

## Measurement of Photochemical Degradation in Certain Plastics by Color Reactions with Phenylenediamines

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### Synopsis

Samples of polyester plastics, upon exposure to solar or carbon-arc radiant energy, were found to form oxidation products which, when reacted with *N,N*-dimethyl-*p*-phenylenediamine (DMPDA), produced yellow to brown reaction products. The extent of the reaction was determined directly by the amount of diamine reacted or indirectly by differential colorimetry. Research with this color reaction was extended into the development of tests for measuring the photooxidative degradation of polyesters, rigid poly(vinyl chloride), acrylics, and cellulose acetate-butyrate plastics. The basic colorimetric method was modified as needed for each of these plastics types, by directly measuring the absorbance of the DMPDA solution instead of measuring the amount of DMPDA reacted, by the use of *o*-, *m*-, and *p*-phenylenediamines as replacements for DMPDA in the color reaction, or by a change in the solvent. The reliability of "yellowness" as an indicator of the photochemical stability of plastics was examined.

The methods selected to evaluate the photochemical degradation of plastics are usually based on the type of plastic under study. For example, glass fiber-reinforced polyesters are evaluated by visual appearance<sup>1</sup> or bulk physical properties,<sup>2</sup> poly(vinyl chloride) by color change or electrical measurements,<sup>3,4</sup> and polyethylene by per cent carbonyl, per cent elongation, or brittleness.<sup>5</sup> While some of these tests may be readily reproducible and provide considerable information about the photostability of a given plastic, a single method is applicable to a few classes of plastics at most.

Gray and Wright<sup>6</sup> described recently a colorimetric method for measuring the photochemical oxidation of polyesters which appears applicable to many types of plastics and, as such, might possibly provide a common basis for comparing the relative photochemical stabilities of several classes of plastics. The method was based on the reaction of *N,N*-dimethyl-*p*-phenylenediamine (DMPDA) with oxidized components on the surface of an exposed plastic producing a yellow-to-brown reaction product. (Plastics were exposed to solar radiation as well as to carbon-arc radiation.) Unexposed plastics gave no reaction with DMPDA. The extent of the reaction was determined directly by the amount of diamine reacted or indirectly by the color formed in the test specimen (by differential colorimetry). The amount of oxidative degradation was shown to vary directly with the ex-

posure duration, and various polyesters were found to degrade at different rates under the same exposure conditions.

The present paper describes an extension of the above research into the development of tests for measuring the photooxidative degradation of polyesters, rigid poly(vinyl chloride), acrylics, and cellulose acetate-butyrate plastics. The previously described test method<sup>6</sup> was modified as needed for each of these plastics types, by directly measuring the absorbance of the DMPDA solution instead of measuring the quantity of DMPDA reacted, by the use of *o*-, *m*-, and *p*-phenylenediamines as replacements for DMPDA in the color reaction, or by a change in the solvent. The reliability of "yellowness" as an indicator of the photochemical stability of plastics was also examined.

## EXPERIMENTAL

### Materials

**Plastics.** The three glass fiber-reinforced polyesters described previously<sup>6</sup> were used in the present work. In addition, 16 other commercial polyesters, as well as one laboratory polyester (styrene-modified) with no glass reinforcement, were included in the program. Commercial poly(methyl methacrylates), with and without glass, clear, cellulose acetate-butyrate sheet, and pigmented poly(vinyl chloride), both white and colored, were examined. All panels were a nominal 2.0 mm. in thickness.

**Diamines.** *N,N*-Dimethyl-*p*-phenylenediamine was obtained as reagent grade dihydrochloride salt from Eastman Organic Chemicals and used without further purification. Reagent grade *o*-, *m*-, and *p*-phenylenediamines were obtained from Eastman Organic Chemicals and used with no further purification.

### Radiant Energy Exposure

The plastics test specimens were exposed as 7 cm. × 15 cm. panels to either solar or carbon-arc radiant energy. After prescribed periods of time, test specimens, 2 cm. × 7 cm., were cut from these panels and the extent of degradation measured by the colorimetric method. Outdoor exposures were made in Washington, D. C., starting in April 1961, on open weathering racks inclined 45° from the horizontal and facing south. The racks were located atop a four-story building and were supported 3-5 ft. above the asphalt-gravel roof. No backing material was used.

Laboratory irradiation was carried out in an Atlas single carbon-arc Weather-Ometer. The ambient air temperature in the vicinity of the samples was 110 ± 5°F. The specimens were inverted at the end of each 22-hr. exposure period, the same side being kept exposed to the carbon arc. No water spray or radiation filters were used; the plastics were exposed to radiant energy only.

