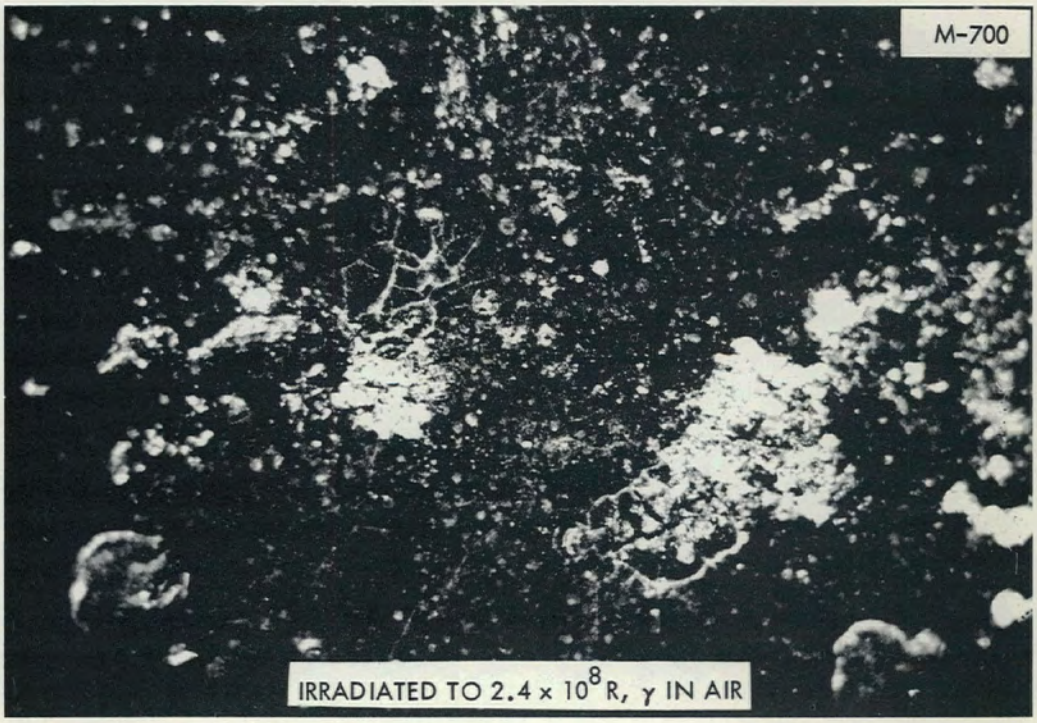


Fig. 3. Effects of Gamma Irradiation on Amercrat-55 on an Aluminum Panel. 50X. Reduced 15%.

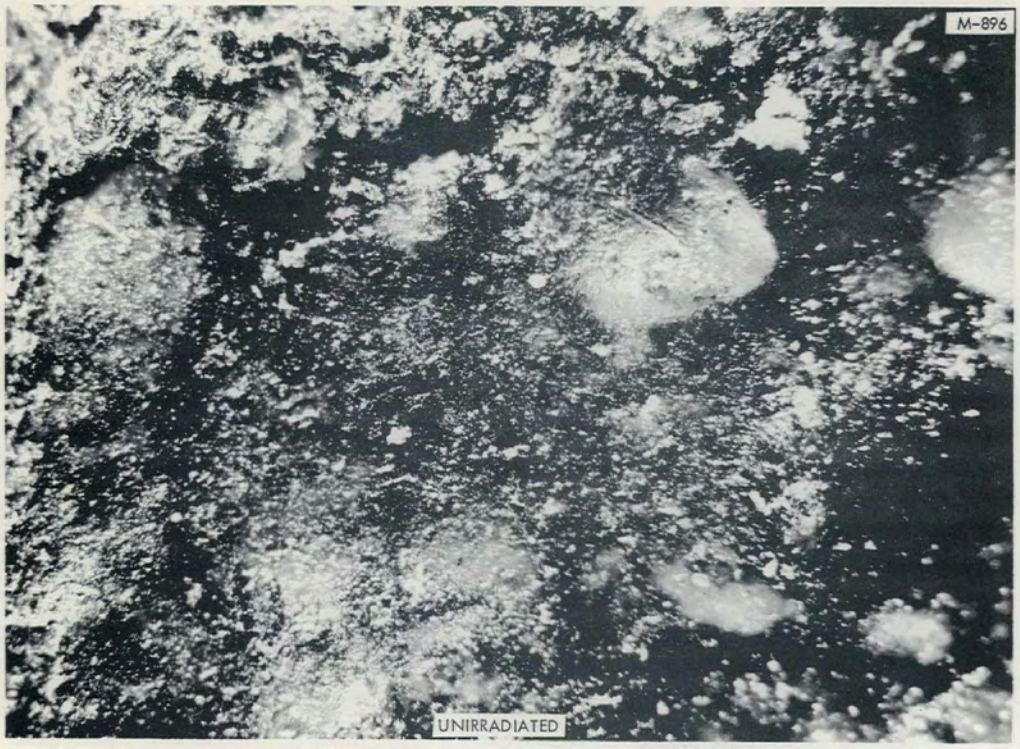
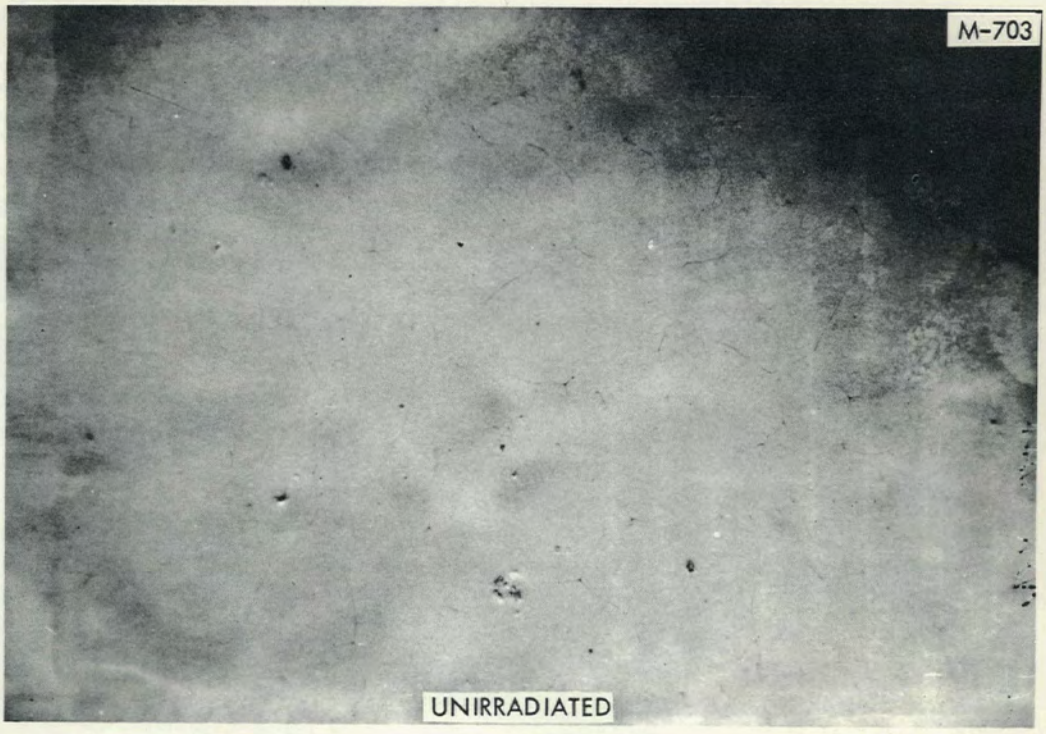


