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DEVELOPMENT OF ULTRAVIOLET LIGHT STABILIZATION METHOD FOR TRANSPARENT POLYARYLSULFONES

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W. A. HENDERSON, JR.
N. D. SEARLE

AMERICAN CYANAMID COMPANY

TECHNICAL REPORT AFML–TR–74–58

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WRIGHT–PATTERSON AIR FORCE BASE, OHIO 45433

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FOREWORD

This report was prepared by the Chemical Research Division of the American Cyanamid Company, Stamford, Connecticut 06904, under USAF Contract No. F 33615-73-C-5168. This contract was initiated under Project Nr. 7340, Nonmetallic and Composite Materials", Task Nr. 734003, "Structural Plastics and Composites". The program was administered by the Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Mr. E. A. Arvay (AFML/MBC) as Project Engineer.

This program was initiated by the use of AFML In-House Laboratory Independent Research Funds.

This project was conducted during the period June 15, 1973 to December 15, 1973. Contained herein are discussions and experimental results concerning the light stabilization of transparent polyarylsulfones.

The principal investigator for this research effort was Dr. A. Zweig.

The following scientists also contributed to the program: Dr. J. S. Brinen, Mr. N. B. Colthup, Mr. R. Evans, Mr. J. P. Falzone, Dr. J. B. Gallivan, Dr. W. A. Henderson, Jr., Dr. N. D. Searle, and Mr. T. Mead.

The report was submitted by the authors in January, 1974.

This technical report has been reviewed and is approved for publication.

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ABSTRACT

The polyarylsulfone polymer is an exceptionally photosensitive plastic the degradation of which is manifested by ultraviolet visible and infrared absorption spectral changes as well as haze development, changes in fluorescence, embrittlement and loss of impact strength. The wavelengths most effective in causing these events are in the short wavelength ultraviolet (310-330 nm) region corresponding to onset of strong absorption by the polymer itself. As the photochemical processes proceed the rate of degradation slows but only after optical properties near the exposed surface have deteriorated to unacceptable levels. The photolysis is independent of moisture but requires oxygen, and generates hydroxylic and carbonyl compounds without an induction period. It produces a radical species not associated with sulfur and it also affects the oxidation state of the sulfur that is present.

The degradation is not accelerated by singlet oxygen sensitizers or significantly quenched by singlet oxygen quenchers, energy transfer agents, antioxidants or antioxidant synergists. It is accelerated by benzophenone and its rate is reduced with UV absorbers particularly hydroxybenzotriazoles which are most effectively competitive for the short wavelength ultraviolet radiation that is primarily responsible for the degradation. The damaging light is absorbed by the polymer itself or a very strongly absorbing impurity with similar solubility characteristics. The specific photochemical and chemical processes responsible for the degradation are unknown. Protective UV light absorbing additives are the only effective means of reducing the photodegradation of this material. The absorbers should be concentrated at the exposed surface for optimum effectiveness. At most they can provide no more than a five-to tenfold decrease in rate of photodegradation of the polymer.

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SECTION I

INTRODUCTION, CONCLUSIONS AND RECOMMENDATIONS

A. INTRODUCTION

Polyarylsulfone plastics which are normally opaque offer a unique combination of thermoplasticity and retention of structurally useful properties at temperatures as high as 500°F.[1] Recently, a new transparent type of polyarylsulfone retaining the desirable thermal stability has been developed for the Air Force for use in aircraft.[2] This polymer is also characterized by exceedingly poor light stability. For example, a prior study showed that 10 days (240 hrs.) of exposure of a sheet (Polymer A) of this material in an Atlas Carbon Arc Fade-Ometer produces a decrease in light transmission from 83.7 to 66.8% and increase in haze from 3.9 to 24.7%.[2] These results, clearly unacceptable for the intended use, are not completely unexpected because a published report had indicated extremely poor light stability in related non-transparent polyarylsulfones.[3]

Efforts to improve the light stability of the transparent polyarylsulfone formulation through the use of commercial additives were hampered by the incompatibility of most of these additives with the high processing temperature (> 500°F) required for fabrication of this plastic.[2] The previous study evaluated 17 commercial UV absorbers, to determine if they could withstand 500°F.[2] These additives all either volatilized or darkened. The six which volatilized were then ground and blended (at 1%) into the polysulfone and sheets were prepared by compression molding. Because of bubbling and volatilization which then occurred the results were unsatisfactory. A liquid stabilizer was evaluated as a dip-coat on the polysulfone but 30 minutes at 300°F removed it through vaporization. The investigators reported that an experimental (unidentified) UV stabilizer had sufficient thermal stability to allow use as a coating. As their data shows (Table 1) this additive does not significantly affect the photoinduced loss in transmission but it does reduce the otherwise severe haze problem.[2]

While these previous efforts served to establish that existing commercial photostabilizing chemical additives do not possess adequate thermal stability for incorporation into polyarylsulfone polymer, they also provide no indication that any additives can produce an adequate photostabilizing effect in this polymer even in the absence of the thermal stability requirement. Photostabilizers which are effective in one material are often ineffective in others because different degradative processes occur. Thus, a research effort to incorporate a given type of photostabilizer into a high-melting polymer would be wasted if the resulting photostabilizing effect proved inadequate.

TABLE 1

Effects of UV Exposure on Polymer A Polyarylsulfone (AFML-TR-72-110 Part I)

Sample	Carbon Arc Exposure (hr.)					
	0		100		240	
	% Trans.	% Haze	% Trans.	% Haze	% Trans.	% Haze
No Coating	83.7	3.9	77.9	5.1	66.8	24.7
Light Stabilizer Coating	77.0	3.6	68.6	4.4	57.3	6.3
Heavy Stabilizer Coating	76.7	3.2	71.4	3.6	68.8	3.8

This report describes our efforts to establish the nature of the process by which the transparent polyarylsulfone polymer supplied to us by the Air Force photodegrades and to determine the type of protection that would be most effective and the degree of protection that the most appropriate treatment with additives would afford. These efforts consisted of detailed spectroscopic and physical measurements and analysis, and incorporation and evaluation of additives in solvent cast films of the polymer. They thus provide information on/or approaches to the photostabilization of the polymers which are independent of the thermal stability problem.

B. CONCLUSIONS

The transparent polyarylsulfone polymer supplied by the Air Force was found to be too sensitive to ultraviolet radiation and the photodegradative processes which take place in this material were found to be too efficient and effective at the exposed surface for additives to provide the desired level of protection under normal outdoor exposure conditions. Lamination of an efficiently UV absorbing, photostable material on the exposed surface of the polymer could provide adequate protection. Such coatings or laminates would be hard to fabricate and if of material other than the polyarylsulfone itself, would not be likely to possess the desired high temperature properties.

C. RECOMMENDATIONS

It is recommended that photochemical reactions of model biphenylsulfones and diphenylether sulfones be investigated. These studies which would include quantum efficiencies, sensitization, oxygen dependence and product determinations would permit characterization of the nature of, and requirements for the oxidative photodegradation occurring in the polyarylsulfone polymer. It would not be possible to obtain this information as readily from studies of the polymer itself. Such studies could lead to the design of new arylsulfone polymers which, while retaining the desirable thermal, optical and mechanical properties, would not exhibit the extreme photosensitivity characteristic of the the present material.

SECTION II

RESULTS AND DISCUSSIONS

A. GENERAL

The initial information sought was the spectral characteristics and activation spectrum for yellowing and for other indicators of photodegradation since these provide clues as to what the responsible absorbing species are and also provide information concerning the wavelengths UV absorbing additives must absorb to best protect the polymer. Compression molded sheet supplied by the Air Force and solvent cast film (~1.2 mil thick), the preparation of which is described in the Experimental section of this report, were both employed in this study. The degradation of the polyarylsulfone was measured by means of changes in ultraviolet, visible and infrared spectral features resulting from exposure to optically dispersed radiation from a filtered high pressure xenon arc approximating sunlight in spectral distribution (details in Experimental section) as well as from exposure to the radiation from a Xenon Weather-Ometer. Other types of spectroscopic and physical measurements were also made to assess the nature of the polyarylsulfone degradation process and the requirements for its most effective inhibition. The specific results of each study are described and discussed in separate sections.

B. ULTRAVIOLET ABSORPTION CHANGES

The ultraviolet absorption spectra of 1 mil solvent cast film before and after exposure to actinic radiation are shown in Figure 1. Initially, the film is transparent to wavelengths longer than 320 nm. Below 320, absorption increases with decreasing wavelength so that by 305 nm less than 1% of the incident radiation is transmitted. This absorption is consistent with the expected long wavelength edge of the benzenoid absorption of a polymer with the claimed structure. Exposure of the film in the Xenon Weather-Ometer for 18 hrs. produced an increase in absorption and a shift in the edge of the absorption spectrum of the film to longer wavelength as shown in Figure 1. Thus, the photodegradation increases the opacity of the film to ultraviolet radiation, reduces the penetration of the radiation and appears to cause further degradation to be confined closer to the exposed film surface.

C. INFRARED SPECTRAL CHANGES

The infrared spectra of a polyarylsulfone film measured before and after exposure to radiation from the Xenon arc Weather-Ometer are shown in Figure 2. Initially, the film shows strong sulfone bands at 1150, 1290, and 1320 cm^{-1} and aryl ether absorption at 1230 cm^{-1}. No trace of

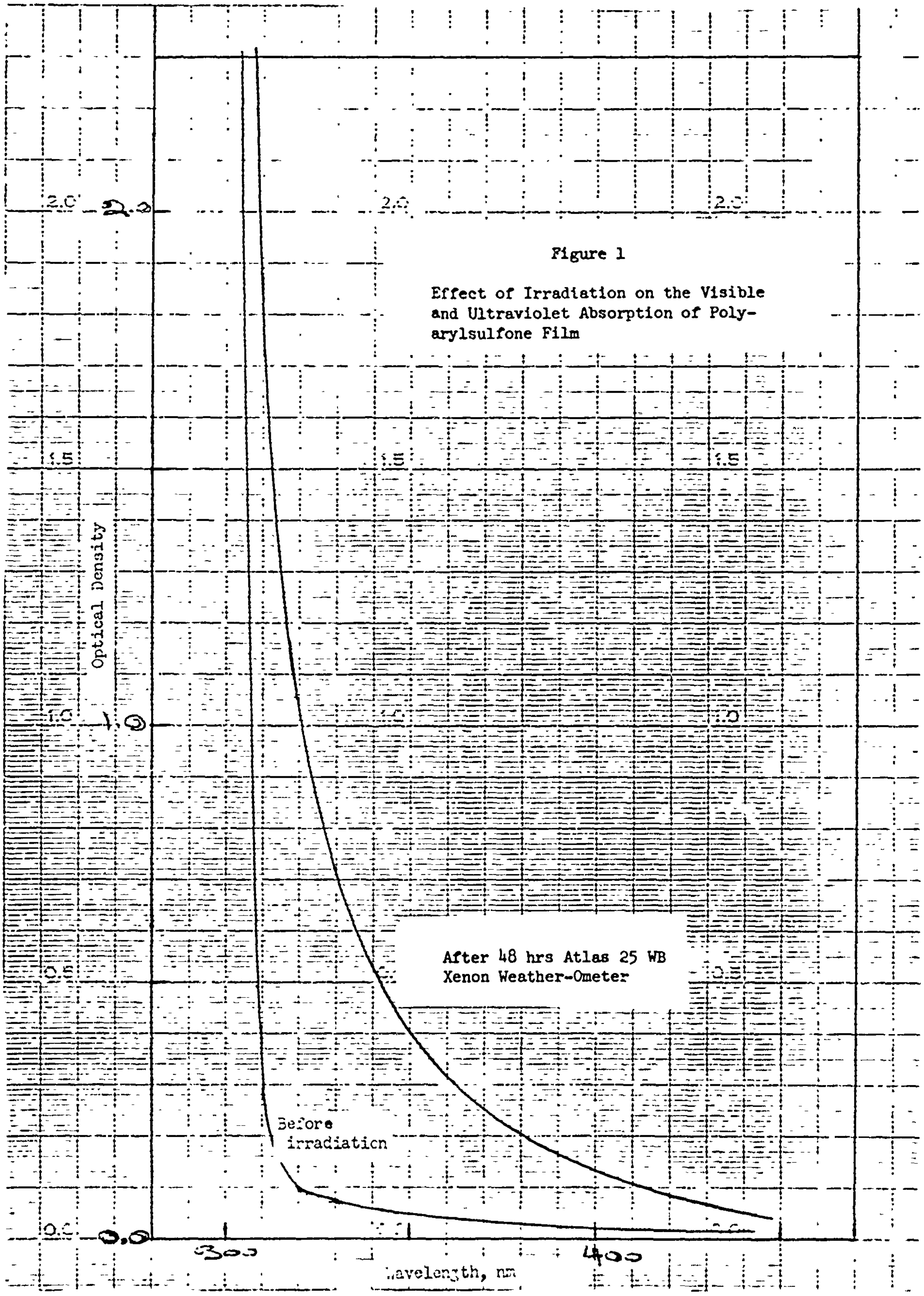
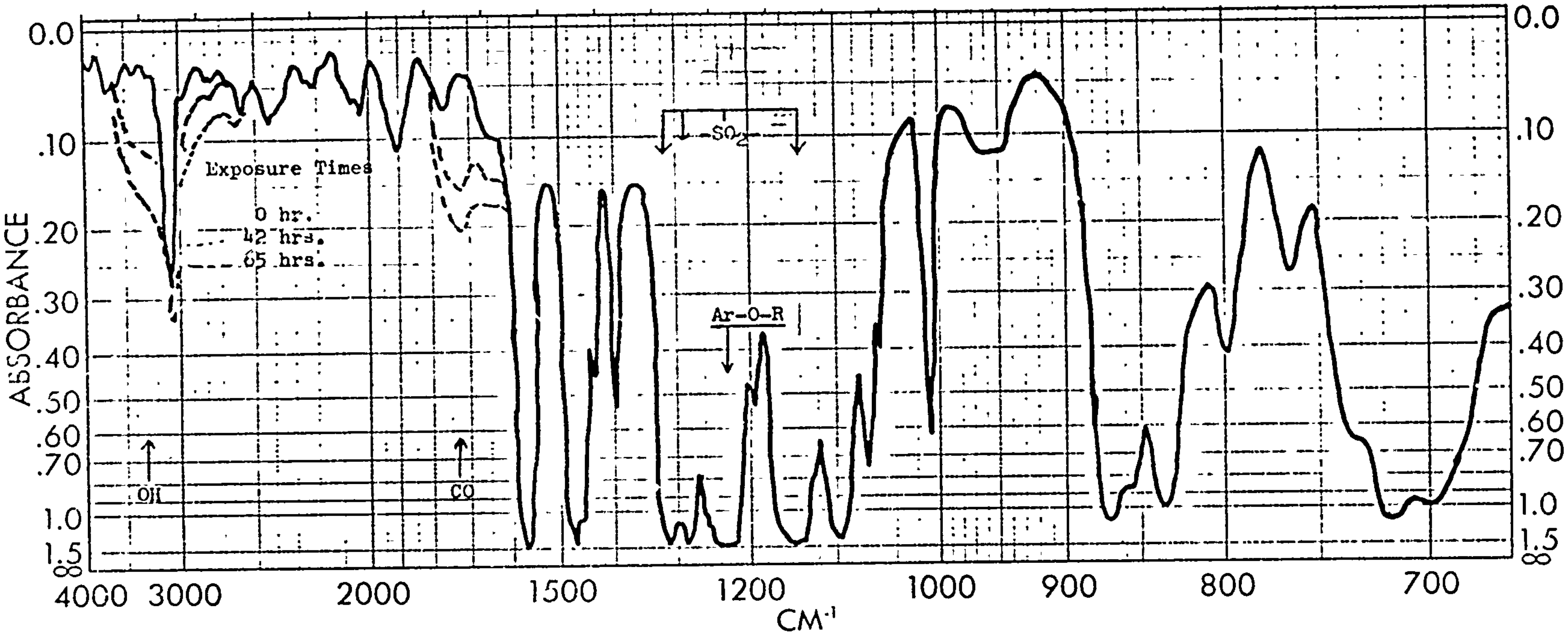


