# INVESTIGATION OF SPACE RADIATION EFFECTS
# IN POLYMERIC FILM-FORMING MATERIALS

By C. Giori
T. Yamauchi
F. Jarke

Prepared under Contract No. NAS1-13292 by
IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois 60616

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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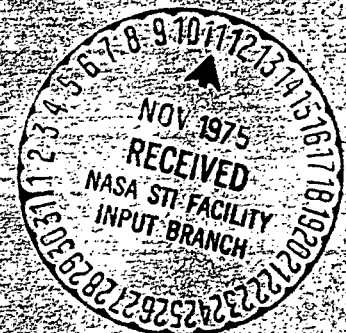
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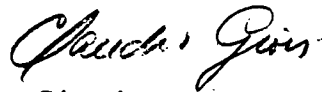NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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16. Abstract

The literature search in the field of ultraviolet radiation effects that was conducted during the previous program, Contract No. NAS1-12549, has been expanded to include the effects of charged particle radiation and high energy electromagnetic radiation. The literature from 1958 to 1969 was searched manually, while the literature from 1969 to present was searched by using a computerized keyword system. The information generated from this search was utilized for the design of an experimental program aimed at the development of materials with improved resistance to the vacuum-radiation environment of space. Preliminary irradiation experiments have been performed which indicate that the approaches and criteria employed are very promising and may provide a solution to the challenging problem of polymer stability to combined ultraviolet/high energy radiation.

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# FOREWORD

This report, entitled "Investigation of Space Radiation Effects on Polymeric Film-Forming Materials" covers the period 6-12-74 through 8-11-75 and was prepared by IIT Research Institute for NASA-Langley Research Center under Contract No. NAS1-13292, IITRI Project No. C6318. The authors wish to acknowledge the cooperation and assistance of Mr. W.S. Slemp, the NASA-Langley Technical Monitor, and of Dr. N. Johnston, also of NASA-Langley Research Center.

Respectfully submitted,
·IIT RESEARCH INSTITUTE

C. Giori
Senior Chemist
Polymer Chemistry Research

APPROVED:

A.M. Stake
Manager
Polymer Chemistry Research

CG:ge

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## 1. INTRODUCTION

The work presented in this report is a continuation of the work initiated during previous NASA Contract No. NAS1-12549 and published in Reference 1. The objective of this study is the development, characterization and testing of high performance materials with improved resistance to the vacuum-radiation environment of space and potentially useful in space applications such as "second surface" mirrors, solar cell adhesives and protective coatings.

The problem of polymer stability to a combined ultraviolet-high energy radiation environment stems from the opposite structural requirements for stability to these two types of radiation: materials with high transparency in the ultraviolet region, such as Teflon, are stable to ultraviolet but unstable to high energy radiation. On the other hand, aromatic polymers that are capable of effectively dissipating high energy radiation through the non-localized $\pi$ electrons are generally unstable to ultraviolet radiation. The work discussed in this report is aimed at achieving superior polymer stability to ultraviolet radiation, charged particle radiation (low and high energy) and combined ultraviolet-charged particle irradiation.

In the first part of this report, the computerized literature search on ultraviolet radiation effects conducted during the previous contract has been expanded to include the effects of charged particle irradiation (both low and high energy) and gamma radiation. Although our main interest is in charged particle radiation, we felt that it was appropriate to include gamma radiation in this review, because the effects produced by gamma radiation are very similar to high energy particulate radiation, and because most of the literature on radiation effects deals with gamma radiation.

In the second part of this report some of the concepts developed as a result of the literature search on ultraviolet effects conducted under the previous contract have been investigated in greater detail. Particular attention has been paid to the study of the various mechanisms by which absorbed ultraviolet energy can be dissipated without degradative effects.

In the third part of this study, a rationale for material selection has been developed and utilized in an experimental program involving short-term in-vacuo ultraviolet exposure tests.

## 2. LITERATURE RETRIEVAL

During the previous program, contract No. NAS1-12549, a
literature search was conducted on the effects of ultraviolet
irradiation on polymeric materials, with particular emphasis on
vacuum photolysis, mechanisms of degradation and energy transfer
phenomena (Ref. 1). During the present program, we have con-
ducted a literature search on the effects of charged particles
and high energy electromagnetic radiation on polymers, with
special consideration to radiation damage in a space environment.

The search of chemical abstracts and NTIS files was con-
ducted by IITRI's Computer Search Center (CSC) by using a com-
puter compatible keyword profile. Table I shows the keywords
that have been utilized. The first category (A) consists of
terms that express the concept of "Radiation Environment" which
is the interaction of interest. The second category (B) consists
of terms that characterize the materials and other interactions
of interest. Common polymer trade-names and abbreviations were
also included.

Each citation card from the computer retrieval contains
the title, author, source, index terms for the references, as
well as a special print-out of those terms that were responsible
for the selection. A final card summarizes the statistics of
the family of keywords, sorted alphabetically. The NTIS com-
puter search (1967-1974) identified approximately 200 pertinent
abstracts. The CA computer search (1969-present) identified
approximately 4,500 references. The period from 1958 to 1969
was searched manually, since it does not currently exist in a
machine readable form. In addition, outside sources were
utilized: the Defense Documentation Center ran an unclassified
search of its holding using a CSC-developed profile form, and
a search of NASA files (including STAR and IAA) was ordered

through the North Carolina Research Triangle Park. Furthermore, the previous study of ultraviolet effects was expanded with a search of the radiation chemistry bibliographies published by the Radiation Chemistry Data Center of the University of Notre Dame, and a manual search of the literature on the photochemistry of specific model structures of interest was conducted. After screening the retrieved citations, about 350 documents were ordered and technically reviewed for the program.

TABLE I
COMPUTER RETRIEVAL KEYWORDS

| A | B |
|---|---|
| *Radiat* | Poly* |
| Proton | Plastic |
| Electron | Coating |
| Charged Particle | Resin |
| Space - environment | Film |
|     - radiation | Vacuum |
|     - Coatings | Absorb* |
| Van Allen Belts | Absorpt* |
| Solar Wind | Degrad* |
| | Damage |
| | Silicone |
| | Nylon |
| | Teflon |
| | Kapton |

## 3. EFFECTS OF PARTICULATE AND HIGH-ENERGY ELECTROMAGNETIC RADIATION

The effects of radiation on polymers have been reviewed in several books (Ref. 2-8) and articles (Ref. 9, 10). Also, a survey of the patent literature with reference to the use of radiation methods in plastic technology is available (Ref. 11) and a review of the technology of radiation processing has been published (Ref. 12). In these reviews, the effect of radiation is discussed primarily in terms of utilization of the radiation for the improvement of specific plastic properties by cross-linking.

The effects of many types of high-energy radiation on polymers have been described, including eletromagnetic radiation (X-rays, gamma rays), and particulate radiation (electrons, protons and neutrons). Although X-rays and gamma rays are similar to ultraviolet radiation in being electromagnetic radiations, their quanta are associated with much higher energies. While the quanta of ultraviolet radiation have energies in the range 50-1000 kcal, particulate and high-energy electromagnetic radiations may have energies up to $10^8$-$10^9$ kcal, more than enough to displace electrons from organic compounds.

The absorption of ultraviolet irradiation occurs at specific groups, and produces electronic excitation that may lead to dissociation into radicals. The absorption of charged particles or high-energy quanta is non-specific with respect to chemical structure, and may result in the displacement of electrons with formation of ion-radicals:

$$A \longrightarrow A_{\cdot}^{\oplus} + e^-$$
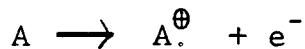
The electron produced can have sufficient energy to leave the zone of primary ionization, and may produce ionization or excitation along the course of its trajectory.

It is important to note that, while displacement of elec-
trons with production of ion-radicals is the primary effect of
high energy radiation, the reactions promoted by the radiation
generally involve free radical mechanisms rather than ionic
mechanisms. An interesting demonstration was given by Tobolsky
(Ref. 13) who showed that on irradiation with beta rays a styrene-
methylmethacrylate mixture, the copolymer obtained was the type
expected for a free radical initiated polymerization. Ionic
initiation would have produced almost pure homopolymers.

There are several ways by which free radicals can form from
the primary products of radiation; generally, an excited molecule
is formed, which can be either in a singlet or triplet state.
This can be formed by recombination of the ion-radical and electron:

$$A \longrightarrow A^{\oplus}_{\cdot} + e^{-} \longrightarrow A^{*}$$
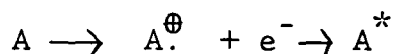
Another possibility is the recombination of the electron
with another molecule to form a negative ion which then combines
with a positive ion:

$$A \longrightarrow A^{\oplus}_{\cdot} + e^{-}$$

$$B + e^{-} \longrightarrow B^{\ominus}_{\cdot}$$

$$A^{\oplus}_{\cdot} + B^{\ominus}_{\cdot} \longrightarrow A^{*} + B^{*}$$
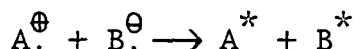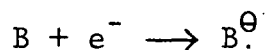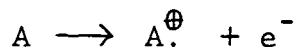
Formation of free radicals results from the decomposition
of the excited molecule, e.g.:

$$(R-R')^{*} \longrightarrow R\cdot + R'\cdot$$

$$(R-H)^{*} \longrightarrow R\cdot + H\cdot$$
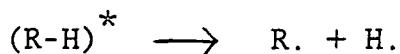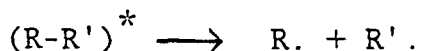
The picture is further complicated because the ions or radicals
themselves may be in an excited state, and produce different
decomposition products. The important point that must be

emphasized is that the lifetime of the ions produced by electron displacement is extremely short, consequently, ionic reactions seldom occur as a result of irradiation.

Chapiro (Ref. 5) classified polymers in two general groups depending on whether the predominant effect of radiation was cross-linking or chain scission (Table 2). However, it should be noted that these two effects are often concurrent and competitive, therefore, clear-cut classifications are impossible. As a general rule, vinyl polymers possessing tertiary carbon atoms in the main chain cross-link as a result of irradiation, whereas vinyl polymers possessing quaternary carbon atoms in the main chain undergo chain scission. This effect is demonstrated by comparing the radiation behavior of polystyrene with polymethylstyrene, and polymethylacrylate with polymethylmethacrylate. This effect is similar to the one already discussed in the case of ultraviolet irradiation (Ref. 1); the lower reactivity of free radicals derived from quaternary carbon atoms was proposed to explain this behavior.

In general, vinyl monomers that have high monomer yields in thermal degradation will degrade by chain-scission upon irradiation, whereas those with low monomer yields will crosslink rather than degrade (ref. 14, 15). The degrading polymers are also those whose monomers have relatively low heats of polymerization (Ref. 16). In addition to the structure with regularly recurring quaternary carbons, the fully halogenated structures (e.g., polytetrafluoroethylene, polychlorotrifluoroethylene) and the monomers with high oxygen content (polyoxymethylene, cellulose) undergo predominant chain-scission by irradiation.

Optical instability (i.e., discoloration) is the most important aspect of radiation damage in thermal control materials

## Table 2

### Crosslinking and Degradation in Irradiated Polymers (Ref.5)

| Crosslinking Polymers | Degrading Polymers |
|---|---|
| Polymethylene (polyethylene) | Polyisobutylene |
| Polypropylene | Poly($\alpha$-methylstyrene) |
| Polystyrene | Polymethacrylates |
| Polyacrylates | Polymethacrylamide |
| Polyacrylamide | Poly(vinylidene chloride) |
| Poly(vinyl chloride) | Cellulose and derivatives |
| Polyamides | Polytetrafluorethylene |
| Polyesters | Polychlorotrifluoroethylene |
| Polyvinylpyrrolidone | |
| Rubbers | |
| Polysiloxanes | |
| Poly(vinyl alcohol) | |
| Polyacrolein | |

for space applications. Production of color is usually ascribed to the formation of multiple conjugated unsaturation or it may be the result of a high concentration of free radicals trapped in the polymer structure.

Formation of volatile by-products is an important phenomenon associated with radiation damage. Most cross-linking polymers, such as polyethylene, polysytrene and polyvinylalcohol, produce hydrogen as the only significant by-product of irradiation, suggesting that cross-linking takes place mainly by elimination of hydrogen between adjacent chains. Degrading polymers generate complex mixtures of volatile by-products whose composition is markedly dependent upon the polymer chemical structure.

As a general rule, polymers containing phenyl groups, either in the main chain or as pendant groups, are more resistant to high-energy radiation than aliphatic polymers. The greater stability is due to the resonance energy of the aromatic structure. Energy from radiation is preferentially absorbed and dissipated by the non-localized $\pi$ electrons. Therefore, the materials having the greater resonance energy have the greater stability towards radiation.

Chapiro (Ref. 5) classified various commercial plastics into twelve groups according to their resistance to radiation damage. This classification is presented in Table III. As expected, the most radiation resistant polymers contain aromatic substituents (groups 1 to 4). Group 12 includes polymers such as Teflon and PMMA that degrade by chain-scission. In the complete absence of oxygen, however, Teflon exhibits better resistance to radiation damage (Ref. 17). Elastomers are also very susceptible to radiation damage. Most rubbers loose their elastic properties for doses of the order of $10^2$ rads (Ref. 5).

Table 3

| Polymer Group | Dose, rads | Observed Changes |
|---|---|---|
| 1. Mineral-filled furan and phenolics | $6.5 \times 10^9$ | Only little darkening in colour |
| 2. Polystyrenes | $6.5 \times 10^9$ | Only little darkening in colour |
| 3. Modified polystyrene | $6.5 \times 10^9$ | Impact strength and elongation decrease to the same value as in unmodified polystyrene |
| 4. Aniline formaldehyde, polyvinylcarbazole | $6.5 \times 10^9$ | Tensile strength decreases a little |
| 5. Polyethylene, nylon | $6.5 \times 10^9$ | Tensile strength increases; impact strength decreases |
| 6. Mineral-filled polyester | $6.5 \times 10^9$ | Tensile strength and impact strength decreases to about 50% |
| 7. Unfilled polyester | $3.3 \times 10^9$ | Tensile strength and impact strength decrease; develop small cracks |
| 8. Phenolics with cellulosic fillers | $2.0 \times 10^9$ | Tensile strength and impact strength decrease; become brittle |
| 9. Melamine and urea formaldehyde | $1.3 \times 10^9$ | Tensile strength and impact strength decrease to about 50% |
| 10. Unfilled phenolics | $6.5 \times 10^8$ | Tensile strength and impact strength decrease to about 50% |
| 11. Poly(vinylidene chloride) poly(vinyl chloride acetate) | $3.3 \times 10^8$ | Soften, blacken, evolve HCl and decrease in tensile strength |
| 12. Casein, poly(methyl methacrylate), Teflon and cellulose derivatives | $6.5 \times 10^7$ | Tensile strength and impact strength decrease to about 50% |

RESISTANCE OF PLASTICS TO RADIATION DAMAGE (Ref. 5)

C6318-8

This effect is particularly pronounced in the presence of oxygen. It has been found that phenyl and other aromatic groups are not only able to dissipate excitation energy without decomposing, but are able to accept energy from alkyl groups, thereby protecting them. This behavior is opposite to the one observed in the case of ultraviolet irradiation.

4.  RADIATION BEHAVIOR OF SPECIFIC POLYMERS

In this section, various polymer structures are reviewed with a discussion of their behavior when exposed to charged particles or ionizing radiation. Particular attention has been given to studies performed in vacuum and to the effect of particulate radiation (protons, electrons) rather than high-energy electromagnetic radiation (X, gamma). Papers that are specifically related to the effect of a simulated space radiation environment on polyfluorocarbons, silicones and polyimides are discussed separately. A literature review on the effects of ultraviolet irradiation was presented in a previous report (Ref. 1).

### 4.1  Polyethylene

The irradiation of polyethylene has received the greatest attention because of the beneficial effects of controlled cross-linking by high-energy radiation. The effects of irradiation depend on whether irradiation is conducted in air or under vacuum. Under vacuum, irradiation results in loss of hydrogen and increase in polymer unsaturation. In air, oxidation also occurs with subsequent appearance of carbonyl structures.

Although the principal volatile product of degradation in vacuum is hydrogen, saturated and unsaturated hydrocarbons are also formed, depending upon the degree of branching of the polymer. Harlen and co-workers (Ref. 18) were able to demonstrate that the hydrocarbon products obtained from a branched polymer were dependent upon the nature of the side groups. The similarity between the radiation behavior of polyethylene and low molecular weight alkanes is indicated by the fact that the average G values for hydrogen formation are 4.1 and 4.6 respectively (Ref. 5). (The G value is the number of chemical events which

result from the absorption of 100 electron volts of energy).
Chapiro (Ref. 5) demonstrated that below the glass transition
temperature (approximately -40°C) $G(H_2)$ is independent of
temperature, whereas above -40°C $G(H_2)$ increases with tempera-
ture. Exactly the same dependence was demonstrated for cross-
linking. This is clearly related to the increased mobility
of the hydrogen atoms and polymer radicals above the glass-
transition temperature.

Koritskii and co-workers (Ref. 19, 20) have demonstrated
the existence in irradiated polyethylene of alkyl radicals which
are possible intermediates in the formation of conjugated double
bonds:

$$\sim CH_2 - \overset{\bullet}{C}H - CH = CH \sim$$
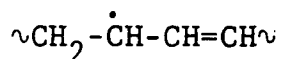
Charlesby and Pinner (Ref. 21) obtained a value of 0.3 for
the ratio of chain-scission to cross-linking in irradiated poly-
ethylene. This indicates that, in spite of the fact that cross-
linking predominates in polyethylene, cleavage of carbon-carbon
bonds also occurs.

Another effect of irradiation is the formation of un-
saturated trans-vinylene structures formed by detachment of an
hydrogen molecule from two adjacent carbon atoms:

$$\sim CH_2 - CH_2 \sim \longrightarrow \overset{H}{\underset{\sim}{\diagdown}} C = C \overset{\sim}{\underset{H}{\diagup}} + H_2$$
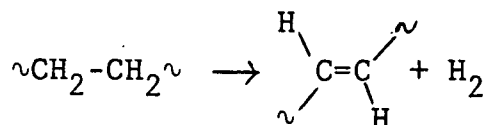
Formation of hydrogen is also involved as a result of cross-
linking:

$$2 \sim CH_2 \sim \longrightarrow \overset{\sim CH \sim}{\underset{\sim CH \sim}{|}} + H_2$$
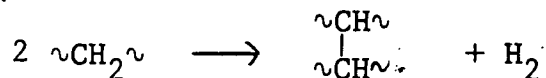
Since formation of hydrogen is associated with both cross-linking and the development of unsaturation, it is expected that:

$$G(H_2) = G(cross\text{-}linking) + G(trans\text{-}vinylene)$$

Charlesby (Ref. 22) found that $G(H_2)$ is slightly larger than expected for this relationship. Chapiro (Ref. 5) suggested that hydrogen may be also produced from intramolecular cyclization, and that this hydrogen accounts for the discrepancy:
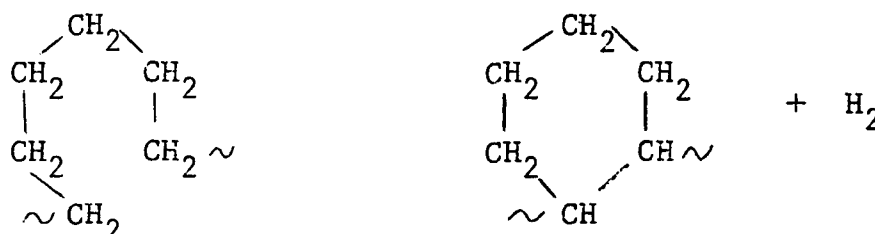


In the presence of oxygen, radiation becomes an initiator of oxidation and results in the formation of carbonyl and carboxyl groups. Peroxides are the primary product of radiation-induced oxidation (Ref. 23).

### 4.2 Polypropylene

Both chain scission and cross-linking are found to occur in irradiated polypropylene in approximately equal amounts (Ref. 76, 77). This is not surprising, in view of the fact that polypropylene has a structure intermediate between poly-ethylene, which predominantly cross-links, and polyisobutylene, which degrades when exposed to radiation.

The most abundant gaseous product is hydrogen, and the second most abundant product is methane (Ref. 78, 79). Traces of higher hydrocarbons with small amounts of CO and $CO_2$ are also found. Formation of hydrogen is accompanied by formation of unsaturation in the polymer, mainly vinylidene group (Ref. 80).

Many studies have been conducted on the ESR spectra of irradiated polypropylene. The predominant type of radical formed at low temperature (-196°C) is most likely one of the following (Ref. 81, 82, 83, 84):

$$-CH_2-\overset{\bullet}{C}-CH_2- \qquad\qquad -CH_2-\overset{|}{C}H-CH_2$$
$$\qquad\ \ |\qquad\qquad\qquad\qquad\qquad |$$
$$\qquad\ \ CH_3 \qquad\qquad\qquad\qquad\ \ CH_2\bullet$$

If the irradiated polymer is allowed to warm to room temperature, or if the irradiation is performed at room temperature, there is a change in the ESR spectrum. These thermally more stable radicals are believed to be allylic radicals having the structures (Ref. 81, 85, 86):

$$-\overset{\bullet}{C}H-CH-C=CH-CH- \qquad\qquad -CH_2-\overset{\bullet}{C}-CH=C-CH_2-$$
$$\quad\ |\qquad\quad\ |\qquad\qquad\qquad\qquad\qquad |\qquad\ |$$
$$\quad\ CH_3\qquad\quad CH_3\qquad\qquad\qquad\qquad CH_3\ \ CH_3$$

## 4.3 Polyisobutylene

Unlike polyethylene and polypropylene, which cross-link, polyisobutylene degrades when subjected to ionizing radiation (Ref. 24, 25), as expected from a structure containing a quaternary carbon atom. A study of the effects of various radiation sources indicates that chain scission is a random process that follows first order kinetics (Ref. 26). The degree of unsaturation increases in proportion to the dose, with formation of 1.87 double bonds/scission. Hydrogen and methane are evolved. Isobutylene monomer formation is small but increases with dosage. The amount of monomer produced by radiation is small compared to that produced by pyrolysis (Ref. 26).

## 4.4 Polystyrene

Although polystyrene is rapidly degraded by ultraviolet light, it is one of the most stable polymers towards high energy radiation, owing to the protective action of the benzene ring (Ref. 27). The protective effect of the aromatic ring can be seen by comparing the rate of cross-linking in polystyrene with polyethylene. The G value for cross-linking in polyethylene is 1.0-2.5 but is only 0.035-0.050 in polystyrene (Ref. 28, 29). Cross-linking of polystyrene occurs to the almost total exclusion of chain-scission.