Fig. 4. Effects of Gamma Irradiation on Ampreg-E on a Concrete Panel. 100X. Reduced 43%.



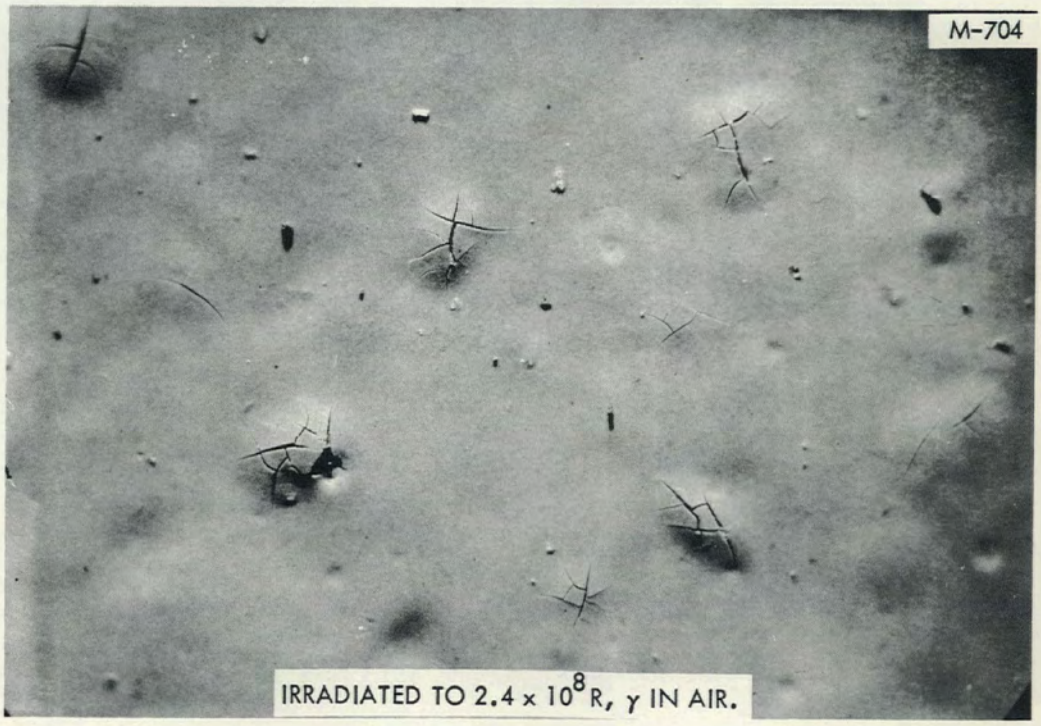
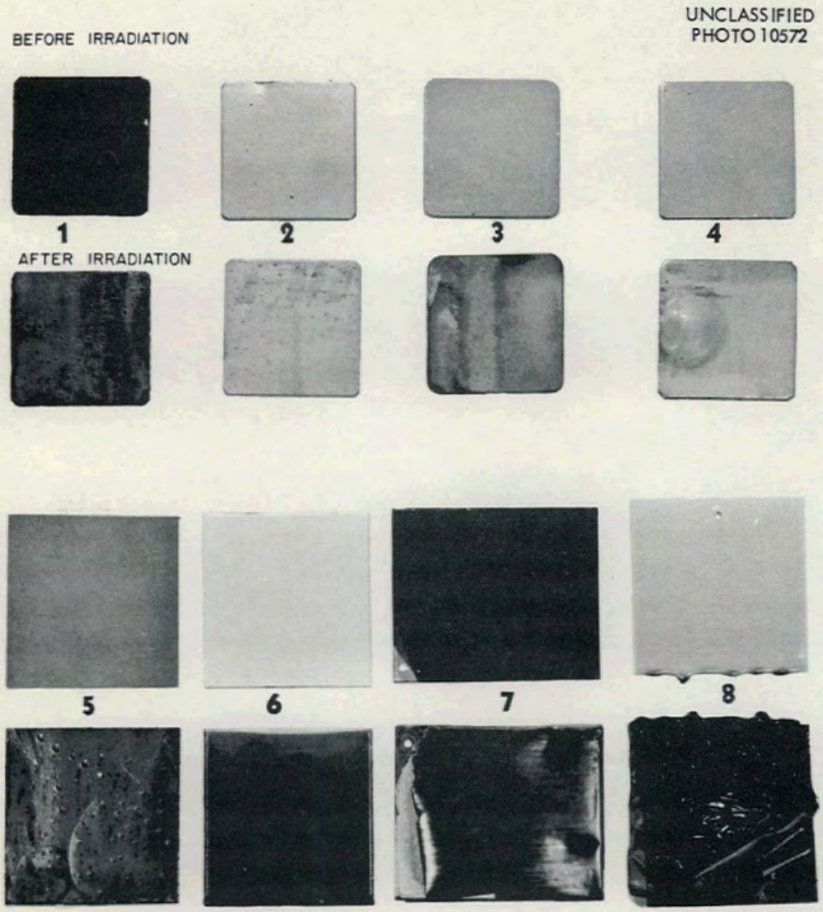


