

## Investigation of the Protective Ultraviolet Absorbers in a Space Environment.

### III. Protective Effectiveness\*

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#### 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 extreme conditions of ultraviolet radiation, temperature, and vacuum. Most surface-coating materials deteriorate to some extent under terrestrial conditions and require the use of additives such as protective ultraviolet absorbers or antioxidants to increase their service life. The more severe conditions encountered above the earth's atmosphere will undoubtedly necessitate the use of one or more types of protective agents 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 effectiveness of the protective ultraviolet absorbers. Two completely different types of protective agents are considered in this study. These are (1) the commercially available absorbers of the benzophenone, benzotriazole, and phenyl salicylate types and (2) certain derivatives of the metal organic compound ferrocene. Their names are given in Table I. The commercially available absorbers have one important feature in common: they have an intramolecular hydrogen bond between a hydroxyl group that is in a position *ortho* to an oxygen or nitrogen atom. This results in the formation of a six-membered chelated ring which contributes to the high photochemical stability of these compounds. Absorbers of this type function by absorbing harmful ultraviolet radiation and dissipating the energy as harmless infrared radiation or heat. The ferrocene derivatives were prepared by the Wyandotte Chemicals Company.<sup>1</sup> Certain of these have structures analogous to the commercial absorbers.

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TABLE I  
 Protective Ultraviolet Absorbers

Compound	Trade name and abbrev.
2,4-Dihydroxy benzophenone	Uvinul 400 <sup>a</sup>
2-Hydroxy-4-methoxy benzophenone	Uvinul M-40, <sup>a</sup> CYASORB UV 9 <sup>b</sup>
2,2'-Dihydroxy-4,4'-dimethoxy benzophenone	Uvinul D-49 <sup>a</sup>
2,2'-Dihydroxy-4-methoxy benzophenone	CYASORB UV 24 <sup>b</sup>
2,2'-4,4'-Tetrahydroxy benzophenone	Uvinul D-50 <sup>a</sup>
Phenyl salicylate	Salol <sup>c</sup>
4- <i>tert</i> -Butyl phenyl salicylate	Light Absorber TBS <sup>c</sup>
5-Chloro-2-hydroxy benzophenone	Light Absorber HCB <sup>c</sup>
Dibenzoylresorcinol	Light Absorber DBR <sup>c</sup> (DBR)
2-(2'-hydroxy-5'-methylphenyl) benzotriazole	Tinuvin P <sup>d</sup>
2,2'-Dihydroxy-4-octyloxy benzophenone	CYASORB UV 314 <sup>b</sup>
1,1'-Ferrocene dicarboxylic acid	None (FDA)
Benzoylferrocene	None (BF)
Dibenzoylferrocene	None (DBF)
2-Hydroxybenzoylferrocene	None (HBF)
2-Hydroxy-4-methoxybenzoylferrocene	None (HMBF)
2-Methoxybenzoylferrocene	None (MBF)

<sup>a</sup> Trademark of Antara Chemicals (General Aniline & Film Corp.).

<sup>b</sup> Trademark of American Cyanamid Company.

<sup>c</sup> Trademark of Dow Chemical Company.

<sup>d</sup> Trademark of Geigy Industrial Chemicals Company.

There are four basic requirements necessary for an ultraviolet absorber to be an effective light stabilizer for polymeric materials. These 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 to evaporation, and that it be compatible with the material in which it is used. Previous studies with the commercial absorbers have shown that the losses due to evaporation are a serious problem only for the more volatile monohydroxy-substituted compounds in certain thermoplastic resins.<sup>2,3</sup> The diffusion and subsequent evaporation of absorbers from most thermosetting resins was found to be negligible. Evaporative losses were also found to be negligible for the ferrocene compounds under high vacuum conditions. Previous photochemical studies have shown that the commercial ultraviolet absorbers are considerably less stable in an extraterrestrial environment<sup>4</sup> than in a terrestrial one. It was concluded that this was due primarily to the higher quantum yield of the second and higher electronic transitions of the absorbers for the short wavelength ultraviolet radiation (2000 to 3000 Å.).

The absorbing properties of the ferrocene derivatives were found to be extremely stable to ultraviolet radiation. These compounds appear to rearrange or decompose to a stable product with similar absorption spectra. Comparison of the photochemical stability of ferrocene, 1,1'-ferrocene dicarboxylic acid and the benzoylferrocenes has shown that the addition of a

benzoyl or an *o*-hydroxybenzoyl group has little effect on the mechanism of decomposition. Increase in the ultraviolet absorption and improved solubility in resins are, however, important advantages gained by benzoyl substitution of ferrocene.

This paper is concerned with the ability of the ultraviolet absorbers to inhibit the degradation of polymeric materials by their filtering action. This property has been termed their protective effectiveness and 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. Both calculated and experimentally determined "protective effectiveness" values have been measured in this work in an effort to determine the effect of these parameters for a wide variety of transparent coating systems.

There is a twofold purpose in beginning a study of this type with the measurement of transparent coatings. First, there is a need for clear coatings in a spacecraft to serve as windows for many types of measuring devices and, second, it was felt that a study of the stability of the resinous binder should be a prerequisite to a study of the more complicated pigmented systems. Many pigments are photosensitive and may affect the stability of the resin by acting as a photosensitizer. Pigments are also absorbers or reflectors of ultraviolet radiation and will compete with the absorbers as protective agents. Similar studies with pigmented systems are in progress now and will be reported at a later date.