Figure 1

Effect of Irradiation on the Visible and Ultraviolet Absorption of Polyarylsulfone Film



Effects of Irradiation on the Infrared Spectrum of Polyarylsulfone Film

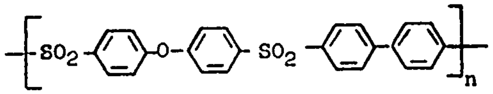


Figure 2

carbonyl due to the DMF solvent used in film preparation could be detected. Exposure to the light in air for periods of 42 and 65 hrs. caused virtually no measurable changes in the strong bands of the polymer but produced significant new absorption in the hydroxyl region (around 3400 cm^{-1}) and the carbonyl region (around 1725 cm^{-1}). The rates of increase in absorption with exposure in the two wavelength regions were comparable and the rate falls off markedly after about 100 hrs. of exposure, at which point the film is extremely fragile. The growth of carbonyl absorption bands is indicative of acid, aldehyde and/or ketone formation, although the intensity and broadness of the hydroxyl absorption suggests that alcohols and/or hydroperoxides are also present. A typical curve for the rate of increase in OH absorption with time of exposure is given in Figure 3; where it is compared with that for a polybutadiene-containing transparent impact polymer which is regarded as having poor light stability. The curves differ in that the polysulfone photodegradation appears to proceed more rapidly and shows no induction period while the impact polymer does. In addition, the effective rate of photoinduced hydroxylic compound formation is markedly higher in the polyarylsulfone than in the impact plastic. The relative peak intensities indicate a carbonyl concentration of no more than 3.5% that of the sulfone. Efforts to see if this proportion could be increased by further irradiation repeatedly failed due to disintegration of the film. From the molecular structure indicated by the manufacturer,[2] and substantiated by the infrared spectrum, it is difficult to establish the reaction sequence or mechanism responsible for carbonyl formation. Possibilities include a) photooxidation of a benzene ring of the polymer or b) photooxidation of an aliphatic compound present in low concentrations.

D. ACTIVATION SPECTRA

Activation Spectra showing the degradation of the thin film as a function of wavelength of irradiation are plotted in Figures 4 and 5. The former is based on visible and ultraviolet absorption changes and the latter is based on formation of infrared-absorbing species in the carbonyl and hydroxyl regions.

The spectra show that the active wavelengths extend from 260 to 380 nm with maximum degradation produced by radiation ranging from 305 to 330 nm. The wavelength peak of the activation spectrum was found to depend on the length of time of exposure and thus on the extent of photodegradation, on the method of measurement of the extent of degradation, and also on the film thickness. The activation spectrum as measured is a function of the spectral emission curve of the light source and the absorption curve of the photosensitive entities in the sample. It falls off rapidly with decrease in wavelength below 305 nm because of the rapid drop off in intensity of the filtered xenon source despite the fact that the sample continues to absorb strongly. Initially, radiation in the region of 305 nm has the greatest actinic effect because it corresponds to the highest intensity of absorbed radiation. As the photodegradation progresses, the reactive species become depleted and the effect is more rapid under the more strongly absorbed shorter wavelengths of irradiation. In addition, the degradation