Fig. 5. Effects of Gamma Irradiation on Corrosite–22 on an Aluminum Panel. 50X. Reduced 15%.



RADIATION DAMAGED PROTECTIVE COATINGS

Dosage – 1×10^9 Roentgens, γ (in air)
Source – Cobalt 60 (5.3 Y, 1.2 MEV)

LIST OF COATINGS

1. AMERCOAT-44 (BLACK)
2. AMERCOAT-33 (GREY)
3. AMERCOAT-1574 (CONTAINING FLAKE LEAD)
4. AMERCOAT-23 (GREY)
5. UCILON-E
6. NUKEMITE-40
7. PRUFCOAT
8. POLYCLAD SEALCOAT-33

ALL SPECIMENS IRRADIATED ON STEEL PANELS UNDER DISTILLED WATER.

Fig. 6. Effects of Gamma Irradiation on Protective Coatings. One-tenth actual size.

TABLE II

RESULTS OF CHEMICAL RESISTANCE AND DECONTAMINATION STUDIES ON MOUNTED COATINGS

Coating	Surface	Dosage(R,γ)	Reagents	Results[1]				
				Acid	Base	Solvent	C/D[2]	DF
1. Alkaloy	Concrete	1.13×10^9	HNO_3-FP Contaminant				R	25-200
	Steel	1.0×10^9	HNO_3, NaOH, Hexone	R	R	R		
3. Amercoat-33	Aluminum	1.0×10^8	HNO_3-FP				R	70-117
7. Amphesive-801	Steel	1.0×10^9	HNO_3, NaOH, Hexone	N	N	N		
9. Barrett Silicone	Concrete	8×10^8	HNO_3-FP				R	12
	Steel	8×10^8	HNO_3, HCl, NaOH, Hexone, HNO_3-FP	N	N	N	N	
10. Corrosite-22	Aluminum	1×10^8	HNO_3-FP				R	560
11. Duralon-36	Concrete	1×10^9	HNO_3-FP				R	40-200
	Steel	1×10^9	HNO_3, NaOH, Hexone, HNO_3-FP	R	R	N		
14. EPON-395	Steel	8×10^8	HNO_3, NaOH, HCl, H_2SO_4, Hexone	R	R	R	R	200
15. EPON-1001	Concrete	1.2×10^9	HNO_3-FP				R	5
	Steel	8×10^8	HNO_3, NaOH, HCl, Hexone, HNO_3-FP	R	R	N	N	
16. Neobon	Steel	1×10^9	HNO_3, NaOH, Hexone, HNO_3-FP	R	R	N	R	3-8
17. Nukemite-40	Steel	1×10^9	HNO_3, NaOH, Hexone	N	N	N		
21. Solar Silicone Alkyd	Concrete	8×10^8	HNO_3-FP				R	8-15
	Steel	8×10^8	HNO_3-FP				N	

1. Symbols for results: R-Resistant
N-Non-resistant

2. C/D: The process of HNO_3-fission product contamination and decontamination.

4.2.2 Unmounted Coatings

The results of studies of gamma radiation damage to unmounted coatings are presented in Table III.

The main requirements for a radiation-resistant strip coat are that the coating surface retain its integrity and the film its flexibility in order that decontamination by coating removal may be carried out with an irradiated coating. In four of the five strip coat tests, the surface remained intact, but the film became brittle and broke during a bending test. It was obvious that these strip coats could not be readily removed after 10^9 R, γ.

The fifth strip coat, G. E. Cocoon, remained flexible, but the surface became very tacky. There was a possibility that the film porosity had increased with irradiation, but no quantitative tests were carried out to establish this point.

The proposed use of both T-locked coatings and flame-sprayed polyethylene called for flexibility of the coatings. The unmounted tests indicated that both types were seriously embrittled by exposure to 10^9 R, γ. However, applications without the need for flexibility (e.g., a T-locked surface for a concrete cell wall) would be possible provided that the sheet porosity had not increased. Again, porosity tests were not carried out.

