

STUDIES ON THE PROTECTIVE ULTRAVIOLET ABSORBERS IN A SPACE ENVIRONMENT

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I. INTRODUCTION

The use of organic coatings in a space environment for the protection of surfaces and for temperature control requires that the organic materials be stable to the extreme conditions of ultraviolet radiation, temperature and vacuum. Most surface coating materials deteriorate to some extent under terrestrial conditions and require the use of inhibitors such as the protective ultraviolet absorbers or antioxidants to increase their service life. The conditions encountered above the earth's atmosphere will undoubtedly necessitate the use of one or more types of protective agent to adequately prolong the life of polymeric materials used for such applications.

The purpose of this investigation is to study the effects of a space environment on the protective ultraviolet absorbers with major emphasis on their stability to evaporation and short wavelength ultraviolet radiation under a high vacuum. The requirements for an effective ultraviolet absorber are that it absorb strongly in the wavelength region to which the plastic is photosensitive, that it itself be relatively stable to this radiation, and that it be compatible with the material in which it is used. Certain benzophenone and benzotriazole derivatives have these desirable properties and have proven themselves invaluable for many terrestrial applications.

The protective ultraviolet absorbers studied in this investigation are presented in Table I.

Table I

PROTECTIVE ULTRAVIOLET ABSORBERS

NAME	TRADE NAME
2,4-dihydroxy benzophenone	Uvinul 400 - Antara Chemicals (General Aniline & Film Corp.)
2-hydroxy-4-methoxybenzo- phenone	Uvinul M-40 - Antara Chemicals Cyasorb UV 9 - American Cyanamid Company
2,2'-dihydroxy-4,4'-dimethoxy- benzophenone	Uvinul D-49 - Antara Chemicals
2,2'-dihydroxy-4-methoxy- benzophenone	Cyasorb UV 24 - American Cyanamid Company
2,2'-4,4'-tetrahydroxy benzophenone	Uvinul D-50 - Antara Chemicals
Phenyl salicylate	Salol - Dow
4-tert-butyl phenyl salicylate	Light Absorber TBS - Dow
5-chloro-2-hydroxy benzo- phenone	Light Absorber HCB - Dow
Dibenzoylresorcinol	Light Absorber DBR - Dow
2-(2'-hydroxy-5'-methyl phenyl) benzotriazole	Tinuvin P - Geigy Ind. Chem.
2,2'-dihydroxy-4-octyloxy benzophenone	Cyasorb UV314 - American Cyanamid Company
1,1'-ferrocene dicarboxylic acid	None

II. ABSORPTION SPECTRA

The near ultraviolet and visible absorption spectra of the protective ultraviolet absorbers have been determined in cyclohexane and absolute ethanol in the region of 2000 to 5000 Angstroms using a Cary Model 14 Automatic Recording Spectrophotometer. The spectra were extended in the vacuum ultraviolet region to 1700 Angstroms in n-hexane and n-heptane solution with a Jarrell-Ash model 78-800 one-meter, normal-incidence vacuum spectrometer. Four typical absorption curves are shown in Figures 1-4. The spectral data for the ultraviolet absorbers have been described in a Wright Air Development Division technical report (1) and will not be discussed in detail in this paper.

All the absorbers have a strong absorption band in the 3000 to 4000 Angstrom region which corresponds to their lowest $\pi \rightarrow \pi^*$ electronic transition. It is the strong absorption and low quantum yield of this lowest energy transition which makes these compounds effective in preventing degradation of plastics exposed to terrestrial sunlight. The absorbers also have a number of other electronic transitions in the shorter ultraviolet wavelength regions; the most intense transitions occur in the vacuum ultraviolet. The stability of the ultraviolet absorbers to extraterrestrial radiation will be determined by the quantum yield for these higher energy transitions.

The position of the absorption maxima vary to some extent with the type of solvent employed. More polar solvents, or those which have the greatest effect on the hydrogen bonding in the molecules, tend to shift the absorption maxima to shorter wavelengths. This effect is quite large for the absorbers containing more than one hydroxyl group.

Table II

EFFECT OF ENVIRONMENT ON LONG WAVELENGTH MAXIMUM
OF PROTECTIVE ULTRAVIOLET ABSORBERS
(Wavelengths in Angstroms)

<u>Compound</u>	<u>Cyclohexane</u>	<u>Ethanol</u>	<u>Cellulose Acetate</u>	<u>Polyester Resin ^A</u>
2-hydroxy-4-methoxy benzo- phenone	3280	3260	3260	3260
2,2'-dihydroxy-4-methoxy benzophenone	3530	3270	3300	3400

^A LAMINAC 4123 polyester resin, phthalic-maleic-propylene glycol, cross-linked with polystyrene.

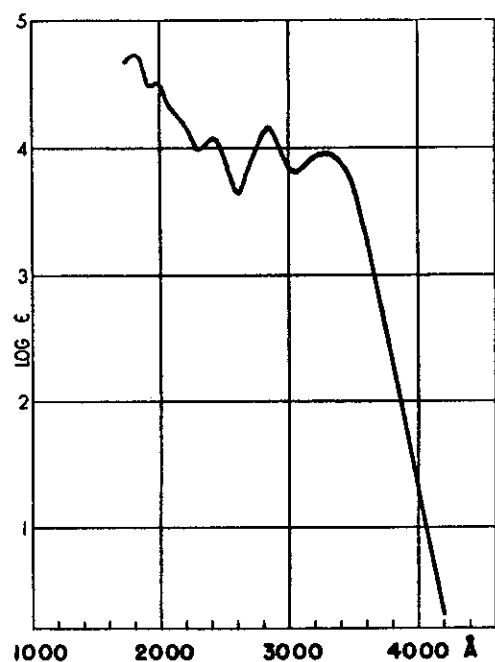


Figure 1. Absorption Spectrum of 2-hydroxy-4-methoxy benzophenone

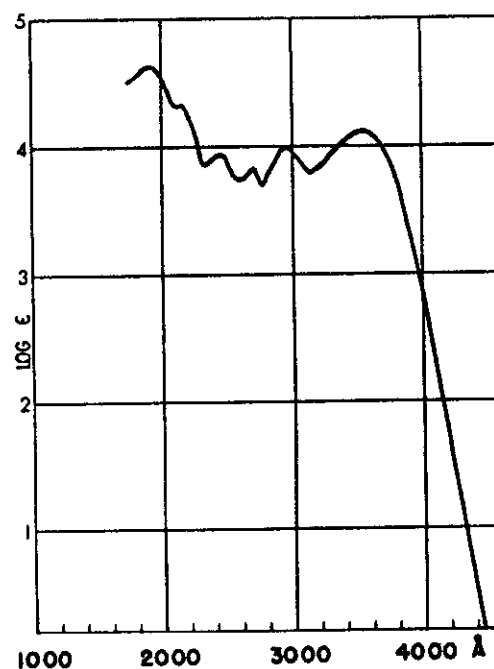


Figure 2. Absorption Spectrum of 2,2'-dihydroxy-4-methoxy benzophenone

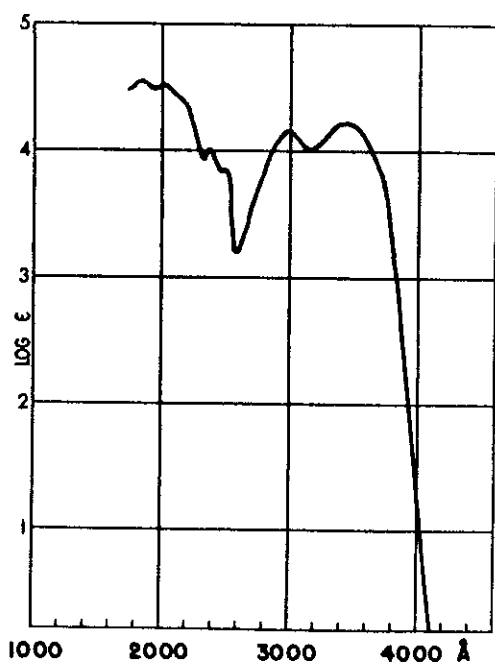


Figure 3. Absorption Spectrum of 2-(2'-hydroxy-5'-methyl phenyl) benzo-triazole

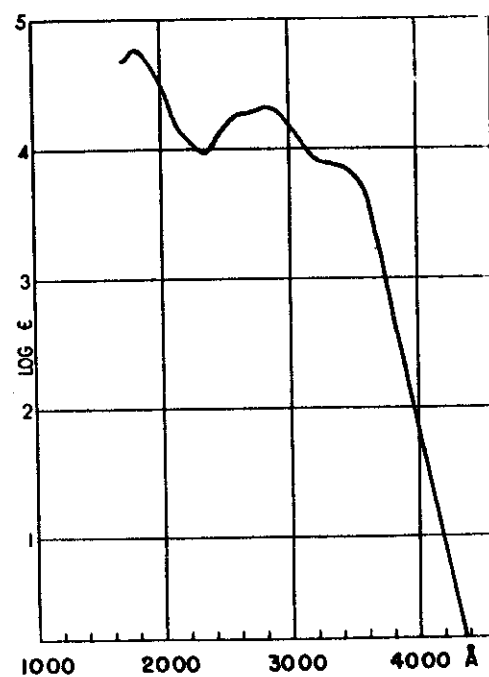


Figure 4. Absorption Spectrum of Dibenzoylresorcinol

III. RATES OF EVAPORATION AND VAPOR PRESSURES

The rates of evaporation and vapor pressures of the pure ultraviolet absorbers have been measured as a function of temperature. The loss by evaporation of the absorbers dispersed in various polymeric systems has been measured under vacuum conditions. The details of the methods used and the results obtained have been published elsewhere(1,2) and will not be discussed here. The conclusions arrived at from this work are summarized as follows:

The volatilities of the protective ultraviolet absorbers in vacuum are sufficiently high to cause appreciable loss in relatively short time.

The volatilities of the benzophenones having more than one hydroxyl group are lower than those of the mono-hydroxy compounds. This is attributed to intermolecular hydrogen bonding by the additional hydroxyl groups.

The rate of evaporation of the protective ultraviolet absorbers from polymeric materials is lowered by an amount vastly greater than that predicted from Henry's law. This is attributed to a diffusion-controlled process which retards evaporation and migration to the surface. The loss of absorber by evaporation in vacuo from thermosetting resins such as melamine-formaldehyde and polyesters was found to be negligible at temperatures up to 150°C. The rate of evaporation in vacuum from thermoplastic resins such as cellulose acetate and methyl methacrylate was found to be appreciable for the more volatile mono-hydroxy benzophenone absorbers at temperatures above 40°C.

IV. PHOTOCHEMICAL STABILITY

This investigation is concerned with the photochemical stability of the protective ultraviolet absorbers under the conditions that exist above the upper atmosphere of the earth. The earth's atmosphere acts as a filter of the sun's radiation, this filtering action being the greatest in the short wavelength ultraviolet and long wavelength infrared regions. Figure 5 illustrates the variation of the intensity of sunlight with wavelength at the earth's surface. It can be seen that practically no light with wavelengths shorter than 2900 Å reaches the earth. There is a further cut-off in the infrared longer than 30,000 Å (3 microns).

In the visible and near ultraviolet regions, sunlight approximates the emission of a 6000° Kelvin blackbody as can be seen in Figure 5. At shorter wavelengths there is evidence (3,4,5) that the sunlight curve falls below the blackbody radiation down to at least 1000 Å. The radiant energy from the sun can be divided into the more familiar spectral regions as follows: Infrared (above 7000 Å) - 40%, visible (4000 to 7000 Å) - 50%, near ultraviolet (3000 to 4000 Å) - 8%, middle ultraviolet (2000 to 3000 Å) - 2%, and the far ultraviolet (below 2000 Å) - less than 0.01%.