### EXPERIMENTAL

The calculations of the protective effectiveness of the ultraviolet absorbers for various polymeric systems were made by means of the spectral energy distribution of sunlight and the absorption spectra of the absorbers and polymers. Eq. (1) gives the expression used for these calculations.<sup>5</sup> The absorption spectra were determined on a Cary Model 14 Automatic Recording Spectrophotometer.

$$PE = \frac{\sum_{\lambda_2} I_0(1 - 10^{-b_1 a_{p\lambda} C_p})}{\sum_{\lambda_1} I_0(1 - 10^{-b_2(a_{p\lambda} C_p + a_{B\lambda} C_B)}) \frac{a_{p\lambda} C_p}{a_{p\lambda} C_p + a_{B\lambda} C_B}} \quad (1)$$

where  $I_{0\lambda}$  = incident intensity at  $\lambda$ ,  $b_1$  = thickness of unprotected polymer in millimeters,  $b_2$  = thickness of protected polymer in millimeters,  $a_{p\lambda}$  = absorptivity of polymer at  $\lambda$ ,  $a_{B\lambda}$  = absorptivity of absorber at  $\lambda$ ,  $C_p$  = concentration of polymer in per cent, and  $C_B$  = concentration of absorber in per cent.

This expression is simply the ratio of the radiant energy absorbed by an unprotected polymer to the energy absorbed by the polymer in a system

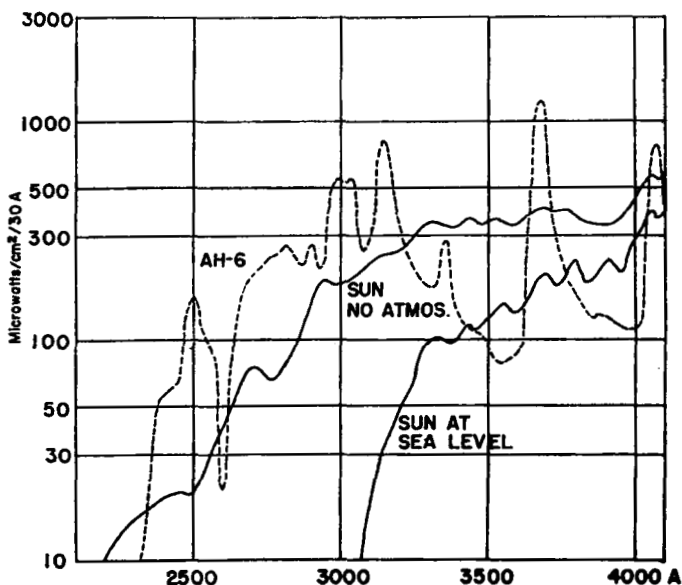


Fig. 1. Ultraviolet spectral energy distribution of the sun with no atmosphere, the sun at sea level, and the 1000 w. AH-6 Lamp.

protected with an ultraviolet absorber. The denominator in this expression will always be less than the numerator since the absorber will prevent part of the incident radiation from being absorbed by the polymer. The more effective the absorber is in this respect, the greater will be the value of the "protective effectiveness."

Calculations of protective effectiveness by means of eq. (1) 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 is achieved completely in a real system, but the use of the calculations is worth while in predicting the degree of improvement that can be obtained initially by the use of an ultraviolet absorber. With eq. (1) it is possible to compare the protective ability of the various absorbers, estimate which polymers are better protected by an absorber, and determine the effect of film thickness and absorber concentration on the effectiveness of the ultraviolet absorber.

The protective effectiveness of the ultraviolet absorbers was determined experimentally by comparing the rate of photochemical degradation of unprotected and protected polymers. A General Electric Type AH-6 water-cooled high pressure mercury arc<sup>6</sup> was used for the photochemical studies. With a quartz outer jacket, the AH-6 lamp gives a strong continuum in the ultraviolet to about 2000 Å. The mercury lines are superposed upon the continuum but are not prominent.<sup>7</sup> 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 Fig. 1).<sup>8,9</sup>

Figure 2 is a photograph of the irradiation chamber and monitoring photocell. The irradiation chambers were designed to permit periodic 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 vacuumtight during the examination. A second valve permits the introduction of various gases into the system. Thermocouple and ion gauges measure the pressure in the irradiation chamber which varies between  $10^{-5}$  and  $10^{-3}$  mm. Hg, depending upon the outgassing properties of the sample.

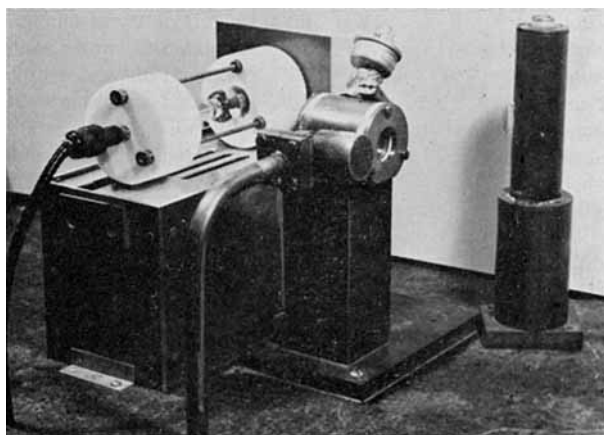


Fig. 2. AH-6 mercury lamp, radiation chamber, and photocell for monitoring energy.