4.2.3 Asphalts and Tars

A need for an exceedingly cheap method of storing indefinitely radioactive waste solutions resulting from the reprocessing of spent reactor fuels prompted an investigation of impervious lining materials for earthen basins. In a survey test program, asphalts, tars, prefabricated asphaltic membranes, soil solidification agents, plastic-filled concrete and polyester resin laminates were investigated. Asphalts and tars, because of cheapness and ease of application, were selected for radiation damage testing and chemical resistivity testing.

Radiation damage testing of several asphalts and tars in a gamma irradiation source up to 10^9 roentgens total dosage shows that both retain their ductility and are hardened (but not excessively) with increasing exposure (see Figure 7 and Table IV). An increase in softening point and a decrease in penetration is indicative of hardening. Note that the origin of each line on Figure 7 is the property of the unirradiated asphalt. From the slopes of the lines, there is evidence that excessive hardness may occur at 10^{10} roentgens.

Asphalts and tars evolve gases (principally hydrogen) during irradiation. The asphalt assumes a vesicular or honeycombed structure of individual cells which would not be expected to develop leaks in actual service. Irradiated tars exhibit this structure to a slight extent.

Chemical tests show that asphalts and tars are adequately resistant to neutralized radioactive wastes up to 200°F, but attack by acid wastes is severe.

TABLE III

STUDIES OF RADIATION DAMAGE TO UNMOUNTED COATINGS

RADIATION DOSAGE - 1.05×10^9 R, γ (IN AIR)

Coating[1]	Polymer Base	Color Change	Flexibility	180° Bend Test	Remarks
A. Strip Coats					
1. A-89-A	Vinyl	Black-unchanged	Stiff	Breaks	Sample Curled
2. Amercoat Strip	Vinyl	White to Gray	Stiff	Breaks	Sample Curled
3. Brevon	Vinyl	Black-unchanged	Stiff	Breaks	Sample Curled
4. G. E. Cocoon	Vinyl Copolymer	Orange to Black	Flexible	Bends	Tacky Surface
5. Tygofilm	Vinyl Copolymer	Blue to Gray	Stiff	Breaks	Not Curled
B. Plastic Sheet					
1. Amer Plate (T-Locked, Black)	Vinyl	Black-unchanged	Stiff	Breaks	Not Curled
2. Amer Plate (T-Locked, White)	Polyethylene	White to Amber	Stiff	Breaks	Not Curled
3. Polyethylene (Flame-Sprayed)	Polyethylene	Red, Yellow, and Blue to darker shades	Stiff	Breaks	Not Curled

[1] For coating manufacturers see Table VI.

TABLE IV

TYPICAL CHANGES IN PHYSICAL PROPERTIES ON GAMMA IRRADIATION OF COAL TAR PRODUCTS[a]

Sample Code	Roofing Pitch		W. G. Millwrap Enamel		Pipeline Enamel		Waterworks Enamel	
Total exposure, roentgens	0	5×10^8	0	5×10^8	0	5×10^8	0	5×10^8
Softening point (ASTM D36), °F	-	-	199	203	192	197	237	248
Softening point (ASTM D61), °F	158	161	-	-	169	168		
Penetration at 77°F, 100 g, 5 sec, mm/10[b]	5.5	5	9	8.5	0	0	15	7.5
Penetration at 32°F, 200 g, 60 sec, mm/10	0	0	1	1	0	0	5	0.5
Penetration at 115°F, 50 g, 5 sec, mm/10	84	70	26	24	1.5	1.5	31	22.5
Ductility at 77°F, 5 cm/min, cm	67	17.5	2	2	0	0	3	1.5
Ductility at 90°F, 5 cm/min, cm					1.5	1		
Ash, %	0.08	1.04[c]	30.7	28.2	16.9	16.8	29	29.5

[a]Test specimens supplied by the Barrett Division of Allied Chemical and Dye Corporation, Edgewater, New Jersey.

[b]The unit mm/10 is used in the trade to indicate 0.1 mm.

[c]Similar to ferric oxide residues; probably due to metallic contamination.