### Color Reactions with Polyesters

The experimental method for treating an exposed polyester with DMPDA, to develop color in the plastic specimen, and subsequent analysis to determine the exact amount of diamine reacted, were previously described in detail.<sup>6</sup> For convenience, a brief summary of the method is presented here.

Upon termination of the irradiation, duplicate specimens of the exposed polyester, together with an unexposed control sample, were reacted with a 50:50 (v/v) benzene-methanol solution of DMPDA (1.0 mg./ml. concentration) for a 2-hr. period.<sup>6</sup> The specimens were then removed from the solution, washed with methanol, and dried. At this point, the exposed specimens were yellow to brown in color, while the unexposed but otherwise treated specimen was essentially unchanged.

An indirect approach was used to determine the amount of DMPDA that reacted with the exposed plastic surface. An aliquot of the solution used to effect coloration in the exposed plastic was treated with benzoyl peroxide to oxidize the unreacted DMPDA. The oxidation reaction produced an intense, pink solution, the intensity of which was dependent upon DMPDA concentration and could be measured quantitatively by absorption spectroscopy. By knowing the amount of DMPDA in the reagent solution before treating the exposed plastic and how much remained after reaction, the amount of DMPDA reacted could be calculated by difference. The amount of DMPDA reacted was then taken as a measure of the extent of polyester degradation.

### Color Reactions with Poly(vinyl Chloride)

Exposed poly(vinyl chloride) (PVC) was found to react with benzene-methanol solutions of DMPDA in a manner similar to that shown by polyesters. A yellow-brown product was formed on the plastic surface along with yellow products in the DMPDA solution. Since the quantitative aspects of the direct determination of DMPDA reacted with exposed PVC had not yet been resolved, relative absorbances of the yellow products in solution were used as a measure of photooxidative degradation. The absorption spectrum of this DMPDA solution showed a peak at 410  $m\mu$ .

A series of white-pigmented PVC samples was exposed to carbon-arc irradiation for varying durations and then treated with DMPDA solutions as follows.

Each PVC test specimen (1.8 cm.  $\times$  7.5 cm.  $\times$  0.15 cm.) was submerged in 25.0 ml. of DMPDA reagent solution. The test tube was stoppered to prevent loss of solvent, placed in a wrist-action shaker, and shaken gently for 2 hr. Then the PVC test specimen was removed from the DMPDA solution, washed with methanol, and allowed to dry. The color of the PVC specimens were determined by the reflectance technique used for polyester specimens<sup>6</sup> which is described in a later section of this paper.

The absorbance of the reacted DMPDA solution at 410  $m\mu$  was determined by using a Beckman Model DU spectrophotometer with matched

1 cm. cells. The absorbance corresponding to the products produced during irradiation was found by subtracting the absorbance of DMPDA solution reacted with unexposed PVC specimen.

### Color Reactions with Acrylic and Cellulosic Plastics

The benzene-methanol solution of DMPDA was of limited use in its application to poly(methyl methacrylate) (PMMA) and cellulose acetate-butyrate (CAB) due to extensive swelling of these plastics by benzene. Therefore, it was necessary to carry out the reaction in another solvent system that would either not cause swelling of the plastic or would dissolve the plastic completely. Experiments with numerous solvent systems proved the latter method the more feasible one. Consequently, the color reactions with PMMA and CAB were carried out by dissolving the plastic specimen completely and measuring color changes of these solutions by absorption spectroscopy.

Glacial acetic acid was found to be a good solvent for PMMA and CAB as well as a suitable medium for the color reaction between DMPDA and exposed PMMA and CAB. In addition to DMPDA, *o*-phenylenediamine (*o*-PDA), *m*-phenylenediamine (*m*-PDA), and *p*-phenylenediamine (*p*-PDA) were found to produce colored solutions when reacted with the exposed plastic under the same conditions. The unexposed specimen did not produce a color reaction.

Solutions of the colored products formed when any one of the diamines was reacted with an exposed plastic surface, were used to obtain transmittance spectra of these products. Inasmuch as the spectra were found to vary with the particular combination of plastic and diamine, the use of four diamines instead of one as colorimetric reagents, permitted the selection of suitable absorbance peaks for relative intensity measurements.

The procedure developed for the color reactions between various diamines and PMMA or CAB in acetic acid was as follows: A 1.0-g. specimen of plastic was dissolved in 40 ml. of reagent grade glacial acetic acid at room temperature. To this solution, an equal volume of 4.79 *mM* phenylenediamine solution was added. The concentration of the plastic in the combined solutions was 1.25 g./100 ml. and that of the diamine was 2.40 *mM*.