Transparent polymer films, 0.001 to 0.003 in. thick, were prepared on 1 in. diameter quartz disks which were placed near the center of the irradiation cell. The thickness of the films was determined with a micrometer from an average of 20 readings. Standard procedures were followed in preparing the films (Table II gives the formulations used). The ultraviolet absorbers were dissolved in the resin solutions prior to laying down the films. Each sample received a total of approximately 50 hrs. of exposure.

Absorption spectroscopy was used to follow the photodegradation of the polymer films. The ultraviolet, visible, and near-infrared spectra of the polymers were determined initially, and at several points during an irradiation period, with a Cary Model 14 Automatic Recording Spectrophotometer. Use was made of the spectral data in calculating the solar absorptivity ( $\alpha_s$ ) which is the fraction of sunlight absorbed by the organic coating (see eq. 2). The calculations were carried out with a Burroughs

205 computer. Absorbance values were taken at 200 Å. wavelength intervals.

$$\alpha_s = \left[ \sum_{\lambda=2200\text{\AA.}}^{\lambda=27000\text{\AA.}} (1 - t_\lambda) H_\lambda \right] / S \quad (2)$$

TABLE II  
Polymer Formulations

Polymer type	Designation	Composition
Melamine-formaldehyde resin	I	100% methylated polymethylol melamine
Melamine-formaldehyde resin	II	100% 2/1 formaldehyde/melamine condensate
Melamine-modified acrylic	III	65% Butyl acrylate-acrylic acid copolymer
Melamine-modified polyvinylacetal	IV	35% Alkylated melamine resin 90% Polyvinylbutyral source A
Melamine-modified polyvinylacetal	V	10% Alkylated melamine resin 90% Polyvinyl butyral, source B
Melamine-modified cellulose ester	VI	10% Alkylated melamine resin 91% Cellulose acetobutyrate
Melamine-modified methacrylic	VII	9% Alkylated melamine resin 80% Methyl methacrylate-methacrylic acid terpolymer
Glycol-modified melamine resin	VIII	20% Alkylated melamine resin 50% Cyclohexane dimethanol
Urea-formaldehyde	IX	50% Alkylated melamine resin 100% Butylated urea-formaldehyde
Melamine alkyd	X	80% Alkyd from phthalic anhydride, C <sub>14</sub> -saturated fatty acids, and glycerine
Styrenated alkyd	XI	20% Alkylated melamine resin 70% Alkyd from phthalic anhydride, C <sub>18</sub> -saturated fatty acids, and
Polyurethane	XII	30% Styrene glycerine 37% Polyester resin
Melamine-modified	XIII	63% Polyisocyanate 85% Polyglycidyl ether of bisphenol A
Silicone alkyd	XIV	15% Alkylated melamine resin 50% Phenylmethyl silicone resin
Polyamine-modified epoxy	XV	50% Melamine alkyd (X) 95% Polyglycidyl ether of bisphenol A
Phenylmethyl silicone	XVII	5% Diethylenetriamine 100% Phenylmethyl silicone
Urea-modified polyvinylbutyral	XVIII	90% Polyvinylbutyral, source A 10% Urea-formaldehyde
Polyvinylacetal	XX	100% Polyvinylbutyral
Cellulose ester	XXI	100% Cellulose acetobutyrate
Polyvinyl alcohol-modified melamine	XXIV	70% 2/1 formaldehyde/melamine condensate 30% Polyvinyl alcohol
Methylmelamine-formaldehyde resin	XXV	100% Methylated polymethyloltrimethyl-melamine

where  $\alpha_s$  = solar absorptivity,  $t_\lambda$  = transmittance at  $\lambda = I/I_0$ ,  $H_\lambda$  = solar energy at  $\lambda$  in milliwatts per square centimeter, and  $S$  = the solar constant (139.5 mw./cm.<sup>2</sup>).

The solar absorptivity was used as a measure of the photochemical stability of polymers because of its relationship to the equilibrium temperature of an object that is exposed to an extraterrestrial environment (satellite or other space vehicle). Equation (3) shows how  $\alpha_s$  is related to the temperature of an object whose heat balance is determined only by radiation processes:

$$T^4 = S\alpha_s A_s / \sigma \epsilon A_\epsilon \quad (3)$$

where  $T$  = equilibrium temperature in degrees Kelvin,  $S$  = the solar constant,  $\alpha_s$  = solar absorptivity,  $\epsilon$  = emissivity (radiation determined by temperature of object),  $\sigma$  = Boltzman-Stefan constant ( $5.67 \times 10^{-12}$  w./cm.<sup>2</sup>/°K),  $A_s$  = cross-sectional area exposed to sunlight, and  $A_\epsilon$  = area emitting.

It can be seen from eq. (2) that the temperature of a spacecraft is determined by the ratio  $\alpha_s/\epsilon$  since the other quantities are constants. Change in this ratio as a result of photochemical degradation of the organic coating will cause a rise or fall in the temperature of the space vehicle with possible subsequent failure of certain critical components. The degradation of many polymers is manifested first by a yellowing or increase in absorption of visible light. This results in an increase in the solar absorptivity with probably very little change in the emissivity (changes in the far infrared absorption or emission would require structural changes in the polymer many orders of magnitude greater than those necessary for yellowing). Measurement of this change in the solar absorptivity as a function of the exposure, therefore, will provide a means of determining the degree of temperature control that can be achieved for a particular coating. Additional advantages are the sensitivity of  $\alpha_s$  to exposure and its applicability to all types of polymers regardless of their initial absorption spectrum.