## 4.5 Poly(α-methylstyrene)

Irradiation with 800 keV electrons causes chain-scission of poly(α-methylstyrene) (Ref. 25). Unlike polystyrene, chain-scission is the main effect in the irradiation of poly(α-methyl-styrene). Once again, it is possible to observe the stabilizing effect of the benzene ring by comparing the G values for chain-

scission of poly(α-methylstyrene) with its aliphatic analog polyisobutylene:

$$\begin{array}{cc}
\overset{\displaystyle CH_3}{\underset{\displaystyle \bigcirc}{-CH_2-\overset{|}{\underset{|}{C}}-}} & \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{-CH_2-\overset{|}{\underset{|}{C}}-}}
\end{array}$$

The G value for chain scission in polyisobutylene is 5 (Ref. 30), while the G value for poly(α-methylstyrene) is only 0.25 (Ref. 31).

## 4.6 Unsaturated Polyhydrocarbons

Elastomers derived from dienes and containing high concentration of unsaturated groups have cross-linking and scission rates that are not greatly different from polyethylene. The G value for crosslinking in natural rubber is 1-1.5 and the scission-to-crosslinking ratio is 0.05-0.10 (Ref. 32). It is uncertain whether cross-linking and chain-scission involve consumption of double bonds. Available data on the rate of disappearance of double-bonds during irradiation of unsaturated polymers such as polybutadiene or natural rubber are in wide disagreement (Ref. 33). There is evidence, however, that polybutadiene saturated by addition of methyl mercaptan is more resistant to irradiation than the unsaturated polymer (Ref. 34).

## 4.7 Poly(methylmethacrylate)

The irradiation of poly(methylmethacrylate) (PMMA) has been extensively investigated, and this polymer was found to be readily degraded (Ref. 25, 26, 35). Alexander and co-workers (Ref. 36) found that degradation is a random chain process and that approximately one ester group was decomposed per each main chain cleavage. Shultz and co-workers (Ref. 37, 38) have

measured changes in molecular weight of 1-mev electron-
irradiated PMMA. Since both weight-average and viscosity-
average molecular weights are linearly dependent on dosage, it
is concluded that no cross-linking occurs during degradation
(Ref. 39, 40). The most peculiar feature of irradiated
poly(methylmethacrylate) is the rapid discoloration, which
deepens from yellow to reddish brown with increasing dose.
This is surprising, in view of the fact that the same polymer
is quite stable to discoloration by ultraviolet irradiation.
The color is uniform throughout the bulk of the polymer and
is stable in nitrogen or vacuum. In air, the color disappears
progressively from the surface throughout the entire sample.
Discoloration appears to be due to a transient species,
most probably free radicals which are trapped within the
solid polymer. The presence of trapped radicals in PMMA was
first suggested by ESR determinations (Ref. 41, 42, 43). The
presence of these radicals is further attested by the ability
of the irradiated polymer to initiate polymerization of mono-
mers (Ref. 44). Wall found that in the solid polymer four
months were required for a 100-fold decay in radical concentra-
tion at room temperature (Ref. 44). Combrisson and Uebersfeld
(Ref. 43) observed a decrease in radical concentration only
after heating to 80°C. Ohnishi and Nitta (Ref. 45) found a
long-lived, heat resistant radical of G=0.16, which has an
activation energy of decay of 28 kcal/mole. The short-lived
radical which is formed by either gamma or electron radiation
at 90°K (G=2.5) has been reported to be $-CH_2-\overset{\bullet}{C}(CH_3)-COOCH_3$
(Ref. 46, 47).

## 4.8  Polyacrylates

Both chain-scission and cross-linking occur when poly-acrylates are exposed to high-energy radiation, cross-linking being the predominant effect.  Various polyacrylates were studied by Shultz and Bovey (Ref. 48).  The value of G(cross-linking) is 0.43-0.57 for all members of the group except the t-butylester, whose value is much lower (0.13-0.16).  Chain-scission appears to follow a molecular mechanism that does not involve free radical formation (Ref. 49).

## 4.9  Polyvinylchloride

When polyvinylchloride is irradiated by high energy radiation, a color change takes place which is associated with the formation of a polyene structure formed by dehydrochlorination (Ref. 50, 51, 52):

$$\sim CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}-CH_2-\underset{\underset{Cl}{|}}{CH}\sim \longrightarrow \sim CH=CH-CH=CH-CH=CH\sim \qquad +HCl$$
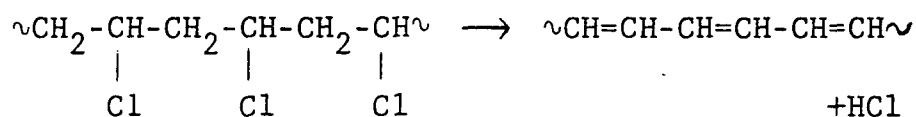
This reaction is similar to the one produced by thermal degradation and by ultraviolet irradiation.

Both cross-linking and chain-scission occur by high-energy irradiation (Ref. 24, 25, 50, 53).  An initial decrease in molecular weight and tensile strength is followed by an increase in these properties.  At higher doses, insolubilization due to cross-linking takes place.  G(cross-linking) is independent of temperature below the glass-transition temperature (80°C), but increases with temperature above the Tg.  The deterioration of polyvinylchloride upon exposure to ionizing radiation is greater in air than in vacuum (Ref. 3).

## 4.10  Polyvinylalcohol

Polyvinylalcohol is cross-linked by ionizing radiation in nitrogen whereas chain scission predominates in the presence of air (Ref. 54). The rate of carbonyl group formation upon irradiation depends upon the rate of chain scission. It appears that scission and cross-linking mainly occur at 1,2-glycol groups incorporated in the polymer during polymerization.

## 4.11  Fluorocarbon Polymers

Polytetrafluoroethylene (PTFE) as well as other fluorocarbon polymers undergo chain scission when exposed to ionizing radiation (Ref. 25, 55, 56). The rapid deterioration of PTFE as a result of irradiation is in striking contrast to its great chemical and thermal stability. Because of the high insolubility of PTFE, the radiation damage has not been studied in terms of molecular weight changes such as osmometry, light scattering or solution viscometry. Other techniques have been used, such as determination of changes in mechanical properties, spectroscopic studies by ESR and NMR, and analysis of gas evolution.

By analogy with polyethylene, which liberates molecular hydrogen in high yield by irradiation, one might expect to find fluorine gas in the irradiation products of PTFE. However, fluorine formation is negligible. Calculations of the energetics of fluorine abstraction and cross-linking in PTFE show that these processes are highly endothermic and unlikely to occur (Ref. 57, 58.).

High energy irradiation causes an increase in the crystallinity of PTFE, as demonstrated by measurements of specific volume (Ref. 59), density and infrared studies (Ref. 60), and X-ray diffraction measurements (Ref. 61). Pinkerton and Sach (Ref. 62) found that the increase in crystallinity is greater in air than in vacuum . The increase in crystallinity is

interpreted on the basis of chain degradation which lowers the molecular weight and increases the ability of the chains to crystallize.

The most noticeable effect of chain scission in PTFE is the loss in mechanical strength. Mechanical strength measurements at various radiation doses were reported by Wall and Florin (Ref. 63) and more recently by Hedvig (Ref. 64). Hedvig's data are shown in Table 4 and indicate a pronounced deterioration at relatively low radiation doses. Although chain scission is the predominant effect of irradiation, changes in tensile properties in the early stages of irradiation indicate that some cross-linking may also take place (Ref. 63). $CF_4$ and saturated fluorocarbons up to 6 carbon atoms were identified by analysis of the gases obtained by irradiation under vacuum. In oxygen, $CF_2O$ was also identified (Ref. 65).

All the studies of ESR spectra of irradiated PTFE show a 10-line spectrum attributed to the radical $\sim CF_2-\overset{\bullet}{C}F-CF_2\sim$ (Ref. 56, 66, 67). This radical combines readily with oxygen (Ref. 67). This combination may be reversed upon heating (Ref. 66).

An important ESR study is that of Hedvig (Ref. 64). Hedvig points out that the in-chain free radicals $-\overset{\bullet}{C}F-$ in irradiated PTFE are stable up to 150°C and that terminal $-CF_2\cdot$ radicals (formed by irradiation under vacuum followed by ultraviolet exposure) are stable up to at least 100°C. Besides the evidence for free radicals, there is some indication of the existence of ionic species in irradiated PTFE, such as a temporary increase in electrical conductivity during irradiation of PTFE (Ref. 2, 68, 69). Although ions may play some role in fluorocarbon radiation chemistry, the radiation chemistry of this polymer is generally interpreted in terms of free radical

TABLE 4

Mechanical Strength and Elongation at Break of Irradiated
PTFE Film*

| Treatment | Dose (Mrad) | Mechanical Strength (kg cm$^{-2}$) | Elongation at break (%) |
|---|---|---|---|
| Untreated | 0 | 269 ± 15 | 129 ± 30 |
| Irrad. in vacuo, measured in air | 10.4 | 136 ± 7 | 10 ± 2 |
| Irrad. in vacuo, oxidized, illuminated with UV light (Hg arc) | 10.4 | 122 ± 5 | 0.4 |
| Irrad. in air | 10.4 | 0 | 0 |

*Film thickness, 0.04 mm.  Data of Hedvig (Ref. 64).

mechanisms (Ref. 56).

Polychlorotrifluoroethylene (PCTFE) behaves upon irradiation in a manner quite similar to PTFE (Ref. 53, 55, 56). Chain scission takes place with no evidence of cross-linking. Very low yields of saturated fluorocarbons are evolved during vacuum irradiation (Ref. 56). The infrared analysis of vacuum irradiated PCTFE shows the presence of double bonds; in air, infrared analysis shows the presence of carbonyl, carboxyl and hydroxyl groups (Ref. 70). ESR studies of PCTFE indicates no detectable radicals in vacuum (Ref. 71).

The copolymer tetrafluoroethylene-hexafluoropropylene degrades by chain scission upon irradiation, in a manner similar to PTFE (Ref. 56). Lovejoy and co-workers (Ref. 72) obtained evidence of cross-linking by melt-viscosity measurements. They found that if irradiation is conducted below the glass transition temperature (80°C), the melt viscosity decreases with increasing radiation dose; above the glass transition temperature, the melt viscosity increases with increasing radiation dose.

It is interesting to note that fluorocarbon polymers containing hydrogen, such as polyvinylfluoride, are found to cross-link by irradiation (Ref. 73, 74, 75). HF evolution has been observed upon vacuum irradiation (Ref. 56).

### 4.12 Polyamides

Aliphatic polyamides such as Nylon 66 become cross-linked with high energy radiation (Ref. 87, 88). When aliphatic polyamides are subjected to high-energy irradiation, formation of free radicals occurs as a result of removal of hydrogen from the carbon adjacent to the amide nitrogen (Ref. 89, 90, 91, 92). The most convincing evidence is obtained from ESR spectroscopy of irradiated samples.

Analysis of the gaseous products of irradiation of poly-
amides have shown that $CO_2$, CO, $H_2$ and $CH_4$ are formed, with $H_2$
as the main product. Production of a transient color by irradia-
tion has been associated with the accumulation of free radicals
(Ref. 92). The color may be yellow, red or blue depending
upon the polyamide structure.

The high degree of specificity in the free radical forma-
tion is ascribed to a concentration of energy in the vicinity
of the amide group prior to the elimination of the α-proton.
Other types of radicals, if they are formed, are expected to
disappear in favor of the α-radical by hydrogen transfer reac-
tions. This evidence is supported by experiments on free radical
production as a result of mechanically induced degradation.

The rate of free radical decay decreases with increasing
the crystallinity of the irradiated polyamide (Ref. 93). As
expected, aromatic polyamides are much more stable to high
energy irradiation than aliphatic polyamides. The greater
stability is demonstrated by comparing the yield of gaseous
products obtained by irradiation of the polyamide from
m-xylylenediamine and adipic acid (Ref. 94) and the polyamide
from m-phenylenediamine and isophthalic acid (Ref. 95).

4.13 Polysulfones

The radiation stability of the polysulfone derived from
bisphenol A and 4,4-dichlorodiphenylsulfone is remarkably
high (Ref. 96):
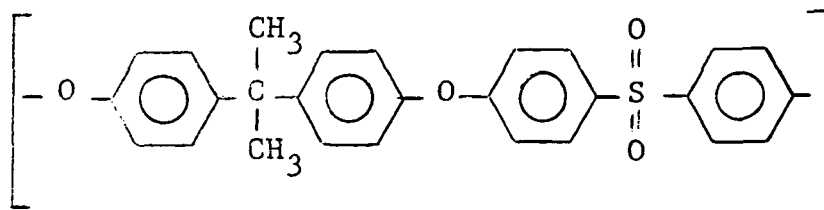
Measurements of gel formation and solution viscosity of irradiated samples indicate that cross-linking and chain scission occur at nearly equal rate.  The high radiation stability of the aromatic polysulfones is in great contrast with their poor ultraviolet stability (Ref. 97, 98), demonstrating once again the protective influence of the benzene ring toward high energy radiation.

Irradiation of the model compound diphenylsulfone results almost exclusively in the elimination of sulfur dioxide and a comparable formation of diphenyl (Ref. 99).  Sulfur dioxide is also the main decomposition product of $\gamma$-irradiated aromatic polysulfones.  $RSO_2$. radicals have been detected by ESR analysis of irradiated sulfones and polysulfones (Ref. 100).

4.14. Polyesters

The transmission of polyethyleneterephthalate decreases as a result of irradiation over a wide wavelength range up to 5200$\overset{o}{A}$ and discoloration occurs.  Partial bleaching is observed on exposure to air, therefore, a distinction has been made between transient and permanent components which are said to make comparable contributions (Ref. 101).  It has been suggested that the permanent component is due to polyphenyl groups (Ref. 102).  Differences between optical density for samples irradiated and maintained in air (to eliminate the transient component) and unirradiated controls revealed a poorly defined maximum at 3250$\overset{o}{A}$ (Ref. 101).

There have been conflicting reports concerning changes in infrared absorption resulting from electron irradiation.  In one case a spectrum was presented covering the range 2-15$\mu$ . in which the only significant change, after a dose of 2000 Mrad was a decrease in absorbance near 2.82$\mu$ which was ascribed to a

decrease in hydroxyl end-groups (Ref. 103). In other experiments, extensive changes were observed after the same dose and throughout the range 4-15μ, which were attributed to a decrease in crystallinity and formation of polyphenyl systems (Ref. 102). Increased absorption near 3.05μ can be assigned to the formation of carboxyl groups (Ref. 104).

The main gaseous products formed during irradiation are $CO_2$, $CO$, $H_2$ and $CH_4$ (Ref. 103, 105). The ESR signals of crystalline samples of irradiated polyethyleneterephthalate have been ascribed to the following radicals (Ref. 106):

I    (95%)
$$-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-O-\overset{\bullet}{C}H-CH_2-$$

II    (5%)
$$-\langle\bigcirc\rangle-\overset{\bullet}{}$$
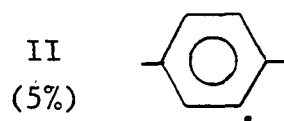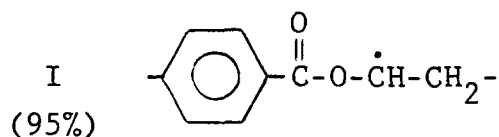
Amorphous samples of PET yield a poorly resolved ESR spectrum. Its features are consistent with radical II but inconsistent with radical I (Ref. 107).

### 4.15 Polysiloxanes

The radiolysis of polydimethylsiloxane causes cleavage of silicon-carbon and carbon-hydrogen bonds:

$$
\begin{array}{c}
CH_3 \\
| \\
\sim Si-O\sim \\
| \\
CH_3
\end{array}
\nearrow
\begin{array}{c}
CH_2\cdot \\
| \\
\sim Si-O\sim \;+\; H\cdot \\
| \\
CH_3
\end{array}
$$

$$
\searrow
\begin{array}{c}
\bullet \\
\sim Si-O\sim \;+\; CH_3\cdot \\
| \\
CH_3
\end{array}
$$
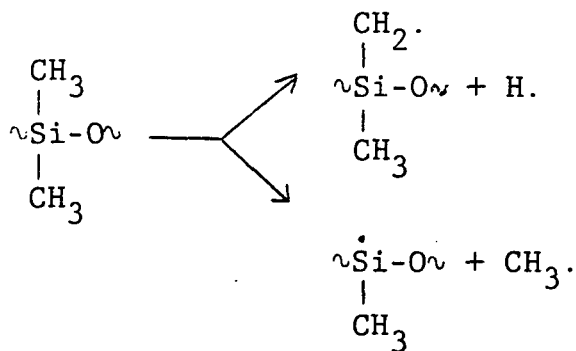
The radicals formed may react further with formation of three types of cross-links:

```
                                            CH
                                            | 3
2 ~Ṡi-O~                                   ~Si-O~
    |                  ───→                  |
   CH3                                      ~Si-O~
                                            |
                                           CH3
```

```
                        CH2·              ~Si-O~
                        |                  |
 ~Ṡi-O~    +    ~Si-O~        ───→         CH2
    |                |                      |
   CH3              CH3                    ~Si-O~
```

```
                                   CH3
                                   |
    CH2·                          ~Si-O~
    |                              |
2 ~Si-O~          ───→            CH2
    |                              |
   CH3                            CH2
                                   |
                                  ~Si-O~
                                   |
                                  CH3
```
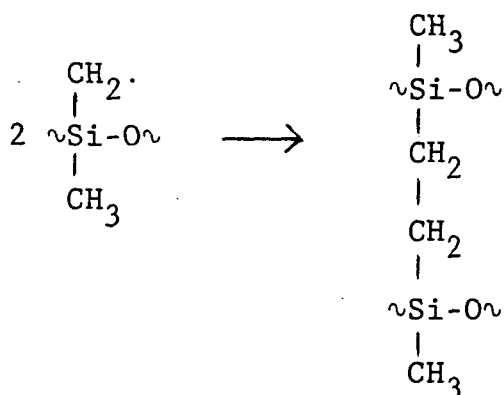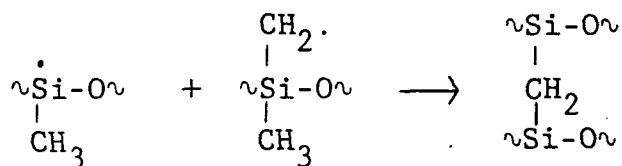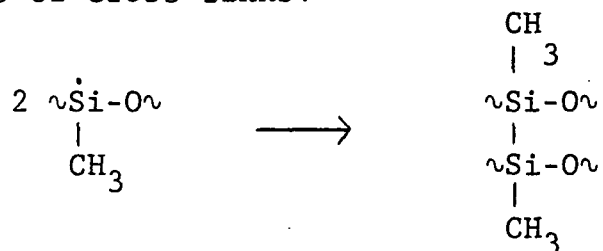
Electron irradiation at 25°C produces the cross-linked groups in the ratio 1/2/0.5 respectively for $\equiv$Si-Si$\equiv$, $\equiv$Si-CH$_2$-Si$\equiv$, and $\equiv$Si-CH$_2$-CH$_2$-Si$\equiv$ (Ref. 108). A similar ratio was obtained by irradiation of the model compound $(CH_3)_3$Si-O-Si$(CH_3)_3$, but the yields were lower.

Hydrogen, methane and ethane are formed by the recombination of H· and CH$_3$· radicals. They are the main gaseous products evolved during irradiation (Ref. 108, 109). Measurements of the effect of radiation intensity and temperature suggest that H· and CH$_3$· radicals may also abstract hydrogen from the polymer and promote formation of new radical species.

Partial substitution of phenyl groups for methyl groups in the polysiloxane chain increases the radiation stability in terms of both gas evolution and cross-linking. Protection of the radiation sensitive methyl group is increased when phenyl and methyl groups are attached to the same silicon atom (Ref. 110).

A comparison of the radiolysis and photolysis of polydimethylsiloxane (Ref. 111, 112, 113) and polyphenylmethyl siloxane (Ref. 114, 110) clearly indicates that presence of phenyl groups decreases ultraviolet stability whereas radiolytic stability is increased.

5. SPACE SIMULATION STUDIES OF CHARGED PARTICLE EFFECTS ON
CLEAR POLYMERS

Silicones, polyimides and fluorocarbon polymers are the
materials that have received the greatest attention in space
applications. Some recent works dealing with the effects of
charged particles radiation on these materials will be reviewed
here. These studies are concerned with space applications such
as solar cell covers, adhesives, clear (non-pigmented) coatings,
and second-surface mirrors.

## 5.1 Fluorocarbon Polymers

Fogdall and co-workers (Ref. 115) reported that metallized
FEP Teflon resists reflectance degradation from electron exposure
until fluences greater than $10^{15}$ electrons/cm$^2$ are reached. All
six varieties studied are altered significantly by exposure to
$10^{16}$ 80-keV electrons/cm$^2$. The Teflon loses its transparent
nature and acquires a crazed, mottled gray appearance. This
changes the coatings' specular quality to a rather diffuse
appearance. Substantial solar absorptance changes result, and
reflectance degradation is observed across the entire 0.25- to
2.5-µ wavelength region measured, in all six Teflon coatings
studied. Exposure to 20-keV electrons causes less extensive
degradation, both in amount and wavelength region affected.

Cunningham and co-workers (Ref. 116) studied the effect of
ultraviolet irradiation and charged particle bombardment on
bare and metallized FEP Teflon films. The metallized FEP films
were: (a) ultraviolet irradiated in vacuum and oxygen; (b)
irradiated with 5,10,25 and 30 keV electrons and protons; and
(c) exposed to simultaneous ultraviolet-proton and ultraviolet-
electron bombardment. The charged particle irradiations indicate
that a measurable change occurs in the spectral reflectance of
both silver and aluminum backed material at a dose of about

$1x10^{15}$ particles/cm$^2$, and that this degradation increases as the total dose is increased. This spectral reflectance change appears first and is the most pronounced in the ultraviolet for a given total dose. At a total dose of $1x10^{16}$ particles/cm$^2$ the surfaces generally look cloudy and oftimes mottled. Upon closer examination this mottling is found to be due to the presence of Litchenberg figures within the teflon-especially in the case of electron irradiation-which are caused by charge storage and subsequent electric discharge. The ultraviolet results confirm that silver coated teflon is stable when irradiated in vacuum and indicate that aluminum coated material undergoes a small decrease in integrated solar absorptance (i.e., an improvement) when so irradiated. Combined ultraviolet and 20 keV protons tend to retard the damage that occurs with protons alone. However, the 5 keV data do not support such a conclusion.