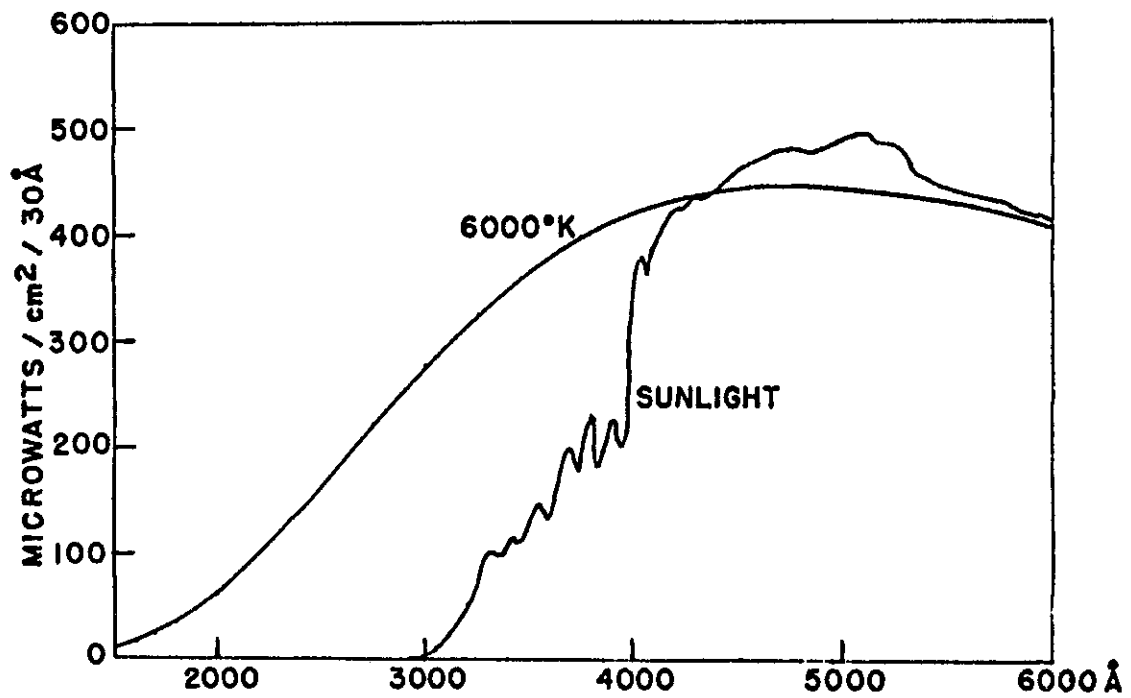


FIG. 5. SPECTRAL ENERGY DISTRIBUTION OF CONNECTICUT JULY SUNLIGHT AND 6000°K BLACKBODY.

The photochemical stability of a compound is a function of the ability of the material to absorb light, the energy of irradiation, and the quantum yield, all integrated over the wavelength region that the source emits. In addition, the strength of the chemical bonds and the means by which a molecule can dissipate the energy it absorbs, whether by its own radiation or by transfer to its surroundings in the form of heat, will also determine its ability to resist degradation. Ultraviolet radiation is responsible for most photochemical reactions by virtue of its ability to rupture many chemical bonds. The shorter wavelengths have higher energy per quanta and are thereby more effective in this respect.

When a molecule absorbs ultraviolet energy, it becomes highly activated or electronically excited. While in the unstable excited state, a molecule may act in one or more of several ways. Each results in a loss of the energy absorbed and a return to the ground state. The excited molecule, for example, may re-emit the absorbed energy at longer wavelengths by fluorescence or phosphorescence. It may return to the normal state as a result of a collision in which the previously absorbed energy is converted into kinetic energy or vibrational energy of the colliding molecules. A third alternative is the initiation of a photochemical reaction by the absorbed energy. The probability for the photochemical process can be represented by the quantum yield for each of the electronic transitions of the molecule. The quantum yield is defined as the number of molecules reacted divided by the number of quanta of energy absorbed.

Many polymeric materials have high quantum yields and degrade quickly when exposed to terrestrial sunlight. Such photochemical reactions can be in many cases suppressed effectively by the use of the protective ultraviolet absorbers. Ultraviolet absorbers protect polymers by preferentially absorbing the ultraviolet radiation by virtue of their strong absorbing properties. They are a unique class of compounds in that they are able to withstand this radiation, i.e., they have extremely low quantum yields for terrestrial radiation.

The more severe conditions encountered by polymeric materials exposed to a space environment will most certainly necessitate the use of protective agents in inhibiting their degradation. It is the purpose of this study to determine the ability of the ultraviolet absorbers to withstand the higher energy short wavelength ultraviolet radiation that is present above the earth's atmosphere. The additional complicating factor of the high vacuum in space requires that the influence of oxygen and other atmospheric constituents be also studied.

1. Experimental Details

A General Electric Type AH-6 (6) water-cooled high pressure mercury arc was used for the photochemical studies in the 2000 to 4000 Angstrom region. With a quartz outer jacket, the AH-6 lamp gives a strong continuum in the ultraviolet to about 2000 A. The mercury lines are superposed upon the continuum but are not prominent (7). The

radiant energy from the lamp is many times stronger than sunlight above the earth's atmosphere and has a relative spectral energy distribution that approximates that of extraterrestrial sunlight (see Table III below).

Table III

COMPARISON OF THE SPECTRAL ENERGY DISTRIBUTION OF THE AH-6 MERCURY ARC
AND THE SOLAR SPECTRAL ENERGY DISTRIBUTION

<u>Wavelength Region (Angstroms)</u>	<u>Solar Energy (milliwatts/cm²)[*]</u>	<u>AH-6 Mercury Arc (milliwatts/cm²)^{**}</u>
2000-2100	0.01	0.02
2100-2200	0.02	0.06
2200-2300	0.03	0.15
2300-2400	0.05	0.50
2400-2500	0.06	1.60
2500-2600	0.10	1.61
2600-2700	0.20	2.02
2700-2800	0.24	3.84
2800-2900	0.34	4.19
2900-3000	0.63	6.05
3000-3100	0.63	7.12
3100-3200	0.76	9.56
3200-3300	1.04	3.79
3300-3400	1.05	3.34
3400-3500	1.13	1.86
3500-3600	1.14	1.41
3600-3700	1.20	9.64
3700-3800	1.26	4.37
3800-3900	1.15	2.29
3900-4000	1.23	1.97
<hr/>		
Total	12.27	65.41

^{*} Values taken from the data of F. S. Johnson (4) using a solar constant value of 2.00 g. cal/cm²/min. or 135 mw/cm².

^{**} Calculated from actinometric and spectral energy distribution measurements (8).

Figure 6 is a photograph of the irradiation chamber and monitoring photocell. The irradiation chamber was designed to permit periodic ultraviolet examination of the samples without exposing them to the atmosphere. Removable quartz windows mounted between silicon "O" rings seal the ends of the cell. A high vacuum valve and demountable coupling permit the chamber to remain vacuum-tight during examination. A second valve permits the introduction of various gases into the system. A thermocouple gauge measures the pressure in the irradiation chamber. Pressure in the cell usually ranges from 10⁻⁵ to 10⁻³ millimeters of mercury depending upon the outgassing properties of the material under

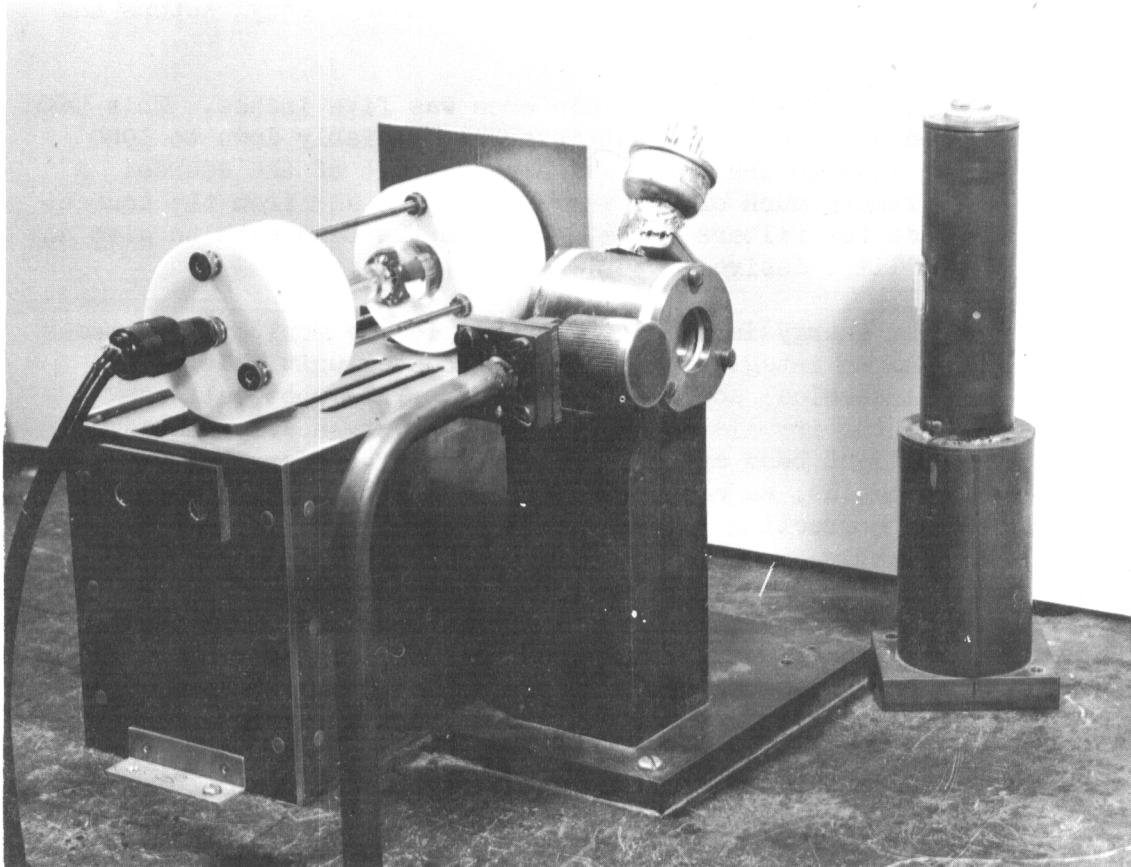


Figure 6. AH-6 Mercury Lamp, Radiation Chamber and Photocell for Monitoring Energy

examination. A copper-constantan thermocouple located in the cell records the temperature of the samples. Samples in the form of one inch diameter disks or films mounted on quartz windows are located near the center of the cell. Melamine-formaldehyde and cellulose acetate films approximately 0.001 cm. thick containing from one to five percent absorber were used for most experiments. The melamine-formaldehyde films were prepared from methyl cellosolve and cured at 140°C. for 20 minutes. The cellulose acetate films were deposited from a mixture of methyl ethyl ketone and methyl cellosolve and air-dried.

The source to sample distance was five inches. This path was not evacuated since air does not absorb appreciably down to 1900 Angstroms, which is also the lower wavelength limit of the source. A fan was used to remove much of the infrared-heated air from the source. Provision was made for filters to be placed in the beam path to give any short wavelength limit desired.

The energy incident on the sample was monitored by means of a photocell and an integrating motor and counter unit that were calibrated with a chemical actinometer (9,10). This photocell is located alongside the irradiation unit and sees very nearly the same portion of the radiant beam as does the sample. The energy actually absorbed by the samples, as contrasted to the energy incident upon them, was calculated by correcting the incident energy for the absorption spectrum of the sample.

Ultraviolet absorption spectroscopy was used to follow the photochemical reactions. Usually the longest wavelength absorption maximum was used as a measure of the amount of absorber reacted because of less interference from absorber and polymer decomposition products.

2. Results and Discussion

The photochemical stability of the protective ultraviolet absorbers was measured under a variety of conditions. Consideration is given first to a comparison of the stability of the absorbers using well defined conditions that simulate an extraterrestrial environment. The remainder of this section is devoted to a study of the effect of certain rate determining variables on the rate of photodecomposition.

A. Stability of the Absorbers

Melamine-formaldehyde was chosen as the standard dispersing media for comparing the photochemical stability of the protective ultraviolet absorbers to short wavelength ultraviolet radiation. Many other polymeric systems were considered, but rejected because of poor thermal or photochemical stability or because losses of absorber by evaporation were pronounced. A number of experiments were performed in cellulose acetate, however, to illustrate this latter effect and to demonstrate whether or not the stability of the absorbers is greatly affected by the type of polymeric system used. The experimental data for melamine-formaldehyde and cellulose acetate are presented in Figures

7-14 and summarized in Tables IV and V. The times required to produce a change in absorbance of 0.200 and 0.400 (which is equivalent to losses of approximately 10 and 20 percent respectively) are used as measures of the photochemical stability of the absorbers.