## RESULTS AND DISCUSSION

The rate of photodegradation of unprotected and protected polymeric systems was determined for the formulations listed in Table II. A summary of these rate data is given in Tables III and IV. The times required to produce an increase in the solar absorptivity of 0.05, 0.10, and 0.15 are used as measures of the photochemical stability of the polymeric systems. The initial  $\alpha_s$  value and the thickness of the polymeric film are also given in Tables III and IV.

A typical set of curves illustrating the changes produced in the absorption spectrum of an unprotected polymer when subjected to irradiation is shown in Figure 3. These data for a melamine alkyd resin demonstrate that the greatest change is produced at the shorter wavelengths. This results in an increased absorption of blue light and hence the polymer

TABLE III  
Photochemical Stability of Unprotected Polymers

Polymer	b, mm.	$\alpha_s^\circ$	Exposure hours in space for:		
			$\Delta\alpha_s =$ 0.05	$\Delta\alpha_s =$ 0.10	$\Delta\alpha_s =$ 0.15
Melamine formaldehyde (dimethylol) (II)	0.012	0.0041	50	1100	20000
Polyvinylbutyral (XX)	0.010	0.0066	162	295	425
Melamine-modified polyvinylacetal (IV)	0.015	0.0386	128	260	420
Urea-formaldehyde (IX)	0.037	0.0052	44	143	260
Urea-modified polyvinyl- butyral (XVIII)	0.004	0.0028	89	139	196
Methyl melamine- formaldehyde (XXV)	0.003	0.0084	56	130	260
Silicone alkyd (XIV)	0.052	0.0031	18	94	238
Polyvinylalcohol-Modi- fied melamine (XXIV)	0.16	0.207	47	100	165
Melamine-modified epoxy (XIII)	0.067	0.0180	19	76	193
Melamine-formaldehyde (polymethylol) (I)	0.045	0.0098	24	76	185
Cellulose acetate butyrate (XXI)	0.005	0.0011	11	128	180
Melamine-modified polyvinylacetal (V)	0.011	0.0055	33	74	128
Melamine-modified cellulose ester (VI)	0.021	0.0044	27	75	121
Melamine-modified acrylic (III)	0.013	0.0131	20	60	135
Glycol-modified melamine resin (VIII)	0.039	0.0062	14	52	110
Melamine-modified methacrylate (VII)	0.027	0.0075	17	40	92
Styrenated alkyd (XI)	0.026	0.0550	11	31	94
Polyamide-modified epoxy (XV)	0.009	0.0116	7	26	74
Melamine alkyd (XI)	0.038	0.0188	9	23	58
Polyurethane (XXI)	0.020	0.0216	5	26	60
Phenylmethyl silicone (XVII)	0.031	0.0064	47	100	165

appears yellow. The near-infrared data were not included since there is very little change in this region.

The data for this melamine alkyd resin are also presented in Figure 4 as a plot of the change in solar absorptivity ( $\alpha_s$ ) versus the logarithm of the exposure time. Two scales are chosen for the abscissa, the experimental exposure time (which has been corrected for variation in source intensity by the monitoring unit) and the equivalent hours in space which is determined by the factor of 5 difference in radiant output between the AH-6 mercury arc and sunlight. The exposure time should be multiplied by an



TABLE IV  
 Photochemical Stability of Protected Polymers

Polymer	Absorber	b, mm.	$\alpha_s^\circ$	Exposure hours in space for:		
				$\Delta\alpha_s = 0.05$	$\Delta\alpha_s = 0.10$	$\Delta\alpha_s = 0.15$
Melamine-formaldehyde (dimethylol) (II)	5% DBR	0.028	0.0852	295	3,100	35,000
	5% BF	0.017	0.0951	1,020	17,800	—
	5% HMBF	0.045	0.3128	2,180	300,000	—
	5% DBF	0.026	0.1236	5,750	225,000	—
	5% MBF	0.035	0.2290	14,500	500,000	—
“	5% HBF	0.013	0.1981	500	8,500	—
Melamine alkyd (X)	1% DBF	0.088	0.4147	70	670	43,500
	1% HBF	0.078	0.5480	50,000	500,000	—
	1% DBR	0.062	0.3177	450	1,050	2,000
“	+ 1% HBF					
“	1% HMBF	0.050	0.2338	260	525	675
“	1% MBF	0.047	0.1218	26	120	415
Melamine-modified polyvinylbutyral (IV)	1% DBR	0.012	0.0398	47	112	160
	5% DBR	0.025	0.0656	80	188	306
	1% HBF	0.039	0.2635	280	22,200	—
	5% HBF	0.026	0.2246	10,000	123,000	—
“	1% DBF	0.048	0.2493	35	320	660
Polyvinylbutyral (XX)	5% DBR	0.019	0.0704	155	380	650
	5% HBF	0.055	0.2548	4,050	179,000	—
Melamine-modified cellulose ester (VI)	5% DBR	0.023	0.0646	32	91	175
Cellulose acetate butyrate (XXI)	5% DBR	0.016	0.0686	66	150	320
	5% HBF	0.021	0.1524	99	221	550
Phenylmethyl silicone (XVII)	1% DBR	0.068	0.1192	27	224	1,800
	5% DBR	0.019	0.0889	29	127	310
	5% HBF	0.053	0.1616	74	360	1,800
Silicone alkyd (XIV)	1% DBR	0.036	0.1246	29	127	378
	1% HBF	0.220	0.3509	2,500	25,000	—
	1% DBF	0.029	0.3275	2,500	25,000	—
	5% HBF	0.064	0.4022	2,450	25,000	—
Urea-formaldehyde (IX)	5% DBR	0.011	0.0628	58	156	283
	5% HBF	0.085	0.2248	1,450	10,000	—
Melamine-modified epoxy (XIII)	1% DBR	0.045	0.0611	52	140	360
	5% DBR	0.036	0.0793	67	179	440
Polyurethane (XII)	1% DBR	0.038	0.0625	25	70	150
	5% DBR	0.036	0.0701	30	81	173
Melamine-formaldehyde (polymethylol) (I)	5% DBR	0.039	0.0825	68	200	472
Melamine-modified Methacrylate (VII)	5% DBR	0.027	0.0128	81	208	505