The diamine-plastic solution was heated in a water bath at 62°C. for 30 min. Under these conditions, solutions containing exposed plastic specimens developed pronounced colors; those with unexposed plastics produced little, if any, color.

The glacial acetic acid solution was cooled to room temperature and the transmittance spectrum from 300–700  $m\mu$  was obtained using a Beckman DK-1 recording spectrophotometer with 1.0 cm. matched silica cells. For all measurements, a glacial acetic acid solution of unexposed plastic, containing no diamine (also 1.25 g./100 ml.) was used in the reference beam to cancel any absorbance caused by the dissolved plastic. The absorbance values at absorption peaks were read from the transmittance spectra of the solutions of exposed and unexposed plastic. The absorbance values ob-

tained from solutions of exposed plastic-diamine were corrected by subtraction of any absorbance given by solutions of unexposed plastic-diamine at the same wavelength. These corrected absorbance values, hereinafter referred to as relative absorbance, were used as a measure of photooxidation of the exposed plastic.

### Color-Change Measurements on Solid Plastic Specimens

The color produced by the DMPDA treatment of the exposed plastics surface provided the basis for an indirect method of correlating photochemical degradation and specimen color. While the nonuniformity of the glass-fiber reinforcement in some plastics precluded the use of absorbance measurement of color, it was possible through the use of a differential colorimeter to measure reflectance values and determine color changes that occurred in an irradiated plastic. Since this method was previously described in detail,<sup>6</sup> a brief description will suffice here.

Measurement of the reflected color of the diamine-treated plastics (polyesters and PVC) were made by use of a Meece tristimulus color difference meter standardized on the green, red, and blue reflectance values of a white glass standard having a 90% reflectance. A similar standard was used as a reference. To obtain color values that would relate instrumental and visual color, the reflectance values were corrected to the modified Adams coordinate system ( $L$  lightness,  $a$  redness-greenness,  $b$  blueness-yellowness).<sup>7</sup> The coordinate values obtained for treated, exposed specimens were corrected by subtracting those found for treated unexposed specimens. This produced color coordinate values ( $\Delta L$ ,  $\Delta a$ ,  $\Delta b$ ) that were dependent only on the amount of diamine reacted with the exposed plastic surface and, were in turn, related to the amount of photochemical degradation. This method, of course, was applicable only to those plastics that were not swollen or dissolved when treated with solutions of the diamines.

## RESULTS

### Polyesters

The exposure of glass fiber-reinforced polyesters to solar or carbon-arc radiant energy resulted in photooxidation which, in all cases, could be measured by the colorimetric method. Sixteen different polyesters were exposed outdoors for periods up to 2 yr. or for 3200 hr. to the carbon-arc. Periodically, specimens were treated with DMPDA in methanol-benzene solution and the amount of DMPDA reacted was determined as well as the colorimetric values ( $L$ ,  $a$ , and  $b$ ) for the color developed in the treated plastic.

Typical data are presented in Table I for six polyesters exposed to solar radiant energy. For each polyester, at the indicated duration of exposure, color change is shown in terms of Adams coordinates as  $\Delta L$ ,  $\Delta a$ , and  $\Delta b$ ; the amount of diamine reacted is given in milligrams per specimen. In general, the amount of DMPDA reacted increased with exposure time, but

TABLE I  
 Effect of Solar Radiant Energy on Polyesters

Polyester	Exposure time, days <sup>a</sup>	Color change <sup>b</sup>			DMPDA, mg./specimen <sup>c</sup>
		$\Delta L$	$\Delta a$	$\Delta b$	
Polyester A	94	-17.48	+3.8	-0.2	0.114
	136	-20.21	+5.4	+11.2	0.25
	214	-22.64	+9.9	+9.0	0.46
	316	-26.58	+12.2	+9.7	0.55
	366	-30.46	+11.8	+9.6	0.57
	658	-34.02	+15.2	+4.9	0.799
Polyester B	94	-8.54	+2.4	+5.4	0.023
	136	-17.04	+3.7	+12.6	0.11
	214	-18.97	+7.8	+21.1	0.30
	316	-17.14	+4.1	+22.5	0.37
	366	-26.35	+10.3	+21.7	0.32
	658	-28.99	+12.4	+8.9	0.73
Polyester C	94	-8.14	+1.3	+9.6	0.046
	136	-12.54	+2.9	+13.2	0.11
	214	-18.01	+4.6	+22.0	0.18
	316	-17.37	+5.2	+19.5	0.21
	366	-19.85	+5.6	+21.4	0.23
	658	-23.62	+7.3	+24.6	0.36
Polyester D	94	-7.31	+3.2	+7.5	0.11
	136	-9.23	+5.1	+10.4	0.16
	231	-15.56	+10.7	+13.7	0.46
	366	-16.92	+8.9	+12.4	0.50
Polyester E	94	-7.13	+1.2	+7.3	0.023
	136	-7.98	+1.9	+11.0	0.023
	231	-14.67	+4.4	+18.6	0.091
	366	-17.98	+5.3	+20.1	0.205
Polyester F	94	-3.90	-0.1	+5.5	0.09
	136	-6.44	+1.0	+7.7	0.11
	231	-13.24	+2.2	+12.4	0.23
	366	-14.59	+2.8	+12.5	0.25