Table IV

PHOTOCHEMICAL RATE DATA FOR THE ULTRAVIOLET ABSORBERS
IN MELAMINE-FORMALDEHYDE

Absorber	Equivalent Hours in Space for		Gamma	Inertia
	$\Delta A = 0.200$	$\Delta A = 0.400$		
1,1'-ferrocene dicarboxylic acid	500	500	0.00	high
2-(2'-hydroxy-5'-methyl phenyl) benzotriazole	140	1900	0.09	0.12
2-hydroxy-4-methoxy benzophenone	20	425	0.15	0.16
4-tert-butyl phenyl salicylate	20	195	0.22	0.49
Dibenzoylresorcinol	28	175	0.25	0.90
2,4-dihydroxy benzophenone	12	83	0.23	0.28
2,2'-4,4'-tetrahydroxy benzophenone	12	72	0.26	0.45
2,2'-dihydroxy-4-methoxy benzophenone	7	40	0.25	0.21
2,2'-dihydroxy-4,4'-dimethoxy benzophenone	6	28	0.28	0.21

Table V

PHOTOCHEMICAL RATE DATA FOR THE ULTRAVIOLET ABSORBERS
IN CELLULOSE ACETATE

Absorber	Equivalent Hours in Space for		Gamma	Inertia
	$\Delta A = 0.200$	$\Delta A = 0.400$		
4-tert-butyl phenyl salicylate	75	650	0.21	1.70
Dibenzoylresorcinol	28	175	0.26	0.92
2,2'-dihydroxy-4- octyloxy benzophenone	20	62	0.49	1.95
2-(2'-hydroxy-5'-methyl phenyl) benzotriazole	17	40	0.59	1.70
2,2'-dihydroxy-4,4'- dimethoxy benzophenone	17	34	0.68	1.80
2,2'-dihydroxy-4-methoxy benzophenone	12	44	0.28	0.52
2,4-dihydroxy benzophenone	10	20	0.59	0.87
2,2'-4,4'-tetrahydroxy benzophenone	7	16	0.57	0.64
2-hydroxy-4-methoxy benzophenone	3	6	0.68	0.32

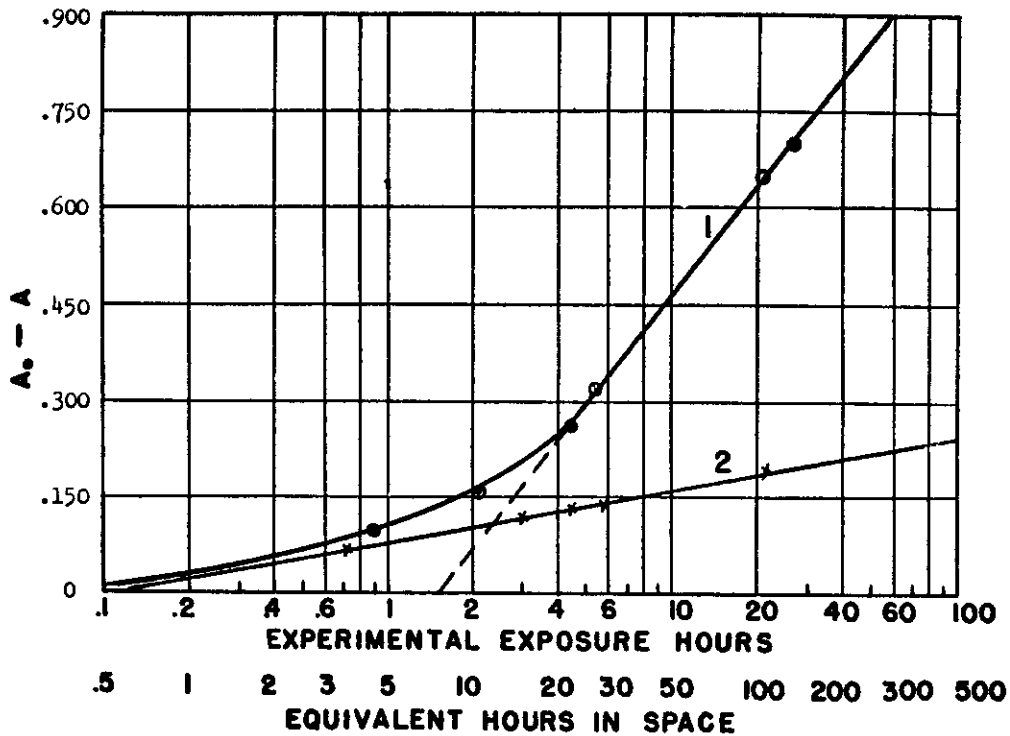


Figure 7. Photodecomposition of 2-(2'-hydroxy-5'-methylphenyl) benzotriazole: (1) Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

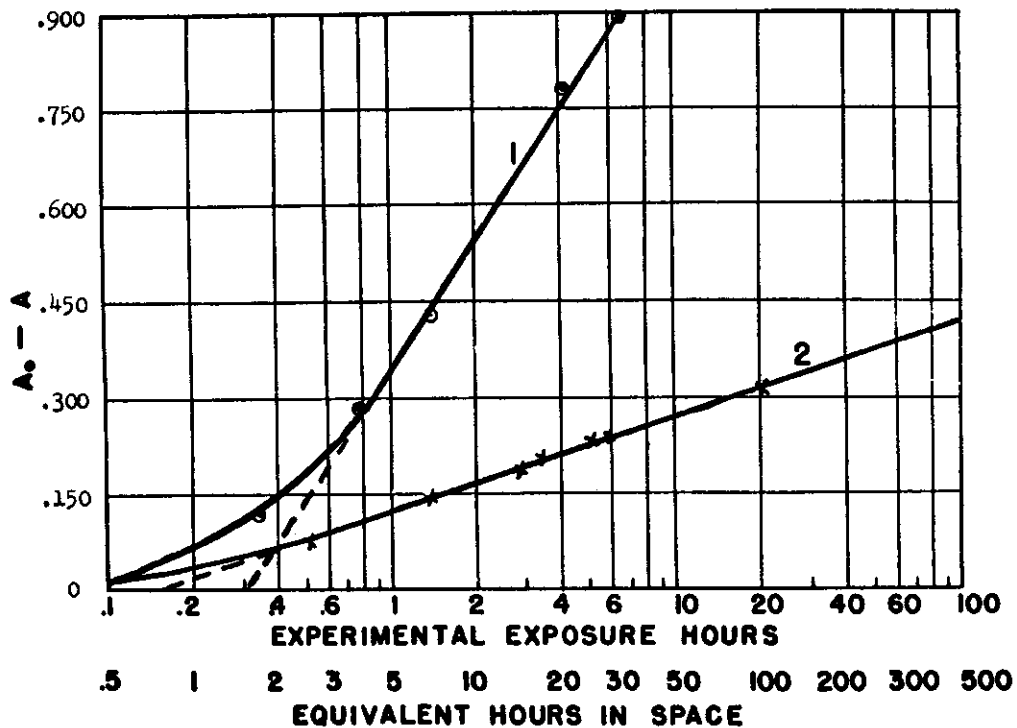


Figure 8. Photodecomposition of 2-hydroxy-4-methoxy benzophenone: (1) In Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

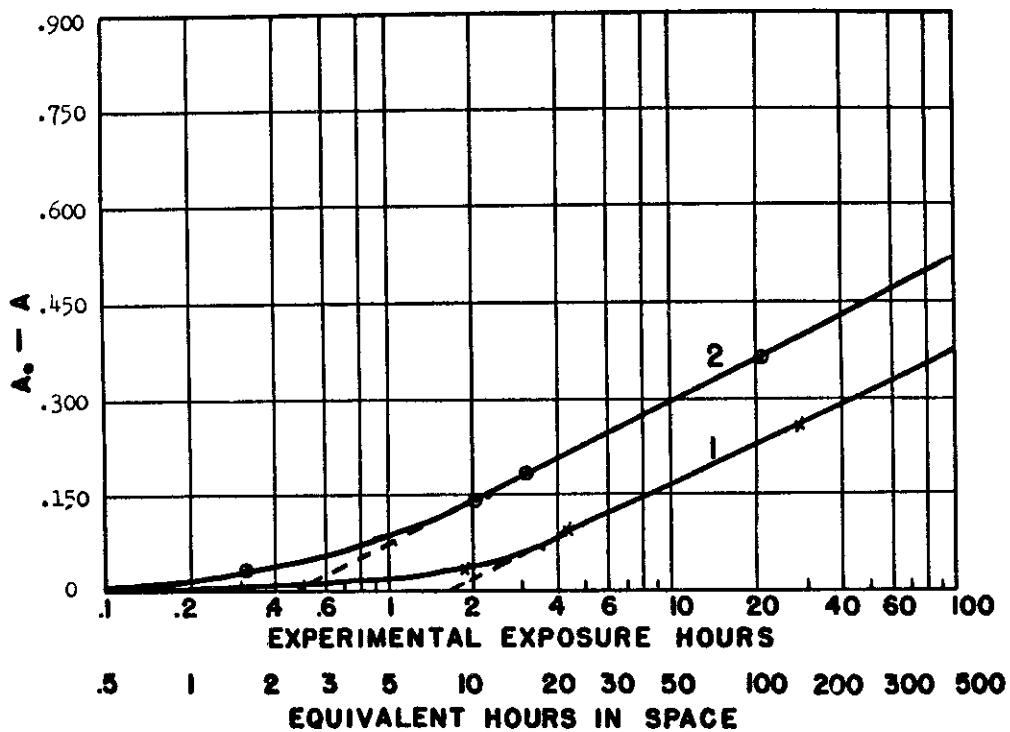


Figure 9. Photodecomposition of 4-tert-butyl phenylsalicylate:
(1) In Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

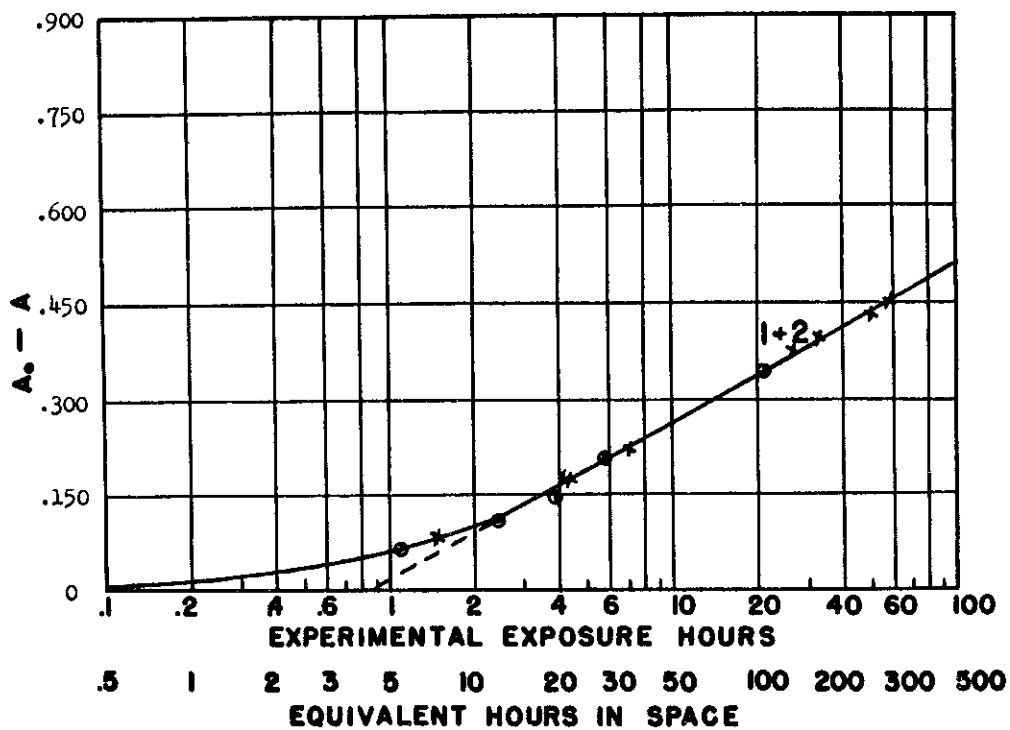


Figure 10. Photodecomposition of Dibenzoylresorcinol: (1) In Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