Schutt (Ref. 117) studied the effect of 30 keV electrons on FEP. Photomicrographs show the presence of Lichtenberg patterns, bubbles and a buckling effect. These effects are discussed in terms of an "electrolysis" mechanisms resulting from charge storage and beam energy thermalization. Expressions are given for surface charge storage and voltage across the sample resulting from such charge accumulation. Buckling is treated on a thermodynamic basis using the Helmholtz free energy and assuming that the distortion develops isothermally. The usefulness of optical measurements for the study of electron damage is questioned. While irradiation with 2-30 keV protons gives reproducible data, irradiation with electrons does not give a degradation sufficiently uniform for optical measurements.

Heaney (Ref. 118) performed optical measurements on aluminum-coated and silver-coated FEP films of various thickness. The data indicate the dependence of solar absorptance and emittance on the Teflon film thickness and the reflectance of the metal underlayer. A correlation between the type of metal used as the reflective coating and the magnitude of radiation - induced degradation shows that Ag-coated Teflon films are less sensitive to damage than aluminized films.

## 5.2 Polyimides

Reflectance degradation in a 2-mil film of Type H Kapton backed by aluminum is strongly dependent upon electron energy. (Ref. 115). The 20-keV electron results are characterized by a peaking of degradation at a wavelength of approximately 0.54µ. The 50-keV electron results and 80-keV electron results show maximum degradation at a wavelength of approximately 0.60µ. For a fluence of $10^{15}$ electrons/cm$^2$, 50-keV degradation is some six times the 20-keV degradation, whereas 80-keV degradation is some eight times that at 20-keV.

## 5.3 Silicones

Pellicori studied the optical properties (Ref. 119) and the radiation stability (Ref. 120) of various silicone bonding agents. Fused silica discs bonded with 0.06-mm layers of various silicone elastomers were subjected to dosages between 1 and 2x10$^6$ rad of 10 MeV electrons. The transmittance of the samples was determined before and after exposure. The best material in terms of radiation stability, low outgassing and thermal shock resistance was DC93-500.

The effects of charged particle irradiation on various silicone encapsulating polymers has been investigated (Ref. 121). Results of irradiation with 2.7 MeV electrons for fluences of $3 \times 10^{16}$ electrons/cm$^2$ show that the most stable of the polymers tested are Sylgard 182 and RTV-615.

The outgassing behavior of silicones in a high-vacuum environment and the characterization of volatile products by liquid-gas chromatography has been reported (Ref. 122, 123).

# 6. ULTRAVIOLET IRRADIATION STUDIES: MATERIALS AND APPROACHES

## 6.1 General Approach

During the previous program, contract NAS1-12549 (Ref. 1), a literature search was conducted on the effects of ultraviolet radiation on polymeric materials, with particular emphasis on mechanisms of degradation and energy transfer phenomena. The various modes by which a polymer dissipates absorbed ultraviolet energy are the following:

$$A + h\nu \longrightarrow A^* \begin{cases} A + h\nu' \text{ (emission)} \\ A + \text{heat (radiationless decay)} \\ C^* \text{ (change of excited state)} \\ B^* + A \text{ (energy transfer)} \\ \text{Chemical reaction} \end{cases}$$
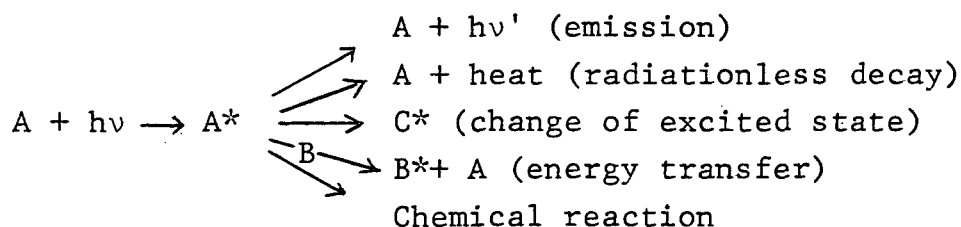
Polymer stability to ultraviolet radiation requires one of the following conditions: (a) ultraviolet transparent structure; (b) structure capable of completely dissipating absorbed ultraviolet energy by non-chemical methods; (c) structure capable of completely dissipating absorbed ultraviolet energy by a chemical rearrangement that does not involve chain cleavage or other undesirable degradative effect.

In the design of an experimental program aimed at the development of materials with improved stability to the ultraviolet radiation environment of space, we have given special consideration to the following basic approaches: (1) preventing energetically favored photodegradation mechanisms (e.g., Norrish Type II) by appropriate polymer structural modifications; and (2) utilizing mechanisms by which ultraviolet absorbed energy is effectively dissipated, namely, fluorescence, radiationless decay, energy transfer to acceptor molecules, and photorearrang-

ments not involving homolytic cleavage. Therefore, we have studied the feasibility of these approaches and we have initiated an experimental program aimed at verifying the applicability of these concepts to the development of ultraviolet-stable polymer structures. The approaches considered and the rationale for selection of polymer structures for ultraviolet testing are described in the following paragraphs.

## 6.2 Photorearrangements of Polymer Structures

An unconventional approach to the problem of ultraviolet stabilization involves the use of structures capable of dissipating absorbed ultraviolet energy by a photo-induced re-arrangement. The chemical rearrangement produced should not be accompanied by cleavage reactions and should not have appreciable effect on the physical and optical properties of the polymer. Along this line of thought, we have reviewed the available literature on the photo-Fries reaction to determine whether this type of rearrangement can be effectively utilized to dissipate absorbed ultraviolet energy in polymer structures. The photo-Fries rearrangement of aromatic polyesters and polycarbonates does not produce chain cleavage. Furthermore, it leads to the formation of a o-hydroxybenzophenone structure that may further stabilize the polymer against photolytic degradation. The Fries rearrange-ment of aromatic polyesters has been described by Maerov (Ref. 124), Rode and co-workers (Ref. 125), Cohen and co-workers (Ref. 126):
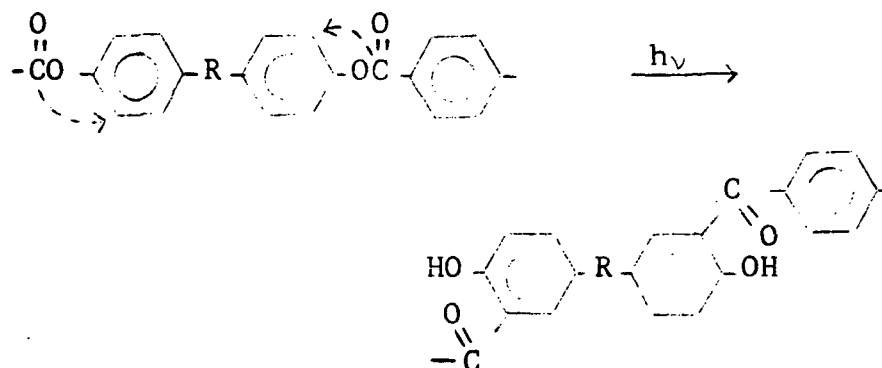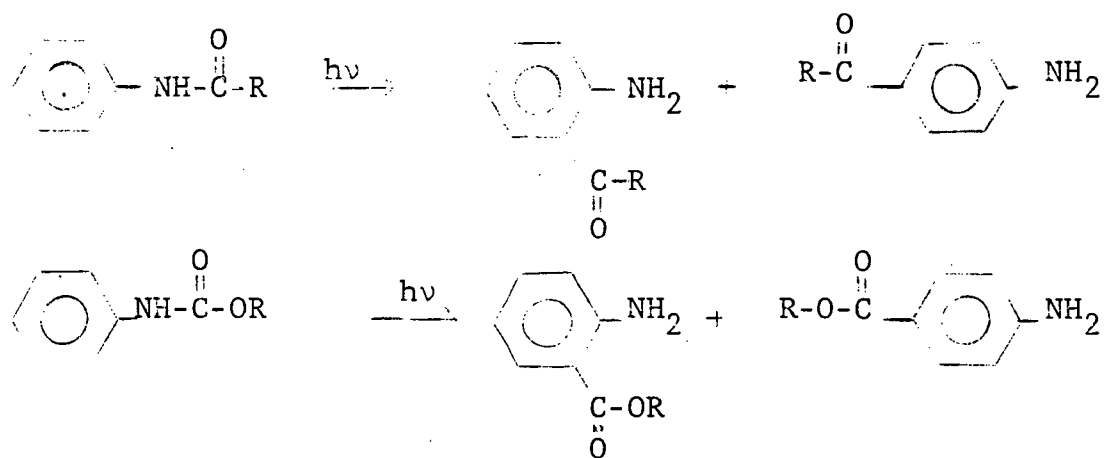
The Fries rearrangement of aromatic polycarbonates has been described by Bellus and co-workers (Ref. 127) and Mullen and co-workers (Ref. 128). It involves a stepwise rearrangement to dihydroxybenzophenone via a phenylsalicylate structure:
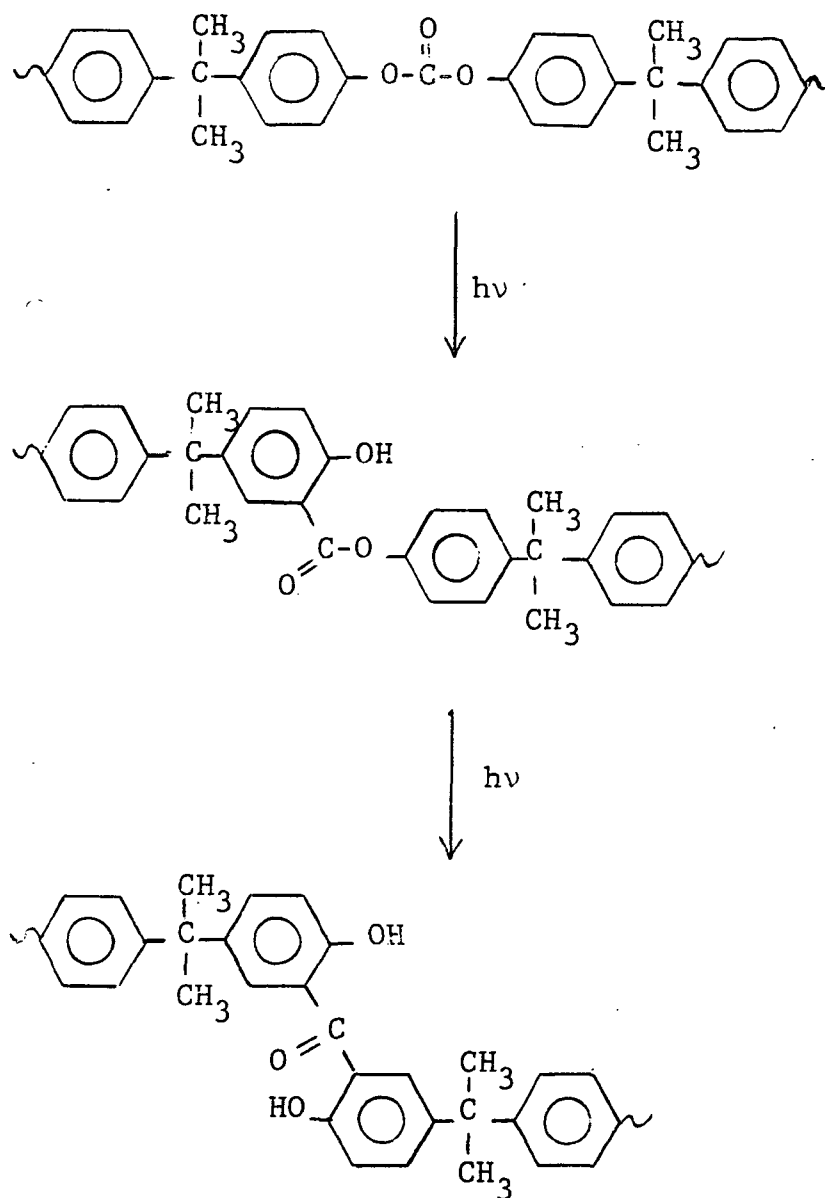
The rearrangement follows essentially the same mechanisms as the photo-Fries of simple organic molecules, such as the rearrangement of phenylacetate into o-and p-hydroxy benzophenone (Ref. 129). In the case of the polyesters and polycarbonates previously mentioned, the para position is occupied and the rearrangement takes place exclusively in ortho.

Photo-Fries rearrangements are also known to occur with N-phenyl substituted amides (Ref. 130) and urethanes (Ref. 131):



Carlsson and co-workers (Ref. 132) proposed that the photolysis of Nomex (aromatic polyamide) involves a similar Fries-rearrangement. Two mechanisms are possible:
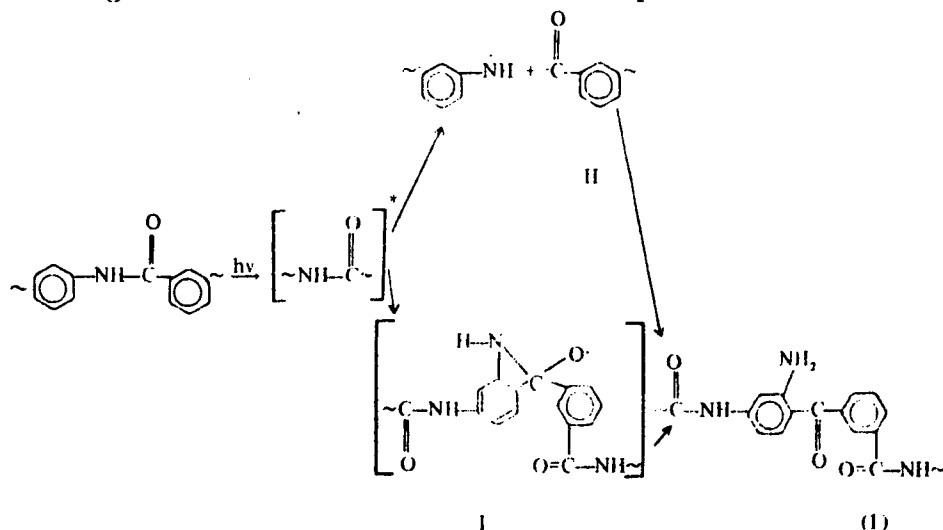
From all the examples reported in the literature it appears that, in conjunction with the Fries rearrangement, other secondary degradative processes occur that lead to cleavage or discoloration. In the case of aromatic polyesters, it has been reported that the Fries rearrangement produces a UV screening effect that protects the substrate (Ref. 126). Unfortunately, surface yellowing occurs (Ref. 124). Therefore, on the basis of the information available from the literature, it is questionable whether the Fries rearrangement constitutes a feasible approach to the problem of polymer stabilization, particularly when stability of optical properties is a critical requirement.

In order to clarify the effect of cleavage reactions and Fries rearrangements in the irradiation of aromatic esters, amides and carbonates, we initiated an ESR study on the following model compounds:
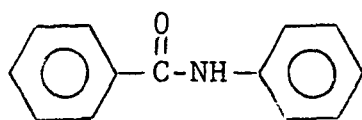
benzanilide
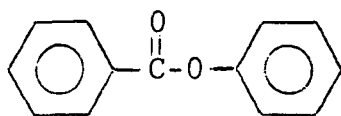
phenylbenzoate
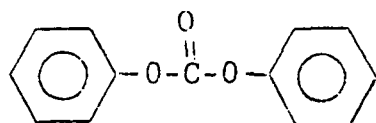
diphenylcarbonate

These model compounds represent the structure of fully aromatic polyamides, polyesters and polycarbonates. Diphenylcarbonate is the only compound examined so far. A sample of this material, previously recrystallized three times from methanol, was placed in a 4mm O.D. quartz ESR sample tube. A piece of rubber tubing and a stopcock were fitted over the opening. The tube was evacuated and sealed via the stopcock. The sample was investigated by ESR at liquid nitrogen temperature using a cold

finger dewar inserted into the ESR sample cavity. The ESR
sample cavity contained an irradiation "window" which allowed
66% of the incident radiation to pass. The irradiation at
2537Å was provided by an Oriel Hg-Ar pen lamp placed immediately
outside the cavity approximately 2.5cm from the sample. Irradia-
tion failed to produce an ESR signal. Irradiation was performed
at 300°K, at 77°K and from 760 torr to as low as $10^{-7}$ torr pres-
sure. No ESR spectra were observed under these conditions.

For comparison purpose, bisphenol-A polycarbonate was
irradiated under the same conditions. The material employed was
"Lexan" previously purified by repeated precipitation from
methylene chloride solution into methanol. No ESR signal was
obtained by irradiation of this material. Finally, bisphenol-A
polycarbonate was irradiated at 77°K and 0.025 torr for 1.5 hr with
an OSRAM 500 watt point source. The energy output of this lamp
is primarily in wavelengths greater than 3000Å. The ESR spectrum
obtained is shown in Fig. 1. The large broad symmetric resonance
can be assigned to a radical species in which the unpaired electron
is localized on a carbonyl group. A possible route of formation is:
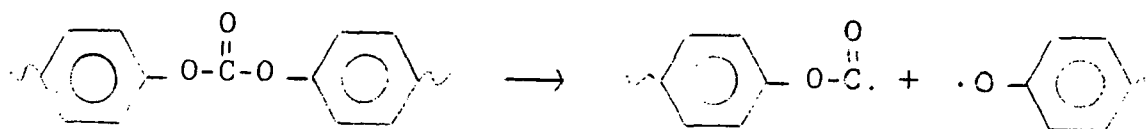


The sharp line overlapping the lower half of the spectrum is due
to free electrons which result from the irradiation of the quartz
tube and dewar assemblies. It is surprising that irradiation of
Lexan for up to 29 hr with the 2537Å lamp produced no signal,
while irradiation with the less energetic OSRAM lamp for only
15 hr produced an ESR signal. Apparently, the damage to poly-
carbonate which results in the formation of low temperature
stable free radicals is wavelength dependent. The effect of
longer wavelength irradiation ( 3000Å) on the model compound
diphenylcarbonate has not been determined. Bisphenol-A poly-
carbonate, purified by reprecipitation, was included in an
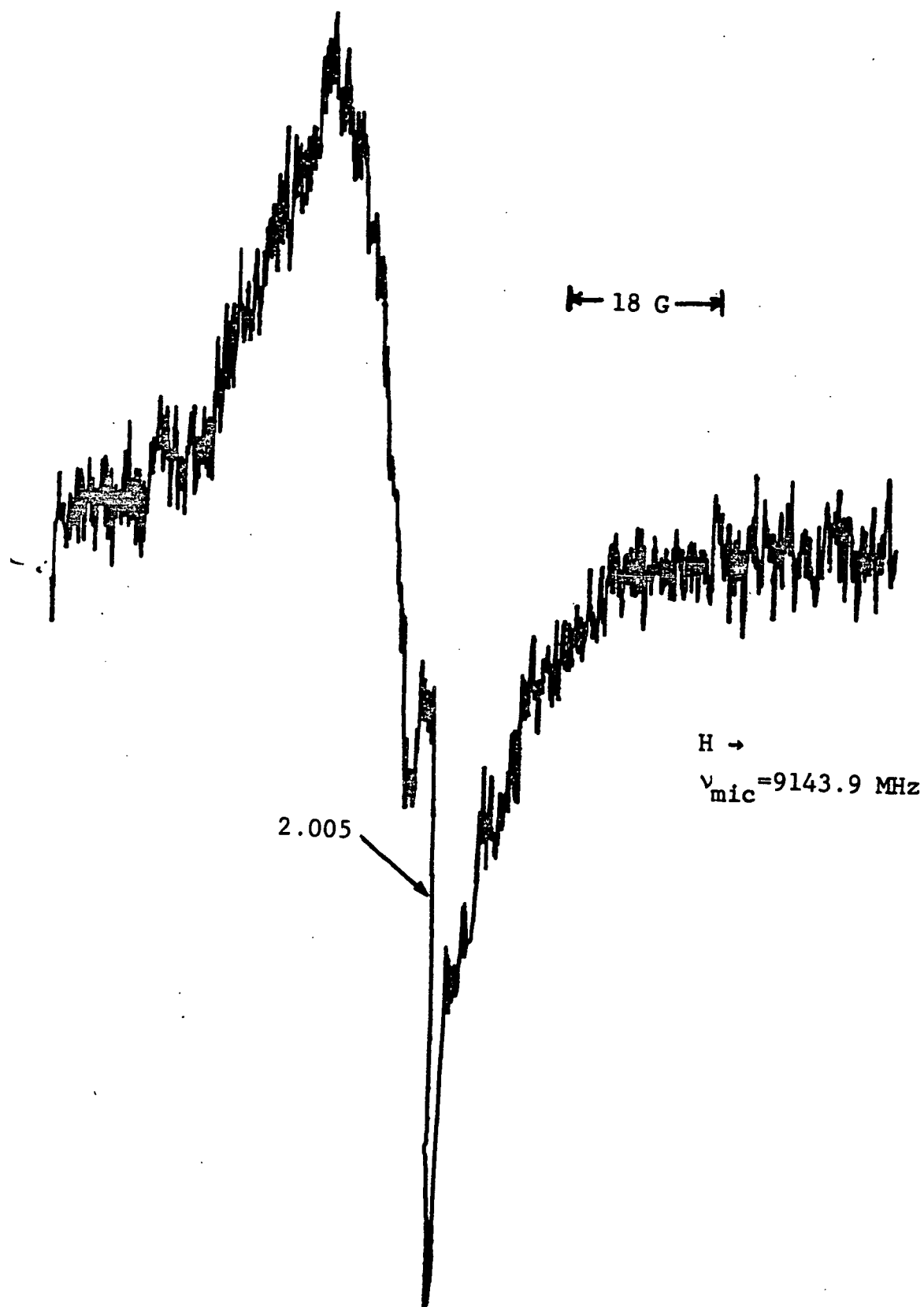ultraviolet exposure test in the IRIF space simulation facility.

Figure No. 1  ESR SPECTRUM OF ULTRAVIOLET IRRADIATED
POLYCARBONATE

39                                        C6318-8

## 6.3 De-excitation of Absorbed Energy

This approach involves the development of a polymer structure capable of dissipating absorbed ultraviolet energy without producing a chemical change. The general modes by which a photoexcited molecule may return to the ground state were discussed in the previous report (Ref. 1). Ultraviolet stabilization may result from three general mechanisms of energy dissipation: (1) quenching of the polymer excited state by energy transfer to acceptor molecules; (2) de-excitation by radiationless decay (emission of heat); (3) de-excitation by fluorescence or phosphorescence. These mechanisms will be reviewed in the following paragraphs.