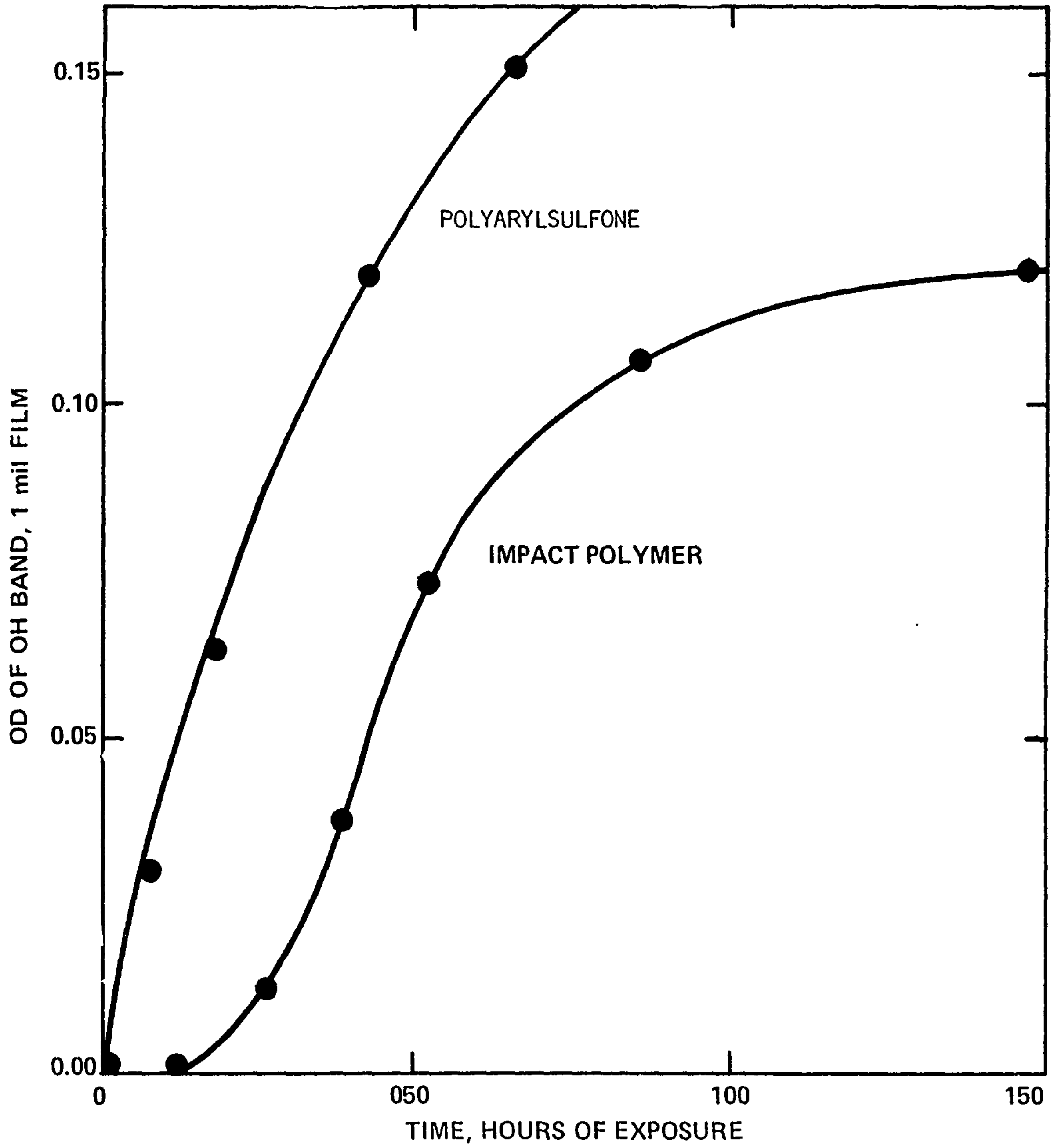


FIGURE 3
COMPARATIVE EFFECTS OF XENON WEATHER-OMETER EXPOSURE
ON IR OF UNPROTECTED CLEAR POLYMER FILMS

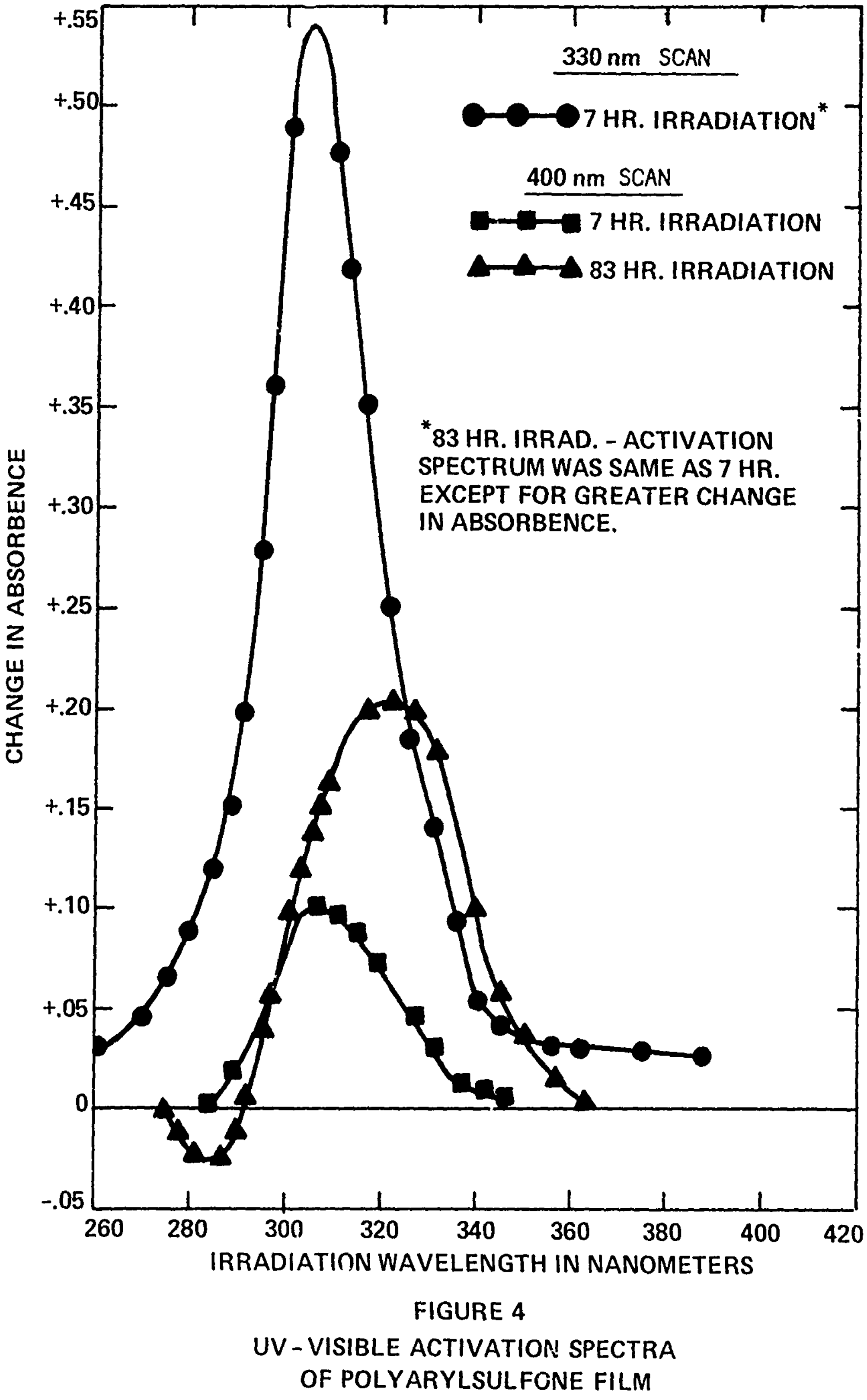


FIGURE 4
UV-VISIBLE ACTIVATION SPECTRA
OF POLYARYLSULFONE FILM

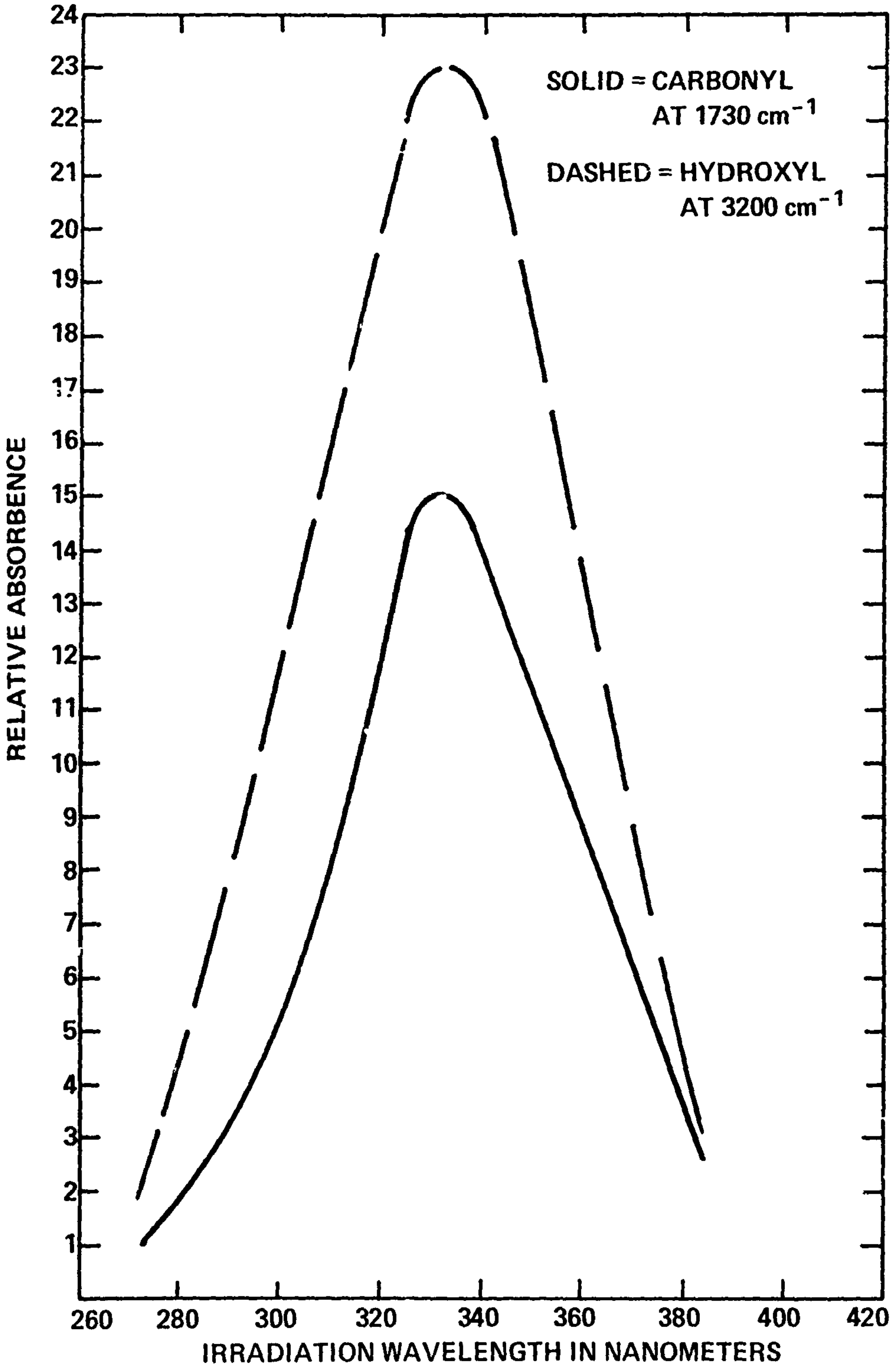


FIGURE 5

IR ACTIVATION SPECTRA
OF POLYARYLSULFONE FILM

products formed, while highly absorbing, do not appear to promote further degradation. This interpretation is based on the fact that the rate of degradation slows down in the area of the sample which was initially most severely affected and the activation spectrum peak shifts to longer wavelengths. This is evident in Figure 4 in comparing the curves obtained after 7 and 83 hours of irradiation using 400 nm as the measuring wavelength. The latter wavelength is more sensitive than 430 nm to increase in opacity and thus allows earlier detection of yellowing. The increased yellow appearance of the material on irradiation results from a general increase in absorption (see Figure 1) which reduces the transmission of blue light (light in the region of 430 nm) more than that of the other colors.

Although the longer the exposure, the greater the increase in opacity, the extent of degradation is clearly not a linear function of exposure. The degradation rate is more rapid initially and decreases with length of time of exposure. The extent of degradation appears to be a logarithmic function of exposure. Thus, 7 hours of irradiation produced a 0.1 absorbence unit increase in opacity to 400 nm in the 1 mil film while 83 hours of irradiation was required to double the initial increase in opacity. The reduction in degradation rate with time is further evidence that the degradation products do not autocatalyze the products, but rather screen the incident radiation from the remaining active sites.

It is surprising that the opacity of the sample is not increased by all wavelengths of irradiation. Thus, on prolonged exposure, short wavelengths, between about 275 and 290 nm, cause a decrease in opacity to visible light, i.e., destroy the yellow species originally present. Although this observation has no immediate practical utility it could be used as a starting point in photochemical mechanism studies.

Since photodegradation of the polyarylsulfone film manifests itself as a general increase in opacity which is most pronounced in the short wavelength region (see Figure 1), the shorter the wavelength of scan, the greater the sensitivity to changes in transmission. Thus, after only 7 hours of irradiation the 330 nm scan of the film produced an increase in opacity greater than 0.5 absorbence units in the area of maximum degradation, i.e., the area exposed to 305 nm. However, in contrast to the 400 nm scan, prolonged irradiation did not produce a shift in the relative sensitivity curve, but merely caused further increase in opacity.

The extent of degradation as a function of time of exposure as well as the peak wavelength sensitivity depends also on the thickness of the sample. For example, the 2 mm thick polysulfone sheet showed significant yellowing when exposed for only 1 hour in the irradiating spectrograph. The area of the sample which was most severely affected increased in absorbence by 0.3 units at 400 nm. The activation spectrum peak, i.e., the incident wavelength region having the maximum effect, was about 320 nm, a 15 nm shift to longer wavelength compared with the 1.2 mil film. After 16 hours irradiation the peak shifted to about 332 nm. The shift to somewhat longer wavelength sensitivity for the thicker sample is explained by its stronger general absorption. The absorption is stronger throughout the entire ultraviolet region. However, combined with the emission characteristics of the radiation source, the highest intensity of absorbed radiation is initially in the region of 320 nm for this sample.

The infrared activation spectra were based on increase in absorption in both carbonyl and hydroxyl regions. The 1.2 mil film was investigated because, unlike the 2 mm sheet, it had sufficient transparency in infrared regions of interest. The curves given in Figure 5 show that wavelengths in the region of 330 nm produce the highest concentration of both carbonyl and hydroxyl groups. The measurements required 83 hours of irradiation since the infrared technique is somewhat less sensitive than the ultraviolet and visible to the effects of photodegradation. For the same length of exposure the infrared activation spectra were similar to that based on the extent of yellowing, suggesting that these different manifestations of degradation arise from the same degradation products. However, this data alone does not unequivocally establish that the yellowing results from the buildup of species containing carbonyl and hydroxyl groups.

E. ENVIRONMENTAL EFFECTS ON PHOTODEGRADATION

Duplicate polyarylsulfone film samples irradiated for 48 hours in the Xenon Weather-Ometer under nitrogen in sealed quartz cells showed no infrared spectroscopic evidence of degradation. When the seals were broken and the same samples were irradiated in air, degradation proceeded as before. In a similar manner it was shown that the reportedly hydroscopic polyarylsulfone film when predried over phosphorus pentoxide and irradiated in dry air photodegraded at the same rate as undried film in the Xenon Weather-Ometer held at 125°F and 50% humidity. Thus, oxygen but not water is a coreactant in polyarylsulfone photodegradation in the atmosphere.

F. CORRELATION OF INFRARED SPECTRAL CHANGES WITH FILM EMBRITTLEMENT

Simultaneous with irradiation and examination by infrared spectroscopy a number of film strips were exposed for evaluation by a simple crease test. This was conducted by flexing and creasing between thumb and forefinger. Initially and through 7 hours of Xenon Weather-Ometer exposure, none of ten strips tested cracked as a result of this treatment. After 9 hours of exposure, ten out of ten strips, crease tested for the first time, cracked. Cracking of the samples in all cases occurred when the optical density at 3400 cm^{-1} had increased from about 0.044 to 0.054. There thus appears to be a correlation between embrittlement and the extent of photodegradation as measured by infrared absorption.

G. TRANSMISSION AND HAZE MEASUREMENTS

Samples of 1/4" polyarylsulfone sheet as supplied by the Air Force (very yellow) were examined for changes in transmission and haze as a function of exposure using ASTM methods 308 and 1003. These samples were exposed in both the Xenon Weather-Omether and the Carbon Arc Fade-Ometer with spectral reading taken on the same area of each piece after 0, 100 and 240 hours of exposure. The results as listed in Table 2 show similar

TABLE 2

Transmission and Haze Measurements on 1/4" Polyarylsulfone Sheet

Exposure (hr.)	Xenon WOM		Carbon Arc	
	% Haze	% Trans.	% Haze	% Trans.
0	14.7	66.0	13.5	67.8
100	13.9	69.2	12.7	62.3
240	28.7	59.6	14.0	59.9

decreases in transmission with the two light sources. However, the Xenon arc which has a smaller total output but a greater output below 350 nm than the carbon arc and a ratio of the two which closely resembles sunlight (Table 3), has a marked deleterious effect on haze after 240 hours of exposure. The visual appearance of the hazed sheet revealed that the depth of penetration of haze extended to much less than 1 mil below the exposed surface.

Weather-Ometer exposure also causes a marked increase in haze in the 1.2 mil films of polyarylsulfone polymers. Increases in yellowness, although real, as shown by the changes in absorption in Figure 1, are not as pronounced in the thin film as in the sheet due to the shorter path length of the light. Haze in film samples containing various additives was found to correlate reasonably well with increase in absorption of the OH band in the infrared, as shown in Table 4.

H. IZOD NOTCH IMPACT TESTS

The tests were run according to ASTM method D 256. Polysulfone notched bars of 1/4" sheet were exposed in the Xenon Weather-Ometer for 0, 100 and 240 hours. The Izod impact strengths averaged for sets of three bars at each time were 0.46±0.03, 0.23±0.00 and 0.23±0.00, ft. lbs./in. respectively. It is clear that photodegradation is essentially complete after less than 100 hours, and that the decrease in strength is quite substantial.

I. ESR EXAMINATION

A Varian 4500 ESR spectrometer was used for the investigation. Irradiation of a sample of the 2 mm thick polyarylsulfone sheet in the ESR cavity with the unfiltered output of a Mercury Arc focussed on the sample at 25°C in air caused a free radical to be formed. This radical produced a featureless ESR signal which grew in intensity with continued irradiation and which slowly decayed with time when the irradiation was stopped. The g value of the radical is approximately 2.003 and it is therefore <u>not</u> a sulfur radical which would have $g \cong 2.02$.[7]

J. ESCA STUDIES

Samples of irradiated and unirradiated polyarylsulfone film were examined by ESCA using the Hewlett-Packard HP-5950A spectrometer. Irradiated material showed a sulfur peak with a bonding energy of 166.7 eV and a carbon peak. Unirradiated film initially showed no sulfur peak and a different carbon peak. After 15 minutes in the instrument under vacuum and exposed to the X-ray beam, the sample developed a spectrum identical to that of the irradiated material. A possible explanation is that a minute film of foreign material is present on the unirradiated film, and that this must be removed to expose the polysulfone. The sulfur peak observed appears to be that of unirradiated material, i.e., sulfone. Freshly exposed surfaces of molded sheets, however, gave ESCA spectra which also initially showed no sulfur electron lines. After approximately 60 minutes of exposure

TABLE 3

Absolute UV Intensities of Weathering Sources at Sample Distance

(Reference 4)

Source	Total UV μW/cm^2	UV Below 350 nm μW/cm^2	Ratio (below 350: total UV)
Sunlight, June 1957, noon, Stamford, Conn.	4,243	1,177	0.276
Sunlight, December 1957, noon, Stamford, Conn.	1,389	257	0.185
Carbon Arc Fade-Ometer	19,531	309	0.016
Xenon Weather-Ometer (Atlas 6000W)	3,735	960	0.257

TABLE 4

Comparative Protective Effects of Additives Based on Generation of Hydroxyl Groups and Haze Resulting from Irradiation of Polyarylsulfone Film

Additive (2 wt.%)	72 hrs. Xenon Exposure	
	% Haze Increase	$A_{3400cm^{-1}}$ Increase
None	7.1	.169
Ni (II) dibutyldithiocarbamate	6.5	.121
Irgastaab 2002	3.7	.155
Uvinul N35	3.7	.072
Cyasorb UV 24	3.3	.076
Tinuvin 327	1.4	.048

to X-rays from the spectrometer a weak sulfur signal was again detected. The behavior was very similar to that of the solvent cast film except that buildup of sulfur lines on X-ray exposure of the film was more rapid. The sulfur lines of the sheet material shifted to higher binding energy (higher oxidation state) as the experiment on the sheet material progressed. Weather-Ometer exposed (48 hrs.) sheet clearly shows sulfur present in an oxidized state. Continued X-ray exposure of this material produced little change in its ESCA spectrum.

K. FLUORESCENCE EMISSION

Visual inspection under black light (365 nm) excitation of unexposed polyarylsulfone film or sheet revealed little emission while after exposure to the dispersed radiation source used to obtain activation spectra; emission was observed which appeared blue-white in the regions exposed to short ultraviolet wavelengths and yellow in regions exposed to longer wavelengths. Since the appearance of emission can be a useful aid to the analysis of photochemical processes, a further quantitative examination was made.

This examination revealed that both unexposed and exposed (100 hr. Xe WOM) 2 mm polyarylsulfone sheet exhibit strong blue (to the eye) fluorescence when excited with short wavelength (~320 nm) radiation. Using a Perkin-Elmer Fluorescence Spectrophotometer model MPF-2A, the emission curves (Figure 6) indicated that the emission peaks near 360 nm in both instances, with about three times greater intensity from the unexposed as the exposed sample. The emission from both samples tails through much of the visible. As shown in Figure 7 these tails extend to at least 600 nm. As shown in Figure 8, the excitation maximum for the fluorescence emission at 360 nm is at about 310 nm in the unexposed film and 320 nm for the exposed film, corresponding roughly to their long wavelength edge of their absorption. The short wavelength excitation (320 nm) in this study permitted detection of UV fluorescence in the unirradiated sample and showed that the species responsible for this fluorescence is being destroyed by irradiation. This is evidently a different fluorescent species than that visually detected under 365 nm excitation. These results thus provide little insight into the degradation problem. A more detailed study of the different fluorescent species which appear to be formed by exposure of the polymer to selected wavelengths of its activation spectrum would be useful in probing the mechanism of photodegradation. Such a study falls outside the scope of the investigation reported here.