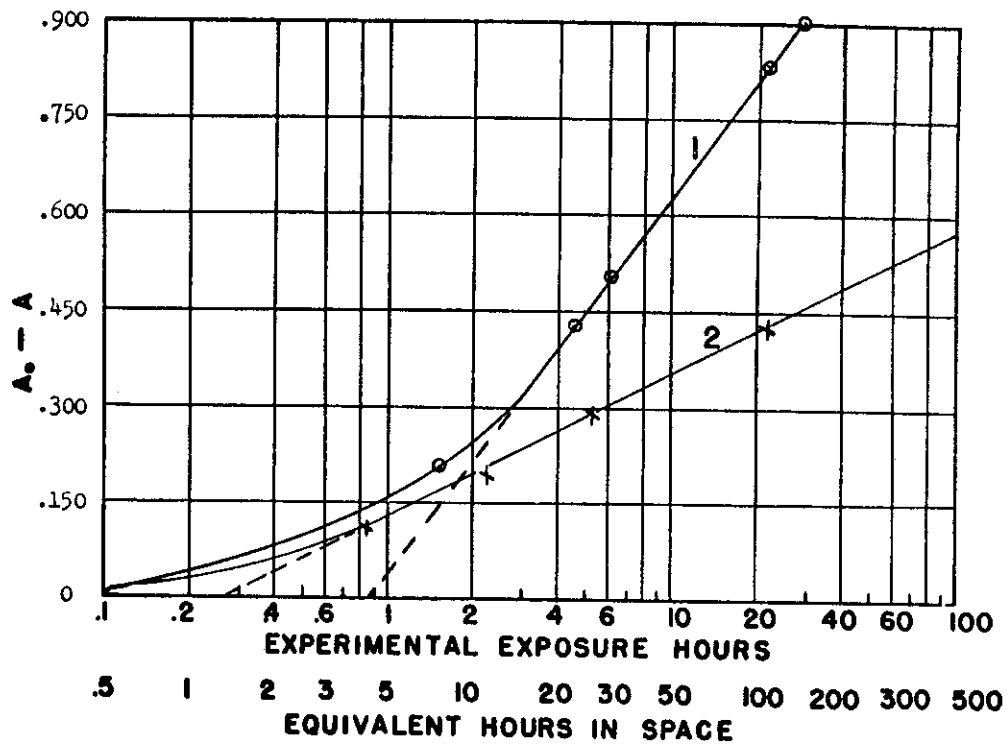


Figure 11. Photodecomposition of 2,4-dihydroxy benzophenone:
(1) In Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

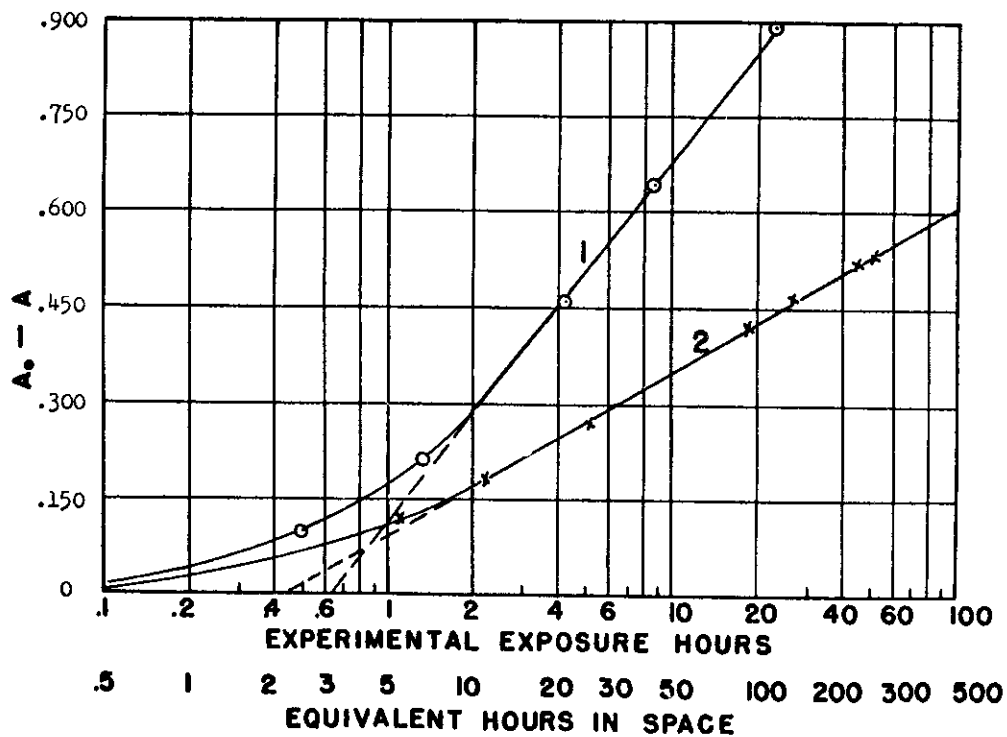


Figure 12. Photodecomposition of 2,2'-4,4'-tetrahydroxy benzophenone:
(1) In Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

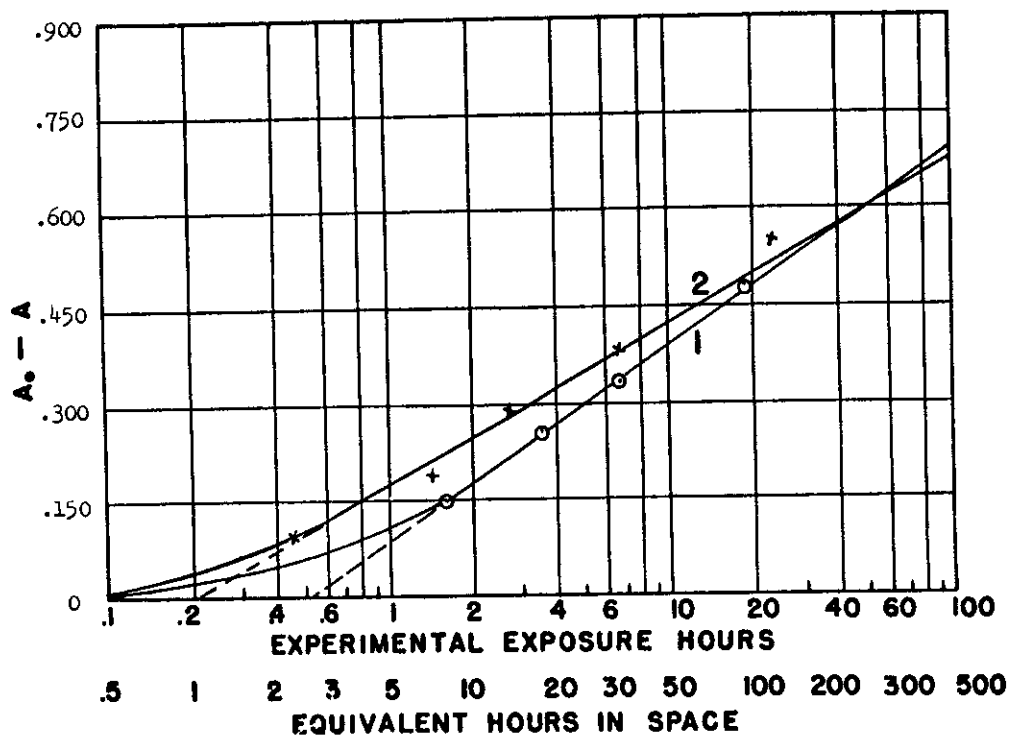


Figure 13. Photodecomposition of 2,2'-dihydroxy-4-methoxy benzophenone:
(1) In Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

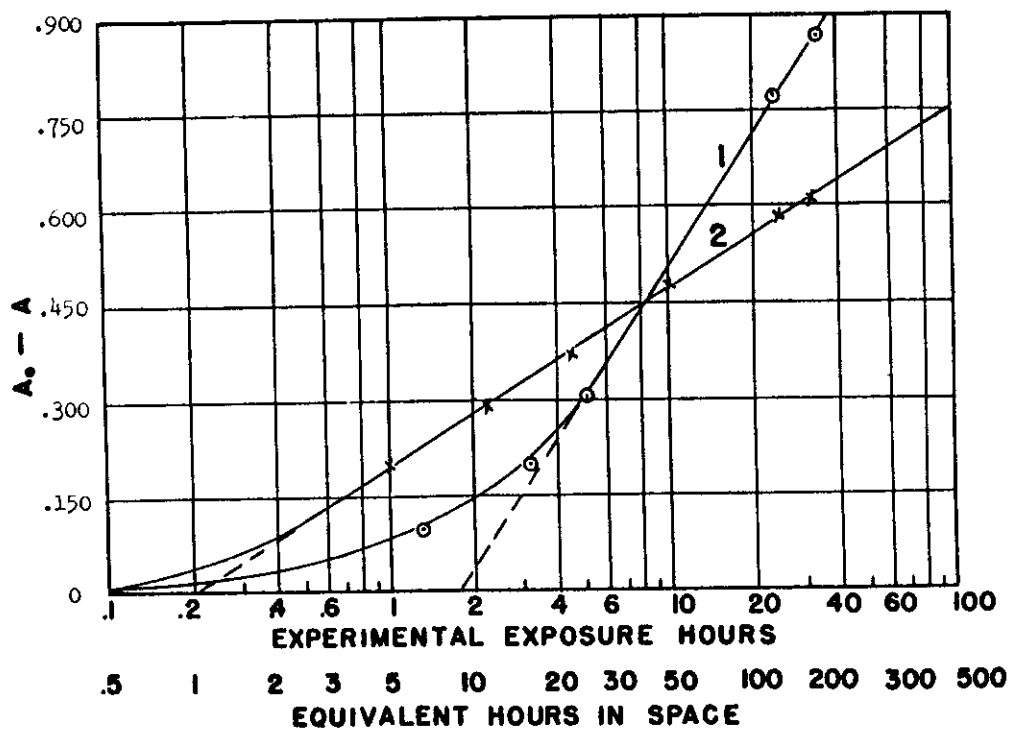


Figure 14. Photodecomposition of 2,2'-dihydroxy-4,4'-dimethoxy benzophenone:
(1) In Cellulose Acetate, (2) In Melamine-Formaldehyde Resin.

The degradation of the ultraviolet absorbers was found to decrease rapidly with time for the polymeric media studied. The results indicated that these reactions were quite complex and that no simple kinetic treatment of the data could be applied. It was empirically determined, however, that the rate data could be expressed by a straight line relationship by plotting the amount of absorber reacted versus the logarithm of the exposure time. This type of treatment is analogous to the Hurter-Driffield law of photographic materials (11,12) (see equation 1 below).

$$A_0 - A = \gamma (\log E - \log i) \quad (1)$$

$A_0 - A$ represents the change in absorbance which is proportional to the amount of absorber reacted. Gamma, known as "photographic contrast", represents the slope of the absorber reacted versus log exposure curve. E is the exposure which is equal to the intensity times the time. (A time value which has been corrected for variations in the intensity of the source by means of the monitoring unit is actually used.) The intercept of the straight line portion of the curve with the exposure or time axis is known as the "inertia" which is represented by i in equation 1. The two constants, γ and i , are functions of the photochemical stability of the absorbers and are given in Tables IV and V. Use is made of these values for extrapolation of the data.

Comparison of the stability of the ultraviolet absorbers in the polymers, melamine-formaldehyde and cellulose acetate, can be made from Tables IV and V. Consideration for the losses by diffusion and evaporation of the more volatile absorbers from cellulose acetate makes a comparison on the basis of photochemical stability possible. 2-hydroxy-4-methoxy benzophenone and 2-(2'-hydroxy-5'-methylphenyl) benzotriazole, two of the most volatile absorbers, have changed most in order of stability. Dibenzoylresorcinol and 2,2'-dihydroxy-4-methoxy benzophenone, which are relatively non-volatile, show nearly the same stability in the two polymers. 4-tert-butyl phenyl salicylate, which undergoes a rearrangement to a dihydroxy benzophenone upon irradiation, is more stable in cellulose acetate. The competing mechanisms of isomerization and degradation may be affected by the solvent in this case. The difference in stability among the other absorbers is not large enough to be significant. Consideration should also be given to the greater transparency of cellulose acetate in the ultraviolet. More radiant energy will be absorbed by the absorbers in this medium which should result in a greater rate of decomposition. However, the greater rate of yellowing for cellulose acetate results in a more equal absorption of the two polymers upon irradiation. From the above considerations it can be concluded that there is probably little difference in the photochemical stability of the ultraviolet absorbers in the two polymeric media, melamine-formaldehyde and cellulose acetate.

From the data in Table IV it is apparent that 1,1'-ferrocene dicarboxylic acid is the most stable absorber. This metal-organic compound, however, is a considerably weaker absorber than the organic types at the longer wavelengths and may thereby be a less effective protecting agent for certain materials. The most photochemically stable organic absorbers under these simulated space conditions are the mono-hydroxy compounds, which is the reverse order to their stability by sublimation (1,2).

B. Rate-Determining Variables

a. Intensity

The photochemical decomposition of the ultraviolet absorbers was found to be directly proportional to the light intensity showing that the "Bunsen-Roscoe reciprocity law" is valid. (The reciprocity law states that the exposure equals the intensity x time.) Figures 15 and 16 illustrate the variation in reaction rate with intensity for 2,2'-4,4'-tetrahydroxy benzophenone and 2-hydroxy-4-methoxy benzophenone. The slope or gamma of the curves is nearly identical. The displacement of the curves along the time axis or the inertia increases proportionately with the decrease in light intensity.