<sup>a</sup> Samples exposed in Washington, D. C., beginning April 1961.

<sup>b</sup> Changes in Adams coordinate values.

<sup>c</sup> Specimen size was 2 × 7 cm.

no two polyesters degraded at the same rate. (The reproducibility between duplicate specimens of a given plastic was  $\pm 0.029$  mg./specimen.) This relationship is demonstrated in Figure 1 for plastics A, B, and C. In the graphic presentation, the seasons of the year are indicated with the day's exposure. Rapid changes took place during the first summer with a subsequent leveling off during the winter and spring seasons. By the end of the second fall season, large changes had again taken place, presumably during the summer, although samples were not evaluated at that time. The general leveling off of photooxidation after one year thus appeared to be a

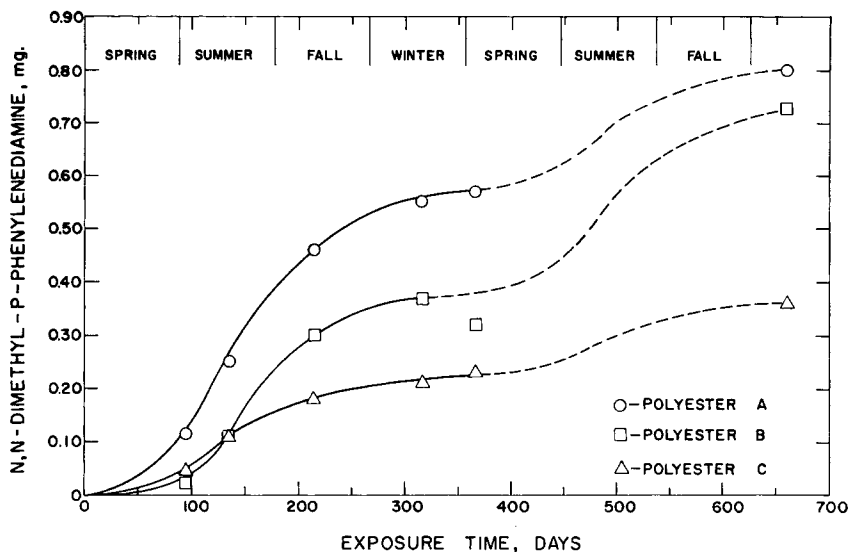


Fig. 1. Amount of *N,N*-dimethyl-*p*-phenylenediamine reacted vs. outdoor exposure times for polyesters A, B, and C.

seasonal effect and not due to the formation of an inert surface film as is found, for example, with bituminous materials.<sup>8</sup>

While the photochemical stability of the three plastics after two years still remained as C, B, and A from most to least stable, the conditions of plastic B appeared to be approaching rapidly that of plastic A. Visual appearance of the untreated plastics confirmed this observation.

The color changes measured on the surface of the DMPDA-treated plastics varied with exposure time. However, the variation with exposure time was not as uniform for the *a* and *b* coordinates as was the amount of DMPDA used. Positive values of  $\Delta b$ , indicating yellowness, were obtained, but with plastic A, for example, there was a maximum  $\Delta b$  after 1 yr. exposure. Undoubtedly, the maxima in  $\Delta b$  were due to the extremely deep color in the treated specimen the measurement of which was beyond the sensitivity of the instrument. To a lesser extent, similar results were found with  $\Delta a$  where positive values indicate redness.

Uniform results were obtained with the lightness coordinate, *L*. As exposure durations increased, the  $\Delta L$  values became increasingly negative, which indicated increasingly darker specimens. Good agreement was found between  $\Delta L$  values and the amount of DMPDA for a given plastic (Fig. 2). It was concluded that  $\Delta L$  was the most significant of the Adams coordinates in measuring the relative photochemical degradation in plastics.