### 6.3.1 Triplet Quenching by Energy Transfer

A typical example of this approach is the use of naphthalene (either as additive or copolymerized vinylnaphthalene) for quenching the excited triplet state of aromatic vinyl polymers, such as polystyrene (Ref. 133, 134, 135), polyvinylketone (Ref. 136, 137), or polyvinylbenzophenone (Ref. 138). However, this approach is limited to excited polymer molecules in the triplet-state, such as aromatic vinyl polymers, and does not have a general applicability.

### 6.3.2 Radiationless Decay

This approach involves the use of a polymer structure capable of reverting from the photo-excited state to the ground state by radiationless transitions. Since this is the mechanism of action of conventional ultraviolet stabilizers, the same concepts that are applicable to the design of ultraviolet stabilizer additives are also applicable to the design of a poly-

meric material possessing the structural characteristics of a
ultraviolet stabilizer incorporated into the polymer molecule.

We found several examples in the literature concerning the
use of reactive ultraviolet stabilizers. Unlike conventional
ultraviolet stabilizers, these are reactive vinyl and acrylic
compounds capable of copolymerizing with conventional monomers
to form ultraviolet stable copolymers. These compounds are
generally characterized by the presence of an o-hydroxy group
capable of forming an intramolecular six-membered hydrogen-
bonded ring capable of deactivating the excited state through
a radiationless transition so that the energy is given up in the
form of harmless heat. It has been reported that these reactive
ultraviolet stabilizers overcome the many problems of conven-
tional ultraviolet stabilizers (e.g., volatility, extractability,
migration, incompatibility, decomposition during processing).
Fertig (Ref. 139) reported the use of salicylates as comonomers:

$$CH_2=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-CH_2 \text{—} \overset{O}{\|} \text{C-O—}$$
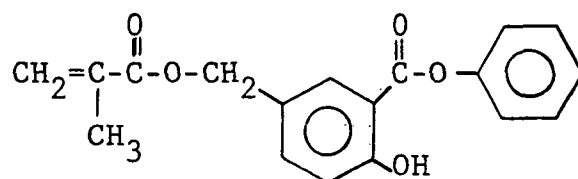
Copolymers of 2% of this material with vinylacetate or vinyl-
chloride provide effective ultraviolet stabilization.

Another example is the use of monomers containing hydroxy-
benzophenone (Ref. 140):

$$\text{—}\overset{C}{\underset{O}{\|}}\text{—}\text{—}O-CH_2-\underset{\underset{OH}{|}}{CH}-CH_2-O-\overset{\overset{O}{\|}}{C}-CH=CH_2$$
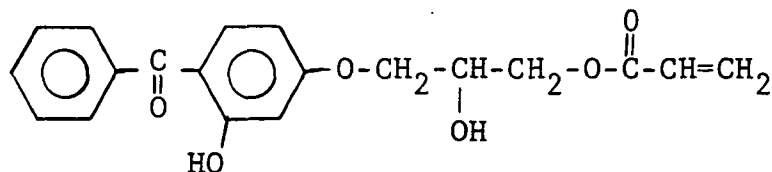
This compound was (a) homopolymerized and blended with PVC,
polyvinylacetate, polyvinylidene chloride, polystyrene, poly-
methyl · methacrylate; (b) copolymerized with the same monomers.
Effective ultraviolet stabilization was observed.

Other examples of ultraviolet absorbing salicylate comonomers are found in the patent literature (Ref. 141):
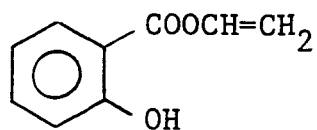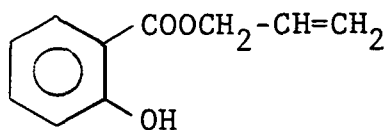


There are more examples in the patent literature of ultraviolet absorbing o-hydroxybenzophenone comonomers (Ref. 142, 143, 144, 145):
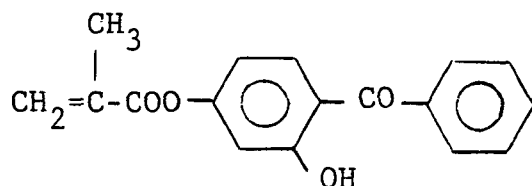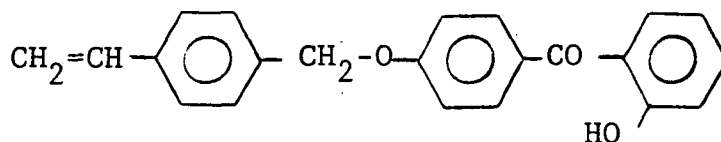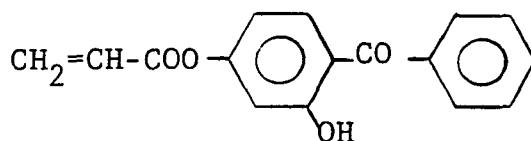


Comonomers containing o-hydroxyphenylbenzotriazole have also been reported (Ref. 146, 147):

C6318-8
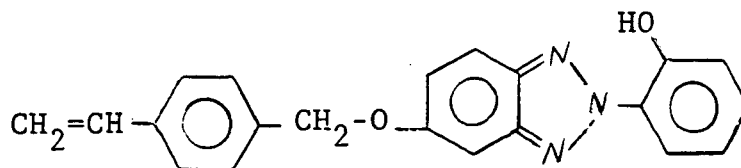
A number of patents cover the use of o-hydroxyphenyl tria-
zine derivatives as ultraviolet stabilizers (Ref. 148):

$$R - \underset{N \diagdown \diagup N}{\overset{N}{\underset{\underset{\underset{X}{\phantom{X}}}{OH}}{\bigcirc}}} - R$$
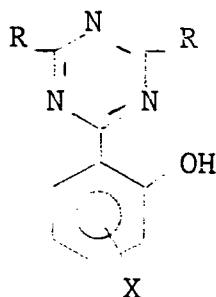
Surprisingly, there is no reference in the literature to the
use of monomeric compounds containing the o-hydroxyphenyltriazine
structure for the synthesis of ultraviolet stable polymers.
Therefore, we decided to investigate the feasibility of using
o-hydroxybenzoguanamine (o-hydroxyphenyldiaminotriazine) as a
reactive intermediate:

$$H_2N - \underset{N \diagdown \diagup N}{\overset{N}{\underset{\bigcirc}{OH}}} - NH_2$$
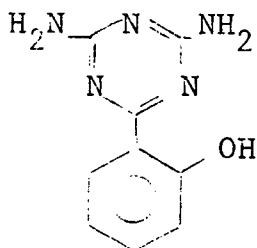
This intermediate is particularly interesting because of its
similarily with benzoguanamine, that forms aminoplastic resins
by reaction with formaldehyde. Thus, we synthesized o-hydroxy-
benzoguanamine that was subsequently utilized as a monomer for
the synthesis of aminoplastic resins:

$$H_2N\text{—triazine—}NH_2 \; (\text{with } N, N, N \text{ ring, C-aryl}) \quad + \quad CH_2O \quad \longrightarrow \quad (HOH_2C)_2N\text{—}\overset{}{}\text{—}N(CH_2OH)_2$$

$$\downarrow$$

$$-CH_2\text{-}N\text{—}\overset{CH_2}{}\text{—}N\text{-}CH_2\text{-}$$
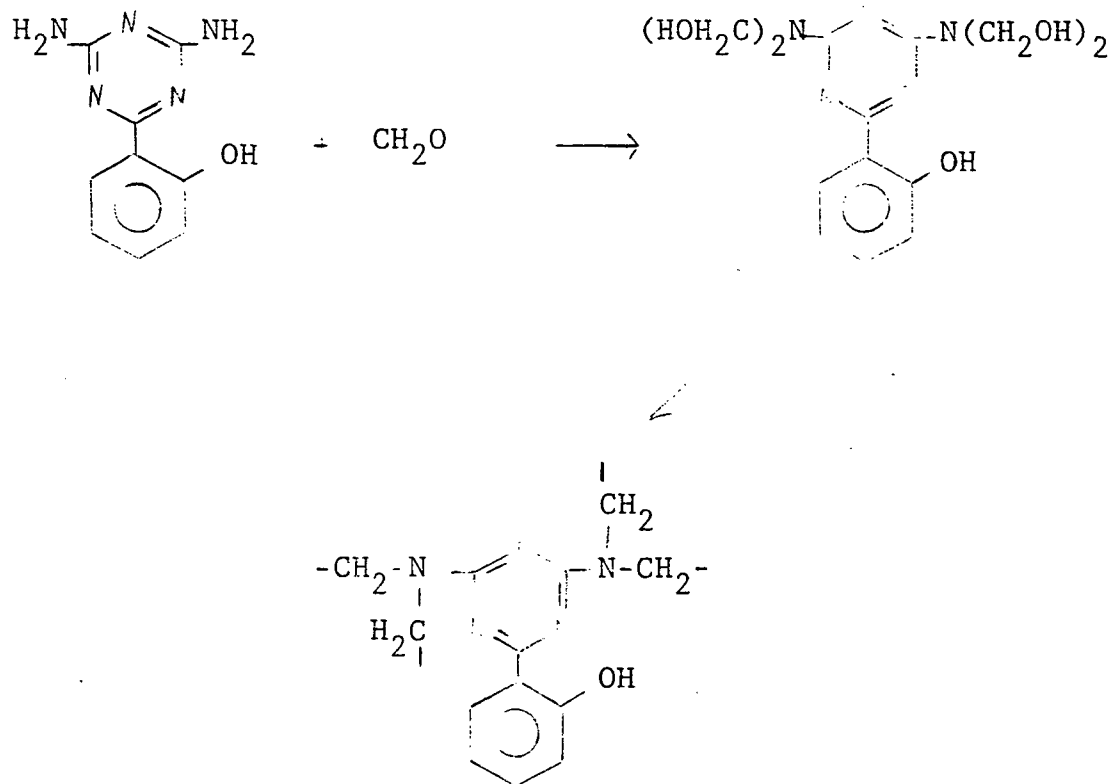
Unlike the other polymer structures containing ultraviolet-
stabilizing groups that have been reported in the literature,
this polymer structure does not possess ultraviolet-absorbing
groups other than the ultraviolet-stabilizing o-hydroxyphenyl-
triazine unit. The homopolymer of formaldehyde with o-hydroxy-
benzoguanamine was synthesized as well as copolymers containing
mixtures of benzoguanamine and o-hydroxybenzoguanamine at various
ratios. The homopolymer of benzoguanamine with formaldehyde was
also synthesized.

### 6.3.3 Fluorescence

Another mechanism of energy dissipation involves reversion to the ground state by photon emission: the excited molecule re-radiates part of the energy at a longer wavelength as fluorescence or phosphorescence, depending on whether the excited state is a singlet or a triplet. We decided to investigate the effects of ultraviolet irradiation on poly-N-vinylcarbazole. Fluorescence emission spectra of poly-N-vinylcarbazole have been reported by Johnson and co-workers (Ref. 149) and by David and co-workers (Ref. 150). Because of its fluorescence characteristics and its ability to form clear films, poly-N-vinylcarbazole was selected for ultraviolet exposure testing:

$$-CH-CH_2-$$
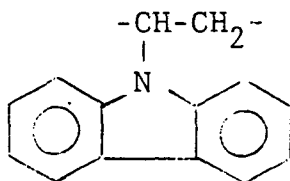
### 6.4 Prevention of Norrish Type II in Aliphatic Polyesters

As indicated in the previous report (Ref. 1), photolysis of polyesters involved decomposition of the ester groups by a Norrish Type II process. It involves a molecular mechanism with formation of an intermediate 6-atom transition stage. In the case of polyethyleneterephthalate, this decomposition reaction can be represented as follows:

$$-Ph-\overset{O}{\overset{||}{C}}-O-CH_2-CH_2- \xrightarrow{h\nu} -Ph-\overset{O}{\overset{||}{C}}$$

$$-Ph-COOH + CH_2=CH-$$
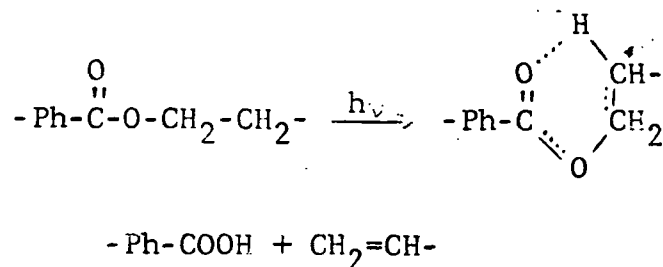
It was thought that a polyester structure with no hydrogen on the carbon atom in β position should possess improved ultraviolet stability since the energetically favored Norrish Type II could not take place.  Therefore, we decided to investigate polyester (and polycarbonate) structures characterized by (a) completely aliphatic structure to reduce ultraviolet absorption and (b) structure disubstituted on the β-carbon to prevent Norrish Type II photodegradation.  A polyester structure that meet these requirements is polypivalolactone, that was selected for ultraviolet testing:

$$-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-O-$$
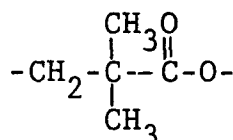
## 6.5  N-Methoxymethylation of Aliphatic Polyamides

Polyamide structures modified by N-methoxymethylation or other substitution on the nitrogen of the amide link were reported to possess good ultraviolet stability (Ref. 151, 152).  Thus, we decided to conduct a comparative study of the ultraviolet stability of Nylon 66 and partially methoxymethylated Nylon 66:

$$\sim(CH_2)_6-NH-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH\sim \qquad \sim(CH_2)_6-\underset{\underset{\underset{OCH_3}{|}}{\overset{|}{CH_2}}}{\overset{|}{N}}-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-NH\sim$$
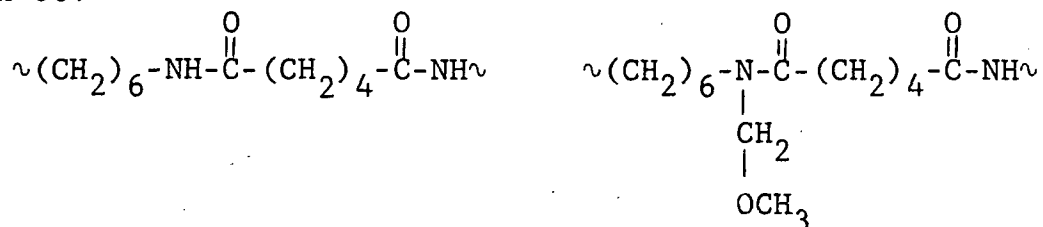
## 6.6  Ultraviolet Transparent Polymers

Since there can be no ultraviolet damage without absorption, the development of a polymer structure highly transparent down to 2000Å appears to be an interesting approach to the problem of ultraviolet stability.

A typical example of transparent structure are the methylsilicones.  Unfortunately, methylsilicones are quite sensitive to the presence of impurities that cause absorption and initiate photodegradation (Ref. 153).  We examined other polymer structures that are fundamentally transparent to the short wavelength ultraviolet and we selected two samples of polyethylene oxide (MW 20,000 and 5,000,000) for ultraviolet exposure testing:

$$\left[-CH_2-CH_2-O-\right]$$
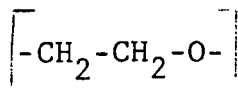
Although polyethylene oxide would have no practical utility because of its water solubility and low softening point, symmetrically disubstituted polyethyleneoxide structures could be synthesized that are solvent resistant and high melting.

# 7. PREPARATION OF SAMPLES FOR TESTING

## 7.1 Polypivalolactone

$$-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}\overset{\overset{O}{\parallel}}{-C-O-}$$
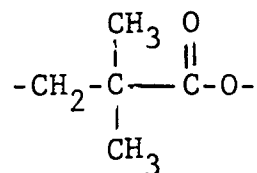
A sample of polypivalolacetone was made available to us by Dr. W.H. Sharkey of the DuPont Co. The polymer is a white powder with an inherent viscosity of 1.38 (0.5% in trifluoroacetic acid at 25°C) and a melting point of 235°C. Solution coating is not feasible with this material because of polymer insolubility. A thin film of polypivalolactone was obtained by melt application at 240°C followed by rapid quenching in cold water to prevent crystallization.

## 7.2 Polyvinylcarbazole
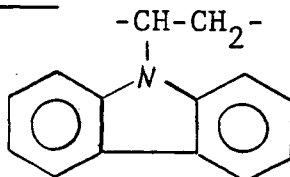
Polyvinylcarbazole (Aldrich analyzed, $M_n$=276,000, $M_w$= 1,410,000) was dissolved in toluene and the solution coated on an IRIF coupon. After evaporation of the solvent at 100°C, a clear coating was obtained.

## 7.3 Polycarbonate
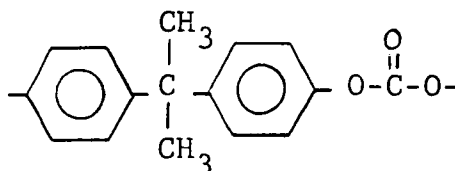
"Lexan" polycarbonate was dissolved in methylene chloride and coagulated into an excess of methanol. Polymer precipitation was repeated three times. After drying, the purified sample

was coated on an IRIF coupon from a methylene chloride solution.

7.4  <u>O.I. 650</u>

$$CH_3-Si \ O_{1.5}$$
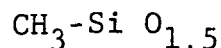
O.I. 650 resin is a monomethyl polysiloxane manufactured by Owens-Illinois. The resin was dissolved in isopropanol and coated on an IRIF coupon. The coupon was cured at 60°C overnight. Curing at higher temperature was not performed since coatings of O.I. 650 become excessively brittle and flake off when the polymer is fully cured. O.I. 650 was tested primarily for reference purpose.

7.5  <u>Polyethylene Oxide</u>

$$-O-CH_2-CH_2-$$
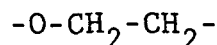
Two samples of polyethylene oxide ($\overline{M}n=20,000$ and $5,000,000$) were obtained from J.T. Baker and Polysciences respectively. They were coated from solutions in methanol and methylene chloride respectively. The coated coupons were dried at 60°C overnight.

7.6  <u>Nylon 66 and Methoxymethylated Nylon 66</u>

Zytel 101 (DuPont Co.) was purified by coagulating a formic acid solution of the polymer into an excess of water. This procedure was repeated three times. After filtering and drying, a portion of the purified Nylon 66 was reacted with methanol and formaldehyde:

$$\begin{array}{ccc} | \\ NH \\ | \\ C=O \\ | \end{array} + CH_2O + ROH \longrightarrow \begin{array}{ccc} | \\ N-CH_2-OR \\ | \\ C=O \\ | \end{array} + H_2O$$
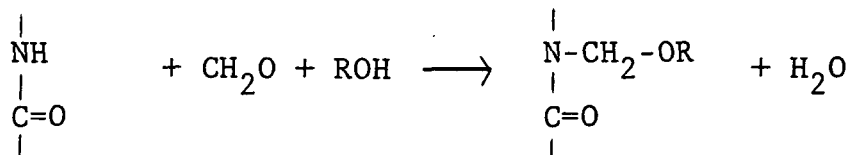
The detailed procedure employed for methoxymethylation is
described in Section 8.1. The extent of conversion of -NH-
groups into N-methoxymethylated groups was determined by infrared
analysis. A comparison of the infrared spectra of Nylon 66 with
methoxymethylated Nylon 66 shows that conversion of -NH- groups
was extensive but not complete. This can be seen by comparing
the relative intensities of the -NH- absorption band ($1540 cm^{-1}$)
with the carbonyl band ($1630 cm^{-1}$) in the two spectra (Fig. 2,3).
Coatings of the two polymers on IRIF coupons were prepared from
formic acid solution (Nylon 66) and from ethanol solution
(methoxymethylated Nylon 66).