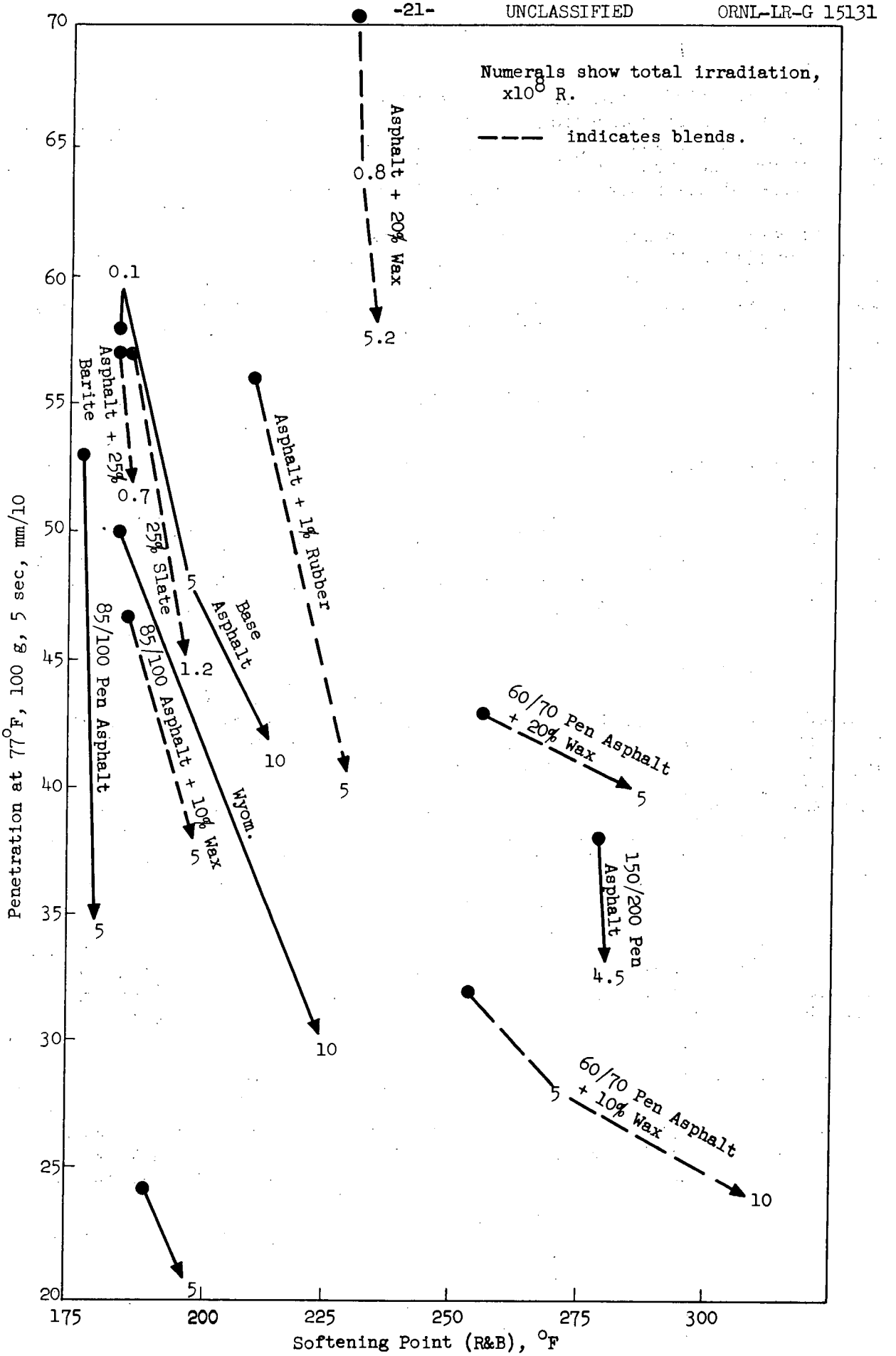


Fig. 7 Softening Point & Penetration Changes on Irradiation of Asphalts

It was concluded that asphalts and tars (if a suitable cheap radiation-resistant reinforcing material for the tar can be found) can be used to contain radiochemical wastes in earthen basins provided: (1) the total dosage does not greatly exceed 10^9 R, γ, (2) the wastes are neutralized, and (3) the temperature of the waste is not permitted to rise above 200°F.

It has been estimated that an earthen basin of 10^6 gallons capacity can be constructed with a 1/2" thick asphalt lining, covered with 2 ft of compacted earth and complete with roof, for 3-5 cents/gallon of stored waste. The complete results of radiation damage studies of asphalts and tars were presented at the Bituminous Symposium of the American Chemical Society, April, 1956.

5.0 GASKET MATERIALS

5.1 Types of Tests

Specimens of gasket materials were placed in leak-proof containers and lowered into a vessel surrounded by cobalt-60 slugs. Radiation intensity varied throughout the tests, but only the total irradiation dosage of each specimen was recorded. Measurements were made of the hardness, tensile strength, percent elongation, shear strength, water absorption, specific gravity, and other properties of the materials after various levels of irradiation.

In early tests, corrosive gases containing fluorine were detected being evolved from irradiated teflon. Tests were made to determine the quantity of fluorine evolved from teflon disks (1 in. dia, 1/8 in. thick) and teflon molding powder during irradiation, the quantity of degraded fluorine within the irradiated disks which was released during the 30-day period immediately following irradiation, and the effects of these gases on stainless steel flanges carrying 50% HNO_3 solutions. To measure the quantity of fluorine evolved, the specimens were immersed in a NaOH solution during irradiation, and the solution was subsequently analyzed for fluoride content. No attempt was made to determine in what compounds the fluorine was evolved.

In many cases only one reading could be obtained from each specimen, so several specimens were necessary for each series of tests. Since perfectly uniform specimens could not be obtained, only changes in properties which were greater than the variations in the specimens could be detected.

5.2 Results of Gamma Stability Tests of Gasket Materials

The most evident observation made from the tests of irradiated gasket material was the difference between the radiation stability of halogenated polymers, teflon and Kel-F, and nonhalogenated polymers, polyethylene and

polystyrene (see Table V). Both teflon and Kel-F evolved corrosive gases and were completely degraded by irradiation to 10^8 R, γ while polyethylene and polystyrene appeared very resistant to irradiation to this level. The only major difference between the behavior of polyethylene and polystyrene was the marked increase in the hardness of polyethylene with irradiation. Polystyrene was the most resistant gasket material tested and probably would be satisfactory for use at irradiation levels up to 10^9 R, γ. However, the rate of hardening of polyethylene may limit its use to less than 10^9 R, γ.

Since inorganic fillers often make organic plastics more resistant to radiation, a 1%-carbon-filled polyethylene sample was tested to compare this material with natural polyethylene. However, any differences between the radiation stability of the natural and carbon-filled polyethylene could not be detected.