additional factor of approximately 6 for a spherical or cylindrical rotating object.

The logarithmic relationship between the degradation or yellowing of polymers and the exposure to light was also observed in the previous studies on the photochemical stability of the ultraviolet absorbers<sup>4</sup> and is analogous

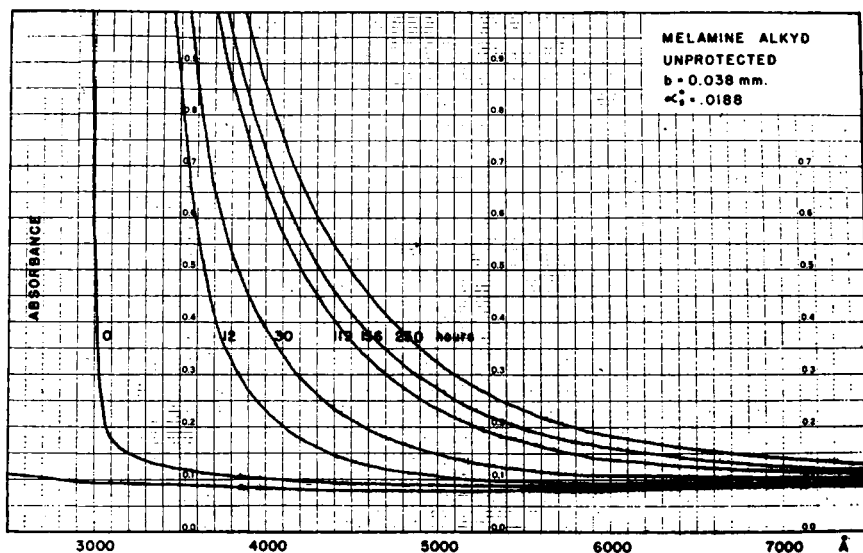


Fig. 3. Spectral curves following photodegradation.

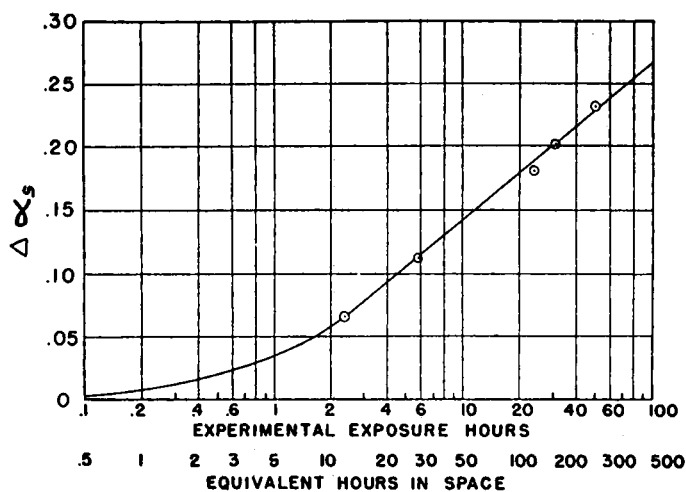


Fig. 4. Photodegradation of melamine alkyd (X), unprotected.

to the Hurter-Driffeld law of photographic materials. This effect is attributed to a rapid decrease in the rate of energy absorption due to the formation of decomposition products which compete with the photosensitive reactants for the incident radiation. It is also possible that the overall rate of yellowing is reduced by a competing fading process whose rate increases with time.

The data in Table III show that the most stable unprotected polymer is the melamine-formaldehyde resin prepared from dimethylolmelamine (II).