### 7.7 Benzoguanamine/O-Hydroxybenzoguanamine/Formaldehyde Resins

O-Hydroxybenzoguanamine was synthesized by reaction of
dicyandiamide with 2-cyanophenol:
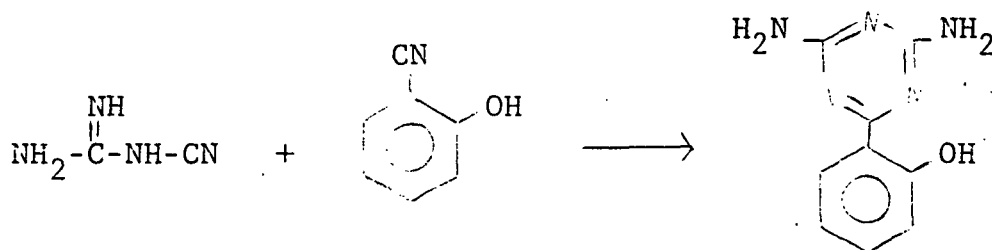


Polymerization of o-hydroxybenzoguanamine with formaldehyde was
performed by condensation in alkaline solution with formaldehyde
(molar ratio, 3/1). A soluble, fusible prepolymer was isolated
that cross-linked on further heating to give a hard coating that
was clear but yellow. A similar procedure was employed for the
polymerization of benzoguanamine with formaldehyde that gave clear
coatings. Copolymers benzoguanamine/o-hydroxybenzoguanamine/
formaldehyde were prepared by co-reacting mixtures of the two pre-
polymers. Copolymers containing 2% and 20% of the o-hydroxybenzo-
guanamine prepolymer were prepared and coated on IRIF coupons.
The color of the copolymer was lighter at lower o-hydroxybenzo-
guanamine concentrations. Details of the synthesis of monomer,
polymers and copolymers are presented in Section 9.2, 9.3 and 9.4.
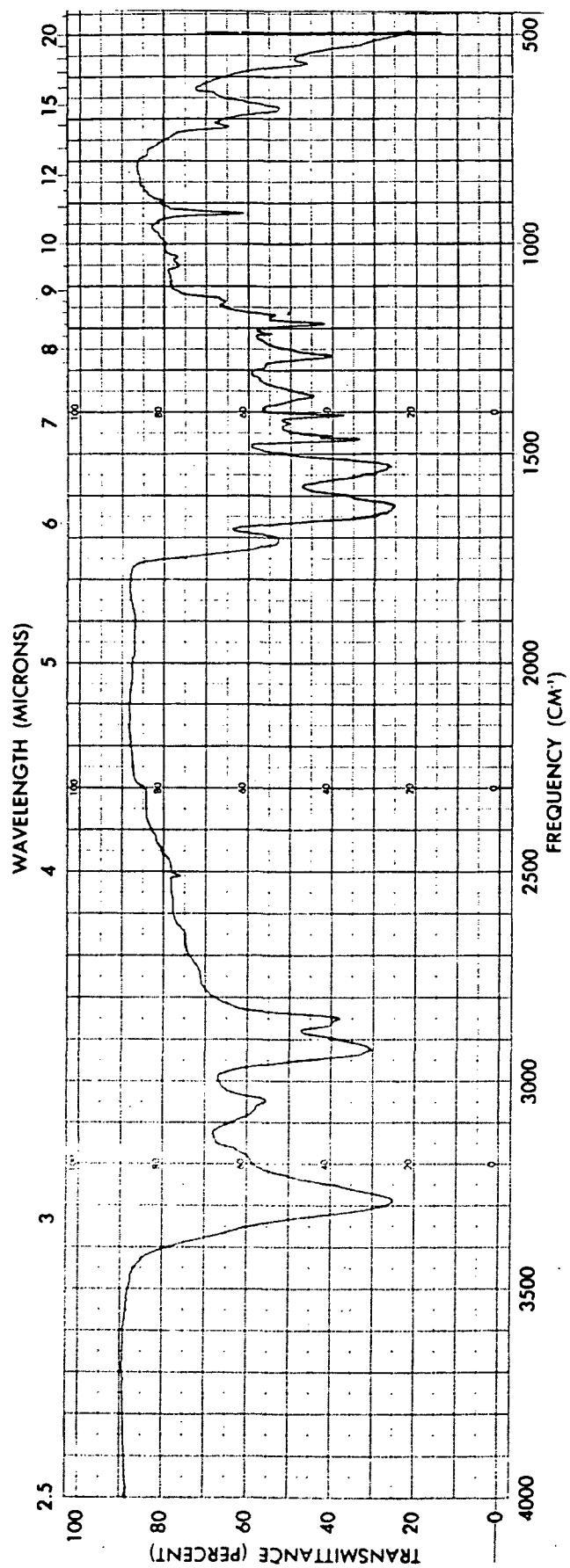
Figure No. 2   IR SPECTRUM OF NYLON 66
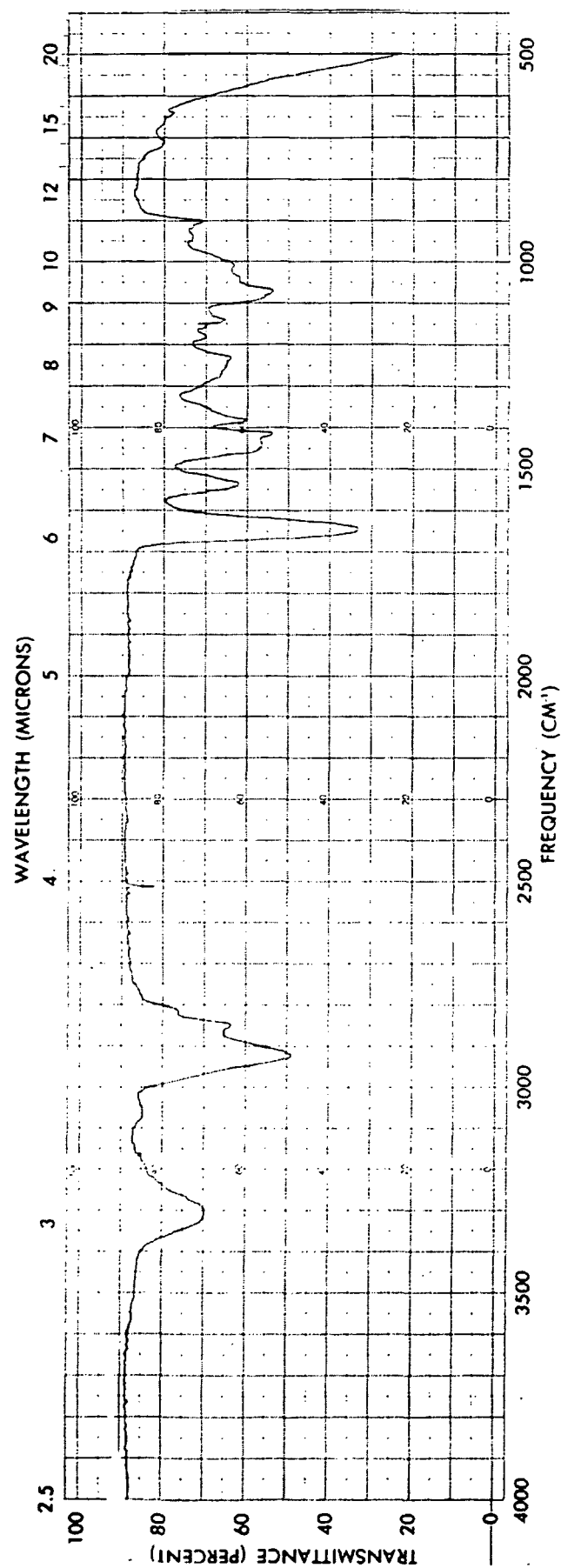
Figure No. 3 IR SPECTRUM OF METHOXYMETHYLATED NYLON 66

C6318-8

8.  ULTRAVIOLET EXPOSURE TESTS

The basic criterion for determining the damage produced
by irradiation in a simulated space environment is the change in
the optical properties of the material.  The materials selected
for ultraviolet exposure testing were coated on aluminum sub-
strates and tested in the IRIF space simulation facility.  All
samples were irradiated in vacuum for a total of 200 equivalent
sun hours (ESH) at one solar constant.  "In-situ" reflectance
measurements were taken at 0, 50, 90 and 200 ESH.  A final
measurement was taken at 200 ESH after bleaching with oxygen.
The experimental procedures employed and the conditions of the
tests are described in section 9.5.  The reflectance data at
various radiation doses are presented in the appendix.  These
data are presented both in graphical and tabular form.  The
graphs show the reflectance curves at various times over the
whole region 0.25-2.6µ.  The tables show the reflectance changes
at selected wavelengths in the ultraviolet and visible region.
As a general rule, optical damage manifests itself as a progressive
decrease in ultraviolet transmittance (measured as double
reflectance) that may reach the visible range and give rise to
yellowing of the polymer.  Therefore, the observation of
changes occurring in this region of the spectrum is very critical.
In some cases, a "bleaching" effect was produced, resulting in
a slight increase in reflectance.

Bisphenol-A polycarbonate (Fig. A-1, Table A-1) degraded
very rapidly, as indicated by a pronounced decrease in re-
flectance both in the UV and visible range.  The sample flaked
off after 100 hr and measurements at longer exposure times could
not be taken.

Both Nylon 66 and methoxymethylated Nylon 66 exhibited a pronounced decrease in reflectance in the ultraviolet and visible region (Fig. A-2, Table A-2; Fig. A-3, Table A-3), indicating that methoxymethyl substitution at the nitrogen of the amide link does not improve the ultraviolet stability of the polymer.

Polypivalolactone (Fig. A-4, Table A-4) exhibited a decrease in reflectance in the ultraviolet region after 50 hr of irradiation, but subsequent doses of ultraviolet radiation produced little or no change.

Polyvinylcarbazole exhibited very good stability (Fig. A-5, Table A-5). Essentially no reflectance change was observed after 100 hr and very little change after 200 hr. This is particularly interesting in view of the aromatic character of the polymer. Because of its aromaticity, polyvinylcarbazole is also expected to exhibit stability to high energy radiation and is a promising candidate for combined environment.

Ultraviolet exposure tests have been conducted on two co-polymers benzoguanamine/o-hydroxybenzoguanamine/formaldehyde having different o-hydroxybenzoguanamine content (2% and 20%-wt.; Fig. A-6, Table A-6; Fig. A-7, Table A-7). The homopolymer o-hydroxybenzoguanamine/formaldehyde has also been tested (Fig. A-8, Table A-8). As expected, these data indicate an increase in UV stability with increasing o-hydroxybenzoguanamine content. An improvement in reflectance was observed as a result of oxygen bleaching of the two copolymers, indicating that the reflectance degradation observed in vacuum is partly due to a transient species. The homopolymer o-hydroxybenzoguanamine/ formaldehyde exhibited excellent stability. Because of the high concentration of non-localized $\pi$ electrons, o-hydroxybenzoguanamine polymers and copolymers are promising materials for combined ultraviolet/high energy radiation environment.

O.I.650 resin (unmodified) was also included in the test for reference purposes (Fig. A-9, Table A-9). This polymer exhibited rather poor ultraviolet stability, confirming previous observations that the O.I.650 resin currently supplied by Owens-Illinois is less stable than earlier batches of this resin.

Two samples of polyethyleneoxide of different molecular weight (M.W.=20,000 and 5,000,000) were tested and found to possess excellent stability (Fig. A-10, Table A-10; Fig. A-11, Table A-11). The high molecular weight polyethyleneoxide in particular exhibited outstanding stability (Fig. A-11, Table A-11). The polyethyleneoxide with a molecular weight of 20,000 showed reflectance degradation after 50 hr irradiation followed by an improvement in reflectance in the far ultraviolet for subsequent doses. The polyethyleneoxide with a molecular weight of 5,000,000 showed no reflectance degradation; on the contrary, a definite improvement in reflectance in the far ultraviolet was observed.

# 9. EXPERIMENTAL

## 9.1 Methoxymethylation of Polyamide

The procedure employed for methoxymethylation was based on the method reported in the literature (Ref. 154). Various ratios of the reagents have been employed in the attempt to maximize the degree of conversion. The highest degree of conversion, as determined by IR analysis, was obtained by using the following procedure:

Zytel 101 (Nylon 66, duPont Co.) was dissolved in formic acid/acetic anhydride (4g polymer/12g solvent). A solution containing paraformaldehyde (12g), methanol (12g) with a trace of potassium hydroxide was prepared. This solution was added to a previously prepared solution of Zytel 101 in formic acid/acetic anhydride (4g polymer/12g solvent). The mixture was stirred for 4 hr at 60°C. After 4 hr, methanol (6.7g) was added and the solution stirred for additional 0.5 hr. The clear solution obtained was poured into a mixture of water/acetone (3:1). Ammonia was added to precipitate the polymer. A glue-like precipitate was isolated, washed with $H_2O$/acetone and dried. This material could be dissolved in ethanol and formed clear, transparent films.

## 9.2 Synthesis of o-Hydroxybenzoguanamine-Formaldehyde Resin

### 9.2.1 Synthesis of o-Hydroxybenzoguanamine

The procedure employed was essentially the same as the one reported in the literature for the synthesis of benzoguanamine (Ref. 155). Unlike benzoguanamine, that precipitates as it forms during reaction, o-hydroxybenzoguanamine does not precipitate out and product separation is difficult because its solubility characteristics are similar to the starting reagents. The following procedure gave o-hydroxybenzoguanamine in low yields:

Dicyandiamide (10.16g, 0.121 mole) and 2-cyanophenol
(12.0g, 0.101 mole) were added to an alkaline solution of methyl
cellosolve (1.29g KOH/25ml) in a 100ml 3-neck flask fitted with
a condenser and thermometer. The flask was heated in an oil
bath at 100-137°C for 20 hr. The solids formed were filtered
and dissolved in hot methanol, concentrated to a small volume
and precipitated in hot water twice. The filtrates were con-
centrated and reprecipitated in water. The precipitate formed
(0.473g) was o-hydroxybenzoguanamine, a light yellow powder
melting at 238-246°C. The IR spectrum of this material is shown
in Fig. 4.

### 9.2.2 Polymerization of o-hydroxybenzoguanamine with Formaldehyde

An alkaline solution of 0.15 ml (0.045g) of 37% formaldehyde
was added to o-hydroxybenzoguanamine (0.102g, 0.49 mole) in a
test tube. The test tube was placed in an oil bath heated at
97-105°C for 15 min. During heating a highly viscous
semisolid phase was formed. The liquid phase was decanted
and the semisolid phase was dried by evacuation. The product
which foamed into a rigid solid was crushed and washed with
water and dried. A light yellow powder was obtained (yield,
0.289g). The softening point of this prepolymer was 110°C, and
the thermosetting temperature 180°C. The composition of this
prepolymer was confirmed by IR analysis (Fig. 5). An IRIF
coupon was prepared by coating a 15% solution of the prepolymer
in acetone. After evaporation of the solvent, the temperature
was gradually increased to 180°C. After 25 min, cross-linking
took place and a clear, yellow, infusible film was formed.

## 9.3 Synthesis of Benzoguanamine/Formaldehyde Resin

Benzoguanamine (K&K; 0.25g, 0.0012 mole) was reacted in a test tube with an alkaline solution of 37% formaldehyde (0.3ml, 0.111g). This mixture was heated in an oil bath at 110°C for 15 min. The reaction product changed from a highly viscous liquid to a white solid. The excess liquid was decanted and the residue evacuated to dryness. The white solid was crushed, washed with water and dried under vacuum. The prepolymer obtained (0.601g) was a white powder, soluble in methanol, insoluble in toluene. The composition was confirmed by IR analysis (Fig. 6). The softening point of the prepolymer was 120°C and the thermosetting temperature 195°C. An IRIF coupon was prepared by coating a 15% solution of the prepolymer in acetone. After evaporation of the solvent, the temperature was gradually increased to 195°C. After 20 min, cross-linking took place and a clear, colorless, infusible film was formed.

## 9.4 Synthesis of Benzoguanamine/o-Hydroxybenzoguanamine/ Formaldehyde Copolymers

Two copolymers were prepared by co-reacting mixtures of the two prepolymers described in the previous paragraphs. The copolymers examined contained 2% and 20%, of the o-hydroxybenzo-guanamine prepolymer. A mixture of the two prepolymers in acetone solution was coated on IRIF coupons. After evaporation of the solvent, copolymerization and cross-linking was conducted by increasing the temperature to 195°C for 30 min.

## 9.5  Irradiation of Coatings and Reflectance Measurements

An irradiation facility known as IRIF was employed (Fig. 7,8).  This facility permits the obtaining of in-situ, absolute, hemispherical reflectance spectra in the 250-2700μ wavelength region.  The ultraviolet source utilized was an A-H6 mercury-argon.  The ultraviolet exposure tests were performed at one solar constant.  The substrate for the coatings was polished aluminum (1/2 x 1 inch coupons).  In-situ reflectance measurements were taken before and after irradiation with a Beckman DK-2A spectrophotometer.  The ESR spectrometer employed in the study of free radical formation in ultraviolet irradiated samples is pictured in Fig. 9.

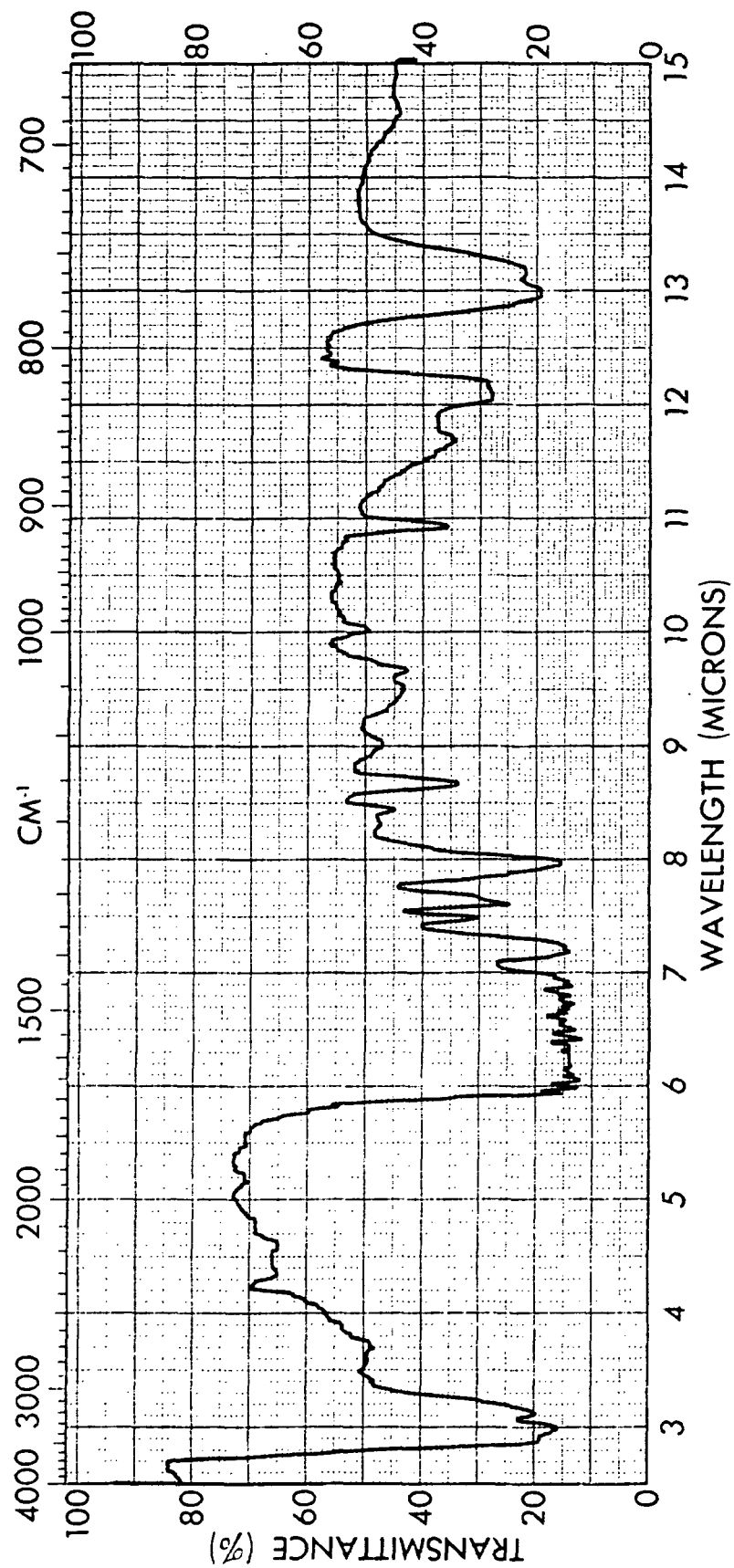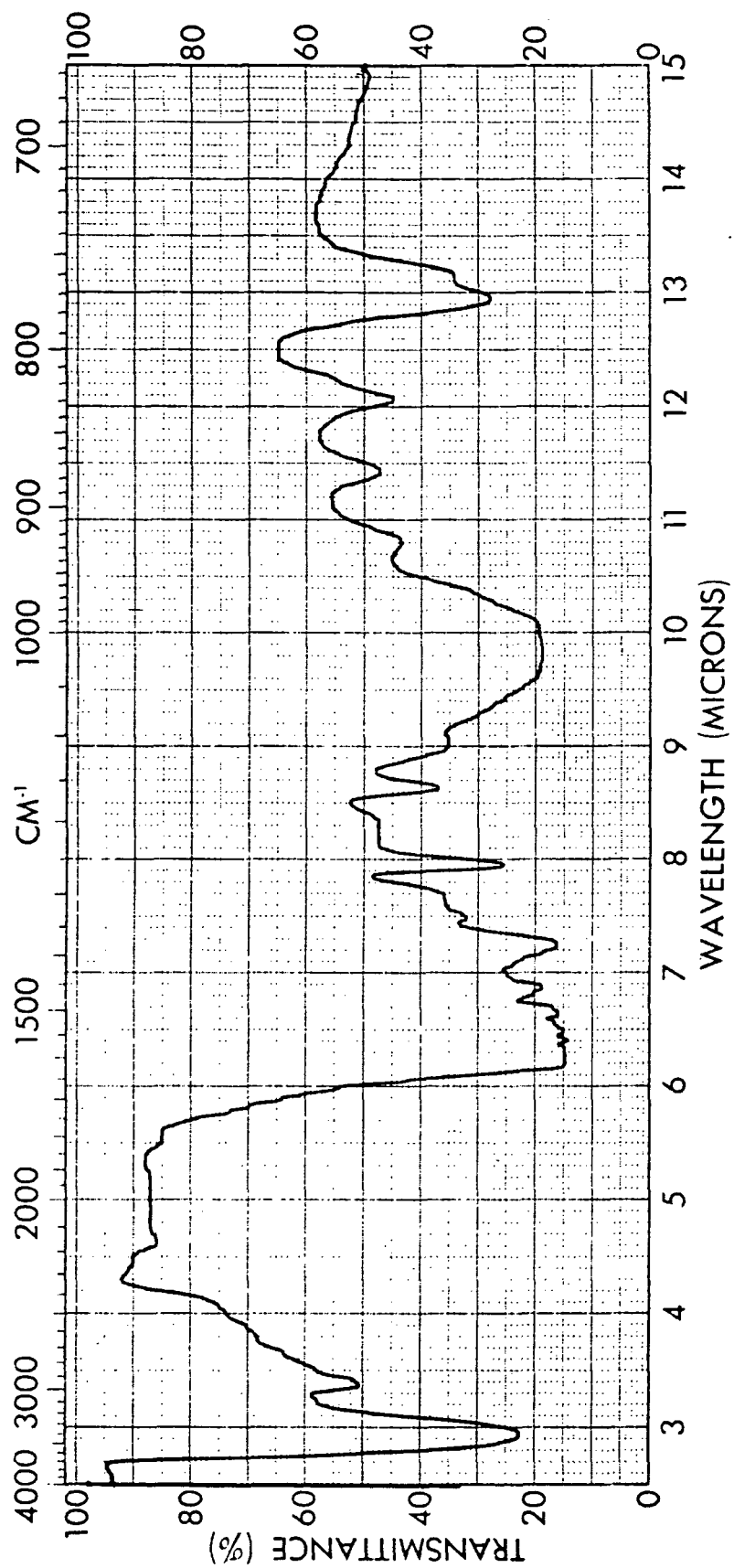Figure No. 4   IR SPECTRUM OF O–HYDROXYBENZOGUANAMINE