L. MASS SPECTROSCOPY

The CEC 21-110B High Resolution Double-Focussing mass spectrometer was employed in an effort to further characterize the products of photolysis of the polyarylsulfone polymer. The only mass peaks that could be detected from this polymer after heating to less than 200°C were at m/e 98, m/e 148 (phthalic anhydride) and m/e 184 ($C_7H_4O_4S$?). Heating samples to above 200°C produced SO_3, SO_2 and other sulfur and oxygen containing moieties but no distinctive product patterns could be discerned.

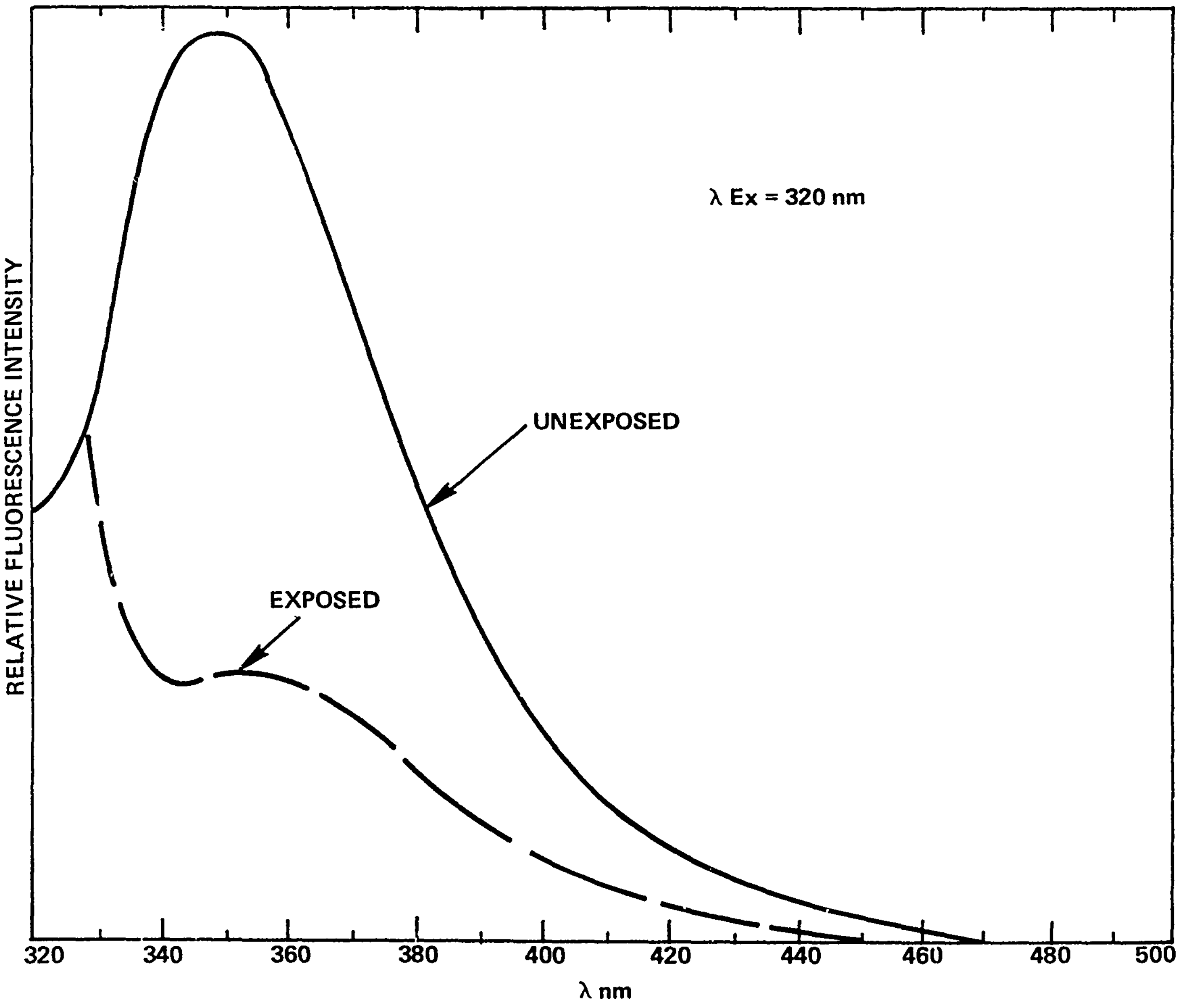


FIGURE 6
POLYARYLSULFONE SHEET FLUORESCENCE

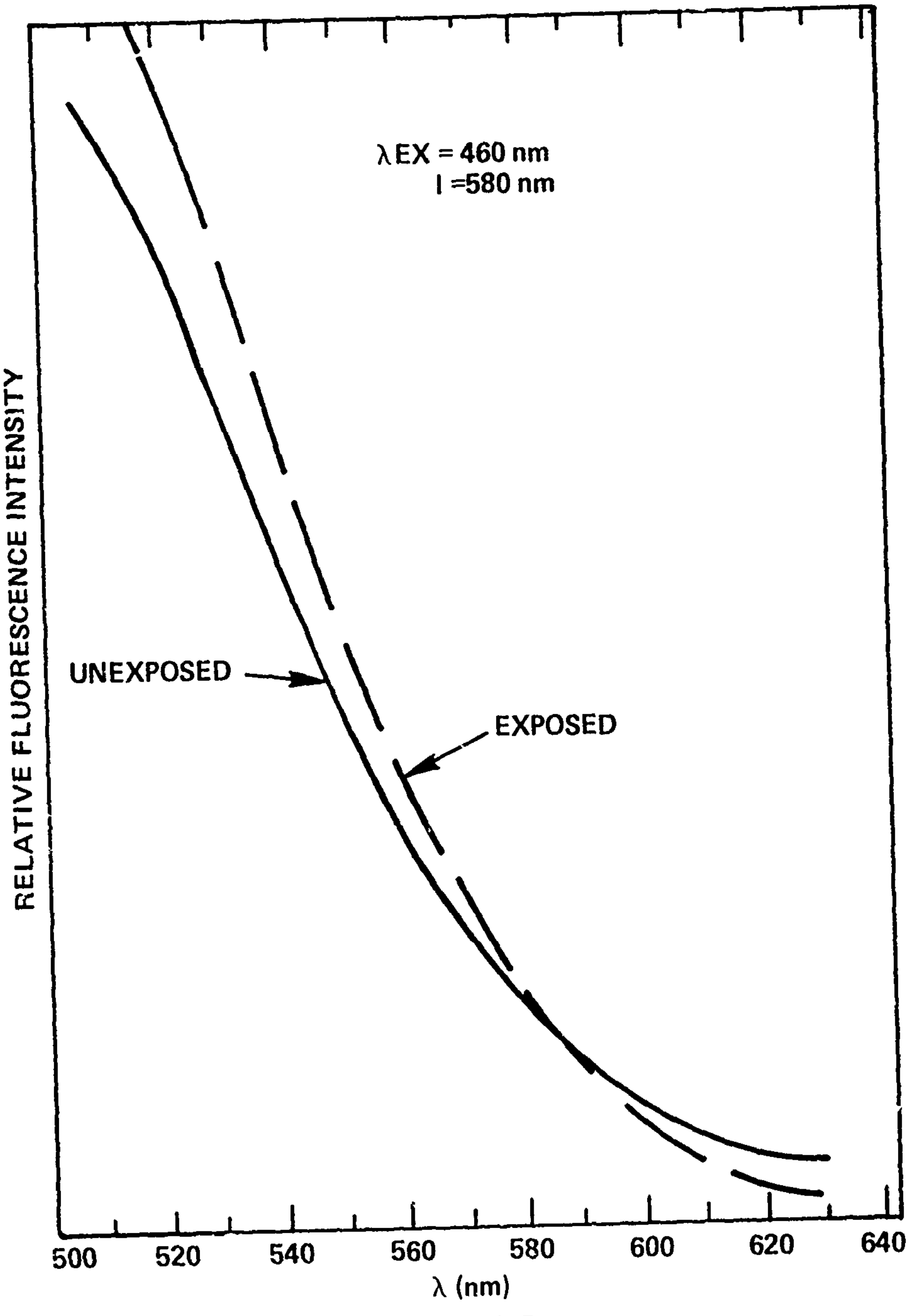


FIGURE 7

POLYARYLSULFONE SHEET FLUORESCENCE
(TAIL OF BLUE FLUORESCENCE EXPANDED)

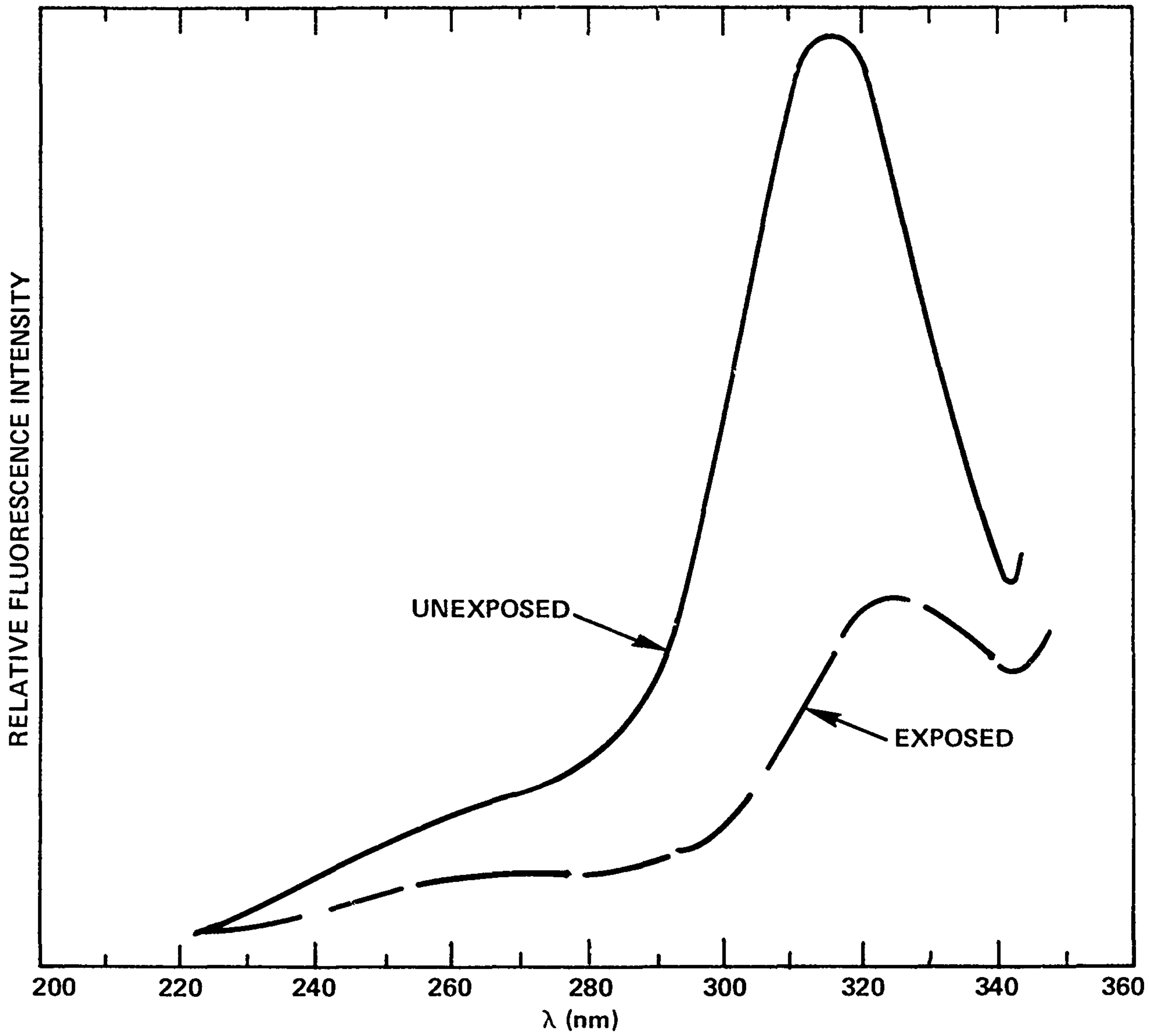


FIGURE 8
POLYARYLSULFONE SHEET
(FLUORESCENCE EXCITATION SPECTRUM)
EMISSION WAVELENGTH 360 nm

M. SENSITIZED PHOTODEGRADATION

Thin films of the polymer were prepared containing amounts of photosensitizers sufficient to give optical densities of about 2 in the UV-visible spectral regions of maximum absorption by the sensitizers. The films were exposed together with blanks (films containing no additives) in the Xenon Weather-Ometer. Photodegradation was followed by measuring increase in absorption at 3400 cm^{-1} in the infrared region. The results plotted in Figure 9, show that typical singlet oxygen sensitizers (Rose Bengal and Rubicene) reduce the rate of increase in the hydroxyl peak, indicating that singlet oxygen is not involved in the photoreaction, and that these sensitizing compounds are acting as light absorbers, effectively competing with the moiety normally responsible for photodegradation. Benzophenone, which functions as a radical chain initiator and/or a direct energy transfer sensitizer, significantly accelerates the rate of polyarylsulfone photodegradation. The film containing benzophenone also becomes much yellower than the blank after irradiation.

N. PHOTOSTABILIZATION THROUGH ADDITIVES

An initial set of formulations of polyarylsulfone films containing photostabilizers of various types at a 1% (by wt.) level was evaluated with and without the presence of a phenolic antioxidant at a 1% by wt. level. The latter was given special attention because esr evidence (Section I) had clearly pointed to radical products of irradiation of the polymer. Degradation was followed by monitoring the increase in hydroxyl absorption at 3400 cm^{-1} in the infrared spectrum of the film. The results of this study are listed in Table 5. Additive names used are commercial designations for the sake of brevity. Table 6 lists the structures and chemical names of all additives investigated. Contrary to our expectations the results show that the phenolic antioxidant had almost no effect on the rate of photodegradation of any of the films. This result indicates that a photoinitiated radical chain process is not a significant cause of the photodegradation of this polymer. Of the compounds studied, an hydroxybenzotriazole (Tinuvin 328) short wavelength UV absorber was the most effective in retarding the photodegradation.