Demonstration of the reciprocity law's validity in these experiments permits the extrapolation of laboratory photochemical rate data to space conditions. The overall radiant energy output of the high pressure AH-6 mercury lamp below 4100 Angstroms was found to be nearly five times that of sunlight above the earth's atmosphere. Multiplication by five of the exposure times determined in these laboratory tests can then be made to approximate conditions above the earth's atmosphere for a surface positioned constantly normal to the sun's rays.

b. Solvent or Dispersing Medium

The photochemical stability of two typical ultraviolet absorbers was studied in a number of liquid solvents. These experiments of course could not be performed in a vacuum, but it was felt that a study of this type would yield much valuable information concerning the mechanism of the photochemical process. The data obtained for 2-hydroxy-4-methoxy benzophenone and 2,2'-dihydroxy-4-methoxy benzophenone are shown in Figures 17 and 18 and Table VI. Absorber concentrations of 0.01% were used in five millimeter cells which gave an initial absorbance of approximately 2.0. The longest wavelength maximum of the absorber was used to follow the reaction. It was noted that shorter wavelength maxima did not decrease as rapidly, indicating that the formation of a simpler conjugated system may be one of the first steps in the reaction. The spectra produced at the shorter wavelengths suggest a benzoic acid type molecule. Also shown in Table VI for comparison are the data for the polymeric dispersing media exposed in air.

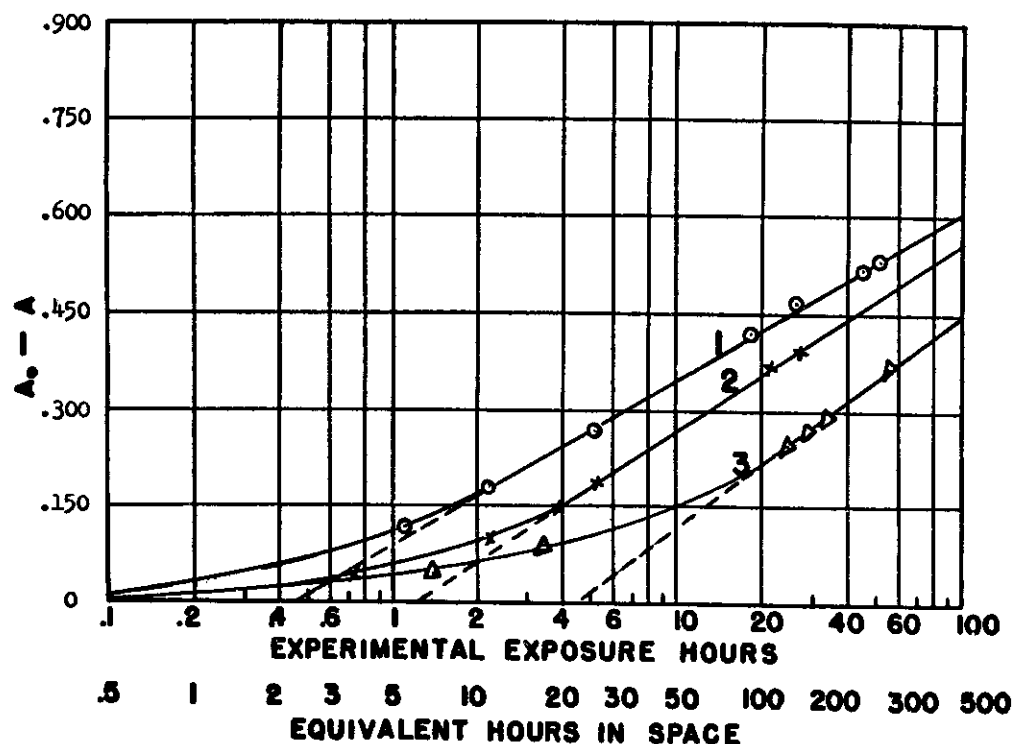


Figure 15. Effect of Intensity on 2,2'-4,4'-tetrahydroxy benzophenone in Melamine-Formaldehyde Resin: (1) In vacuum at 80°C., (2) In vacuum at 80°C. with 40% screen, (3) In vacuum at 80°C. with 15% T screen.

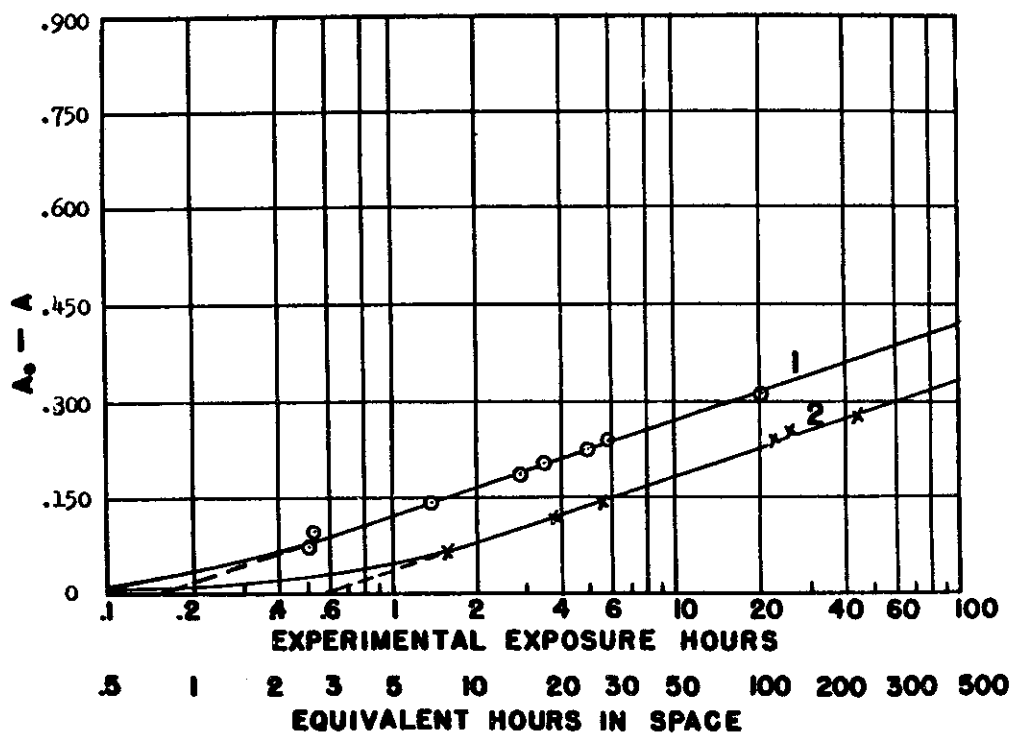


Figure 16. Effect of Intensity on 2-hydroxy-4-methoxy benzophenone in Melamine-Formaldehyde Resin: (1) In vacuum at 80°C., (2) In vacuum at 80°C. with 25% T screen.

Table VI

EFFECT OF SOLVENT OR MEDIUM ON THE RATE OF PHOTODECOMPOSITION OF THE ABSORBERS EXPOSED IN AIR

Solvent	2-hydroxy-4-methoxy benzophenone		2,2'-dihydroxy-4-methoxy benzophenone	
	Hours Exposure for $\Delta A = 0.400$	Hours Exposure for $\Delta A = 0.800$	Hours Exposure for $\Delta A = 0.400$	Hours Exposure for $\Delta A = 0.800$
n-heptane	1.5	2.9	3.5	7.1
ethylene glycol	2.4	3.0	1.9	2.6
ethanol (absolute)	3.9	4.9	1.7	2.9
methanol (absolute)	5.1	6.9	1.4	2.8
cellulose acetate	10.5	24.0	7.7	125.0
melamine-formaldehyde	103.0	----	7.0	600.0

It is obvious from these data that the solvent or dispersing medium plays a very important role in the photochemical reaction. In n-heptane the reactions are zero-order which is typical of many photochemical processes. Most probably the simplest mechanism occurs for this relatively inert solvent. The decomposition of 2,2'-dihydroxy-4-methoxy benzophenone in the alcoholic solvents also appears to be nearly zero-order but occurs at a faster rate. The alcohols evidently weaken the stability of this absorber but probably do not take part in the reaction. The decomposition of 2-hydroxy-4-methoxy benzophenone in the alcoholic solvents proceeds slowly at first then increases very rapidly. For this mono-hydroxy absorber, the alcohols apparently exert an initial stabilizing influence which is later overcome by the formation of more highly reactive free radicals or other sensitizers. It should be pointed out that the exceptional resistance to ultraviolet radiation exhibited by the absorbers is attributed to the formation of a six-membered chelated ring due to a hydrogen bond between a hydroxyl group and an oxygen or nitrogen atom which greatly increases the stability of the aromatic system. This stability would undoubtedly be affected by the ability of the solvent to strengthen or weaken this hydrogen bond.

The most significant result from these data is the much higher rate of decomposition observed for the liquid solvents compared with the solid polymers. This effect becomes more noticeable at longer exposures where the reaction rate in the polymeric systems is rapidly decreasing. The greater reactivity of the absorbers in the liquid solvents can be attributed to their greater mobility in these media which would increase the probability of reaction as well as maintain the system homogeneous by mixing. In the polymeric media the absorber nearest the irradiated surface would be consumed and be replaced by

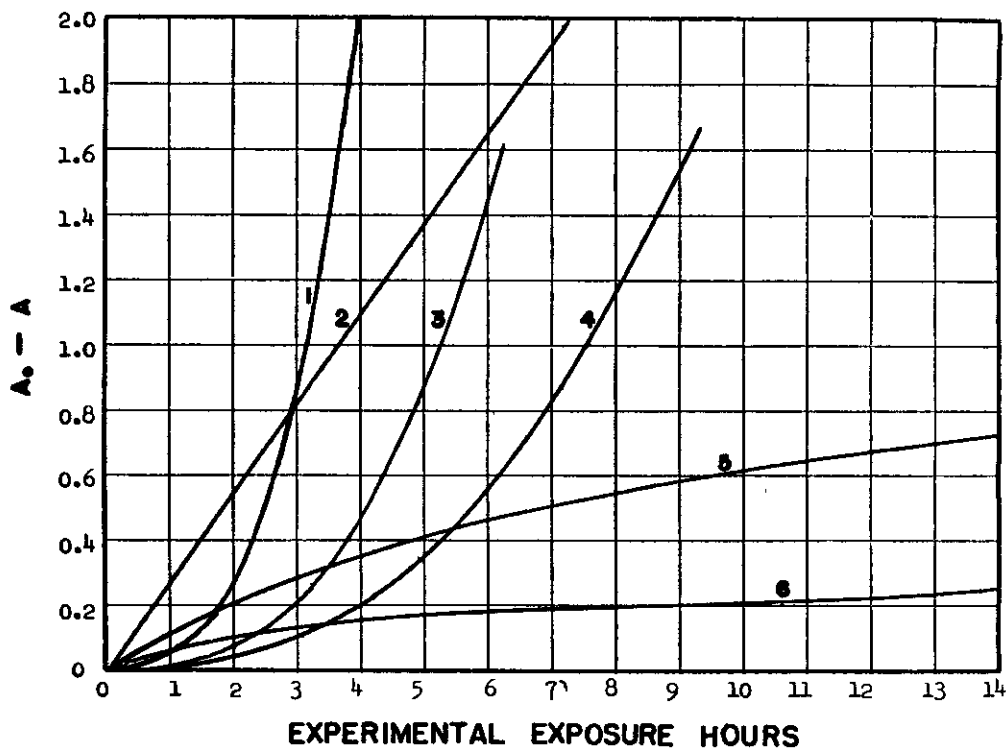


Figure 17. Effect of Solvent on 2-hydroxy-4-methoxy benzophenone: (1) Ethylene glycol, (2) n-heptane, (3) Ethanol, (4) Methanol, (5) Cellulose Acetate, (6) Melamine-Formaldehyde Resin.