TABLE V  
Experimental and Calculated Protective Effectiveness

Polymer	Absorber	PE	
		Exptl.	Calcd.
Melamine-formaldehyde (dimethylol) (II)	5% DBR	3.5	3.1
"	5% BF	18.3	—
"	5% HBF	43.6	1.8
"	5% DBF	160.0	—
"	5% HMBF	154.0	—
"	5% MBF	375.0	—
Urea-formaldehyde (IX)	5% DBR	1.3	7.9
"	5% HBF	51.5	5.9
Silicone alkyd (XIV)	1% DBR	1.5	1.6
"	1% HBF	200.0	1.4
"	5% HBF	200.0	2.1
"	5% DBF	200.0	—
Melamine alkyd (X)	1% DBF	260.0	—
"	1% HBF	5000.0	1.2
"	1% DBR	43.0	1.6
"	+		
"	HBF		
"	1% HMBF	21.0	—
"	1% MBF	5.1	—
Melamine-modified polyvinylbutyral (IV)	1% DBR	0.4	1.8
"	5% DBR	0.7	3.9
"	1% DBF	1.1	—
"	1% HBF	43.9	1.5
"	5% HBF	275.0	4.1
Phenylmethyl silicone (XVII)	1% DBR	20.9	1.4
"	5% HBF	32.5	1.9
"	5% DBR	10.1	2.5
Polyvinylbutyral (XX)	5% DBR	1.3	4.4
"	5% HBF	320.0	2.3
Cellulose acetate butyrate (XXI)	5% DBR	3.0	3.2
"	5% HBF	4.5	—
Melamine-modified methacrylate (VII)	5% DBR	5.1	4.1
Melamine-modified epoxy (XIII)	1% DBR	2.1	1.7
"	5% DBR	2.7	3.3
Melamine-formaldehyde (polymethylol) (I)	5% DBR	2.7	2.9
Melamine-modified cellulose ester (VI)	5% DBR	1.3	2.7
Polyurethane (XII)	1% DBR	3.5	1.4
"	5% DBR	4.0	3.2
Melamine-modified polyvinylbutyral (V)	5% DBR	1.6	1.8

Unfortunately, this material is not particularly suited as a surface coating. Polyvinylbutyral (XX), melamine-modified polyvinylbutyral (IV), urea-modified polyvinylbutyral (XVIII) and urea-formaldehyde (IX) follow in that order. In general, the more transparent polymers are the most photochemically stable. The more highly absorbing alkyd resins are the least stable to ultraviolet radiation. All the polymers, however, are considerably less stable than when exposed to a terrestrial environment.

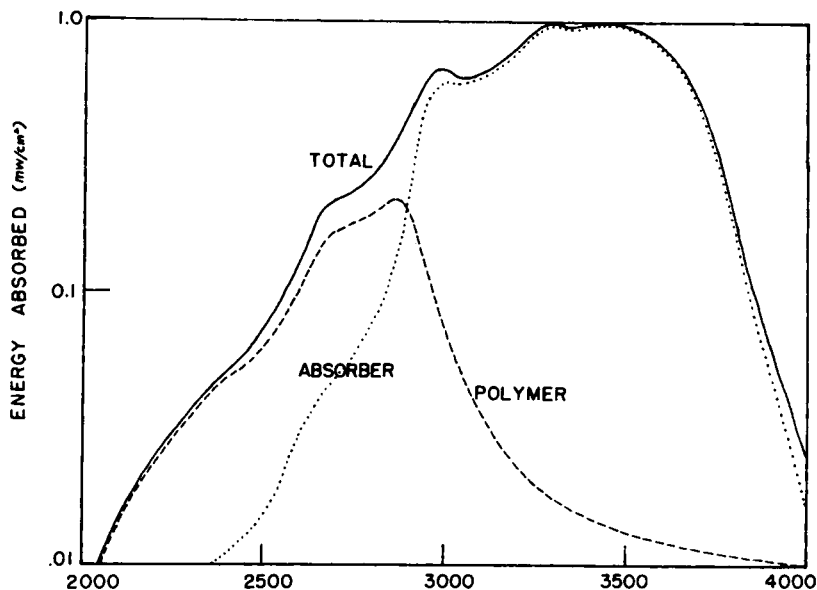


Fig. 5. Extraterrestrial radiation absorbed by a silicone alkyd resin containing 1% dibenzoylresorcinol (film thickness = 0.036 mm.).

A comparison of the experimental and calculated "protective effectiveness" is shown in Table V. The experimental values were determined from the data in Tables III and IV by averaging the ratio of the exposure hours in space required to produce solar absorptivity increases of 0.05, 0.10, and 0.15 for the corresponding protected and unprotected polymers. The values at 0.15 were omitted when large extrapolations of the exposure times were required. The calculated values were obtained by means of eq. 1 with the appropriate thickness and absorber concentration data given in Tables III and IV for unprotected and protected polymers, respectively.

The agreement between the experimental and calculated protective effectiveness values for dibenzoylresorcinol dispersed in many of the polymeric formulations was found to be good. The values are low, however, which demonstrates that the commercially available ultraviolet absorbers do not provide good protection for polymers in an extraterrestrial environment. The protection afforded polymers by dibenzoylresorcinol is an order of magnitude less than that obtained for terrestrial conditions. It can be concluded from these data that this loss in effectiveness is due to the strong absorption of the polymers relative to the absorbers at the shorter wavelengths (below 3000 Å.). This reasoning is illustrated in Figure 5 where the solar energy absorbed by a polymer and absorber in a protected system as a function of wavelength is shown. It can be seen that at the longer wavelengths the ultraviolet absorber is absorbing most of the energy. At the shorter wavelengths the polymer is absorbing a large fraction of the radiation and the absorber becomes a less effective screening agent.