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Figure No. 5   IR SPECTRUM OF O-HYDROXYBENZOGUANAMINE/FORMALDEHYDE RESIN
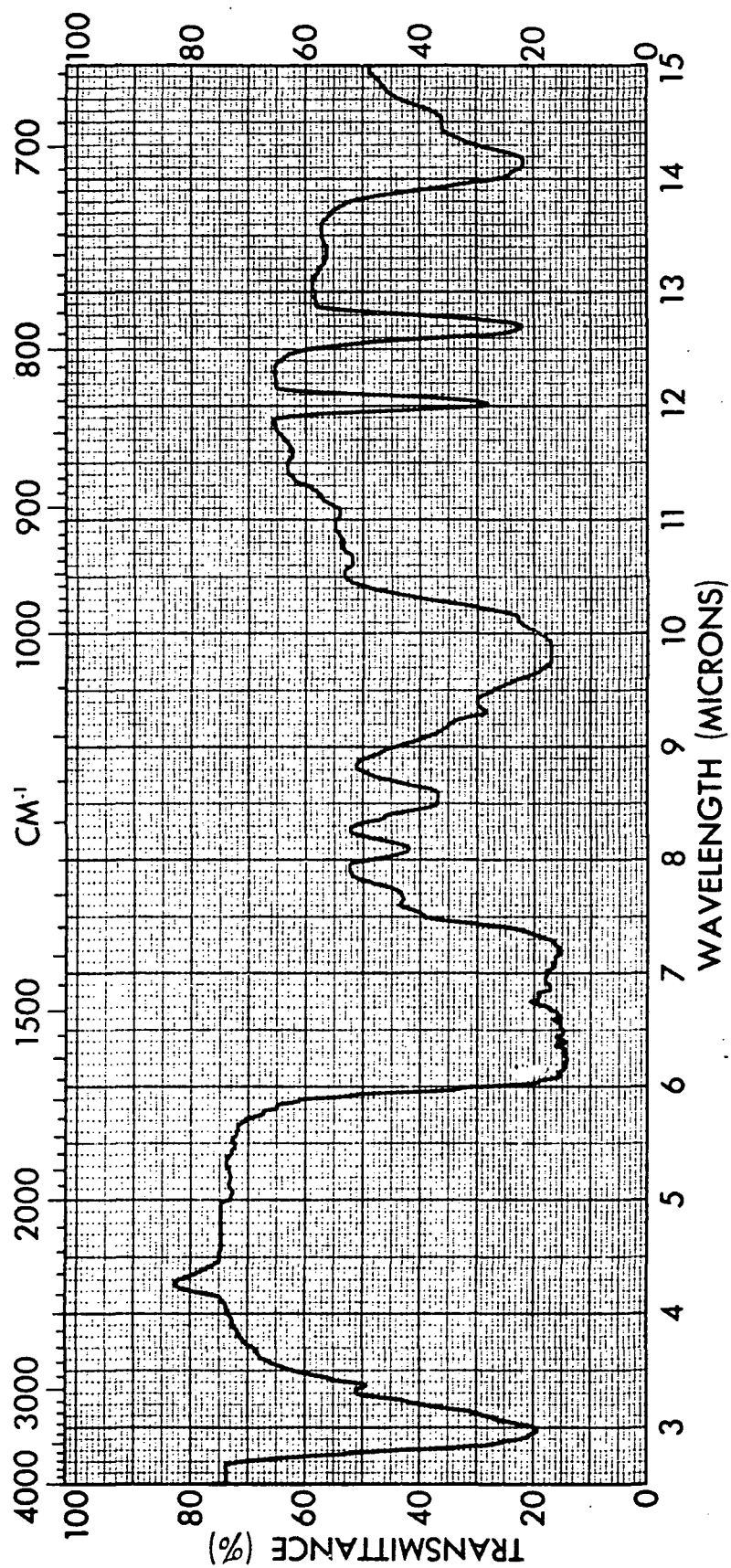
C6318-8

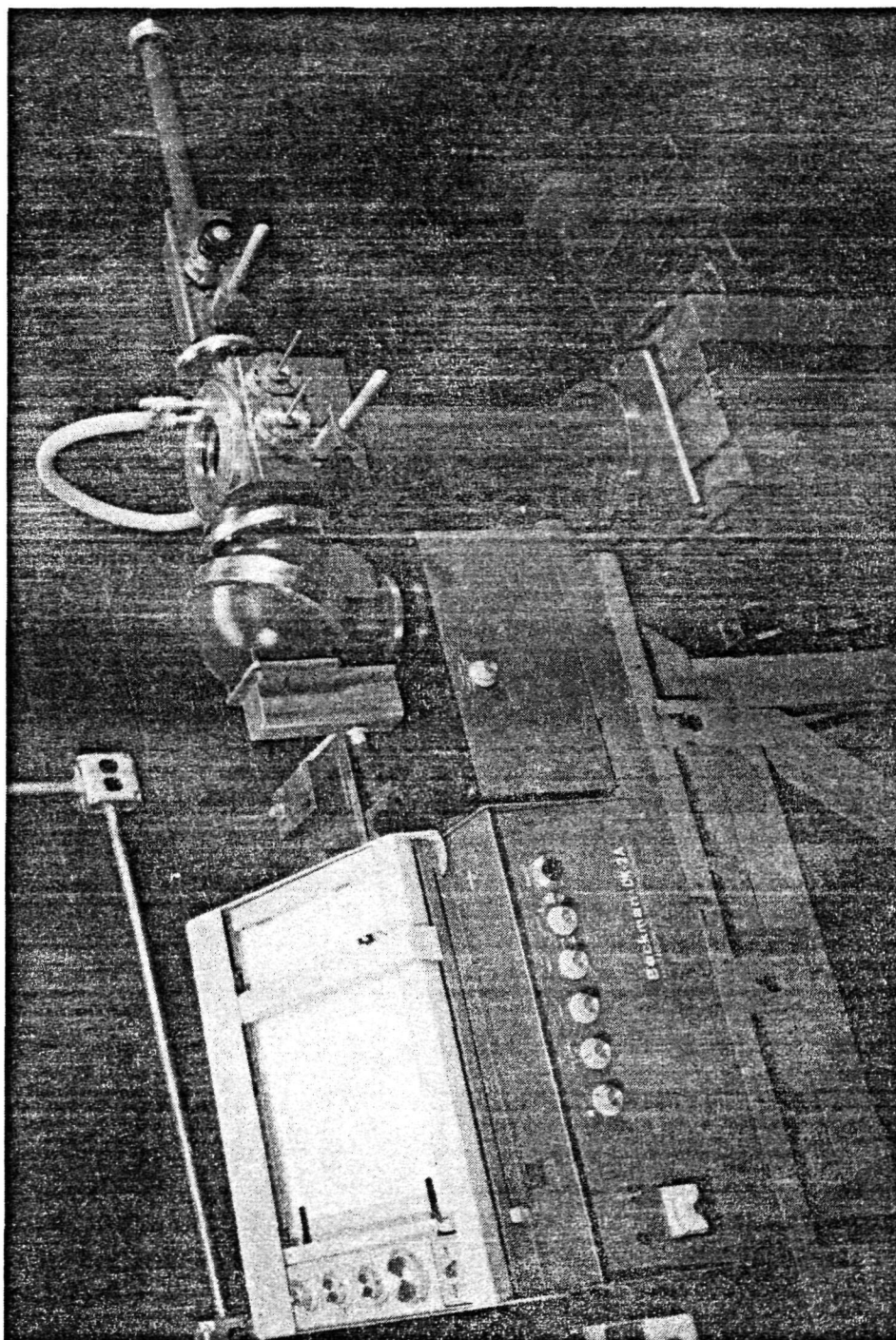Figure No. 6   IR SPECTRUM OF BENZOGUANAMINE/FORMALDEHYDE RESIN

C6318-8

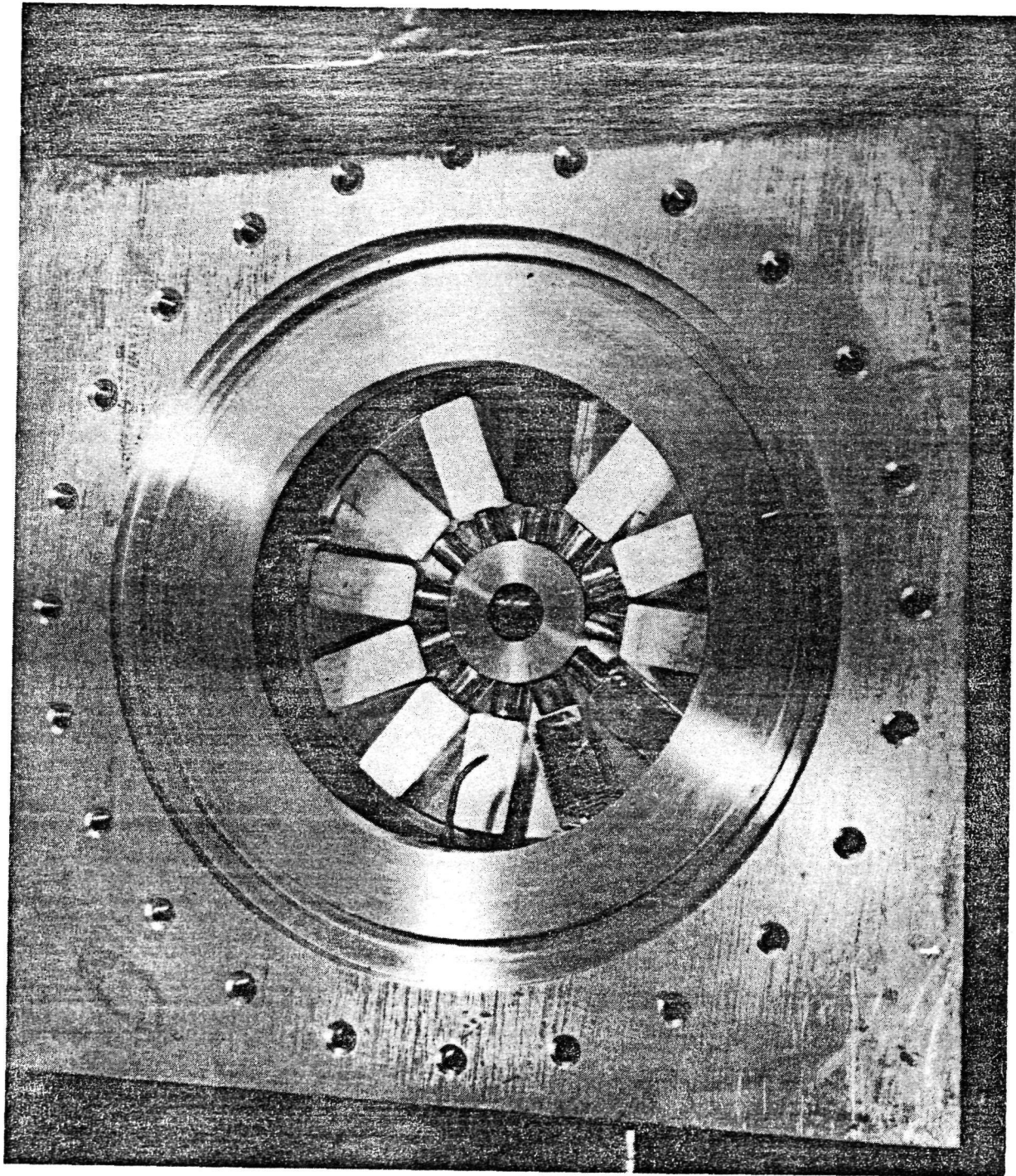Figure No. 7

THE IRIF CONNECTED TO THE BECKMAN DK-2A

C6318-8

Figure No. 8

TOP VIEW OF THE IRIF'S UV-IRRADIATION CHAMBER

C6318-8
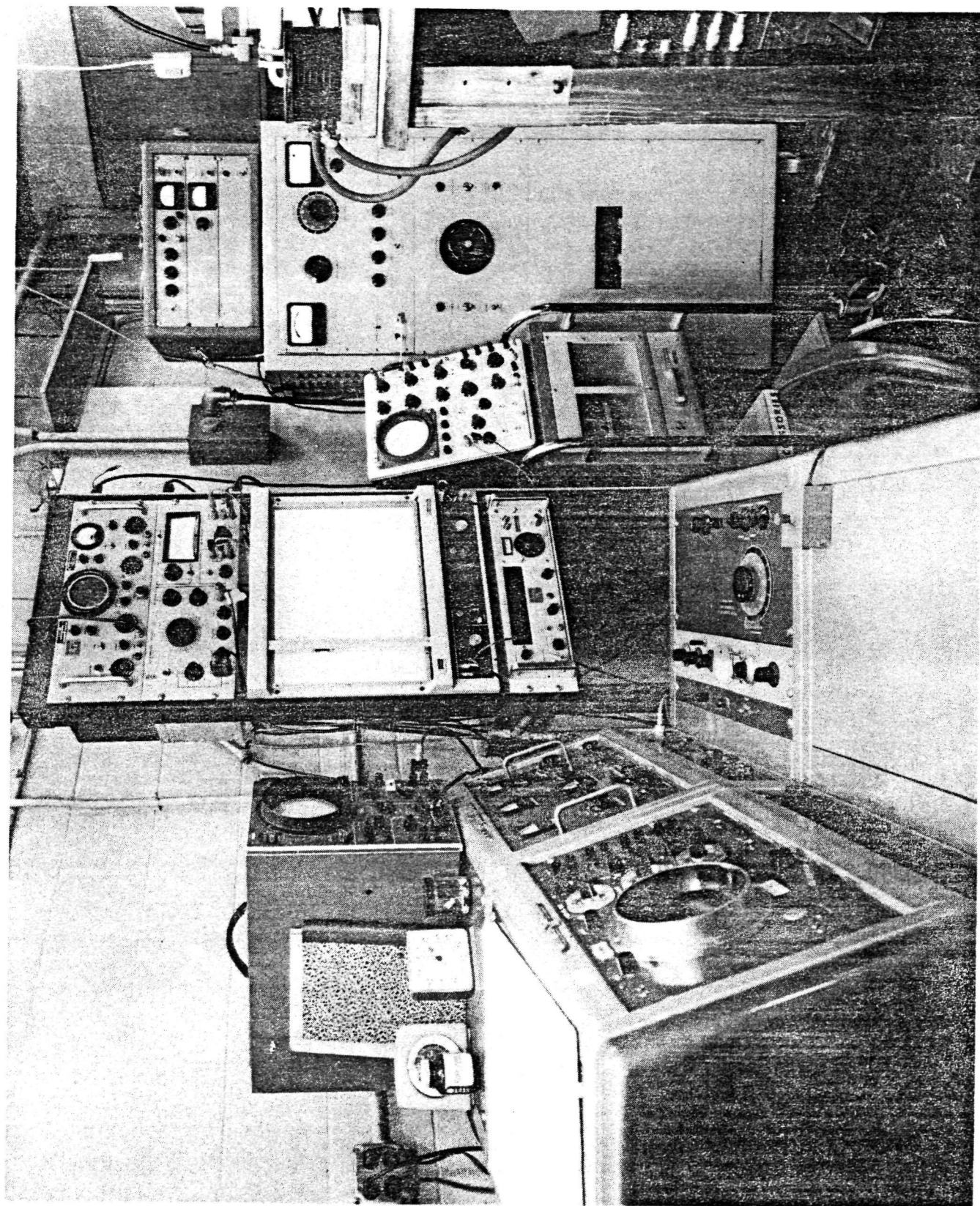
Figure No. 9  THE ELECTRON SPIN RESONANCE SPECTROMETER

65

## 10. CONCLUSIONS AND RECOMMENDATIONS

The main accomplishment of this program was the development of a rationale for material selection from the analysis of a computerized literature search in the field of radiation effects, and the design of an experimental program aimed at the development of high performance materials with improved resistance to the vacuum-radiation environment of space. The preliminary ultraviolet exposure tests presented in this report have shown the applicability of these concepts and the feasibility of these approaches.

The observed ultraviolet stability of polyvinylcarbazole is particularly interesting in view of the aromatic character of this polymer. Because of its aromaticity, polyvinylcarbazole is also expected to be stable to high energy radiation; and because of its photoconducting properties, it is also expected to exhibit low static charge build-up in a charged-particle environment. Since polyvinylcarbazole is a polymer exhibiting pronounced fluorescence, it is recommended that a detailed study of the optical properties and fluorescence emission of polyvinylcarbazole at various ultraviolet excitation wavelengths be included in a continuation of this study. If it appears that polymer fluorescence is in fact related to ultraviolet stability, this study should be expanded to include in addition to polyvinylcarbazole, other fluorescent polymers such as polyvinyl-naphthalene and polyacenaphthylene.

Another approach that appears very promising involves the formulation of amino resins incorporating o-hydroxybenzoguanamine as an ultraviolet-stabilizer comonomer. This study should be expanded to include the synthesis of melamine/o-hydroxybenzoguan-amine/formaldehyde compositions and the evaluation of the effect of o-hydroxybenzoguanamine concentration on the ultraviolet

stability of the copolymer. Such copolymers are also expected
to be stable to high energy radiation because of the high
concentration of non-localized $\pi$ electrons.

The study of polymer structures capable of undergoing
ultraviolet-induced Fries rearrangements is not recommended for
further study. It appears that in conjunction with the photo-
Fries, other secondary degradative processes occur that lead to
polymer discoloration. Therefore, the Fries rearrangement does
not appear to be a feasible approach to the problem of ultraviolet
stabilization.

The excellent stability exhibited by polyethyleneoxide
indicates that aliphatic polyethers are a promising class of
ultraviolet resistant polymers. Unfortunately, polyethyleneoxide
would have no practical utility because of its moisture
sensitivity and low softening point. The study of aliphatic
polyethers from symmetrically substituted epoxides, such as
tetramethyleneoxide, is recommended for further study. These
polyethers are expected to exhibit ultraviolet stability com-
parable to polyethyleneoxide but superior physical and thermal
properties because of the chain stiffening effect imparted by
symmetrical side groups.

Another promising approach involves the utilization of
aliphatic polyester structures in which the energetically favored
Norrish type II photodegradation reaction is prevented by
appropriate structural design. This study should be expanded
to include aliphatic polycarbonates based on diols with no hy-
drogen in $\beta$ position with respect to the hydroxyl group, such
as tetramethylcyclobutanediol or neopentylglycol.

APPENDIX

## Table A-1
### CHANGE IN REFLECTANCE (R) OF IRRADIATED POLYCARBONATE
### IN THE UV-VISIBLE REGION

| Wavelength (μ) | ΔR (50 hr) | ΔR ( 90 hr) | ΔR (200 hr) | ΔR (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | +4 | - | - | - |
| 0.325 | -34 | - | - | - |
| 0.377 | -38 | -44 | - | - |
| 0.457 | -9 | -17 | | |
| 0.554 | -3.5 | -5 | - | - |
| 0.700 | -1 | -1 | - | - |

## Table A-2
### CHANGE IN REFLECTANCE (R) OF IRRADIATED NYLON 66
### IN THE UV-VISIBLE REGION

| Wavelength (μ) | ΔR (50 hr) | ΔR ( 90 hr) | ΔR (200 hr) | ΔR (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | +2 | - | -3 | -3 |
| 0.325 | -5 | - | -20.5 | -20.5 |
| 0.377 | -1 | -2 | -18 | -18 |
| 0.457 | 0 | 0 | -11 | -11 |
| 0.554 | +1 | -1 | -3 | -3 |
| 0.700 | +1 | +2 | +2 | +2 |

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Figure A-1

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
POLYCARBONATE ON ALUMINUM SUBSTRATE

Figure A-2

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
NYLON 66 (Zytel 101) ON ALUMINUM SUBSTRATE

Table A-3

CHANGE IN REFLECTANCE (R) OF IRRADIATED METHOXYMETHYLATED
NYLON 66 IN THE UV-VISIBLE REGION

| Wavelength (μ) | ΔR (50 hr) | ΔR ( 90 hr) | ΔR (200 hr) | ΔR (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | -12 | - | -13.5 | -14 |
| 0.325 | -24 | - | -43 | -43.5 |
| 0.377 | -9 | -18 | -45 | -46 |
| 0.457 | -1 | -5 | -26 | -27 |
| 0.554 | -1 | 0 | -9 | -10 |
| 0.700 | +1 | +2 | -1 | +1 |

Table A-4

CHANGE IN REFLECTANCE (R) OF IRRADIATED POLYPIVALOLACTONE
IN THE UV-VISIBLE REGION

| Wavelength (μ) | ΔR (50 hr) | ΔR ( 90 hr) | ΔR (200 hr) | ΔR (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | -7 | - | -5 | -5 |
| 0.325 | -31.5 | - | -35 | -35 |
| 0.377 | -20 | -20 | -21 | -19 |
| 0.457 | -2 | -2 | -5 | -4 |
| 0.554 | 0 | 0 | -2 | -1 |
| 0.700 | +1 | +2 | +3 | +4 |
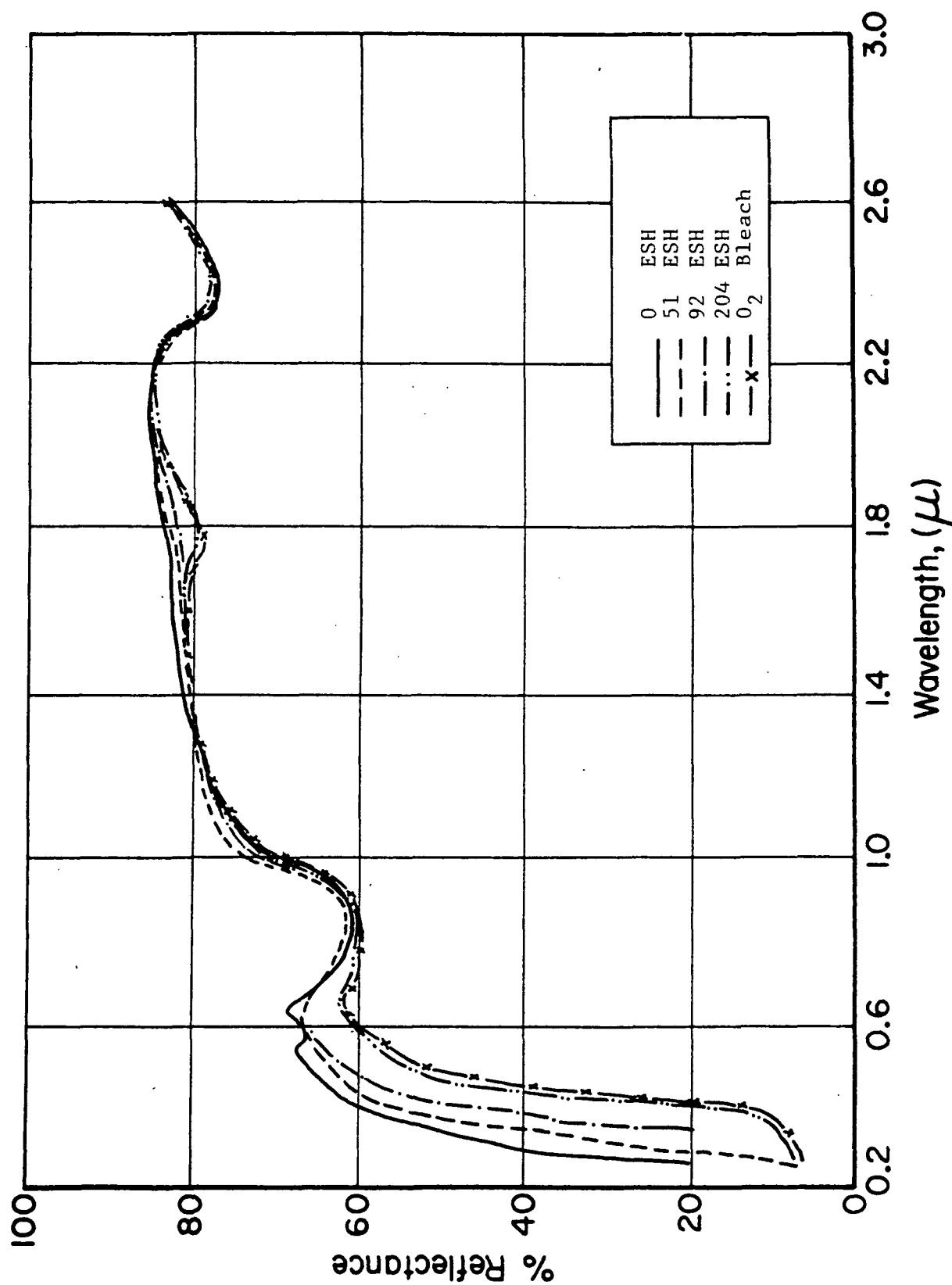
Figure A-3