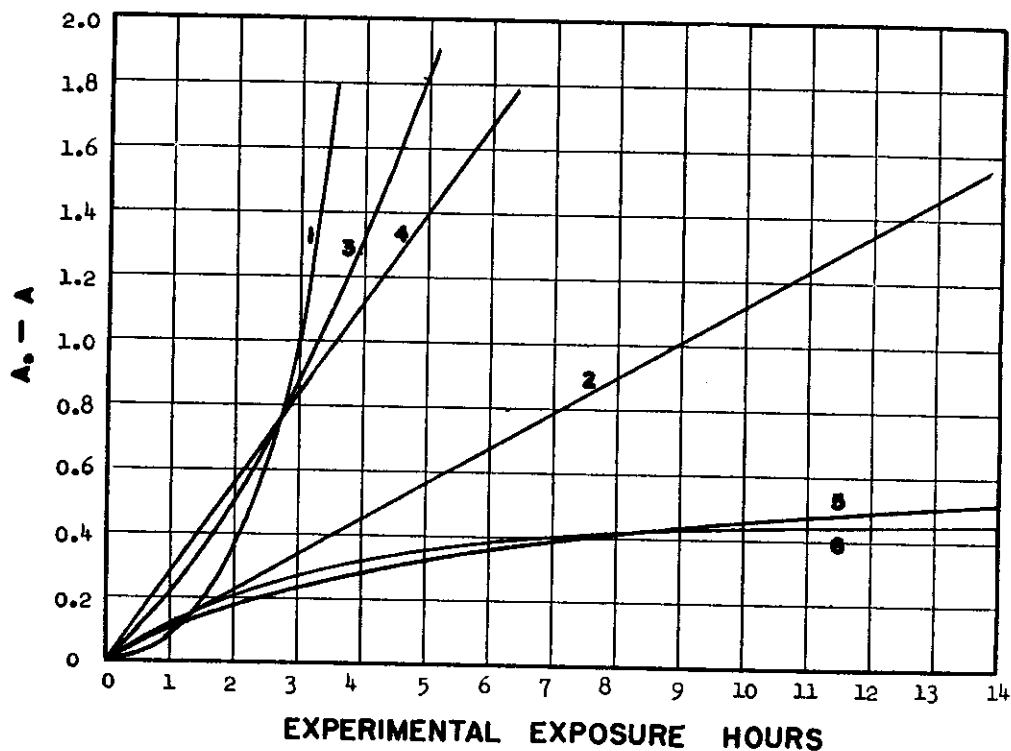


Figure 18. Effect of Solvent on 2,2'-dihydroxy-4-methoxy benzophenone: (1) Ethylene glycol, (2) n-heptane, (3) Ethanol, (4) Methanol, (5) Cellulose Acetate, (6) Melamine-Formaldehyde Resin.

highly absorbing decomposition products from both polymer and absorber which would act as filters and protect the unreacted absorber from further degradation. The very low diffusion rate of the absorbers in these polymers would prevent replacement of the reacted absorber. From this reasoning and the earlier observation that the rate of decomposition of the absorber is proportional to the light intensity, it can be concluded that the rapid, logarithmic decrease in the reaction rate observed in the polymeric media is due to a rapid decrease in the rate of energy absorption by the absorbers. To determine if consideration of these factors would produce a rate expression consistent with the observed data, however, would be very difficult because of the variation of these effects with the wavelength of light.

c. Vacuum and Temperature

The primary photochemical process which involves the formation of an activated absorber molecule is independent of both the temperature and atmosphere. Both of these variables, however, will have an influence on the secondary thermal processes that follow. In addition, the temperature can effect the rate of diffusion of the reactants and products and increase the probability of collisions and of loss by evaporation.

To study the effect of vacuum on the rate of photochemical degradation, the ultraviolet absorbers were exposed in air in both melamine-formaldehyde and cellulose acetate under the same irradiation conditions as for the vacuum experiments. The higher temperature obtained by the samples exposed in vacuum made it necessary to raise the temperature for the air exposures by heating with an infrared lamp. The temperature dependence for the photochemical reactions in air was studied by a second set of experiments in which the samples were not heated. These data are shown in Figures 19-22 and Table VII.

Table VII shows that both temperature and a lack of air have more pronounced effects in cellulose acetate. This can be interpreted as meaning that the photochemical reaction is at least partially dependent upon the rate of sorption and diffusion of atmospheric gases such as oxygen or water vapor in this medium. In melamine-formaldehyde resins these effects are quite small which is consistent with the previous observation that the rate of diffusion of the absorbers through melamine-formaldehyde is considerably lower than through cellulose acetate. A lower diffusion rate for oxygen might also be predicted.

Two other experiments were performed to support this conclusion. Neither prior treatment of the melamine-formaldehyde samples with oxygen or nitrogen nor their exposure in an atmosphere of pure oxygen had any effect on the rate of reaction. Similar experiments performed for cellulose acetate show that oxygen has a detrimental effect.

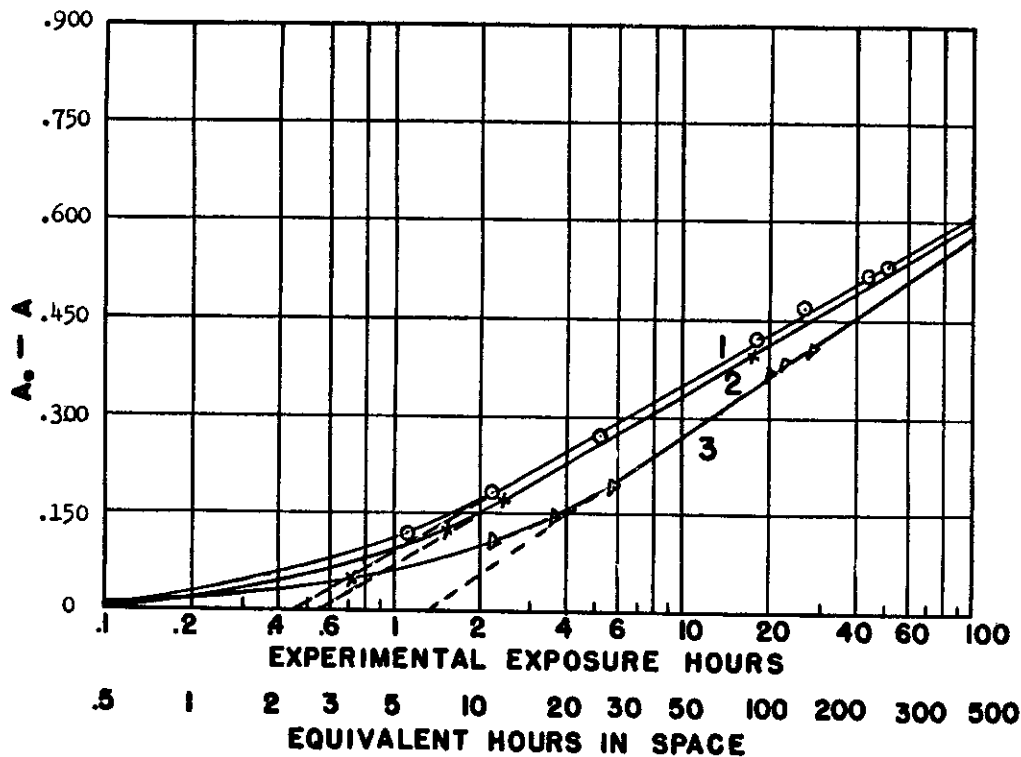


Figure 19. Effect of Vacuum and Temperature on 2,2'-4,4'-tetrahydroxy benzophenone in Melamine Formaldehyde Resin: (1) In vacuum at 80°C., (2) In air at 70°C., (3) in air at 40°C.

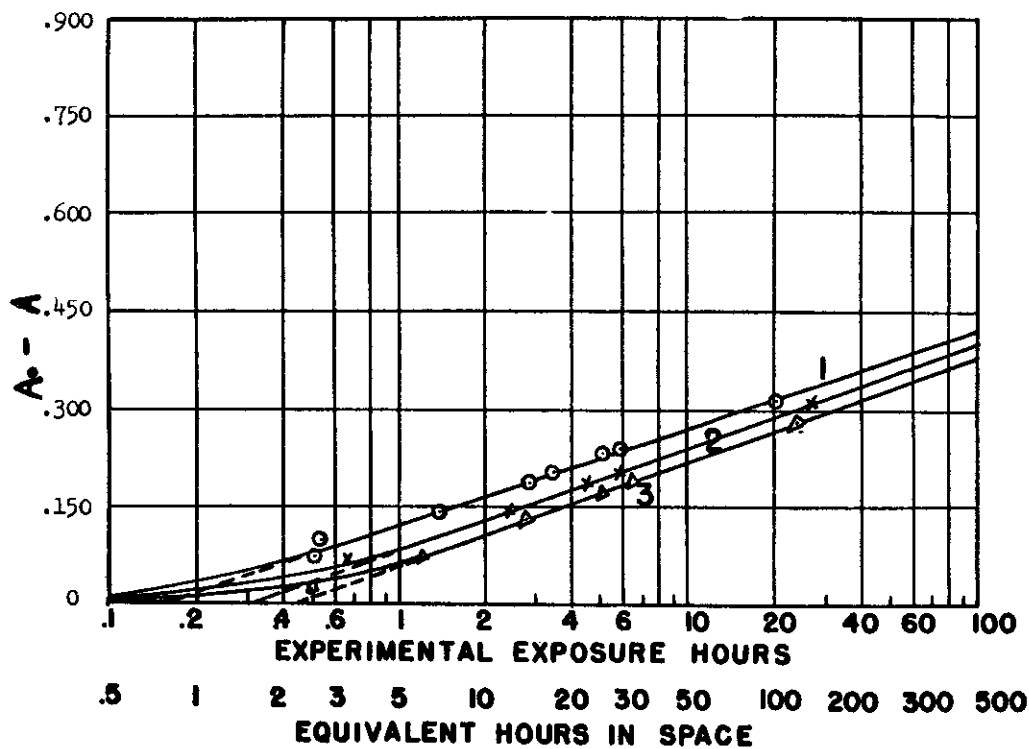


Figure 20. Effect of Vacuum and Temperature on 2-hydroxy-4-methoxy benzophenone in Melamine Formaldehyde Resin: (1) In vacuum at 80°C., (2) In air at 70°C., (3) In air at 40°C.

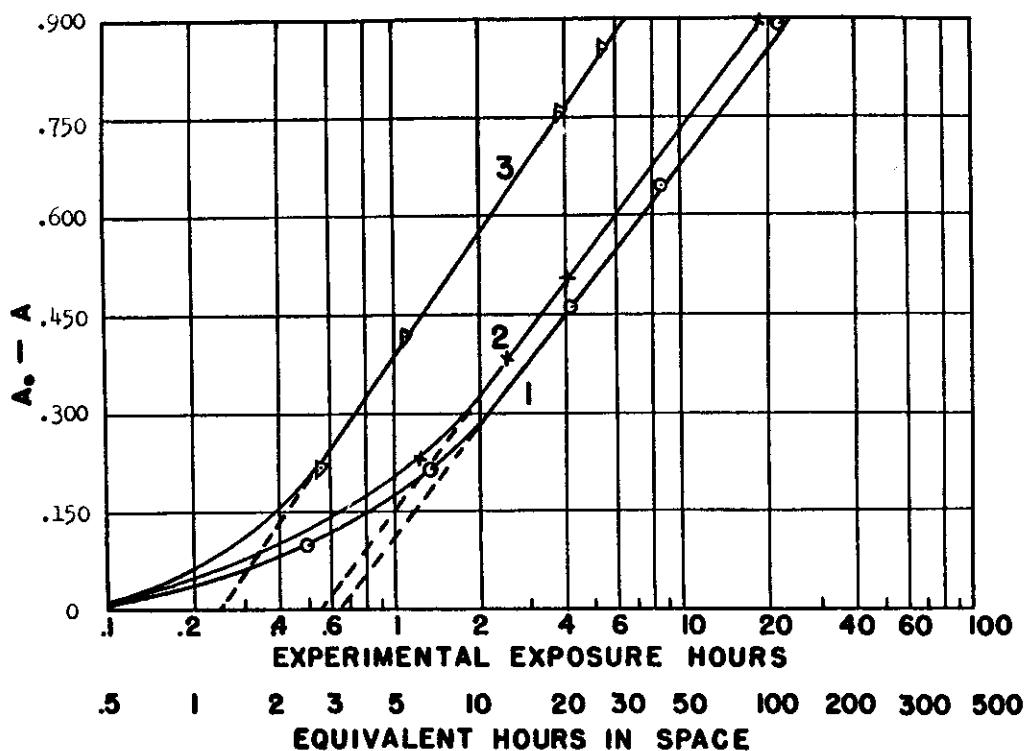


Figure 21. Effect of Vacuum and Temperature on 2,2'-4,4'-tetrahydroxy benzophenone in Cellulose Acetate: (1) In vacuum at 80°C., (2) In air at 40°C., (3) In air at 70°C.