The effects of carbon-arc exposure for durations up to 3200 hr. are shown in Figure 3, where photodegradation is indicated by the amount of DMPDA reacted with the exposed specimens. Three significant factors are indicated by this graph: (a) there is a steady increase in photodegradation with ex-

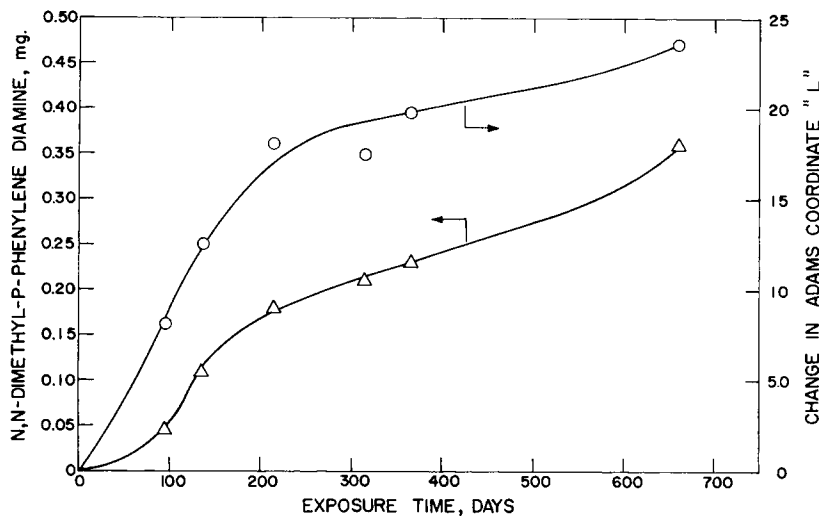


Fig. 2. Amount of *N,N*-dimethyl-*p*-phenylenediamine reacted and specimen color change ( $\Delta L$ ) vs. outdoor exposure time for polyester C.

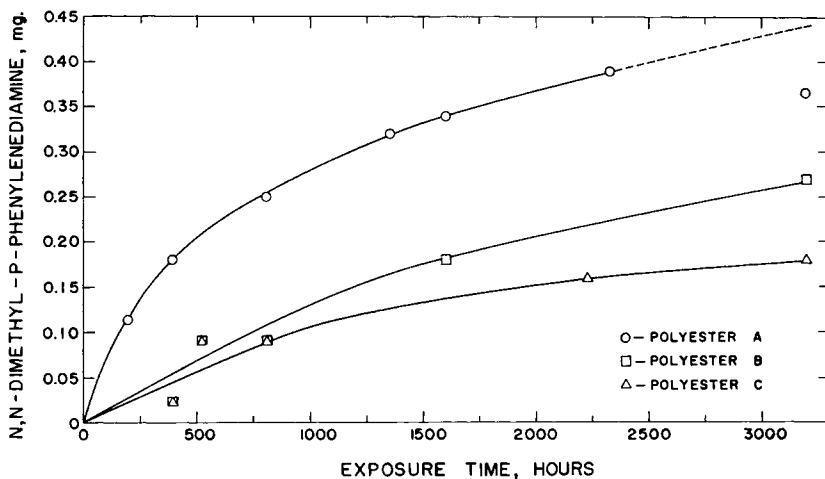


Fig. 3. Amount of *N,N*-dimethyl-*p*-phenylenediamine reacted vs. carbon-arc exposure times for polyesters A, B, and C.

posure time, (b) the relative order of degradation for plastics A, B, and C is the same as that found in outdoor exposures, and (c) the photodegradation rate is steady as contrasted with the "seasonal" effect in outdoor exposures.

In Table II, the effects of carbon-arc irradiation of pigmented polyesters are shown. The pattern of photodegradation with exposure time is similar to that of the unpigmented plastics. For a given exposure time, less reaction appears to take place in the pigmented plastics. For example, in unpigmented plastic A after 2000 hr. (from Fig. 3) the amount of DMPDA



TABLE II  
Effect of Carbon-Arc Radiant Energy on Pigmented Polyesters

Polyester	Exposure time, hr. <sup>a</sup>	Color change <sup>b</sup>			DMPDA, mg./specimen <sup>c</sup>
		$\Delta L$	$\Delta a$	$\Delta b$	
Polyester A (white)	509	-5.02	+6.1	+10.0	0.046
	1030	-9.81	+9.3	+11.8	0.180
	1987	-14.38	+11.2	+11.7	0.250
Polyester D (white)	509	-5.38	+7.7	+11.0	0.091
	1030	-8.46	+10.1	+13.6	0.160
	1987	-9.86	+11.3	+13.9	0.205
Polyester D (green)	509	-8.91	-4.5	+7.2	0.046
	1030	-8.02	+2.0	+6.0	0.068
	1987	-10.77	+5.9	+8.8	0.160

<sup>a</sup> Exposed in Atlas single-arc Weather-Ometer at  $125 \pm 5^\circ\text{F}$ .