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
METHOXYMETHYLATED NYLON 66 ON ALUMINUM SUBSTRATE
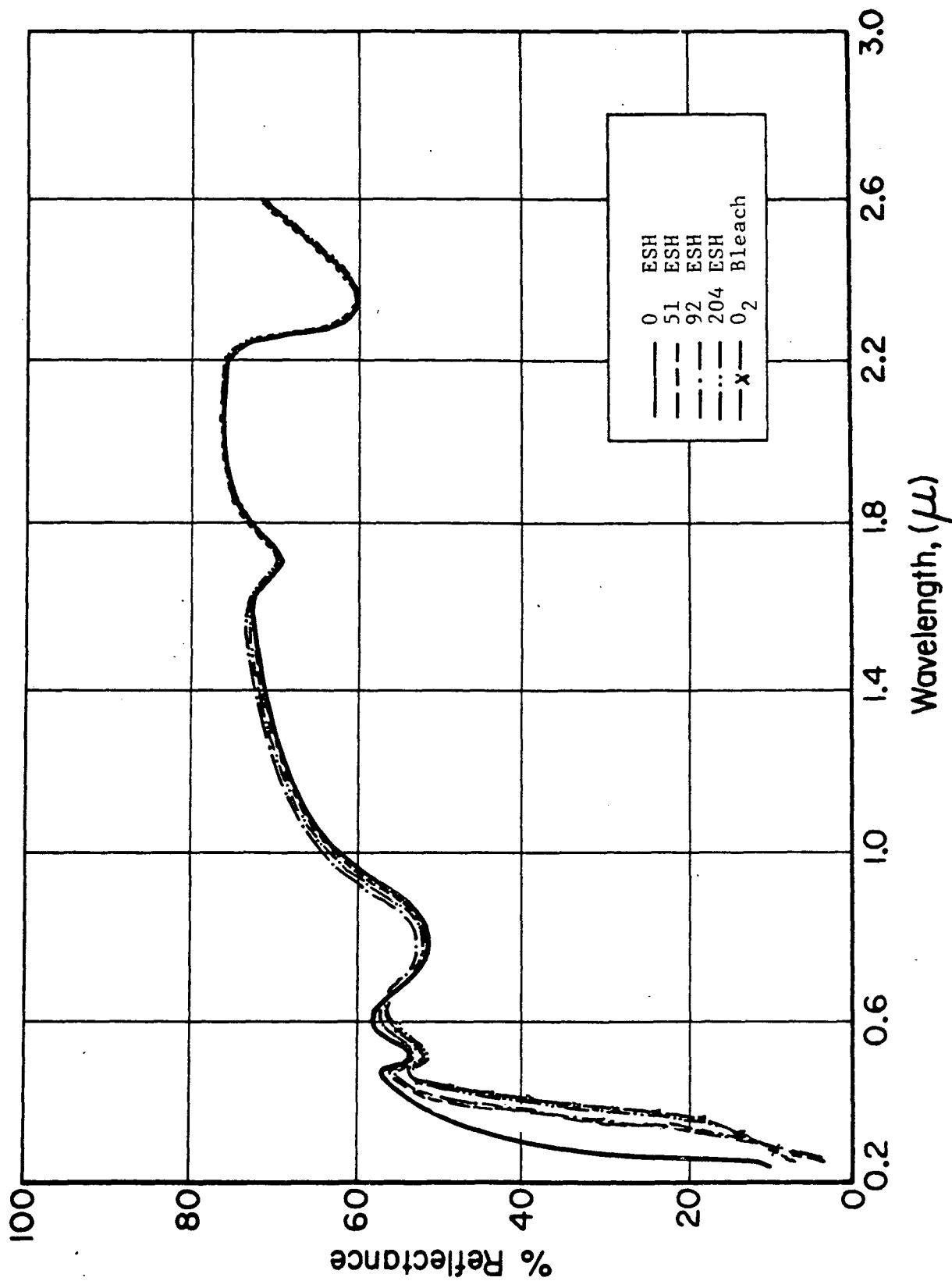
Figure A-4

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
POLYPIVALOLACTONE ON ALUMINUM SUBSTRATE

## Table A-5

### CHANGE IN REFLECTANCE (R) OF IRRADIATED POLYVINYLCARBAZOLE IN THE UV-VISIBLE REGION

| Wavelength ($\mu$) | $\Delta R$ (50 hr) | $\Delta R$ (90 hr) | $\Delta R$ (200 hr) | $\Delta R$ (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | -3 | - | -4 | -5 |
| 0.325 | -1 | - | 0 | -2.5 |
| 0.377 | -1 | 0 | -4 | -5 |
| 0.457 | -1 | 0 | -3 | -4 |
| 0.554 | -1 | 0 | -1 | -2 |
| 0.700 | 0 | 0 | 0 | 0 |

## Table A-6

### CHANGE IN REFLECTANCE (R) OF IRRADIATED BENZOGUANAMINE/ o-HYDROXYBENZOGUANAMINE/FORMALDEHYDE RESIN IN THE UV-VISIBLE REGION (o-HYDROXYBENZOGUANAMINE, 2% WT.)

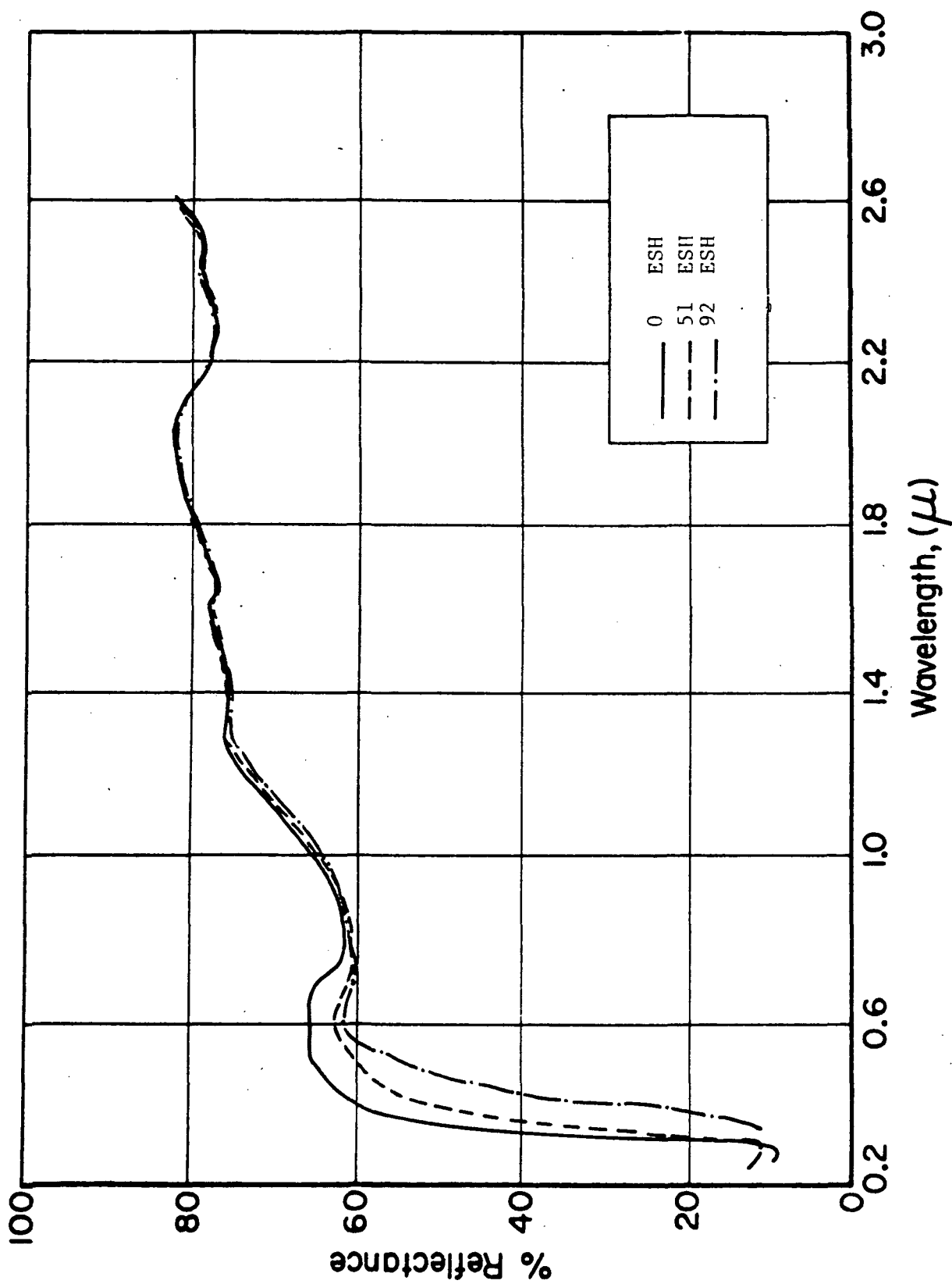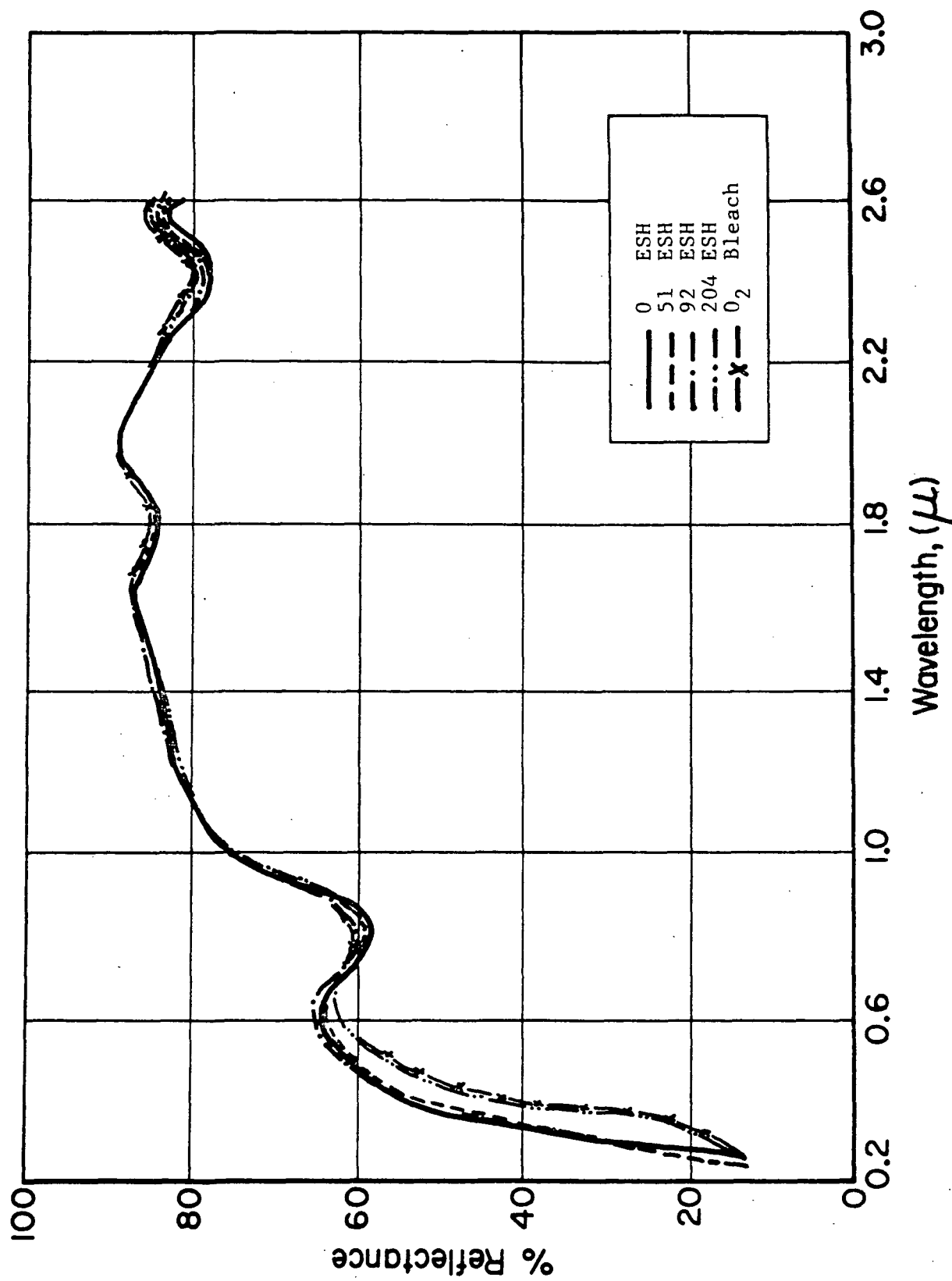| Wavelength ($\mu$) | $\Delta R$ (50 hr) | $\Delta R$ (90 hr) | $\Delta R$ (200 hr) | $\Delta R$ (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | +2.5 | 0 | +1.5 | +.5 |
| 0.325 | +.5 | -1 | -.5 | -.5 |
| 0.377 | +4 | 0 | 0 | 0 |
| 0.457 | -4 | -8 | -10 | -8 |
| 0.554 | -2 | -2 | -5 | -2 |
| 0.700 | -1 | -1 | -2 | +1 |
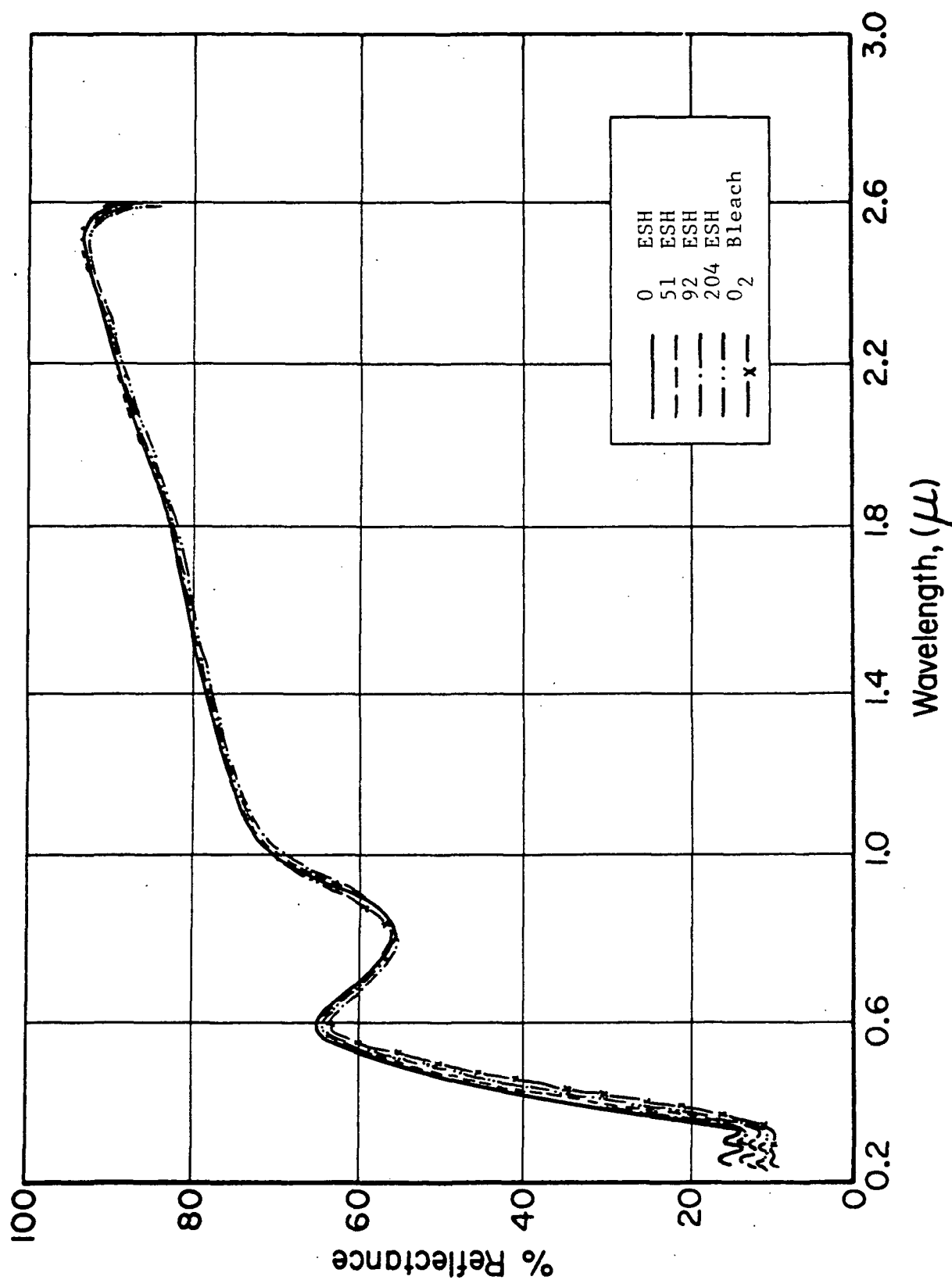
Figure A-5

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
POLY-N-VINYLCARBAZOLE ON ALUMINUM SUBSTRATE

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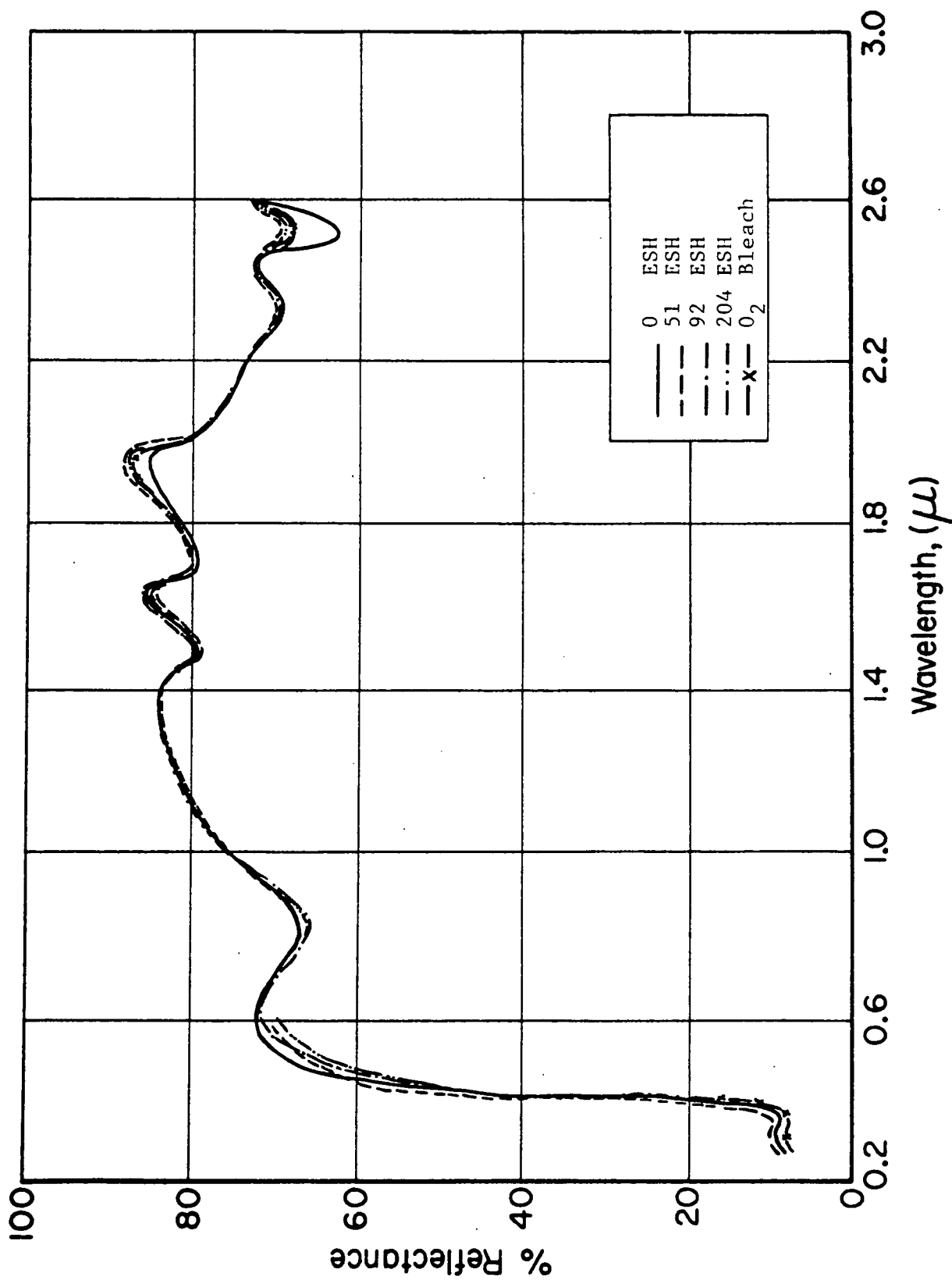
Figure A-6

EFFECT OF UV IRRADIATION ON THE REFLECTANCE
OF BENZOGUANAMINE/O-HYDROXYBENZOGUANAMINE/
FORMALDEHYDE RESIN (2% O-HYDROXYBENZOGUANAMINE)

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Table A-7
CHANGE IN REFLECTANCE (R) OF IRRADIATED BENZOGUANAMINE/
o-HYDROXYBENZOGUANAMINE/FORMALDEHYDE RESIN IN
THE UV-VISIBLE REGION (o-HYDROXYBENZOGUANAMINE, 20% WT)

| Wavelength ($\mu$) | $\Delta R$ (50 hr) | $\Delta R$ * ( 90 hr) | $\Delta R$ * (200 hr) | $\Delta R$ * (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | | -1 | -.5 | 0 |
| 0.325 | | -2 | -2 | -1 |
| 0.377 | | -1 | -1 | 0 |
| 0.457 | | -1 | -4 | -2 |
| 0.554 | | -2 | -3 | 0 |
| 0.700 | | 0 | 0 | +1 |