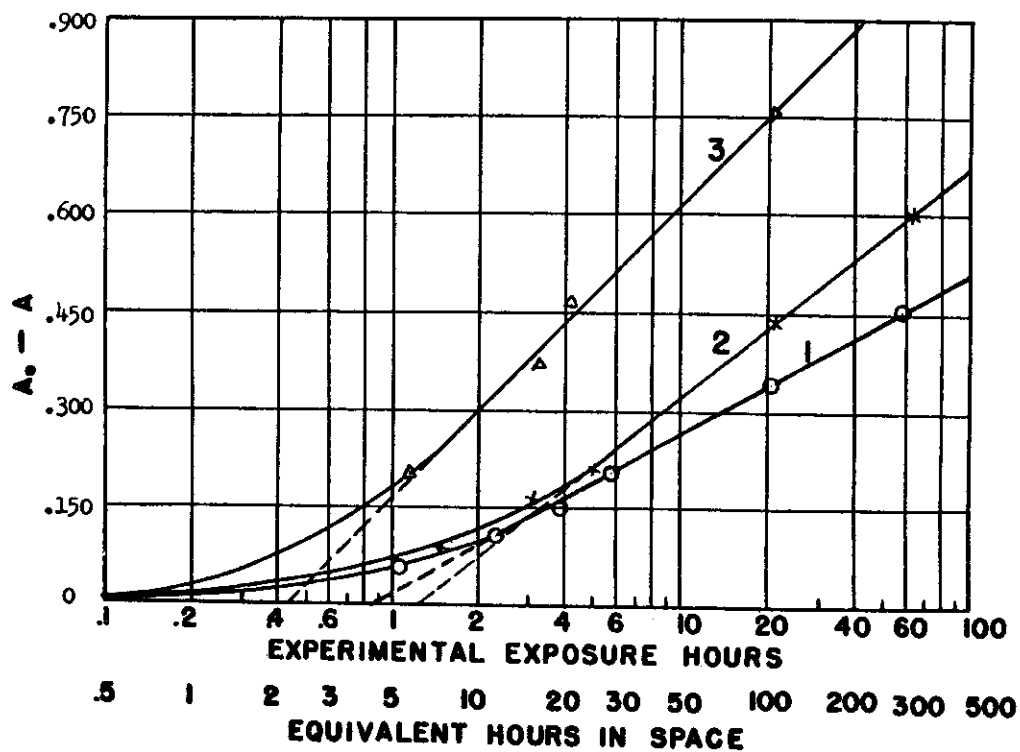


Figure 22. Effect of Vacuum and Temperature on Dibenzoylresorcinol in Cellulose Acetate: (1) In vacuum at 80°C., (2) In air at 40°C., (3) In air at 70°C.
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TABLE VII

EFFECT OF VACUUM AND TEMPERATURE ON THE PHOTOCHEMICAL STABILITY OF THE
ULTRAVIOLET ABSORBERS

Absorber	Medium ★	Conditions	Equivalent Hours in Space for $\Delta A =$	
			0.200	0.400
2-hydroxy-4-methoxy benzophenone	MF	vacuum, 80°C.	20	425
2-hydroxy-4-methoxy benzophenone	MF	air, 70°C.	28	475
2-hydroxy-4-methoxy benzophenone	MF	air, 40°C.	36	516
2,2'-4,4'-tetrahydroxy benzophenone	MF	vacuum, 80°C.	12	72
2,2'-4,4'-tetrahydroxy benzophenone	MF	air, 70°C.	15	78
2,2'-4,4'-tetrahydroxy benzophenone	MF	air, 40°C.	30	133
2,2'-4,4'-tetrahydroxy benzophenone	CA	vacuum, 80°C.	7	16
2,2'-4,4'-tetrahydroxy benzophenone	CA	air, 70°C.	2	5
2,2'-4,4'-tetrahydroxy benzophenone	CA	air, 40°C.	6	14
Dibenzoylresorcinol	CA	vacuum, 80°C.	28	175
Dibenzoylresorcinol	CA	air, 70°C.	6	17
Dibenzoylresorcinol	CA	air, 40°C.	25	90

★ MF = melamine-formaldehyde resin
CA = cellulose acetate

d. Wavelength

The effects of the short wavelength ultraviolet radiation and the high vacuum of space on the stability of the protective ultraviolet absorbers are the primary considerations in this work. To determine the effects of these parameters simultaneously would essentially be making a comparison of terrestrial and extraterrestrial conditions. Since considerably more is known about the stability and effectiveness of the absorbers under terrestrial conditions (13,14,15,16), it was felt that such a comparison would be helpful in the interpretation of the data and in the determination of their usefulness in a space environment.

The terrestrial exposure conditions were obtained by using a pyrex filter that absorbed all radiation from the AH-6 lamp below 3000 Angstroms and by allowing the samples to be exposed to air. Melamine-formaldehyde was used as the dispersing medium as loss by evaporation is negligible and the effect of temperature is small. The data obtained are shown in Table VIII along with the extraterrestrial results.

Table VIII

ABSORBER STABILITY UNDER TERRESTRIAL AND EXTRATERRESTRIAL CONDITIONS

Absorber	Hours Exposure for $\Delta A = 0.200$		Ratio Δ
	Terrestrial	Extraterrestrial	
1,1'-ferrocene dicarboxylic acid	> 500	> 500	—
2-(2'-hydroxy-5'-methyl phenyl) benzotriazole	370	140	3
2-hydroxy-4-methoxy benzophenone	300	20	15
2,2'-4,4'-tetrahydroxy benzophenone	315	13	24
2,2'-dihydroxy-4-methoxy benzophenone	315	7	45

Δ Terrestrial/Extraterrestrial

The protective ultraviolet absorbers were found to be considerably less stable under extraterrestrial conditions, the average loss in stability over terrestrial conditions being a factor of 22. Since the effect of vacuum was shown previously to be small, the above differences can be attributed almost entirely to the wavelength of the radiation, i.e., the quantum yield of the absorbers for the shorter wavelength radiation is much higher than for radiation above 3000 Å. Because the stability of the absorbers is actually determined by the sum of the quantum yields of the individual electronic transitions and the spectral energy distribution of the source, it is logical to conclude from the above results that the lowest energy transition has an extremely low quantum yield. It is very likely, therefore, that the decomposition of the absorbers under terrestrial conditions can be attributed to that part of the band of the second electronic transition which extends into the region above 3000 Angstroms.

From Table VIII it can be seen that there is little difference under terrestrial conditions in the photochemical stability of the four organic absorbers tested. The three benzophenone derivatives contained one, two and four hydroxyl groups, and the other compound is a mono-hydroxy, substituted benzotriazole. It was reported earlier that the mono-hydroxy absorbers were the most stable under extraterrestrial conditions. The very weak absorption below 3000 Angstroms exhibited by the benzotriazole derivative probably accounts for the exceptionally high stability to short wavelength radiation found for this compound. By this same reasoning the benzotriazole would be a less effective absorber for extraterrestrial radiation. It is possible that the differences observed for the benzophenone derivatives may be explained by consideration of their structures in the several excited states involved which may vary with the number of hydroxyl groups and the strength of the intramolecular hydrogen bond. The metal-organic absorber, 1,1'-ferrocene dicarboxylic acid, exhibited excellent stability under both terrestrial and extraterrestrial conditions. Little decomposition of this material was noted after 500 hours exposure.

V. PROTECTIVE EFFECTIVENESS OF THE ULTRAVIOLET ABSORBERS

The ability of a protective ultraviolet absorber to inhibit degradation of polymers is dependent upon a number of factors such as the spectral energy distribution of the incident radiation, the absorption spectra of the polymer and absorber, the photochemical stability of both the absorber and polymer as a function of wavelength, the thickness of the polymeric film or sheet, and the concentration of absorber. C. D. Miller (17) described a mathematical expression which relates the "increase in service life" of a protected polymer to a number of the above factors. Miller's expression, however, used a "protected polymer absorptivity" term which is difficult to evaluate experimentally. A similar expression has been derived using the ratio of the light energy absorbed by an unprotected polymer to the energy absorbed by a polymer protected with an ultraviolet absorber. We have termed this ratio as being the "protective effectiveness" of the absorber.

-
- A "Protective Effectiveness" should not be confused with the quantity termed "Absorbing Effectiveness". "Absorbing Effectiveness" is the sum of the products of the intensity of the light source multiplied by the absorptivity of the pure protective absorber; its units are in "watts per gram". It is an idealized measure of the maximum amount of energy which a quantity of a protective absorber could possibly absorb from a given light source. No "shadowing" or self-absorption of energy is assumed, as well as no competition from a medium such as a polymer for the incident energy.

$$PE = \frac{\sum_{\lambda_1}^{\lambda_2} I_{0\lambda} (1 - 10^{-b a_p \lambda})}{\sum_{\lambda_1}^{\lambda_2} I_{0\lambda} (1 - 10^{-b(a_p \lambda C_p + a_B \lambda C_B)}) \cdot \frac{a_p \lambda C_p}{a_p \lambda C_p + a_B \lambda C_B}} \quad (2)$$

where I_0 = incident intensity at λ
 $b\lambda$ = thickness of polymer in millimeters
 a_p = absorptivity of polymer at λ
 a_B = absorptivity of absorber at λ
 C_p = concentration of polymer in percent
 C_B = concentration of absorber in percent

Calculations of "protective effectiveness" by means of equation 2 assume that the quantum yield for the polymer is independent of wavelength and that the ultraviolet absorber is perfectly stable. In addition, it has to be assumed that degradation products do not absorb and that the absorption spectrum of the polymer does not change during degradation. None of these conditions are achieved completely in a real system, but the use of equation 2 does seem worthwhile for predicting the degree of improvement that can be obtained by the use of an ultraviolet absorber. With equation 2 it is possible to compare the protective ability of the various absorbers, estimate which polymers are better protected by an absorber and to determine the effect of film thickness and absorber concentration on the effectiveness of the ultraviolet absorber. Equation 2 predicts that an ultraviolet absorber becomes less effective as the thickness of the polymer film decreases; this has been found to be true for a number of polymer systems, especially for paints and other thin surface coatings.

The effectiveness of 2-hydroxy-4-methoxy benzophenone in protecting a polyester resin was determined experimentally under both terrestrial and extraterrestrial conditions. The polyester resin studied was Laminac 4123 molded into sheets approximately one-eighth of an inch thick. The protected resins contained 0.25% 2-hydroxy-4-methoxy benzophenone. The resins were irradiated with a 1000 watt high pressure mercury arc which is approximately five times as intense as sunlight above the earth's atmosphere. Filters were used to obtain short wavelength limits of 2000 and 3000 Angstroms to correspond approximately to the short wavelength limits of extraterrestrial and terrestrial sunlight. In addition the experiments were performed both in air and in vacuo to study the effect of atmospheric constituents as well as the wavelength of irradiation. The yellowing of the polymer at 4300 Angstroms was used as a measure of the degradation incurred. These data are presented in Figures 23 and 24 and tabulated in Table IX. Included in Table IX are the experimentally determined and calculated "protective effectiveness".

Table IX
PROTECTIVE
EFFECTIVENESS OF 2-HYDROXY-4-METHOXY BENZOPHENONE IN A POLYESTER RESIN

Lower Wavelength Limit, A.	Atmosphere	Hours for ΔA of 0.100 ($\Delta T = 11\%$)		Protective Effectiveness (Experimental)	Protective Effectiveness (Calculated)
		Unprotected	Protected		
2000	Vacuum	0.7	2.0	2.8	2.5
2000	Air	2.0	5.5	2.7	2.5
3000	Vacuum	3.0	33.0	11.0	13.0
3000	Air	3.5	100.0	28.0	13.0

The calculated "protective effectiveness" was determined by means of equation 2 from the absorption spectra of the polyester and 2-hydroxy-4-methoxy benzophenone (1) and the spectral energy distribution of the mercury arc (1,8). The good agreement between the calculated and experimental values indicates the usefulness of this expression. It should be pointed out that the calculated "protective effectiveness" assumes that the rate of reaction is proportional to the energy absorbed. Figures 23 and 24 show that this is not the case for polyesters. The reaction is actually slowing down with time. It would be expected then that the greatest disagreement between the observed and calculated "protective effectiveness" would occur for the longest exposures.

It can be concluded from Table IX that the effectiveness of 2-hydroxy-4-methoxy benzophenone in protecting a polyester is considerably less for the shorter wavelengths and that the loss in effectiveness is due primarily to the stronger absorption of the polymer at the short wavelengths. Evidence that the quantum yield for the unprotected polyester is nearly constant with wavelength is shown in Figure 25 by the almost identical yellowing curves obtained when comparison is made on an energy-absorbed basis for the 2000 and 3000 Angstrom wavelength limit conditions. The rate of energy absorption was determined to be twice as great in the former case.

It can be seen from Table IX that a lack of oxygen causes an increase in the rate of yellowing of polyester resins. This can be attributed to the inhibition of an oxygen-dependent fading reaction under vacuum conditions, which is known to occur simultaneously with the yellowing process for exposures in air (18).

It becomes apparent from the above data that the present protective ultraviolet absorbers will not be completely suitable for protecting strongly absorbing polymers from degradation due to the shorter ultraviolet wavelengths. It seems reasonable to suggest that only the more transparent polymers be used for space applications. This eliminates any polymers containing aromatic or conjugated groupings. A program is being established to investigate this approach by determining the ultraviolet absorption spectrum of a wide variety of polymers. Calculations will be made of their "protective effectiveness" with various ultraviolet absorbers and the most favorable combinations tested experimentally.