<sup>b</sup> Changes in Adams coordinate values.

<sup>c</sup> Specimen size was  $2 \times 7$  cm.

reacted was 0.385 mg. With white plastic A for a similar period of time, only 0.25 mg. of DMPDA reacted. Similar effects were observed with other clear and pigmented polyesters. The green pigmented polyester D showed less reaction with DMPDA than did the white polyester D. The high  $-\Delta L$  values found with the green specimen were probably an indication of pigment change as well as degradation of the polyester.

### Poly(vinyl Chloride)

Rigid poly (vinyl chloride) was exposed to carbon-arc radiant energy for durations up to 1030 hr. Photooxidation was detected by DMPDA treatment of the exposed plastics and subsequent measurement of the changes in the Adams coordinate values by differential colorimetry. In addition, the relative absorbances of the DMPDA-PVC reaction products in benzene-

TABLE III  
Effect of Carbon-Arc Radiant Energy on Rigid Poly(vinyl Chloride)<sup>a</sup>

Exposure time, hr. <sup>b</sup>	Changes in Adams coordinate values <sup>c</sup>			Relative absorbance, (410 m $\mu$ ) <sup>d</sup>
	$\Delta L$	$\Delta a$	$\Delta b$	
96	-2.55	+0.1	+6.7	0.160
221	-6.71	+1.9	+7.0	0.243
441	-10.05	+3.2	+10.4	—
512	-11.46	+3.3	+7.5	0.289
1030	-19.36	+5.8	+8.1	0.412

<sup>a</sup> Pigmented (white) commercial product.

<sup>b</sup> Exposed in Atlas single-arc Weather-Ometer at  $125 \pm 5^\circ\text{F}$ .

<sup>c</sup> Specimens treated with benzene-methanol solutions of *N,N*-dimethyl-*p*-phenylenediamine for 2 hr. at room temperature.

<sup>d</sup> Absorbance obtained by reaction described above. Each entry is an average of two values.

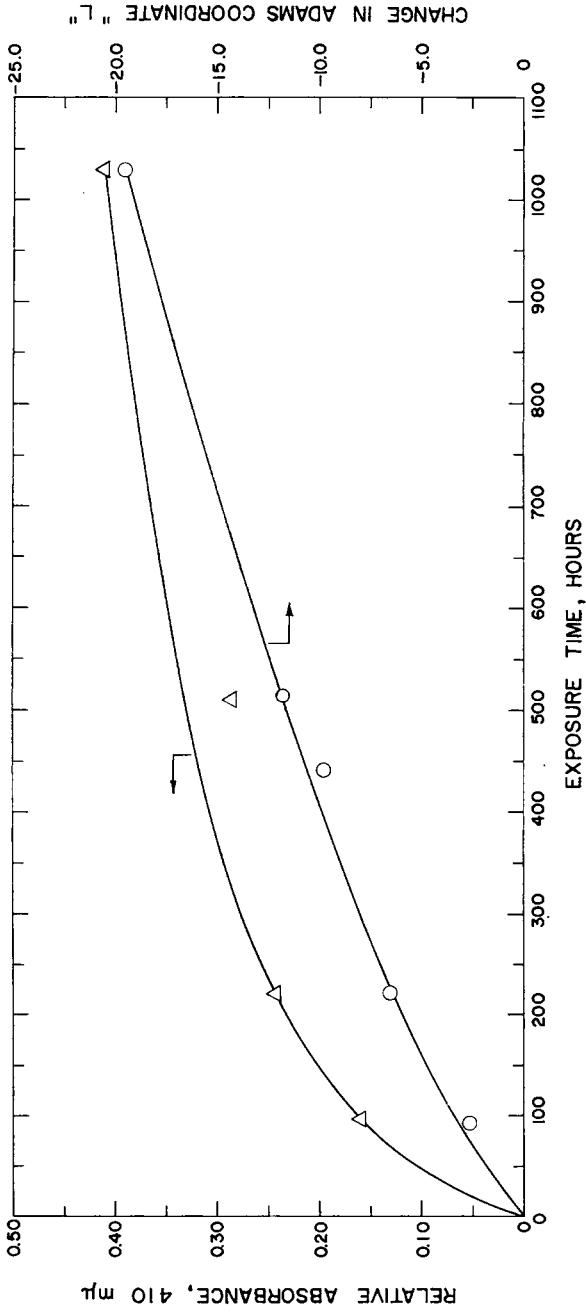


Fig. 4. Relative absorbance at 410 mμ and specimen color change (ΔL) vs. carbon-arc exposure time for poly(vinyl chloride).

methanol solution were measured at 410  $m\mu$  where a distinct absorbance peak was found. Exposure data are given in Table III for a commercial, pigmented (white) specimen of PVC.