A new set of twelve polyarylsulfone film formulations was prepared, each film containing a different additive at a 2 wt.% level. The additives included materials which function as UV and visible light absorbers, as energy quenchers (including singlet oxygen quenchers), and as antioxidant synergists. These films were then exposed to the Xenon Weather-Ometer and their infrared spectral characteristics monitored as a function of time of exposure. The results as listed in Table 7 point to the hydroxybenzotriazole UV absorbers as being the most effective class of materials in reducing the rate of photooxidation of the polyarylsulfone film. As judged by comparisons of increase in absorption at 3400 cm^{-1} on exposure in the Weather-Ometer, these additives decreased the rate of degradation to one-fifth that of a blank. Four other light absorbing stabilizers, Cyasorb UV-531, Cyasorb UV-24, Uvinul® N-35 and N-p-phenylazophenylmaleimide afforded somewhat less protection. Four nickel chelates, Cyasorb UV-1084®, Cyasorb UV-2408®, nickel dibutyldithiocarbamate and Irgastaab® 2002 believed to function through energy quenching, were ineffective. Similarly, an antioxidant synergist, DLTP, also gave no stabilization.

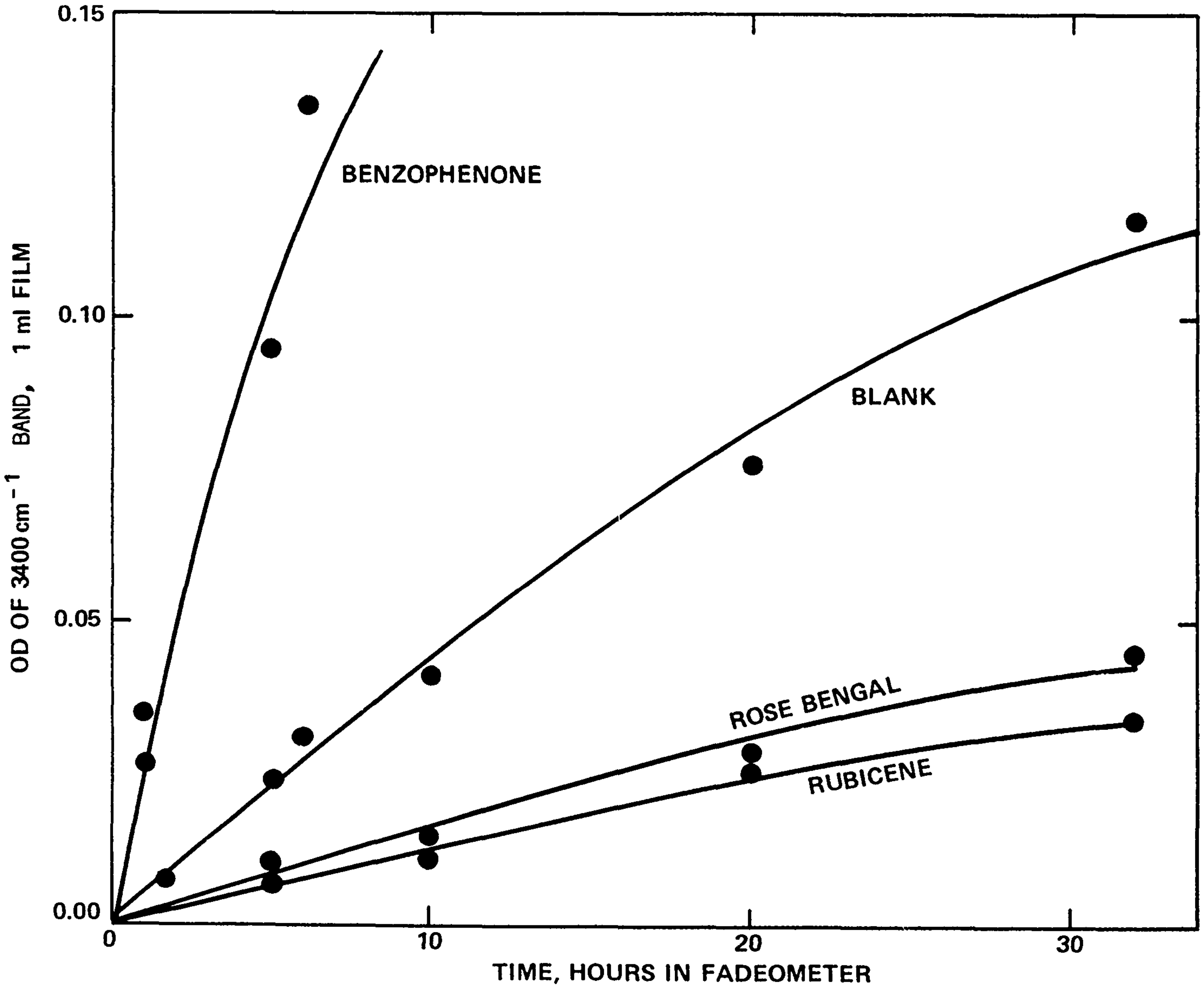


FIGURE 9
EFFECT OF SENSITIZERS ON PHOTODEGRADATION
POLYARYLSULFONE FILM

TABLE 5

Generation of Hydroxyl Groups on Exposure of Polyarylsulfone Film Formulations to Xenon Weather-Ometer (Initial Study)

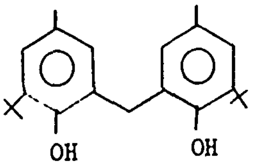
Increase in OD at 3400 cm^{-1} (OH)

Additive (1 wt.%)	No Other Additive		1% Irganox 1010	
	24 hr.	48 hr.	24 hr.	48 hr.
None	0.076	0.124	0.090	0.138
Cyasorb UV 2408	0.092	0.142	0.095	0.142
Cyasorb UV 1084	0.086	0.135	0.094	0.145
Tinuvin 328	0.033	0.063	0.033	0.054
Cyasorb UV 531	0.047	0.091	0.071	0.106

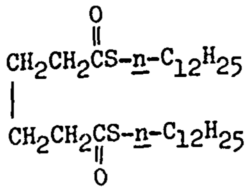
TABLE 6

Additive Identification

Antioxidant 2246

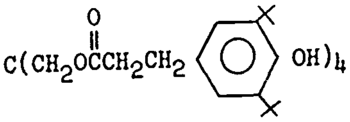


DLTDP

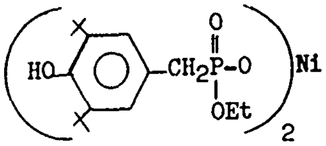


$$\begin{array}{l} CH_2CH_2\overset{O}{\overset{\|}{C}}S\text{-}\underline{n}\text{-}C_{12}H_{25} \\ | \\ CH_2CH_2\underset{O}{\underset{\|}{C}}S\text{-}\underline{n}\text{-}C_{12}H_{25} \end{array}$$

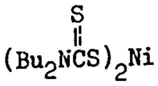
Irganox 1010



Irgastaab 2002

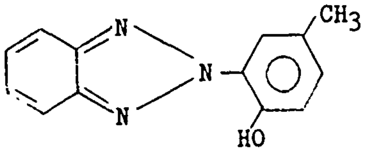


Nickel dibutyldithiocarbamate

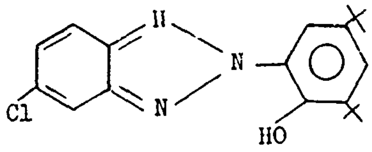


$$(Bu_2N\overset{S}{\overset{\|}{C}}S)_2Ni$$

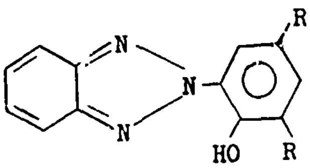
Tinuvin P



Tinuvin 327



Tinuvin 328



Cyasorb UV-24

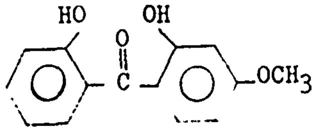
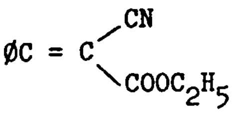


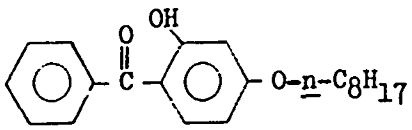
TABLE 6 (Continued)

Uvinul N35

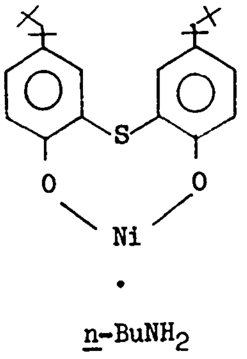


$$\phi C = C\begin{matrix} \diagup CN \\ \diagdown COOC_2H_5 \end{matrix}$$

Cyasorb
UV-531



Cyasorb
UV-1084



Cyasorb
UV-5411

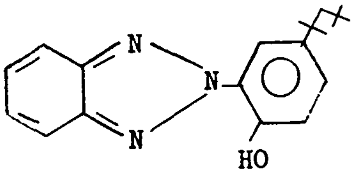


TABLE 7

Generation of Hydroxyl Groups on Exposure of Polyarylsulfone Film Formulations to Xenon Weather-Ometer (Second Study)

Additive (2 wt.%)	Increase in OD at 3400 cm^{-1} (OH) at Time (hrs.)					
	24	48	72	96	144	154
None	0.075	0.145				
Cyasorb UV-5411	0.068	0.124				
Tinuvin P	0.031	0.050	0.065			
Tinuvin P		0.037		0.063	0.083	
Tinuvin 327		0.037		0.063	0.097	
Tinuvin 328		0.049		0.063	0.088	
Azomaleimide		0.049		0.095	0.138	
DLTDP		0.125		0.149		
Cyasorb UV-24		0.060	0.076			0.120
Cyasorb UV-1084	0.072	0.112				
Uvinul N 35		0.050	0.072			0.114
Irgastab 2002		0.127	0.155			
Ni (II) dibutyl-dithiocarbamate		0.101	0.121			
Cyasorb UV-800		0.098	0.116			0.165

O. PROTECTIVE LAMINATES

Polyarylsulfone film was laminated to 2 mil Korad® A-CV photostable film by oven heating at 230°C and rolling. The initial rate of photodegradation of the polysulfone when Weather-Ometer exposed through the protective laminate (an acrylic polymer containing a UV absorber) is less than one-tenth that without the laminate. This result shows that very considerable screening significantly reduces the rate of photodegradation of the polyarylsulfone polymer. The acrylic laminate, however, does not have the thermal stability required for the polyarylsulfone applications.

P. PROTECTIVE ADDITIVES SUMMARY

A graphic representation of the effects of various types of additives on the rate of photodegradation of polyarylsulfone film is given in Figure 10. The results indicate that once excitation energy reaches the polysulfone the degradation that is produced cannot be mitigated through energy transfer or antioxidants. Competitive absorption of UV radiation at or near the plastic surface therefore appears to offer the best practical approach to stabilization.

Q. RESIDUAL ABSORPTION ANALYSIS

Using a procedure described in the literature[5], determination of residual absorption (fraction of incident light normally absorbed by the polymer which is still absorbed by the polymer in the presence of the additive) at 310 nm in eleven different 1 mil films each containing 2% of a UV absorber was made. Because the polymer itself absorbs more than 40% of the incident 310 nm light, the equations for calculating residual absorption are only approximate. The values obtained, however, as shown in Figure 11, indicate a relationship with the effectiveness of the additives as photostabilizers. Additive formulations with the least ($\approx$25%) residual absorption at this wavelength (the wavelength of maximum polyarylsulfone photosensitivity) were those that contained the hydroxybenzotriazoles, the most effective photostabilizers located to date. These results permit an approximate determination of the UV stabilizer requirements for a desired level of polyarylsulfone photostability performance. Maximum performance can be expected with materials having highest absorption in the 310 nm region per unit weight, and which are present in the highest practical concentration in the first few mils of the exposed surface of the sheet. Because of the strong absorption by the polyarylsulfone in this wavelength region, however, a greater than order of magnitude decrease in rate of photodegradation of this polymer by less than a 5% concentration of additive does not appear feasible.

R. SURFACE COATED SHEET

Since virtually all photodegradation of transparent polyarylsulfone sheet takes place in the first mil of exposed surface, efforts were turned to devising means for optimum protection of this volume with solution cast PAS film containing the relatively effective light absorbing additives. Direct casting of DMF solutions containing the polymer