The evolution of corrosive gases from gaskets during irradiation is a very important consideration in the design of a radiochemical plant, as these gases not only indicate deterioration of the gasket but also may damage flanges or other equipment present. No evolution from teflon was detected at radiation levels less than 10^6 R, γ (see Figure 8). The appreciable quantity of fluorine given off by the teflon disks during the 30-day period following irradiation and the difference between the quantity of fluorine evolved from the disks and the molding powder demonstrate the accumulation of released fluorine within the specimen before diffusion through the surface. Data on fluorine evolution from polymonochloro trifluoroethylene and more complete data on changes in the physical properties of Kel-F were reported by Byrne et al. (1)

The effect of these gases on stainless steel flanges immersed in 50% HNO_3 is shown in Figure 9. A light-brown area was noted on the flange where the steel had been in contact with teflon. Microscopic examination of this area revealed masses of tiny pits. All other surfaces of the flange remained as "bright" as before the test. Control specimens of stainless steel in the gamma field (without contact with teflon) were corroded by 50% HNO_3 at a rate less than one mil per year. No difference could be detected between the corrosion rates of the control specimens with and without irradiation.

In tests of properties most important to elastomers, hycar and silicone rubber appeared stable at irradiation levels not greater than 10^7 R, γ (see Table VI). However, between 10^7 R, γ and 10^8 R, γ there were considerable changes in the properties of both materials. It may be noted that after 10^8 both types of silicone rubber have deteriorated to materials with approximately the same mechanical properties. (See values at 10^8 R, γ of tensile strength, elongation and hardness.)

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(1) Ind. Eng. Chem., 45, 2549 (1953).

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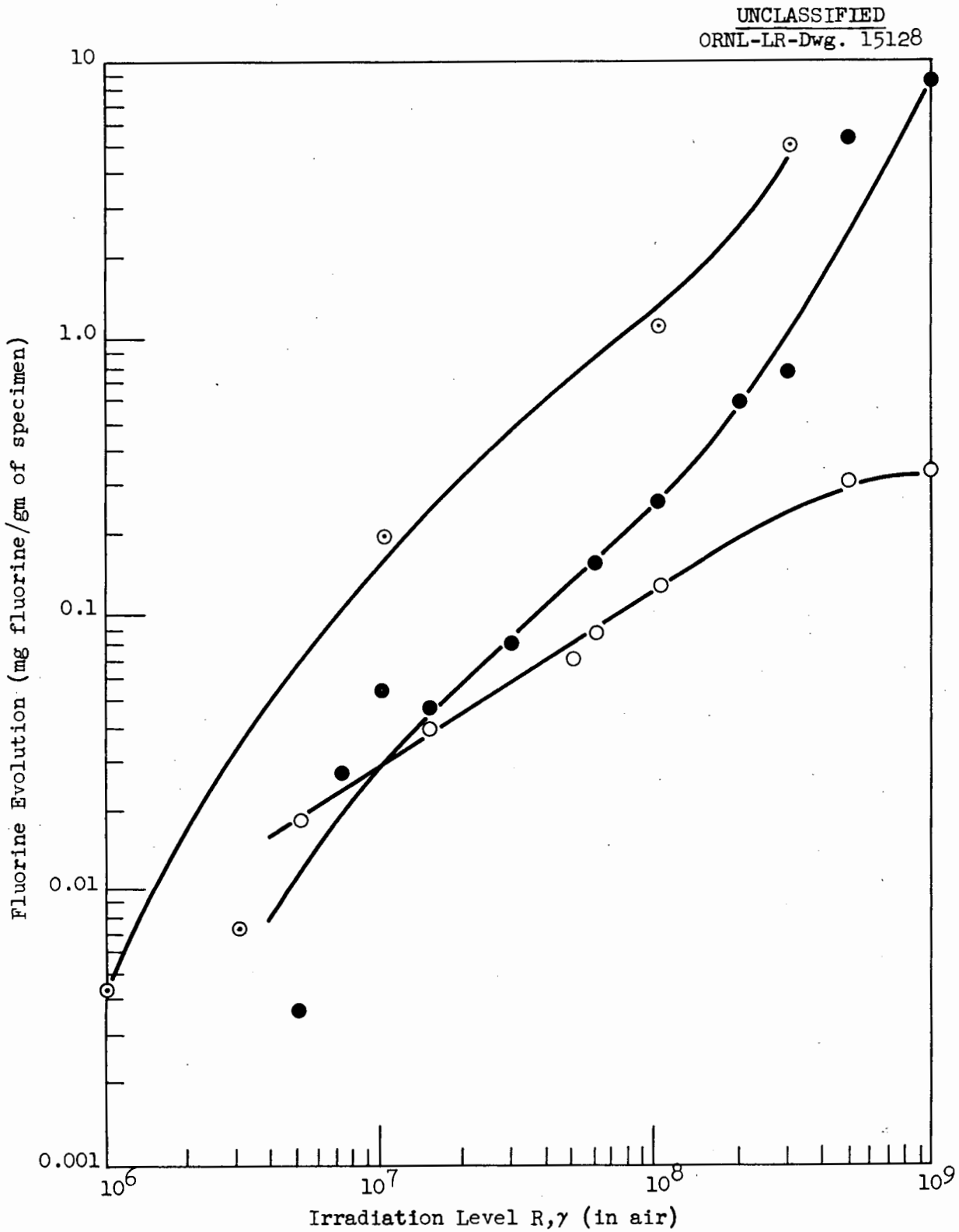
TABLE V