In general, the results with PVC were like those with the polyesters. For increasingly longer periods of exposure, the treated samples became darker, i.e., exhibited larger negative  $\Delta L$  values. Also the relative absorbances at 410  $m\mu$  increased with exposure time. The  $\Delta L$  values and absorbances are plotted against exposure time in Figure 4.

By means of the Adams coordinate value  $\Delta L$ , a direct comparison may be made of the change in lightness in the DMPDA-treated PVC with the white pigmented polyesters treated similarly after given exposure periods to the carbon arc. After approximately 500 hr. exposure, the PVC specimen ( $\Delta L = -11.46$ ) was darker upon diamine treatment than the white polyester A ( $\Delta L = -5.02$ ) or white polyester D ( $\Delta L = -5.38$ ). Similar differences existed at the 1030-hr. exposure duration. On the basis of these limited data, it appeared that the glass fiber-reinforced polyesters were less sensitive to carbon-arc radiation than was the rigid PVC.

### Poly(methyl Methacrylate)

Commercial samples of poly(methyl methacrylate) were exposed to radiant energy from a carbon arc for durations up to 3192 hr. and to solar radiant energy for 1 yr. For evaluation of photodegradation, the exposed specimens were dissolved in glacial acetic acid and treated with either DMPDA, *m*-PDA, or *o*-PDA. With *m*-PDA solutions, relative absorbance peak intensities were measured at 342 and 400  $m\mu$ ; with DMPDA at 344

TABLE IV  
Effect of Carbon Arc and Solar Radiant Energy on Poly(methyl Methacrylate)<sup>a</sup>

Ex- posure time	Relative absorbance <sup>b</sup>					
	<i>m</i> -PDA		DMPDA		<i>o</i> -PDA	
	342 $m\mu$	400 $m\mu$	344 $m\mu$	420 $m\mu$	340 $m\mu$	460 $m\mu$
	Carbon arc <sup>c</sup>					
0 hr.	0	0	0	0	0	0
500	0.072	0.069	0.014	0.020	-0.007	0.004
800	0.087	0.085	0.026	0.029	0.005	0.014
1600	0.116	0.100	0.039	0.035	0.036	0.027
3192	0.156	0.154	0.041	0.059	0.093	0.182
	Solar <sup>d</sup>					
214 days	0.074	0.078	0.027	0.034	0.039	0.084
366	0.084	0.078	0.036	0.030	0.050	0.081

<sup>a</sup> Colorless commercial product.

<sup>b</sup> Absorbance of acetic acid solutions of the exposed plastic and the indicated diamine.

<sup>c</sup> Exposed in Atlas single-arc Weather-Ometer at  $125 \pm 5^\circ\text{F}$ .

<sup>d</sup> Exposed in Washington, D. C., beginning April 1961.

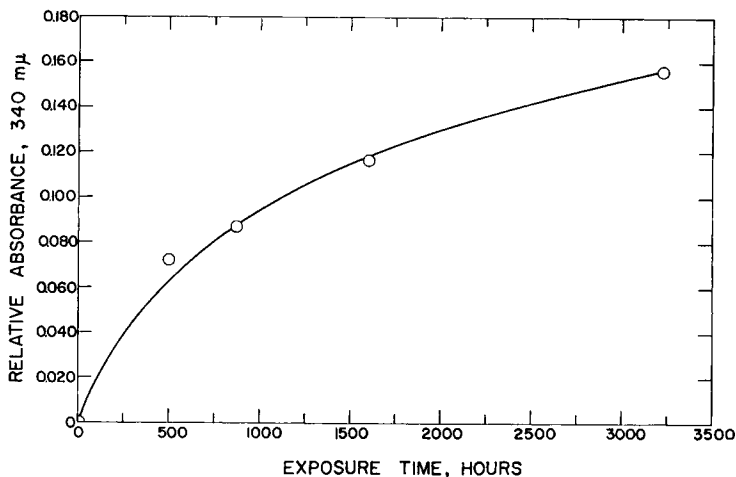


Fig. 5. Relative absorbance at 340  $m\mu$  vs. carbon-arc exposure time for poly(methyl methacrylate).

and 420  $m\mu$ ; and with *o*-PDA at 300 and 460  $m\mu$ . Exposure and photodegradation data on one PMM plastic are given in Table IV.