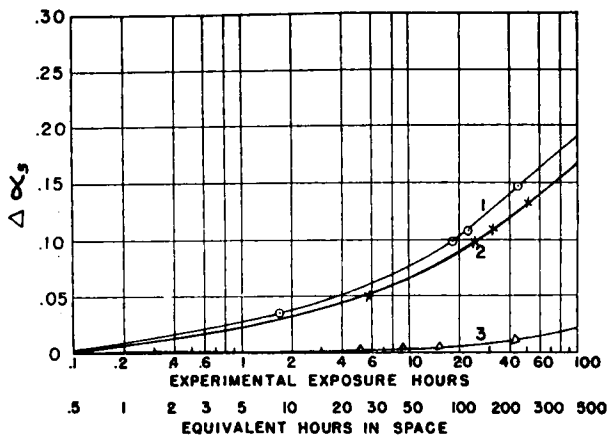


Fig. 6. Photodegradation of silicone alkyd (XIV): (1) unprotected; (2) protected with 1% dibenzoylresorcinol; (3) protected with 1% *o*-hydroxybenzoylferrocene.

The ferrocene derivatives were found to be extremely effective in protecting many of the organic coatings. The stabilizing ability of *o*-hydroxybenzoylferrocene for a silicone alkyd resin is demonstrated in Figure 6. The protection afforded by dibenzoylresorcinol is also shown for comparison. The ferrocene additive increased the useful life of this resin by a factor of 200, compared with less than 2 for dibenzoylresorcinol. The effectiveness of a number of ferrocene derivatives in protecting a variety of coating systems is presented in Table V. Protective effectiveness values from 30 to 5000 were obtained at the 1% and 5% levels. These experimental values were factors of 10–1000 higher than those predicted by the calculated PE, which demonstrates that the ferrocene compounds are not acting simply as internal filters as do the organic absorbers (the protective effectiveness calculations assume that the absorbers are completely stable). Benzoylferrocene, dibenzoylferrocene, 2-hydroxy-4-methoxybenzoylferrocene, and 2-methoxybenzoylferrocene were also found to be unusually effective.

It is interesting to note from Table V that the ferrocenes are effective in stabilizing a wide variety of polymeric types. In particular, the large change in solar absorptivity of the highly photosensitive alkyd resins is almost entirely eliminated (see Fig. 6). This is highly desirable since the alkyds are excellent coating resins. The most stable formulation was 1% 2-hydroxybenzoylferrocene in melamine alkyd (IX). The addition of 1% dibenzoylresorcinol to this system, however, reduced the effectiveness of the ferrocene. The more light-stable melamine-formaldehyde and urea-formaldehyde resins are also afforded a high degree of protection by the ferrocenes. These polymers, however, are not good film formers and would be of less value than the alkyds. Certain of the more transparent polymers are also stabilized by the ferrocenes. Polyvinylbutyral (XX) and melamine-modified polyvinylbutyral (IV) protected with 2-hydroxybenzoyl-

ferrocene were found to be good combinations. On the other hand, dibenzoylferrocene in melamine-modified polyvinylbutyral (IV) and 2-hydroxybenzoylferrocene in cellulose acetate butyrate (XXI) gave no better protection to these polymers than did dibenzoylresorcinol.

It is not clear at this time whether the ferrocenes are actually preventing degradation of the polymers or are obscuring the yellowing process by virtue of their absorption in the visible region. From Table V it can be seen that the polymers containing ferrocenes have much higher initial solar absorptivities than those protected with the benzophenone-type absorbers. Most of the higher solar absorptivity can be attributed to the ferrocene absorption in the 3500 to 5000 Å. region. This is the spectral region associated with the greatest increase in absorption resulting from polymer degradation (see Fig. 3). The solar absorptivity of a protected polymer, therefore, would be insensitive to further increases in absorption resulting from degradation (energy absorbed is proportional to  $1 - \text{transmittance}$ ). Evidence to support this idea can be found in Table V where there is a general correlation between the initial solar absorptivity and the stability of the polymers. It is important to note here that it is necessary to have an absorber with a very high inherent stability in order to maintain the situation described above for a reasonable length of time. This attribute of the ferrocenes certainly contributes to their high effectiveness.

It is also possible that the ferrocenes are preventing degradation of the polymers as a result of an energy transfer mechanism. It is difficult to determine whether this is the case from the ultraviolet spectra, since the ferrocene absorption masks that of the polymer. In an effort to determine whether structural changes in the polymers are taking place, infrared spectroscopy was used to follow the degradation of several polymers containing ferrocenes. The results were inconclusive, as little change could be detected for either unprotected or protected polymers. The changes created in the polymers that contribute to its yellowing are evidently of such a low order of magnitude that they cannot be detected by the relatively insensitive infrared methods.

The high effectiveness as ultraviolet light stabilizers found for the ferrocenes demonstrates that these compounds will be useful for the protection of surfaces used for temperature control of space vehicles. The color of the ferrocenes will limit their applicability to coating systems having a solar absorptivity greater than 0.20. The high solar absorptivities that can be obtained for coatings by the incorporation of a ferrocene suggests that the temperature control may be achieved by adjustment of the concentration of absorber and the film thickness rather than by pigmentation.