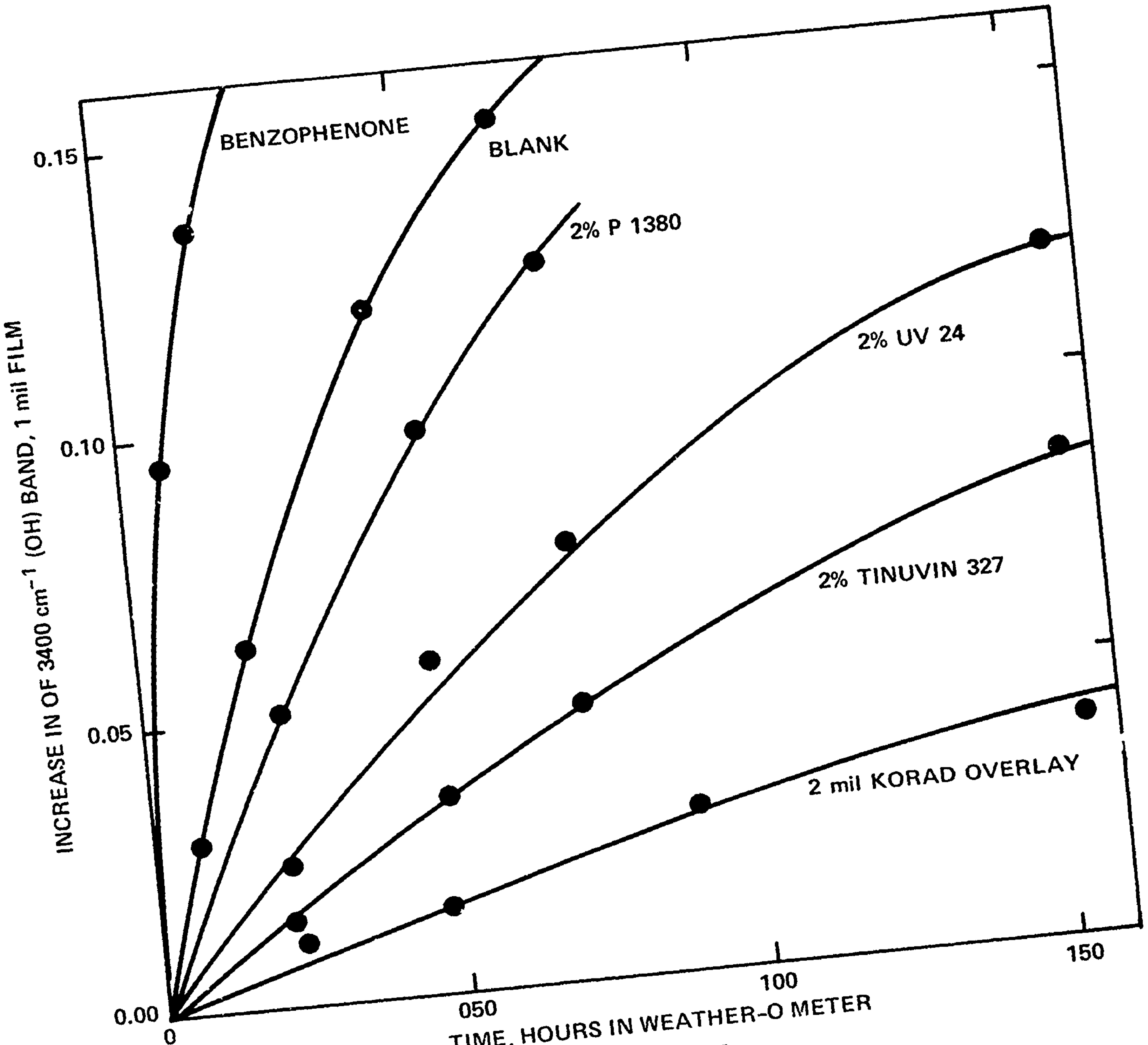


FIGURE 10
STABILIZATION OF CLEAR POLYARYLSULFONE FILM

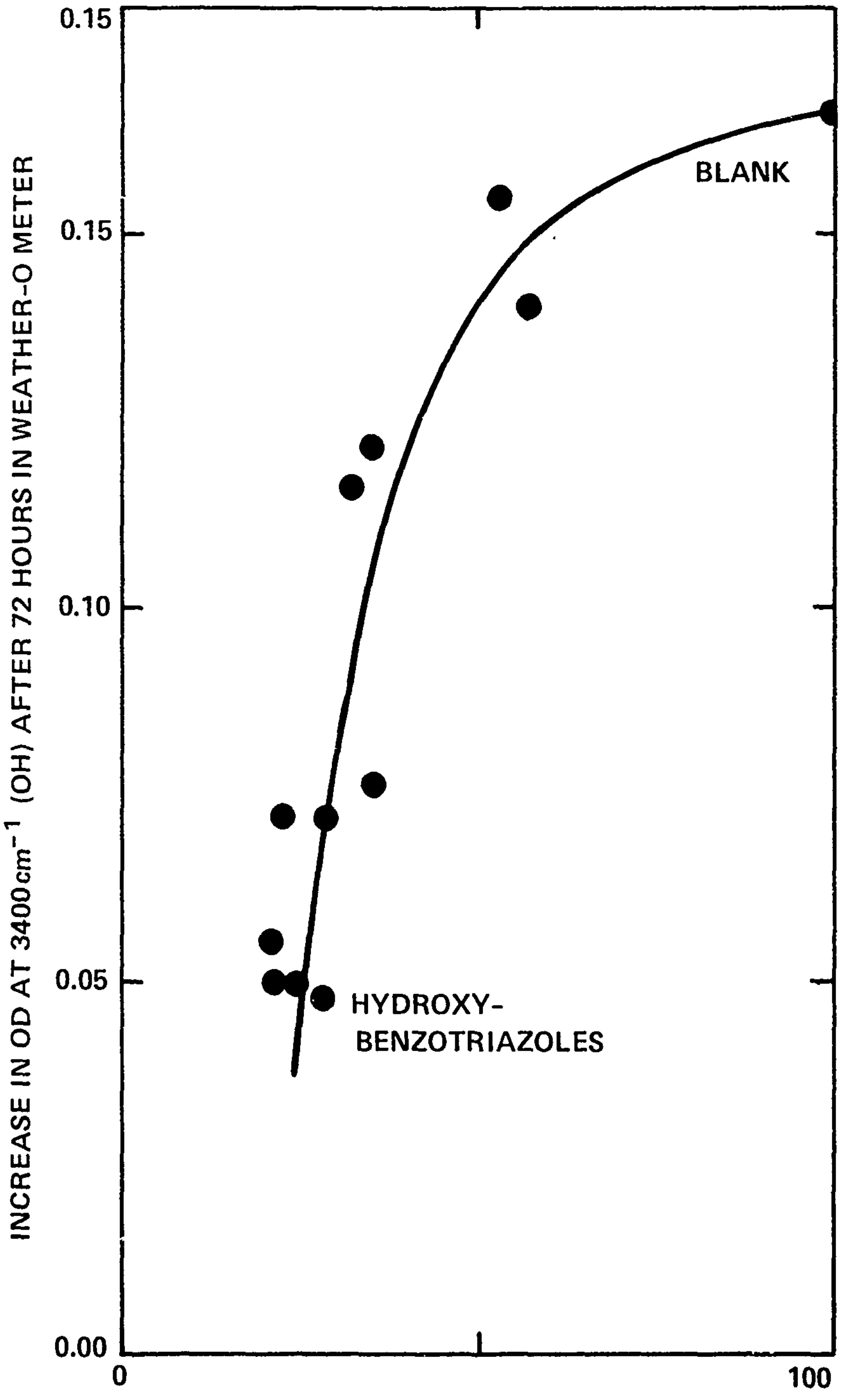


FIGURE 11
PROTECTION OF POLYARYLSULFONE
FILM AS FUNCTION OF RESIDUAL
ABSORPTION OF UV ABSORBER

and additive on the polymer sheet and subsequent vacuum drying (0.3 mm, 25°, 4 hr.) followed by heating (230°, 0.5 hr.) at reduced pressure produced severe bubbling in all test specimens. Examination showed that the bubbling extended throughout the PAS sheet thickness. Uncoated PAS sheet did not bubble when subjected to this treatment. As an alternative approach we turned to lamination of pre-formed film on sheet. Solution cast films of PAS and additive prepared on glass surfaces, dried to varying degrees, peeled and hand-rolled onto PAS sheet consistently failed to laminate at temperatures up to 230°C. Although higher temperatures and greater pressures might produce satisfactory lamination, such efforts fall beyond the scope of this investigation. Extensive efforts in this direction did not appear to be warranted since the film studies showed that the degree of stabilization afforded by the best stabilizers are insufficient for the Air Force requirements.

S. POLYMER PURIFICATION STUDIES

Although the photochemical evidence obtained in this investigation points to the polyarylsulfone polymer itself being the light absorbing species responsible for degradation of its properties, a short wavelength absorbing impurity may be invoked as an alternative causative agent. This agent cannot be a thermal degradation product formed during molding, since solvent cast films show photodegradative characteristics identical to those of molded sheet.

In order to establish whether readily separable impurities cause polyarylsulfone photodegradation, solutions of the polymer were partially precipitated by addition of ethanol in one case and a 1:1 mixture of benzene and n-hexane in the other. In both cases the precipitated polymer, which represented about one-half of the initial amount, was separated, washed once with the solvent that had been used to precipitate it, and then redissolved in DMF and cast into film. As shown in Table 8, no significant difference in rate of photodegradation between standard polyarylsulfone film, prepared from "as is" polymer and from reprecipitated polymer could be detected. We conclude that if an impurity is the cause of this photodegradation it must have solubility as well as absorption characteristics very similar to that of the polymer itself.

T. POSSIBLE PHOTODEGRADATIVE MECHANISM

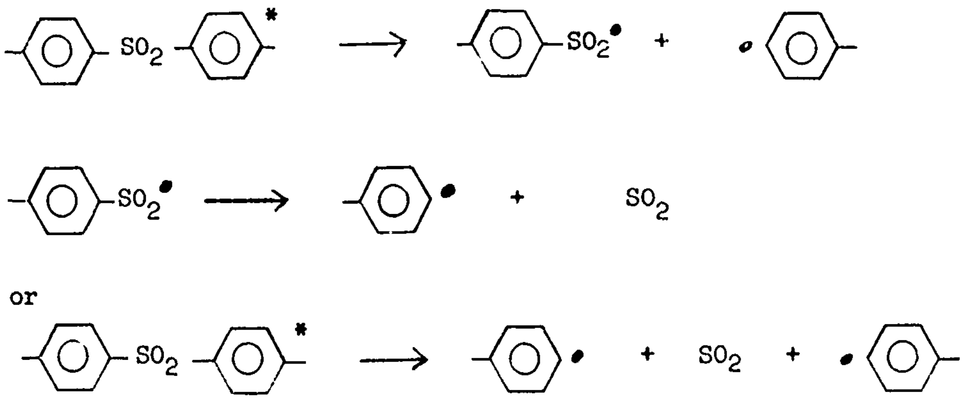
The light absorbing species responsible for the photodegradation of the polysulfone may be (1) the phenyl groups of the polymer itself with absorption in the long wavelength tail of their absorption band, (2) strongly absorbing impurities present in the polymer chain at low concentrations, or (3) impurities not part of the polymer itself. Several observations suggest that (1) or (2) or both are responsible for photodegradation; possibly the most convincing of these being that purification of the polymer by reprecipitation does not decrease its photosensitivity. Photodegradation can be sensitized, however, as witness the results with benzophenone. The possibility that benzophenone acts as a hydrogen abstractor rather than an energy transfer sensitizer is regarded as unlikely since the hydrogen atoms on a benzene ring are usually very resistant to abstraction.

TABLE 8

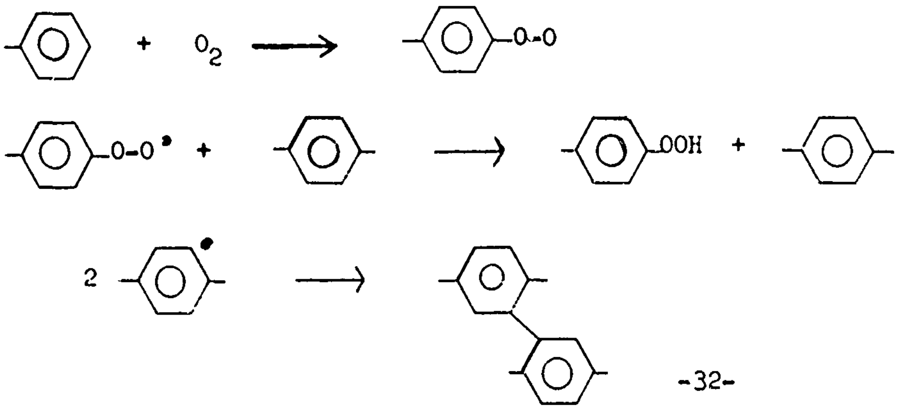
Effect of Polymer Purification by Reprecipitation on Rate of Photogeneration of Hydroxyl Absorption in Polyarylsulfone Film

Film	Relative Thickness (mg/cm^2)	Δ OD (3400 cm^{-1}) at Time (hr.)	
		24	48
Standard	183	0.075	0.116
Hexane-Benzene ppt.	181	0.071	0.105
Standard	117	0.071	0.101
Ethanol ppt.	124	0.071	0.105

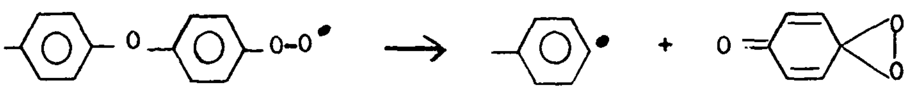
Consequently, it appears that the polymer chain itself is photoexcited. The electronically excited polymer may then degrade via a singlet state and SO_2 extrusion, a process which could be very rapid, perhaps proceeding via predissociation. Alternatively, the polymer may degrade via its triplet excited state formed either by sensitization or by intersystem crossing from the singlet. It has been shown by Cava, et. al.[6] that reaction of sulfones can occur via the triplet. These investigators have shown that photoextrusion of SO_2 from sulfones on irradiation can be a facile process, and this step is probably the first one to occur after excitation of the polymer. Such loss of SO_2 has been reported previously for other polysulfones by Gesner and Kelleher.[7] As shown below, this may be either a one-step or two-step process, but in either case, the net result is the formation of terminal phenyl radicals on the broken polymer chain.



The phenyl radicals formed will, in the presence of oxygen, react rapidly to form peroxy radicals. The 2.003 g ESR peak observed both in this study and by Gesner and Kelleher[7] is most probably due to an oxygen radical, thus supporting the above mechanism. Sulfur and carbon radicals, while probably formed, would not have lifetimes sufficient to be detected in air although they might be observable in deoxygenated polymer. The peroxy radicals may then abstract hydrogen from the benzene rings of the polymer, giving phenyl radicals of a second type. Radicals of the second type are not terminal, and coupling reactions of these can lead to crosslinking and polymer embrittlement. The hydroperoxides formed by hydrogen abstraction are themselves photosensitive and can react to give other reactive radical species.

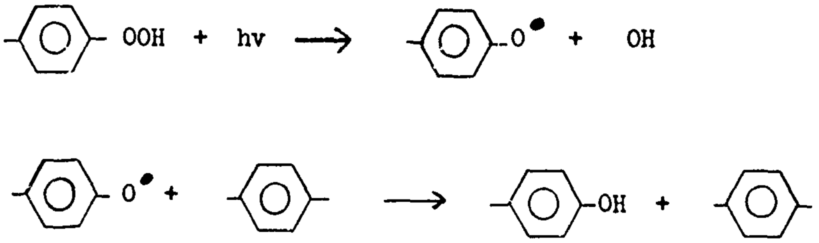


Those phenyl groups of the polymer chain situated between a sulfone and an ether linkage have open to them a further pathway for reaction, one which might possibly explain part of the extreme photoreactivity of the Air Force polymer. That is, formation of a quinonoid species as shown below. Such a species would be very reactive and would also absorb strongly in the ultraviolet. Although it is more probably just an intermediate, its presence could explain some of the carbonyl band development in the infrared spectrum.