THE EFFECTS OF GAMMA IRRADIATION ON THE PHYSICAL PROPERTIES OF ORGANIC GASKET MATERIALS

Irradiation Level Roentgen, γ (in. air)	Specific Gravity (g/cu cm)	Per Cent Change	Tensile Strength (psi $\times 10^{-3}$)	Per Cent Change	Shear Strength (psi $\times 10^{-3}$)	Per Cent Change	Elongation (%)	Per Cent Change	Breaking Energy (ft-lb per in. of notch)	Per Cent Change	H_2O Absorbed (%)	Per Cent Change	Haze (%)	Per Cent Change	Rockwell Hardness (R scale)
							Polyethylene								
0	0.914		1.56		1.89		325		11.2		0.026		1.72		−8.5
10^8	0.920	+0.66	1.64	+5.1	1.81	−4.2	28	−92	5.6	−50	0.035	+35	1.83	+6.4	14.3
10^9	0.921	+0.77	1.90	+21.8	1.91	+1.1	7.6	−98	2.9	−74	0.027	+2	98	+5600	49.2
							Polyethylene, 1% Carbon Filled								
0			1.59		1.76		450		10.3						−6
5×10^8			1.65	+3.6	2.09	+18.7	10-30	−95	3.1	−70					34
10^9			1.80	+19.6	2.15	+22.3	10-30	−95	2.9	−72					66
							Polystyrene								
0	1.049		4.64		5.9		0.75		0.45		0.054		12.5		124
10^6			4.2	−9	5.5	−7	0.78	+4	0.29	−35					124
10^7			5.4	+16	6.1	+3	1.03	+37	0.23	−50					124
10^8	1.051	+0.19	3.3	−29	5.6	−5	0.45	−40	0.30	−33	0.089	+65	8.3	−34	122
10^9	1.053	+0.38	5.0	+8	5.6	−5	0.99	+32	0.19	−58	0.089	+65	14.2	+14	121
							Teflon								
0	2.14		3.76		3.01		175		2.65		0.0053		5.5		
10^8	2.21	+3.3	Failed		0.483	−84	Failed		0.37	−86	0.014	+170	14.6	+165	
10^9	2.19	+2.3	Failed		0.094	−95	Failed		0.30	−90	0.345	+550			
							Kel-F								
0			2.55		3.41		264								
10^6			2.40	−5.9	3.65	+7.0	230	−13							
10^7			1.67	−34.5	1.85	−45.7	73	−72							
10^8			Failed		Failed		Failed								



⊙ Evolution from teflon molding powder during irradiation

● Evolution from teflon disks (1" dia, 1/8" thick) during irradiation

○ Evolution from teflon disks during 30 day period following irradiation

Figure 8
Fluorine Evolution from Teflon

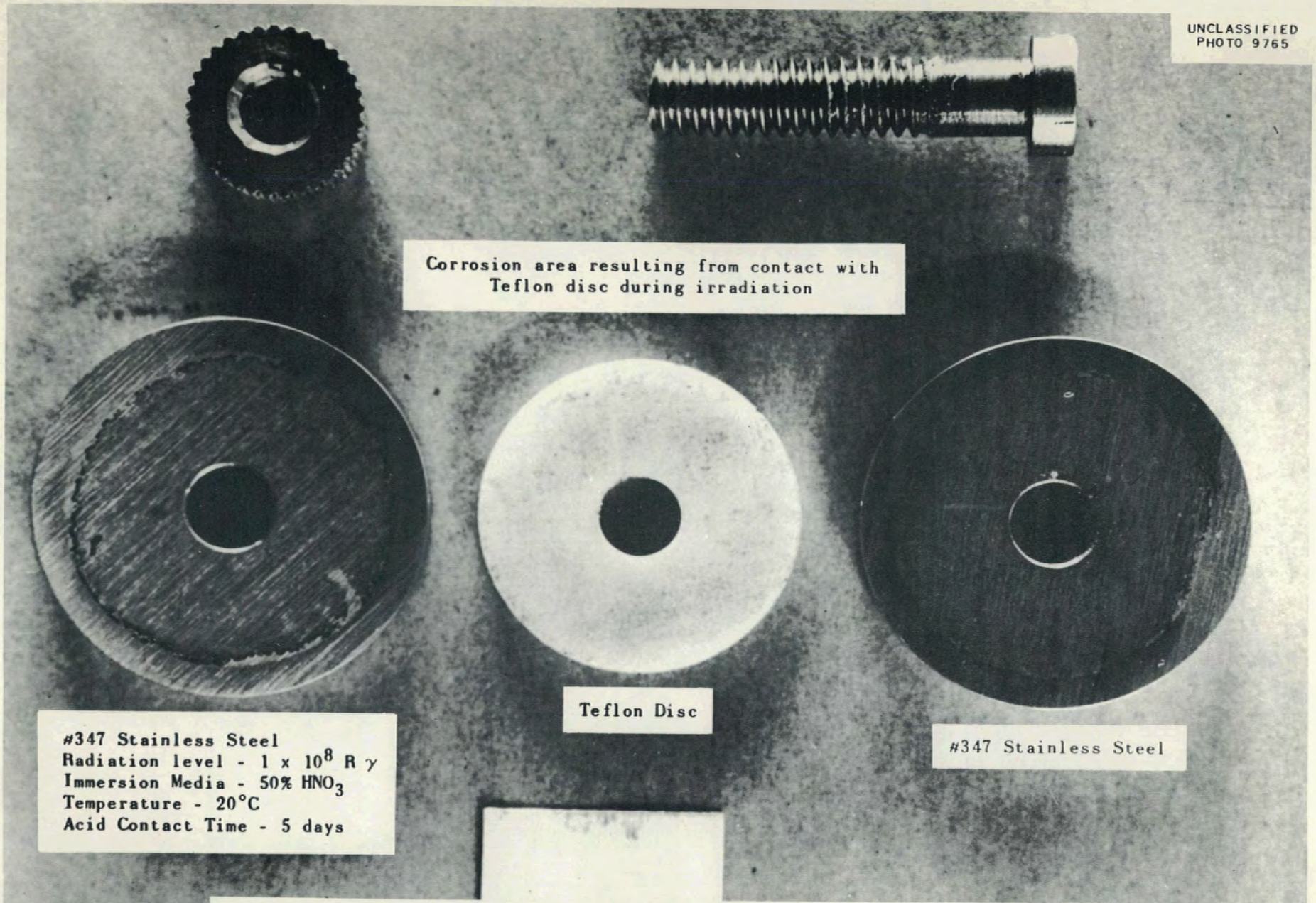


Fig. 9. The Corrosion of Stainless Steel in Contact with an Irradiated Telfon Gasket.