*$\Delta R$ values are referred to 50 hr readings

Table A-8
CHANGE IN REFLECTANCE (R) OF IRRADIATED o-HYDROXYBENZO-
GUANAMINE/FORMALDEHYDE RESIN IN THE UV-
VISIBLE REGION

| Wavelength ($\mu$) | $\Delta R$ (50 hr) | $\Delta R$ ( 90 hr) | $\Delta R$ (200 hr) | $\Delta R$ (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | -8 | -8 | -8 | -8 |
| 0.325 | -5.5 | -5 | -3 | -4 |
| 0.377 | +1 | +2 | +5 | +4 |
| 0.457 | -1 | -1 | +1 | +1 |
| 0.554 | -2 | -2 | +1 | 0 |
| 0.700 | 0 | 0 | +2 | +2 |

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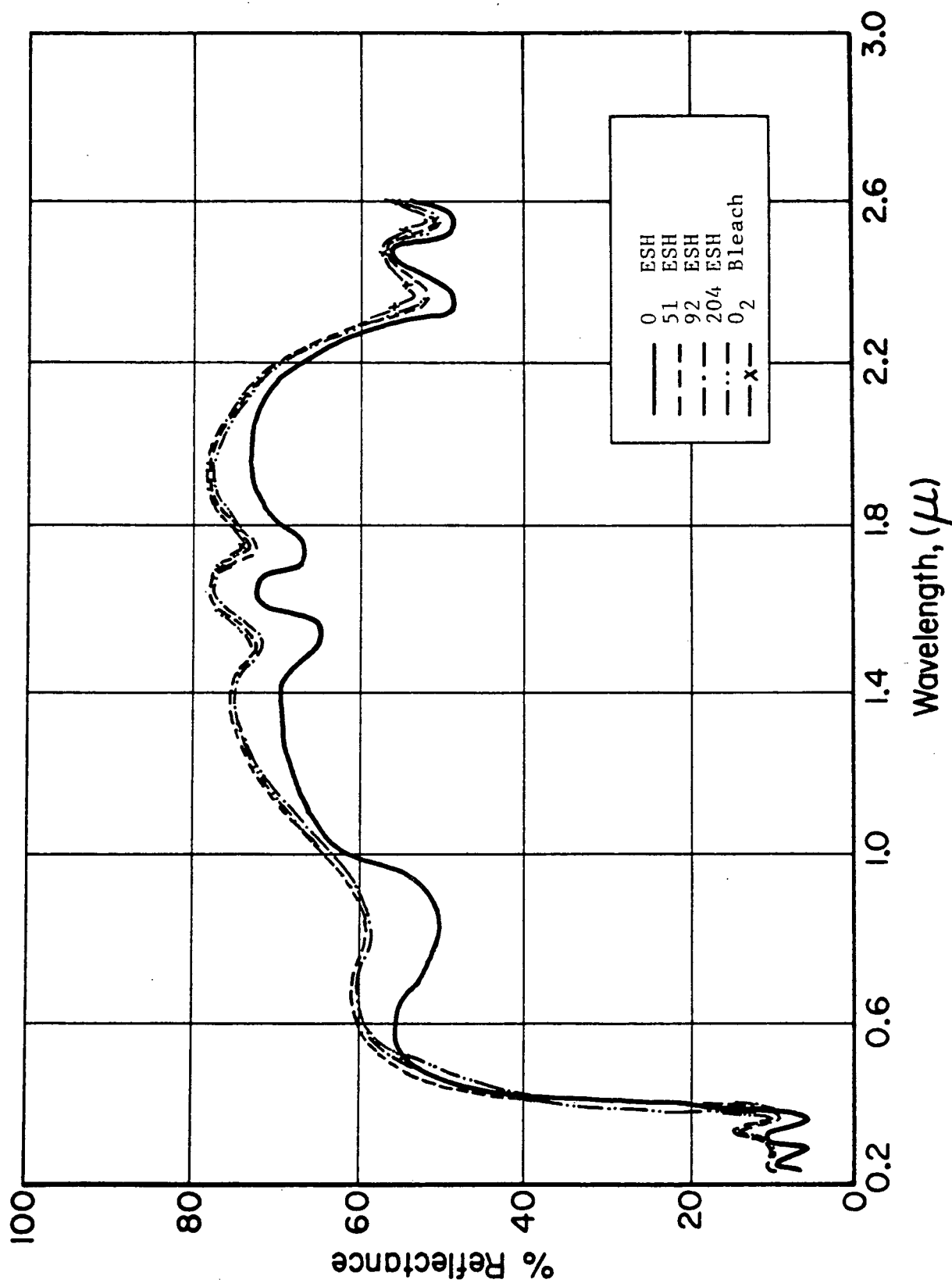
Figure A-7
EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
BENZOGUANAMINE/O-HYDROXYBENZOGUANAMINE/
FORMALDEHYDE RESIN (20% O-HYDROXYBENZOGUANAMINE)
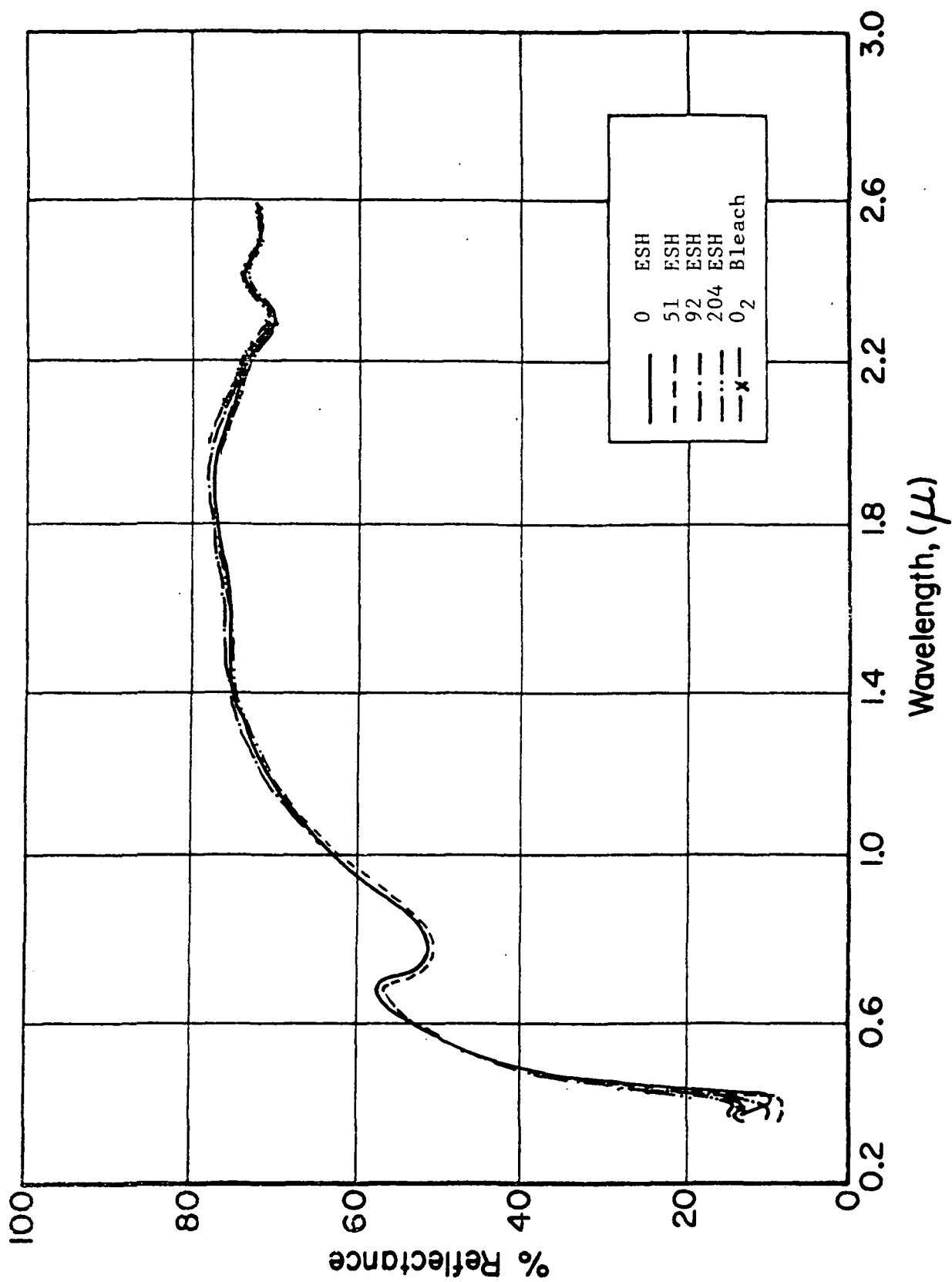
Figure A-8

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
O-HYDROXYBENZOGUANAMINE/FORMALDEHYDE RESIN ON ALUMINUM SUBSTRATE

Table A-9

CHANGE IN REFLECTANCE (R) OF IRRADIATED O.I. 650 RESIN
IN THE UV-VISIBLE REGION

| Wavelength (μ) | ΔR (50 hr) | ΔR ( 90 hr) | ΔR (200 hr) | ΔR (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | -25 | - | -12.5 | -11.5 |
| 0.325 | -15 | - | -13 | -14 |
| 0.377 | -9 | -10 | -10 | -8 |
| 0.457 | -2 | -3 | -3 | -2 |
| 0.554 | 0 | -1 | -1 | 0 |
| 0.700 | 0 | +1 | +2 | +2 |

Table A-10

CHANGE IN REFLECTANCE (R) OF IRRADIATED POLYETHYLENEOXIDE
(M.W. = 20,000) IN THE UV-VISIBLE REGION

| Wavelength (μ) | ΔR (50 hr) | ΔR ( 90 hr) | ΔR (200 hr) | ΔR (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | -12 | - | -2.5 | -5 |
| 0.325 | -14 | - | -7.5 | -9 |
| 0.377 | -9.5 | -4.5 | -4.5 | -5.5 |
| 0.457 | -1 | 0 | 0 | -2 |
| 0.554 | -.5 | -.5 | -1 | -1 |
| 0.700 | +1 | +1 | +2 | +3 |
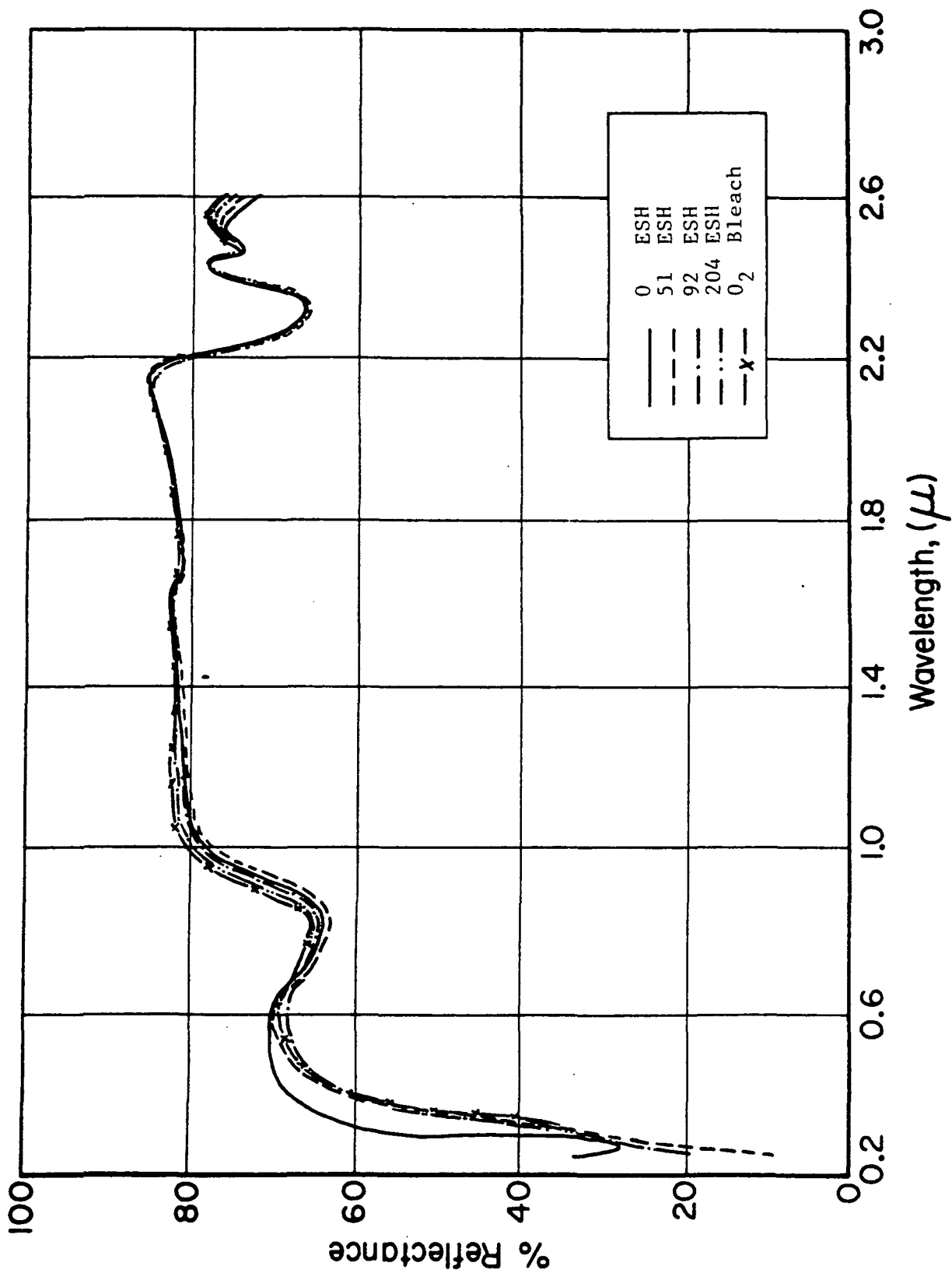
Figure A-9

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF O.I. 650
RESIN ON ALUMINUM SUBSTRATE

C6318-8
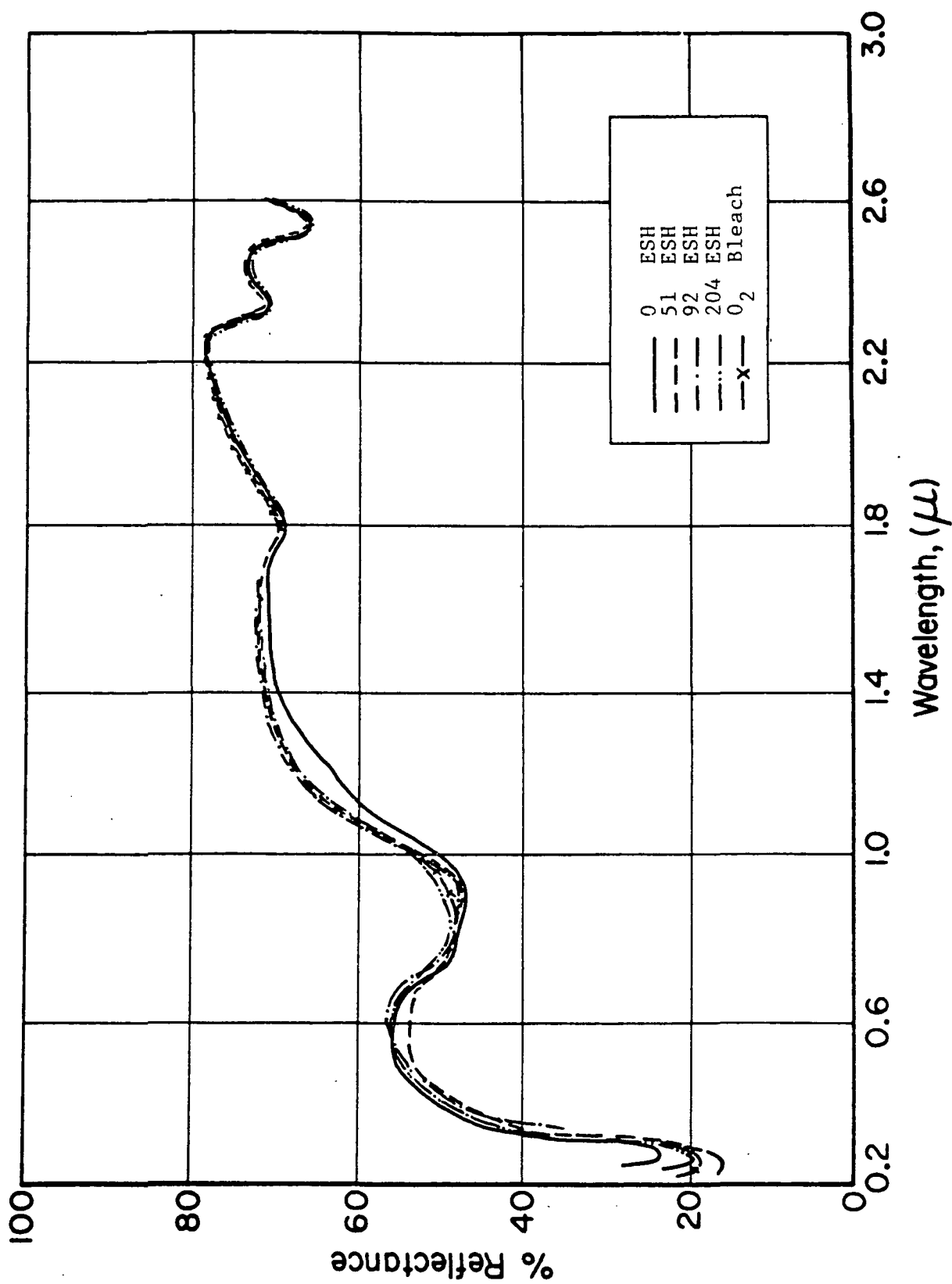
Figure A-10

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF
POLYETHYLENEOXIDE (M.W. = 20,000) ON ALUMINUM SUBSTRATE

## Table A-11

### CHANGE IN REFLECTANCE(R) OF IRRADIATED POLYETHYLENEOXIDE (M.W. = 5,000,000) IN THE UV-VISIBLE REGION

| Wavelength (μ) | $\Delta R$ (50 hr) | $\Delta R$ ( 90 hr) | $\Delta R$ (200 hr) | $\Delta R$ (200 hr $O_2$ bleach) |
|---|---|---|---|---|
| 0.250 | +6.5 | - | +9.0 | +7.5 |
| 0.325 | +3 | - | +3.5 | +1 |
| 0.377 | +1 | +1 | -1 | -1 |
| 0.457 | 0 | +1 | 0 | -1 |
| 0.554 | 0 | +1 | 0 | -1 |
| 0.700 | +1 | +1 | +2 | +2 |
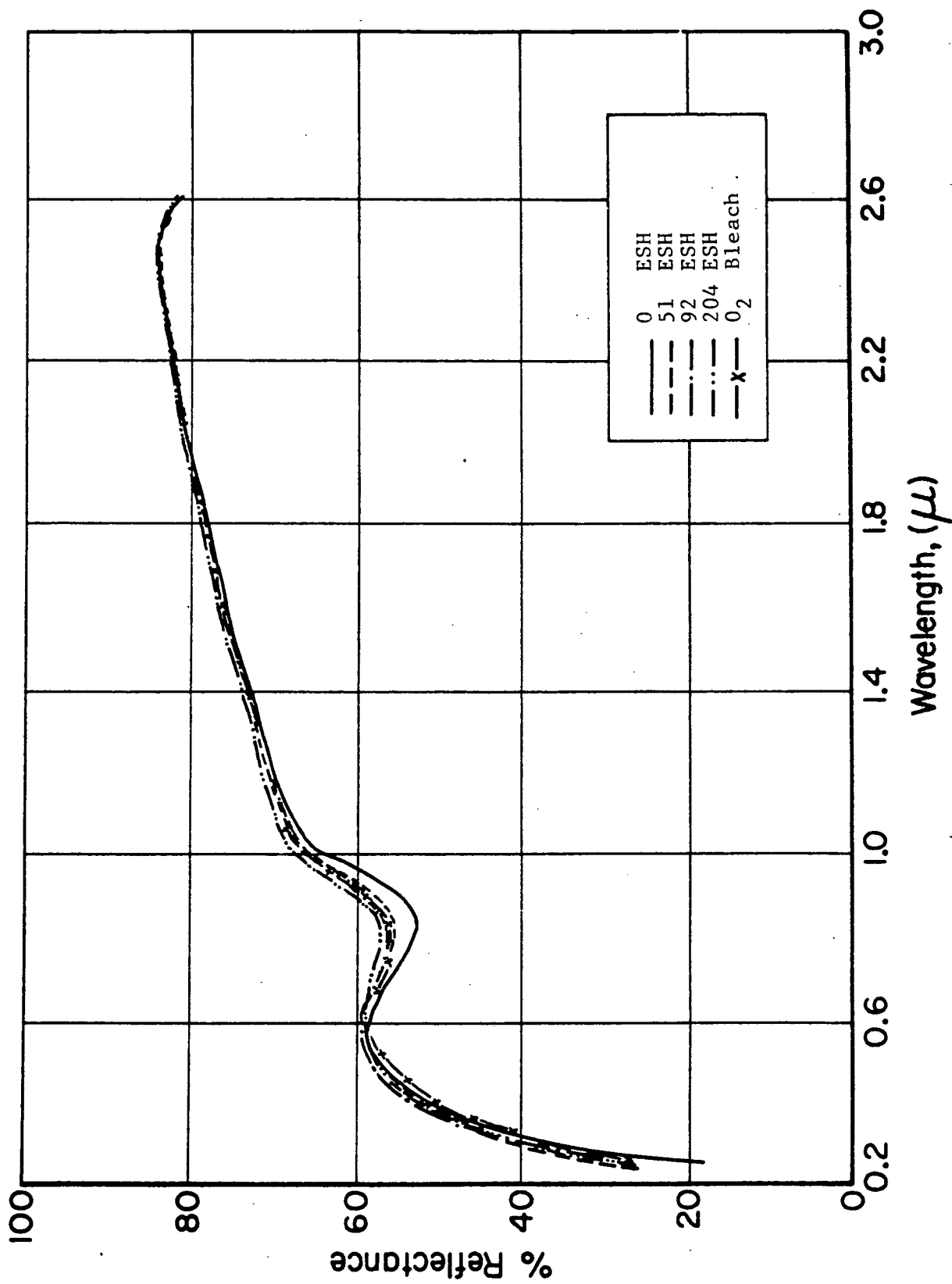
Figure A-11

EFFECT OF UV IRRADIATION ON THE REFLECTANCE OF POLYETHYLENEOXIDE
(MW = 5,000,000) ON ALUMINUM SUBSTRATE

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