If the above type of sequence does not occur, the absence of aliphatic carbon in the Air Force polymer, unlike the polysulfone studied by Gesner and Kelleher[7] makes it difficult to envision conventional routes to the carbonyl species seen in the infrared. The process may be related to the reported[8] photooxidation of benzene to a dialdehyde which occurs with cleavage of the benzene ring. The latter process was implicated as a possible cause of polystyrene yellowing.[8]

The hydroxyl band seen in the infrared spectra is very probably due to hydroperoxide and hydroxyl groups formed by hydroperoxide photodegradation as shown below. Radicals formed in this process will lead to still further photodegradation, and will also possibly generate carbonyl-containing products.



Photodegradation was not observed in the absence of air. However, the criterion used was the presence or lack of hydroxyl or carbonyl absorption in the infrared, and these require oxygen for their formation. Chain scission and SO_2 extrusion could occur even in the absence of oxygen. Gesner and Kelleher, for example, observed virtually the same rate of photodegradation of their polysulfone in undegassed and degassed solution as measured by their physical properties.[7] Although there may be a certain amount of chain repair by recombination of terminal radicals in a "solvent cage" in the absence of oxygen, it is likely that properties such as solubility or molecular weight would show significant changes as a result of irradiation of the polymer even in the absence of oxygen.

SECTION III

EXPERIMENTAL

A. THIN FILM PREPARATION

The polyarylsulfone powder supplied by the Air Force was found to be insoluble in acetonitrile, acetone and ethanol-pyridine mixtures and slightly soluble in chloroform and toluene. Ten percent solutions of the polymer could be prepared in N-methylpyrolidone and hexafluoroacetone, and concentrations of the polymer as high as 20% could be obtained in N,N-dimethylformamide (DMF) and in 1:1 toluene:DMF solutions.

Optically clear thin films were best prepared from the 20% DMF solutions by casting with a doctor blade since the less concentrated polymer solutions had inadequate viscosity leading to non-uniform films. The castings were made on a flat glass plate with the Gardner Knife set at 7 mil. The glass plate containing the fresh casting was immediately transferred to a vacuum oven in which the pressure was reduced to 1 mm at 25°C and held under these conditions for 1 hr. Delay in transferring to the oven results in water vapor condensation in the drying film and consequent irregularities in the final product. The first films prepared were then held at 125°C and 1 mm for a further 18 hrs. This produced high quality film measuring 1.2 mil in thickness. It was subsequently determined that the more volatile additives would be lost by the curing procedure and it was found sufficient to simply heat at 230°C for 30 minutes. The latter time-temperature requirements were found to be an essential minimum for complete removal of solvent. In a few instances where the additives incorporated in the coating solution for purposes of sensitization of photodegradations were found to volatilize under these conditions, they could be sublimed into previously dried supported film by heating both additive and film in a closed container at 230°C. Average additive concentrations in the films were then determined by ultraviolet spectroscopy.

B. ACTIVATION SPECTRA MEASUREMENTS

Irradiation of 1" x 3" samples with dispersed energy was carried out using a fast quartz prism spectrograph (Figure 12) and a 900 watt high pressure Hanovia^{DC} Xenon arc (538C9) filtered with a Corning 9700 glass filter, Color Spec. No. 9-53, placed between the lens system and the spectrograph. The filter served to screen out radiation below 260 nm. Thus, the samples were exposed to somewhat higher energy radiation than that transmitted by the usual Pyrex glass filter (Corning 7740) having a cut-off at 280 nm used to simulate terrestrial sunlight near sea-level.

The spectral energy distribution of the filtered Xenon radiation is compared with that of terrestrial and extraterrestrial sunlight in Figure 13. The data for the filtered Xenon arc radiation was obtained from the transmission curve of a typical Corning 9700 filter given in the Corning filter catalog and spectral distribution measurements previously obtained for an unfiltered 900 watt Hanovia Xenon arc. Thus, it represents an

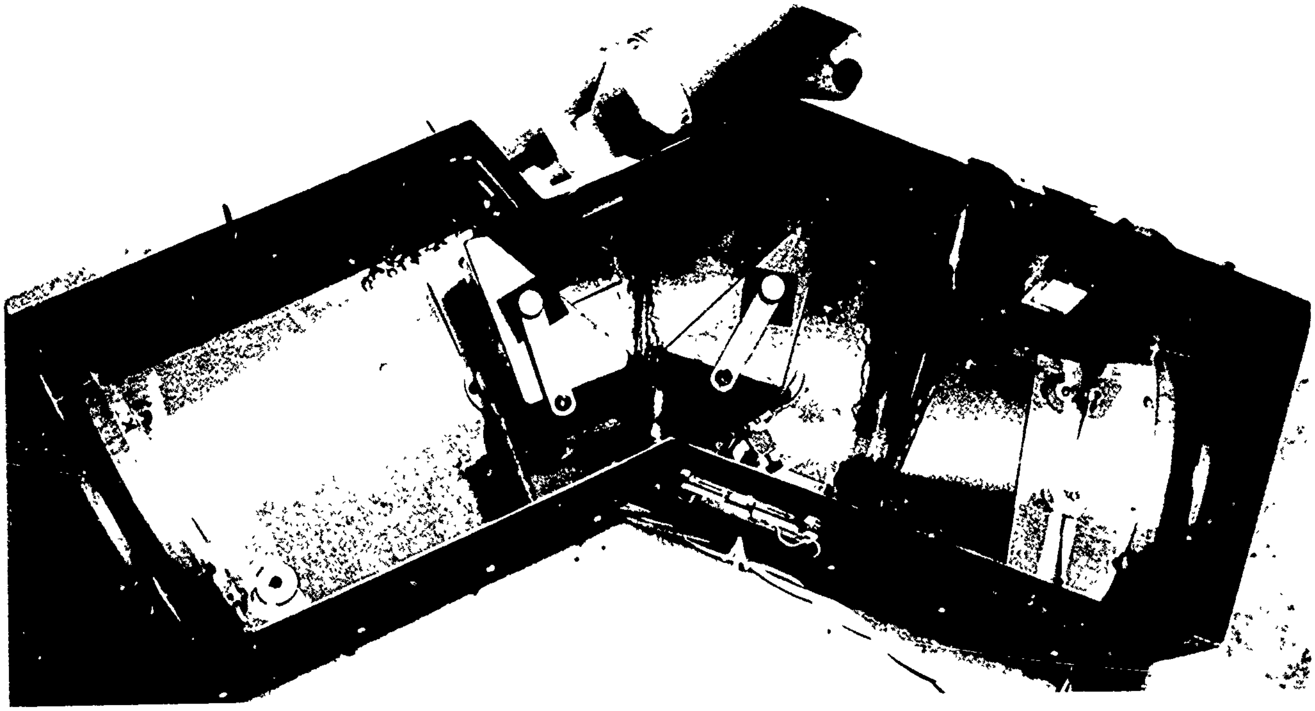


FIGURE 12

Fast Quartz Prism Spectrograph

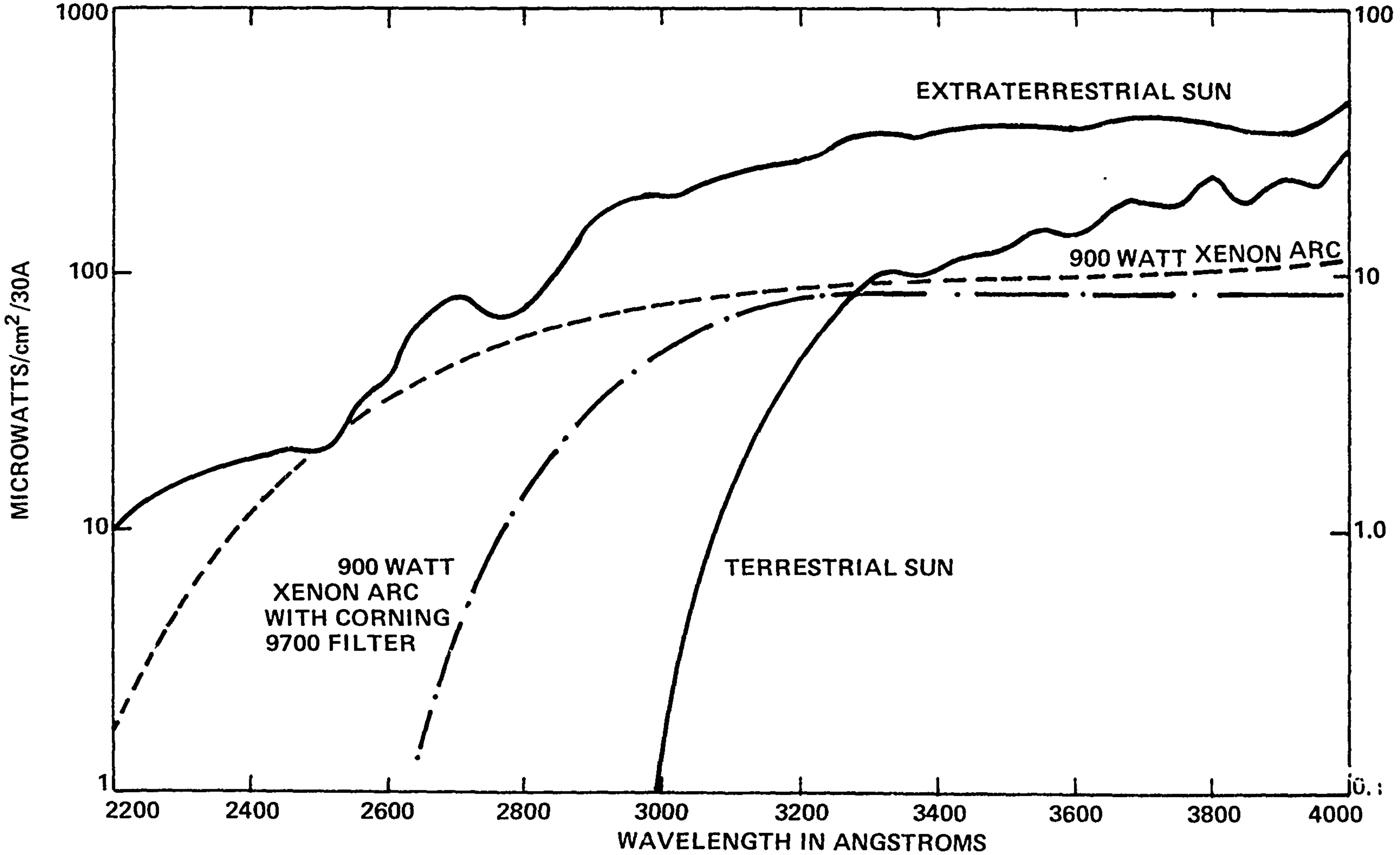


FIGURE 13

SPECTRAL DISTRIBUTIONS FROM VARIOUS SOURCES estimate of the spectral radiation incident on the slit of the spectrograph. No attempt was made to determine the spectral distribution incident on the sample at the back end of the spectrograph. It is assumed that the transmission of the spectrograph as a function of wavelength is relatively constant over the region of the actinic wavelengths, i.e., from about 260 to 400 nm.

The fast quartz spectrograph constructed at the Stamford Laboratories of American Cyanamid Company and pictured in Figure 13 consists of two 30° crystal quartz prisms approximately 4" high placed in tandem to refract the beam which is made parallel by a 9" diameter, 6" focal length concave front surfaced mirror. The refracted beam is focussed at the exit plane by a similar concave mirror and a small plane mirror. The effective speed of the spectrograph is about f/2, i.e., less than theoretical since the prism faces are smaller than the collimated beam.

The wavelength range focussed on the exit slit is determined by an external micrometer and cam which adjusts the prism rotation and by the size of the fixed exit slit. The latter is 30 mm wide and the micrometer is set to allow the sample to be exposed to the entire range of ultraviolet and visible wavelengths available. The dispersion of the spectrograph ranges from less than 10 nm/mm at the short wavelength end to more than 30 nm/mm at the long wavelength end.

In order to maximize the intensity at the sample-plane the Xenon arc radiation is focussed on the 0.5 mm wide entrance slit of the spectrograph by means of a quartz lens system as shown in Figure 12. The latter consists of two 2" diameter lenses each mounted in its own brass tube which is fitted into opposite ends of a larger brass tube support. The lens closest to the light source has a speed of f/1.25 and the one which focusses the beam on the entrance slit of the spectrograph has a speed of f/2. The light between the two lenses is parallel so that the distance between them is unimportant.

The dispersed radiation from about 260 to 630 nm is spread over a 15 mm wide by 10 mm high area of the sample placed in the exit focal plane at the back end of the spectrograph as if it were a photographic plate. The sample is irradiated for a length of time sufficient to produce a measurable change in ultraviolet, visible or infrared absorption characteristics compared with the unirradiated sample. Changes in fluorescence were determined visually in this study.

The position of incident wavelengths on the sample plane of the spectrograph is determined by exposing a photographic plate in the position of the sample to the radiation of a low pressure mercury arc serving as a line source. A GE AH-3 mercury lamp without its glass envelope is placed in front of the entrance slit of the spectrograph masked down to an aperture of about 0.2 mm. A neutral density filter is used to further reduce the intensity of light. An Eastman Kodak SA-1 emulsion photographic plate is cut down to 1" x 3", placed in the sample plane with the left edge against a fixed stop, and exposed for several seconds by temporarily removing a shutter placed between the lamp and slit. The plate is developed in the usual manner, i.e., for 5 minutes using D-19 developer.

The exposed plate, i.e., the spectrogram, contains mercury lines of accurately known wavelengths. The positions of these wavelengths on the plate relative to the left edge are the same as the positions of the same wavelengths originating from the Xenon arc. Thus, the spectrogram can be used to calibrate the scales of the spectrophotometric densitometer attachments to the Cary 14 and infrared instruments (described below) with respect to wavelengths from the Xenon source incident on the sample in the spectrograph.

C. MEASUREMENT OF DEGRADATION

1. Ultraviolet and Visible Spectrophotometry

Changes in ultraviolet and visible absorption as a function of wavelength of irradiation were determined by means of a microdensitometer attachment to the Cary Model 14 Spectrophotometer described below. The extent of yellowing was based on absorption changes at 400 nm. The effects on ultraviolet absorption were measured at 330 nm. The sample was scanned before and after irradiation with the instrument set at the predetermined wavelength. From the relation between the chart traces and counter readings, the change in absorption is determined as a function of sample position. The change in absorption is then plotted as a function of wavelength of irradiation through use of a calibration curve based on a mercury line spectrogram. The plot showing the change in absorption as a function of wavelength of irradiation is referred to as the activation spectrum.