TABLE VI

THE EFFECTS OF GAMMA IRRADIATION ON THE

PHYSICAL PROPERTIES OF ELASTOMERS

Irradiation Level Roentgen, γ (in air)	Tensile Strength (psi x 10^{-3})	% Change		Elongation (%)		% Change		Shore Hardness	% Change
Silicone No. 12602									
0	0.277	-		58		-		62	-
10^4	0.245	-12		50		-14		65	+ 4.8
10^6	0.260	- 6.1		62		+ 6.9		66	+ 6.5
10^7	0.282	+ 1.8		25		-57		74	+19
10^8	0.151	-46		5		-91		95	+53
Silicone No. 12603									
0	0.555			36				84	
10^4	0.540	- 2.7		36		0		84	0
10^6	-	-		-		-		85	+1.2
10^7	0.528	- 4.9		25		-31		87	+3.6
10^8	0.135	-76		5		-86		86	+2.4
Hycar No. OR-25[1]									
	A	B	A	B	A	B	A	B	A	A
0	2.74	2.26	-	-	275	365	-	-	72	-
10^4	1.88	2.33	-32	+ 3.1	230	371	-16	+ 1.6	77	+ 6.9
10^6	2.42	2.40	-12	+ 6.2	255	358	- 7	- 1.9	78	+ 8.3
10^7	2.59	2.64	- 5	+17	208	185	-24	-49	81	+13
10^8	1.63	2.04	-40	- 9.7	35	32	-87	-91	92	+28
Hycar No. PA-21[1]									
	A	B	A	B	A	B	A	B	A	A
0	1.36	1.57	-	-	190	145	-	-	71	-
10^4	1.29	1.40	- 5.1	-11	155	130	-18	-10	70	- 1.4
10^6	1.33	1.40	- 2.2	-11	150	130	-21	-10	73	- 2.9
10^7	1.33	1.38	- 2.2	-12	135	106	-29	-27	72	+ 1.4
10^8	0.81	0.97	-40	-38	50	41	-74	-72	80	+13

[1] Two series of tests (A and B) were made with these materials.

6.0 ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of the following in carrying out the radiation damage test program.

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2. George A. West, Frank L. Rogers, G. R. Guinn, R. J. McNamee, Union Carbide Nuclear Company (Oak Ridge National Laboratory).

3. Dr. Mack Tyner, Jr., University of Florida.

4. J. N. Hunsberger, E. I. du Pont de Nemours and Company, Incorporated.

5. The various companies supplying specimens. (See Table VII).

TABLE VII

MANUFACTURERS OF ORGANIC PROTECTIVE COATINGS AND GASKETS

	Manufacturer
A. Mounted Coatings	
1. Alkaloy-550, Amphesive-801, Ampreg-E, Neobon, Zerox-110	The Atlas Mineral Products Company Houston, Texas
2. Amercoat-23, 33, 44, 55 and 1574 SE	Amercoat Corporation South Gate, California
3. Barrett Silicone	Barrett Varnish Company Cicero, Illinois
4. Corrosite-22	Corrosite Corporation New York, New York
5. Duralon-36	U. S. Stoneware Akron, Ohio
6. Du Pont White	E. I. du Pont de Nemours and Company, Inc. Wilmington, Delaware
7. Dyna-clad	Merchants Chemical Company, Incorporated New York, New York
8. Epon-395	The Glidden Company Chicago, Illinois
9. Epon-1001	Shell Chemical Corporation New York, New York
10. Nukemite-40	Nukem Products Corporation Buffalo, New York
11. Phenoline-3, Polyclad Sealcoat	Carboline Company St. Louis, Missouri
12. Prufcoat	Prufcoat Laboratory, Incorporated Cambridge, Massachusetts
13. Solar Silicone Alkyd	Solar Corporation Milwaukee, Wisconsin
14. Ucilon	United Chromium, Incorporated New York, New York

TABLE VII (Cont'd)

	Manufacturer
B. Unmounted Coatings	
1. A-89-A-Black	Gordon-Lacey Chemical Products Company New York, New York
2. Amercoat Strip, Amerplate (T-Locked, Black and White)	Amercoat Corporation South Gate, California
3. Brevon-Black	Atlas Powder Company N. Chicago, Illinois
4. G. E. Cocoon	R. M. Hollingshead Corporation Camden, New Jersey
5. Tygofilm-Blue	U. S. Stoneware Akron, Ohio
6. Flame-sprayed Polyethylene	The Powder Weld Process Company Brooklyn, New York
C. Gaskets and Elastomers	
1. Polyethylene, Plain and Carbon-filled	American Agile Corporation Cleveland, Ohio
2. Polystyrene	Dow Chemical Company Midland, Michigan
3. Teflon	E. I. du Pont de Nemours and Company, Inc. Wilmington, Delaware
4. Kel-F	Kellex Corporation New York, New York
5. Silicone Rubber - 12602 and 12603	General Electric Company Waterford, New York
6. Hycar Rubber - PA-21 and OR-25	B. F. Goodrich Chemical Company Cleveland, Ohio