## CONCLUSIONS

1. The ultraviolet absorbing properties of a number of ferrocene derivatives were found to be extremely stable to extraterrestrial ultraviolet radiation. The ferrocene compounds appear to rearrange upon irradiation

to a stable product with a similar ultraviolet absorption spectrum. The benzoylferrocenes are the strongest absorbers and undergo the least amount of change upon irradiation.

2. The photochemical stability of a wide variety of unprotected surface coating formulations exposed to extraterrestrial conditions was found to be poor. The coatings yellowed severely, which resulted in a large increase in their solar absorptivity. A melamine-formaldehyde resin (dimethylol) was the most stable polymer tested. The alkyd resins were the least stable.

3. The effectiveness of ultraviolet absorbers of the benzophenone and benzotriazole type in protecting organic coatings exposed to an extraterrestrial environment was found to be considerably less than that in terrestrial conditions. This was attributed to the strong ultraviolet absorption of the polymers at the shorter wavelengths, which competes with the absorber for the incident radiation. Calculated PE values, with the use of the absorption spectra of both polymer and absorber, were in good agreement with the experimental data. Reduction in the rate of yellowing of the coatings by a factor of 2 to 5 were obtained by the use of these absorbers.

4. Certain benzoyl-substituted ferrocene compounds were found to be extremely effective in protecting many types of polymeric coatings exposed to a space environment. The ferrocene derivatives reduced the change in the solar absorptivity of the coatings by a factor of 30 to 5000. The most light-stable formulation was 1% *o*-hydroxybenzoylferrocene in a melamine alkyd resin. The experimental protective effectiveness of the ferrocenes was 1 to 3 orders of magnitude higher than those predicted by the calculated PE, which demonstrates that these metal-organic compounds are not acting as internal filters as do the organic absorbers. The high effectiveness of the ferrocenes may be attributed to their high absorption in the spectral region associated with the absorption of polymer decomposition products (3500 to 5000 Å.). This initial high absorption minimizes the sensitivity of the solar absorptivity to further changes in absorption in this spectral region. Another possibility is that an energy transfer mechanism between the polymer and absorber is taking place.

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### Synopsis

The effectiveness of the ultraviolet absorbers in protecting organic coatings exposed to an extraterrestrial environment from photochemical degradation was studied for the commercially available absorbers and certain errocene derivatives. The change in solar absorptivity of the coatings was used as a measure of the degradation incurred, these data being obtained from the ultraviolet, visible, and near-infrared absorption spectra of the polymers. Ultraviolet absorbers of the benzophenone and benzotriazole type used for terrestrial applications were found to be considerably less effective in a space environment. This was attributed to the strong ultraviolet absorption of the polymers at the shorter wavelengths, which competes with the absorber for the incident radiation. Certain benzoyl-substituted ferrocene compounds were found to be extremely effective in protecting many types of polymeric coatings. The benzoylferrocenes are highly colored materials (red to orange) whose absorbing properties are extremely stable to ultraviolet radiation.

### Résumé

On a étudié l'efficacité des absorbants d'ultraviolet dans la protection vis-à-vis de la dégradation photochimique des revêtements organiques exposés à un milieu extraterrestre, et ce pour des absorbants disponibles dans le commerce et certains dérivés du ferrocène. La variation de l'absorption solaire des revêtements a été utilisée comme mesure de la dégradation subie; ces données étant obtenues aux dépens des spectres d'absorption des polymères dans l'ultraviolet, le visible et le proche infrarouge. On a trouvé que les absorbants d'ultraviolet du type benzophénone et benzotriazol, utilisés pour des applications terrestres étaient considérablement moins efficaces dans un entourage spatial. On a attribué ceci à la forte absorption des polymères dans l'ultraviolet aux longueurs d'ondes plus courtes; il en résulte une compétition avec l'absorbant pour le rayonnement incident. On a trouvé que certains composés du ferrocène à substituant benzoylé étaient extrêmement efficaces en ce qui concerne la protection de nombreux types de revêtements polymériques. Les benzoylferrocènes sont des matières très colorées (rouge à orange) dont les propriétés absorbantes sont extrêmement stables au rayonnement ultraviolet.

### Zusammenfassung

Die Wirksamkeit von Ultraviolettabsorbieren beim Schutze organischer Überzüge in ausserirdischer Umgebung gegen photochemischen Abbau wurde an handelsüblichen Absorbieren und einigen Ferrocenderivaten untersucht. Die Änderung der Solarabsorptionsfähigkeit der Überzüge wurde als Mass für den aufgetretenen Abbau benützt; die Daten wurden aus den Absorptionsspektren der Polymeren im Ultraviolett, Sichtbaren und nahem Infrarot erhalten. Die für irdische Anwendung gebräuchlichen Ultraviolettabsorber vom Benzophenon- und Benzotriazoltyp erwiesen sich im Raume als beträchtlich weniger wirksam. Das wurde auf die starke Ultraviolettabsorption der Polymeren bei kürzeren Wellenlängen zurückgeführt, die mit dem Absorber um die einfallende Strahlung konkurriert. Gewisse benzoyl-substituierte Ferrocenverbindungen erwiesen sich beim Schutze vieler Typen von Polymerüberzügen als äusserst wirksam. Die Benzoylferrocene bilden hoch gefärbte Stoffe (rot bis orange), deren Absorptionsfähigkeit gegen Ultraviolettstrahlung sehr stabil ist.

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