The adapter to the Cary 14 spectrophotometer specially built for activation spectra measurements is shown in Figure 14. It essentially converts the spectrophotometer into a microdensitometer which automatically scans the sample and produces a chart trace of the transmission of 0.5 mm wide areas at any wavelength of choice in the ultraviolet, visible or near infrared regions. A motor drive, continuously moves the sample at a uniform rate of 2 mm/minute across the 0.5 mm fixed slit in the sample beam of the spectrophotometer. The rate is regulated by the pitch of the worm to which the sample holder is attached and the speed of the motor.

The sample holder (5), slit (4), carriage for sample holder and platform fit inside the cell compartment of the spectrophotometer. The set screw coupling (3) at the end of the worm is attached through a spring-type flexible coupling to a small 60 cycle 115 volt Furst 4 rpm synchronous motor (2). The miter gear, coupling and motor are outside the cell compartment. The motor shaft is engaged by means of the miter gear to a revolution counter attached to the outside wall of the cell compartment. The counter is calibrated in terms of distance across the sample from the window edge of the sample holder which is related to wavelength of incident light in the irradiating spectrograph by means of the mercury spectrogram. The spectrogram is measured as if it were a sample and the mercury line positions on the spectrogram are related to the counter readings. A smooth calibration curve is then plotted to allow the complete range of incident wavelengths to be correlated with the photodegradation effects on the sample.

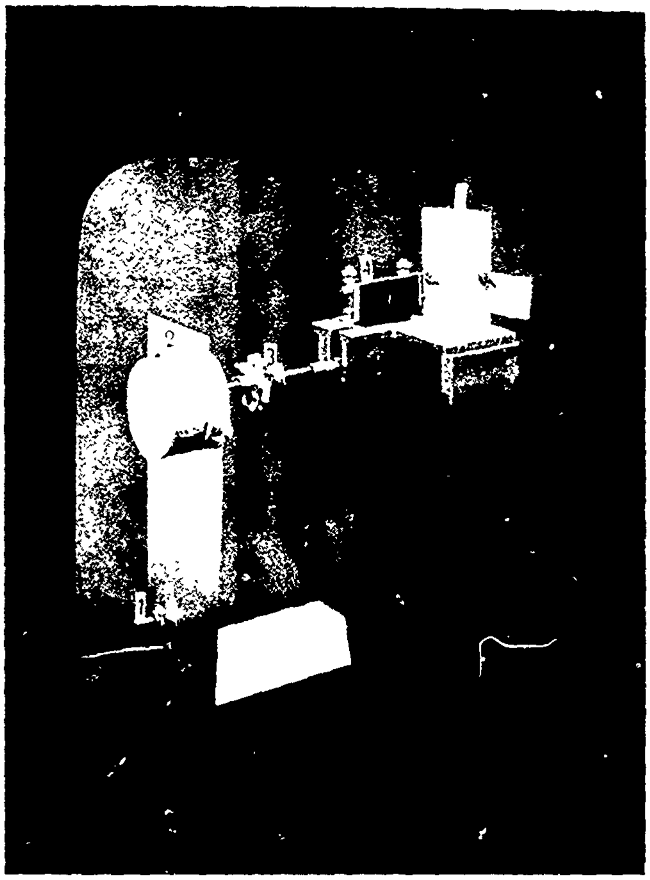


FIGURE 14

Drive Train for Activation Spectra Measurements

2. Infrared Spectrophotometry

Infrared measurements were made with devices and techniques analogous to those described for the ultraviolet and visible regions.

Reference to Figures 15 and 16, full-scale photographs of the film scanning device, will clarify the ensuing description of the sample handling procedure.

The film specimen is cemented or taped to a rigid plastic frame which is then inserted vertically under the two brass spring clamps. The dimensions of the frame are in the order of 1" x 2 1/2" x 1/8". Care is taken to butt the left edge of the frame flush against the galvanized metal wall which is attached to the rotatable screw. The latter has a scale on a disc mounted close to the knurled nut at one end. The scale has 50 graduations and one complete turn of the screw equals one millimeter of translational travel of the film sample. A linear scale, graduated in millimeters, may be seen mounted perpendicular to the disc and at the extreme left edge of the device. There are thirteen usable turns to the screw and, hence, 13 millimeters of film travel across the mechanical slit in the scanner. The slit is approximately 0.3 mm x 5 mm and transmits 55% of the available energy when used in conjunction with a beam condenser attachment (See Figure 16). The latter effects a tenfold reduction in beam area, the normal, focussed source image having the approximate dimensions of 2 x 15 mm.

The regions of interest are from 1650-1850 cm^{-1} (carbonyl) and 3200-3800 cm^{-1} (hydroxyl). The procedure for film measurements is generally as follows:

The beam condenser and film scanning assembly with specimen in place is aligned in the sample compartment of the spectrometer to yield the maximum transmission possible at a non-absorbing frequency, usually 1990 cm^{-1}. The knurled knob is rotated clockwise until the zero position on the linear scale is attained. The film area is then scanned in the two regions of interest previously designated.

The screw is then rotated one complete turn in a counter-clockwise direction and the scanning procedure is repeated. Generally, eleven additional positions, one turn (1 mm) apart are examined, even though the narrowest element of area that could be scanned consecutively is limited by the width of the slit of the scanner (0.3 mm). Hence, three times as many area elements could be analyzed, if desired.

After the film is exposed to ultraviolet radiation for the required time, the analysis is repeated point by point as described. Each element of film area is identified by positional number on the horizontal linear scale. The change in absorbence for each of the regions of interest is obtained by comparison of peak heights before and after irradiation, as measured by the conventional baseline technique. A plot of these data for each of the two regions as a function of the linear scale value isolates the position showing the maximum increase in absorption. The scan positions previously calibrated by a mercury spectrogram yields the frequency of radiation responsible for the maximum absorbence change.

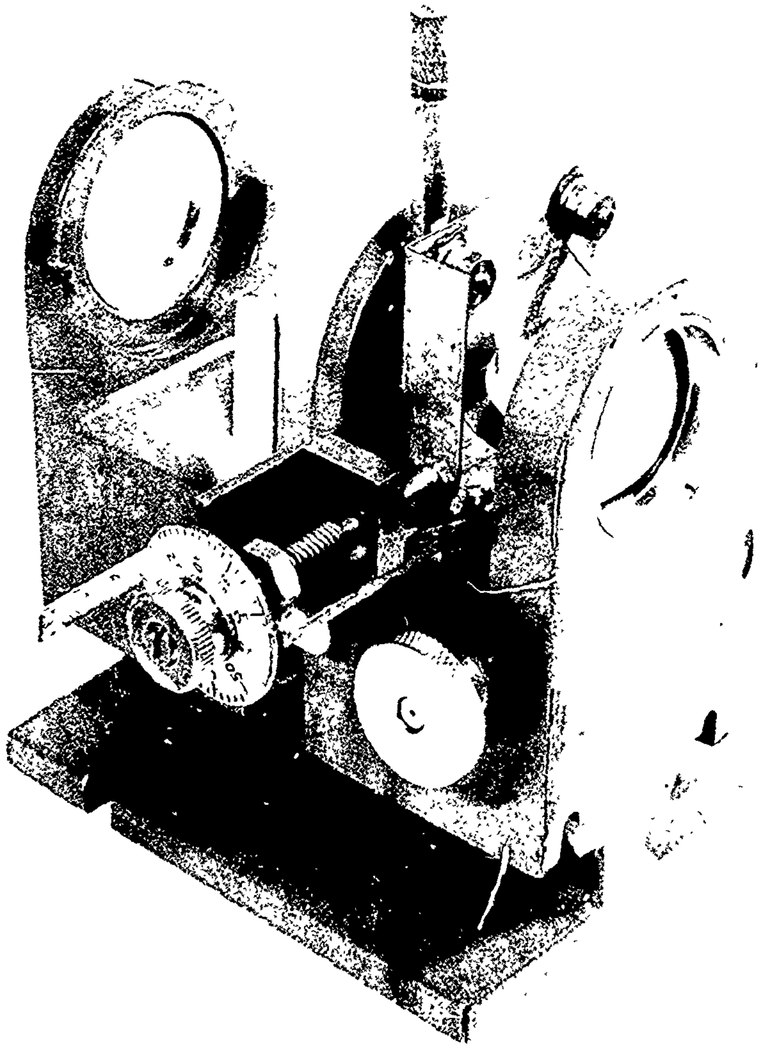


FIGURE 15

Adapter to Infrared Spectrophotometer
for Activation Spectra

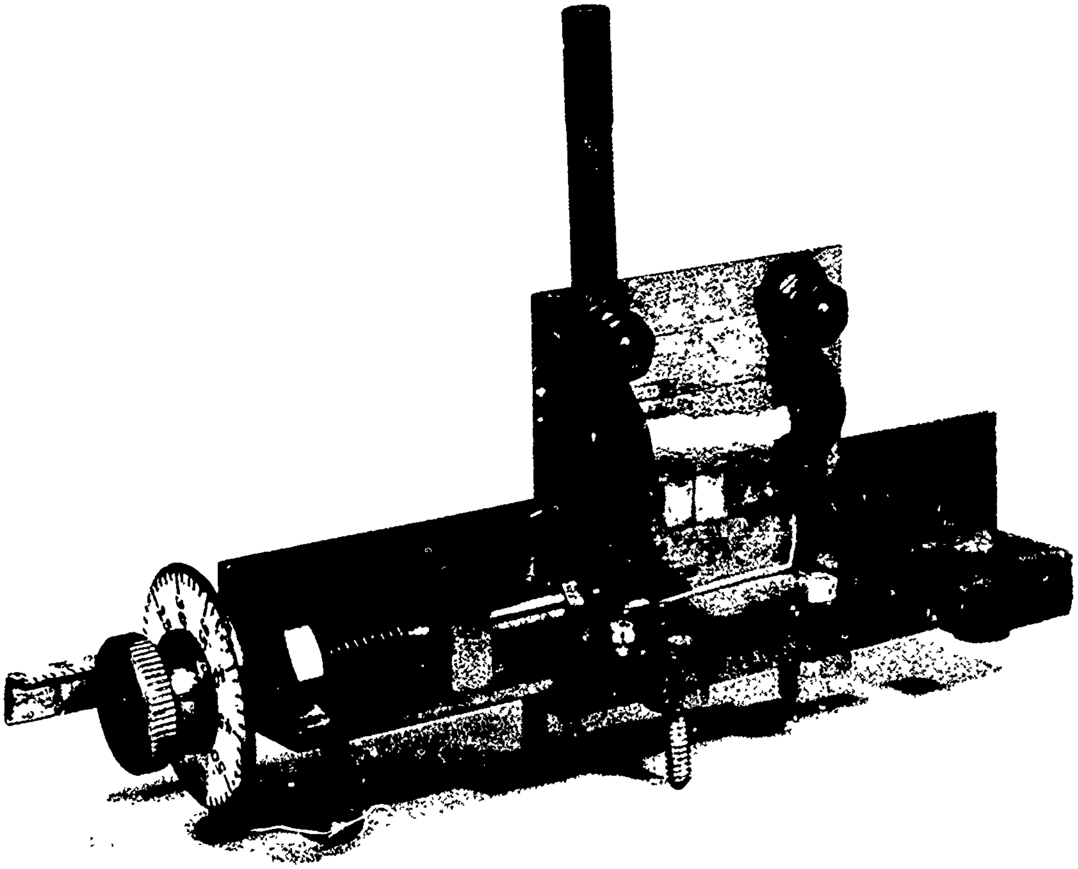


FIGURE 16

Sample Holder for Infrared Activation Spectral Measurements

SECTION IV

REFERENCES

1. R. P. Bringer and G. A. Morneau, Applied Polymer Symp., 11, 189 (1969).
2. R. L. Burns, H. A. Vogel, and A. T. Worm, Technical Report AFML-TR-72-110, December 1972.
3. W. M. Alvino, J. Appl. Polymer Sci., 15, 2521 (1971).
4. R. C. Hirt and N. Z. Searle, Applied Polymer Symp., 4, 61 (1967).
5. H. J. Heller, European Polymer Journal Supplement, 105 (1969).
6. M. P. Cava, R. H. Schlessinger, and J. P. van Meter, J. Amer. Chem. Soc., 86, 3173 (1964); M. P. Cava and R. H. Schlessinger, Tetrahedron, 21, 3073 (1965).
7. B. D. Gesner and P. G. Kelleher, J. Appl. Polymer. Sci., 12, 1199 (1968).
8. K. Wei, V. C. Mani, and J. N. Pitts, Jr., J. Amer. Chem. Soc., 89, 4225 (1967).

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13 ABSTRACT

The Air Force polyarylsulfone polymer is an exceptionally photosensitive plastic the degradation of which is manifested by ultraviolet, visible and infrared absorption spectral changes as well as haze development, changes in fluorescence, embrittlement and loss of impact strength. The wavelengths most effective in causing these events are in the short wavelength ultraviolet (310-330 nm) region corresponding to onset of strong absorption by the polymer itself. As the photochemical processes proceed the rate of degradation slows but only after optical properties near the exposed surface have deteriorated to unacceptable levels. The photolysis is independent of moisture but requires oxygen, and generates hydroxylic and carbonyl compounds without an induction period. The degradation is not accelerated by singlet oxygen sensitizers or significantly quenched by singlet oxygen quenchers, energy transfer agents, antioxidants or antioxidant synergists. It is accelerated by benzophenone and its rate is reduced with UV absorbers particularly hydroxybenzotriazoles which are most effectively competitive for the short wavelength ultraviolet radiation that is primarily responsible for the degradation. The damaging light is absorbed by the polymer itself or a very strongly absorbing impurity with similar solubility characteristics. The specific photochemical and chemical processes responsible for the degradation are unknown. Protective UV light absorbing additives are the only effective means of reducing the photodegradation of this material. The absorbers should be concentrated at the exposed surface for optimum effectiveness. At most they can provide no more than a five-to-tenfold decrease in rate of photodegradation of the polymer

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