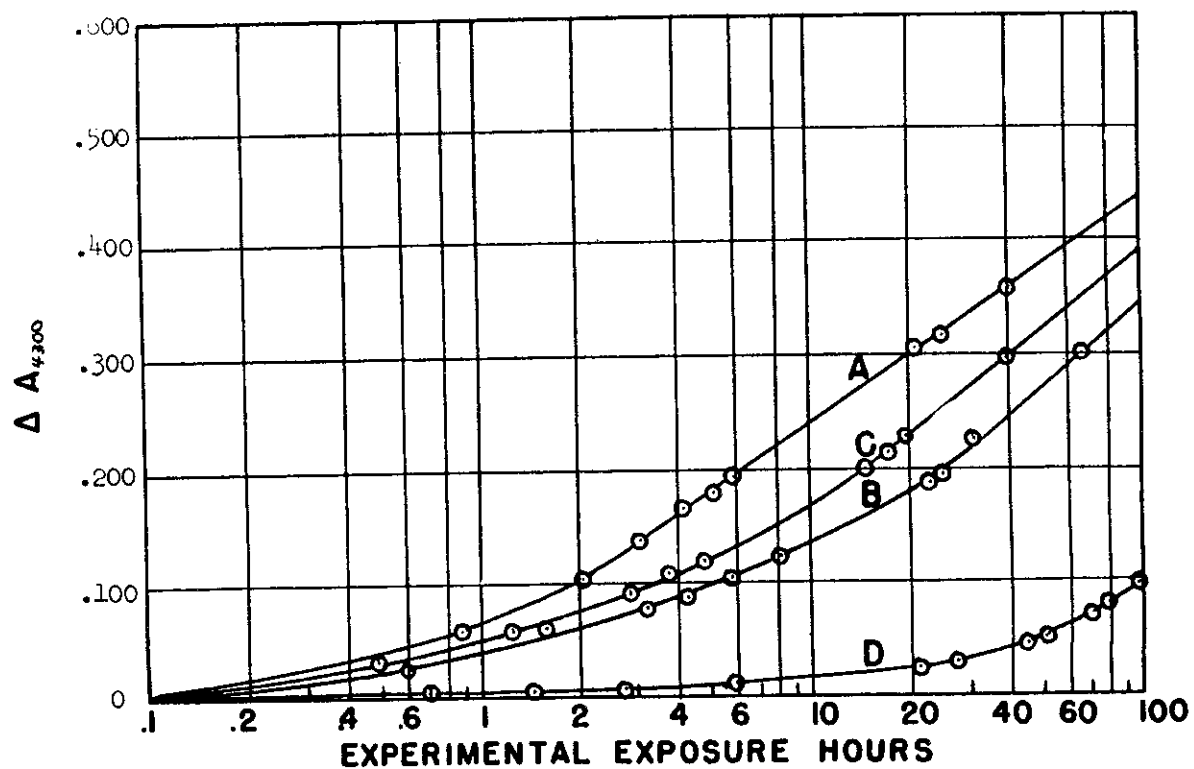


Figure 23. Photochemical Yellowing of Polyester Resins in Air:

- A. Unprotected, irradiated above 2000 Angstroms
- B. Protected, irradiated above 2000 Angstroms
- C. Unprotected, irradiated above 3000 Angstroms
- D. Protected, irradiated above 3000 Angstroms

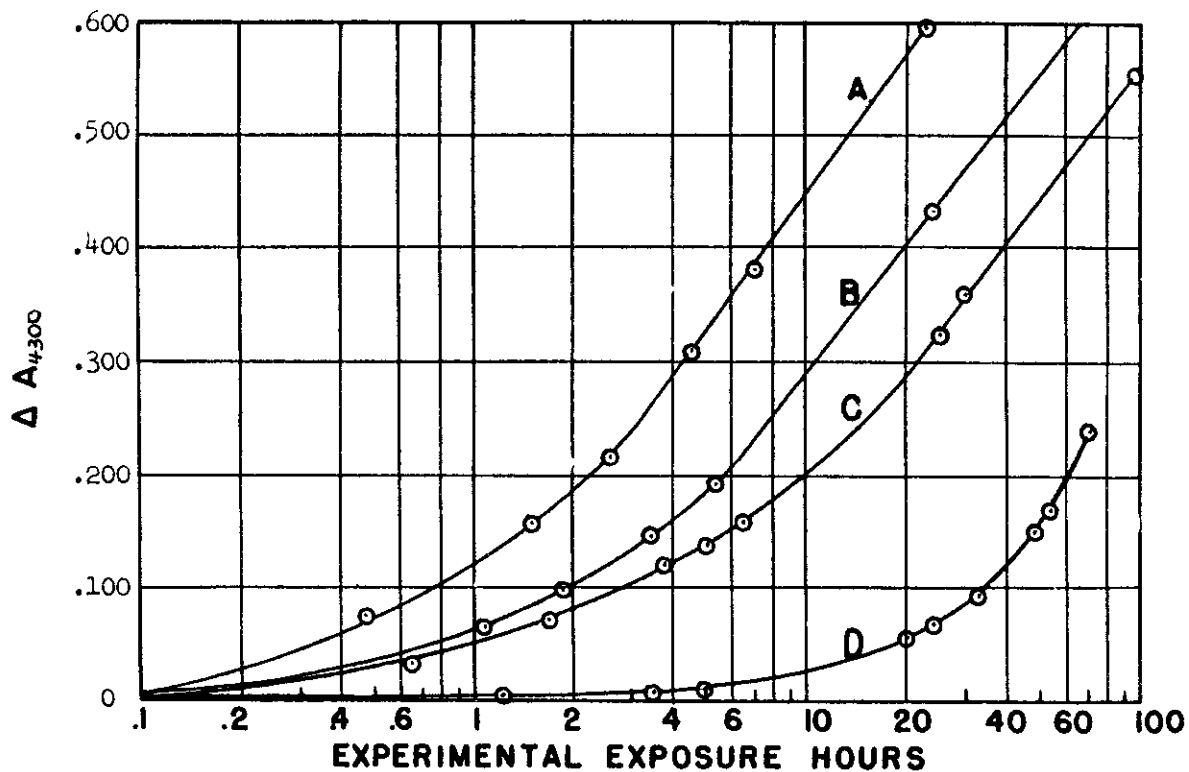


Figure 24. Photochemical Yellowing of Polyester Resins in Vacuum:

- A. Unprotected, irradiated above 2000 Angstroms
- B. Protected, irradiated above 2000 Angstroms
- C. Unprotected, irradiated above 3000 Angstroms
- D. Protected, irradiated above 3000 Angstroms

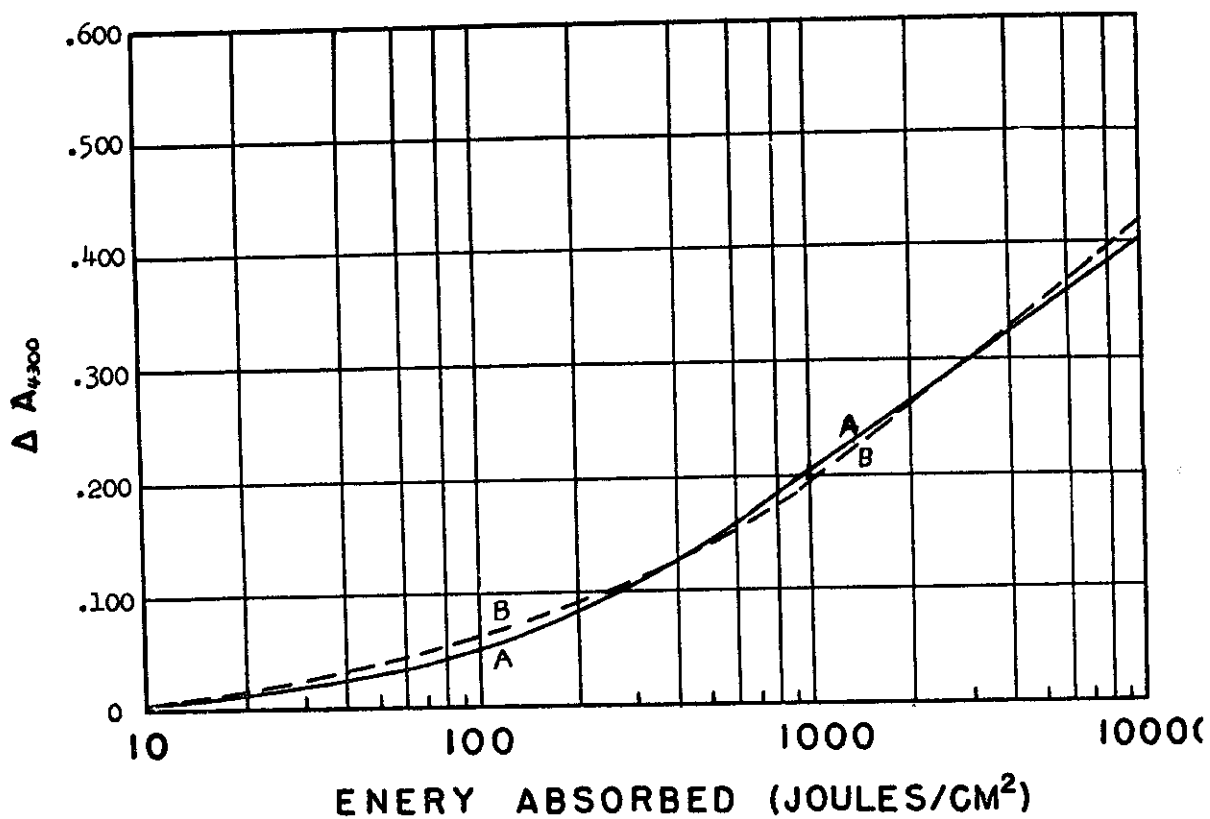


Figure 25. Extent of Yellowing vs. Energy Absorbed for Unprotected Polyesters

- A. Irradiated above 2000 Angstroms
- B. Irradiated above 3000 Angstroms

Consideration will be given to the photochemical and thermal stability of the unprotected polymers in making these selections.

V. CONCLUSIONS

1. Comparison of the photochemical stability under simulated terrestrial and extraterrestrial conditions show the ultraviolet absorbers to be considerably less stable in a space environment. This loss in stability is due primarily to the higher quantum yield of the absorbers for the short wavelength ultraviolet radiation (2000 to 3000 Angstroms). The high vacuum or the absence of air was found to have a relatively small effect, the magnitude of which depended upon the diffusion of atmospheric gases and absorber through the polymer.
2. Ultraviolet absorbers of the benzophenone and benzotriazole type containing more than one hydroxyl group are less photochemically stable than the mono-hydroxy compounds, which is the reverse order to their stability by sublimation. The metal-organic compound, 1,1'-ferrocene dicarboxylic acid, was the most stable absorber examined. This compound is a relatively weak absorber at wavelengths above 2900 Angstroms but may be effective against the short wavelength radiation.
3. The validity of the "reciprocity law" was demonstrated by showing that the exposure time required to produce a given loss in photochemical stability of the absorbers was inversely proportional to the light intensity. This permits extrapolation of laboratory data to space conditions.
4. The rate of photochemical decomposition of the ultraviolet absorbers was found to be highly dependent upon the dispersing media or solvent. For absorbers dispersed in polymers, the rate of reaction decreased rapidly with exposure; the kinetic data could be expressed by a straight line relationship by plotting the amount of absorber reacted versus the logarithm of the exposure time. For the liquid solvents the rate of photodecomposition was much higher, being zero-order for n-heptane. The rapid decrease in reaction rate for the polymers is attributed to a decrease in the rate of energy absorption by the absorbers resulting from competition for the light energy by the polymer and decomposition products from both absorber and polymer.
5. The ability of an ultraviolet absorber to protect a polyester resin from photochemical degradation in a space environment is considerably less than for terrestrial conditions. This is due to the strong ultraviolet absorption of the polyester at the shorter wavelength which competes with the absorber for the incident radiation. Calculated "protective effectiveness" values using the absorption spectra of both polymer and absorber were in good agreement with the experimental data. The quantum yield for the degradation of polyester resins was found to be independent of wavelength (2000 to 4000 Angstroms).

6. The reduced ability of the ultraviolet absorbers to adequately protect strongly absorbing polymers from degradation by the short wavelength ultraviolet radiation lowers their effectiveness for long exposures to space environment. Increased concentrations would improve the situation somewhat. Their use in more transparent polymers would be limited by the inherent stability of both absorber and polymer.

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