While PMMA is well known for lack of change in light transmission characteristics,<sup>9</sup> significant changes were shown to have occurred by the diamine treatment of exposed specimens and subsequent measurement of absorbance intensities at certain wavelengths in the ultraviolet and visible regions. The data indicate that gradual photooxidation occurs with exposure time. While there is reaction with all three diamines, the greatest changes are indicated with *o*-PDA and *m*-PDA. The results with the latter are plotted in Figure 5. (An indication of the type of compounds formed when PMMA and CAB undergo photooxidation is described elsewhere.<sup>10</sup>)

### Effect of Environmental Exposure on Yellowness in Polyesters

It was observed that during the solar irradiation of polyesters in oxygen and in nitrogen, respectively, the samples exposed in nitrogen exhibited far greater yellowness than did those in oxygen. Samples exposed in air were intermediate in yellowness.\* The change in Adams coordinate *b* (yellowness) was measured by differential colorimetry in the exposed but untreated specimens. The data (Table V) show values of +2.6, +5.5, and +6.3 for samples exposed in oxygen, air, and nitrogen, respectively. For the lightness coordinate *L*, the value for the polyesters exposed in oxygen was +0.31, while that of the samples in nitrogen was -0.65.

Upon treatment of the irradiated polyesters with DMPDA, it was soon established that extensive photooxidation had occurred in the samples exposed in oxygen, but very little reaction had taken place in the nitrogen

\* Results for exposures in air are not directly comparable since these exposures were not made in Pyrex tubes as were the plastic specimens irradiated in oxygen and in nitrogen.

TABLE V  
Comparison of Nitrogen, Oxygen, and Air as Environmental Media for Solar Irradiation of Polyester A<sup>a</sup>

Exposure medium	Changes in Adams coordinate values			DMPDA reacted, mg./specimen <sup>b</sup>
	$\Delta L$	$\Delta a$	$\Delta b$	
Before diamine treatment				
Oxygen	+0.31	-0.8	+2.6	—
Nitrogen	-0.65	-0.9	+6.3	—
Air <sup>c</sup>	-1.90	-0.7	+5.5	—
After diamine treatment				
Oxygen	-22.08	+5.5	+11.8	0.433
Nitrogen	+1.61	-0.5	+3.2	0.046
Air <sup>c</sup>	-17.48	+3.8	-0.2	0.114

<sup>a</sup> Samples exposed outdoors for three months.

<sup>b</sup> Specimen dimensions were  $2 \times 7$  cm.

<sup>c</sup> Air exposures were made on open panels. Oxygen and nitrogen exposures were made in Pyrex glass tubes.

atmosphere. The amount of DMPDA which reacted with the oxygen-exposed samples was 0.433 mg./specimen; that with nitrogen-exposed specimens was 0.046 mg./specimen. Thus, approximately a 10-fold difference was observed.

The results with Adams coordinate  $L$  confirmed those based on the amount of DMPDA reacted. A value of +1.61 was found with the diamine-treated specimens that had been exposed in nitrogen. A value of -22.08 was obtained with similarly treated samples irradiated in an oxygen atmosphere. Air-exposed samples produced an intermediate value of -17.48.

The rate of yellowness formation in exposed plastics is used frequently in an index of photochemical stability.<sup>11</sup> The experimental results shown in Table V, however, cast considerable doubt on the significance of yellowness as a measure of overall photodegradation. Exposure of polyesters to solar radiant energy in nitrogen produces yellowness that cannot be attributed to a photochemical process involving reactions with oxygen. While there is no evidence for the formation of nitrogen compounds in the present work, O'Neil<sup>12</sup> has shown that nitrogenous materials are necessary to produce yellowing in linseed oil and suggested the formation of pyrrole compounds; experimental evidence indicated that the yellow compounds were not simple products of oxidation. Conversely, Wright, Campbell, and Fridinger<sup>13</sup> have shown photooxidation to be the main degradation reaction in asphalt upon exposure to the radiant energy of a carbon arc.

## SUMMARY AND CONCLUSIONS

The experimental data presented in this paper provide the basis for a number of conclusions on the measurement of photodegradation in plastics by color reactions with various diamines.

(1) The reaction of DMPDA with an irradiated polyester to produce a yellow to brown color reaction on the exposed surface appears to have more general application. No exceptions were observed in the solar and carbon-arc irradiation of sixteen polyesters for periods up to 2 yr. outdoors and/or for 3200 hr. in the accelerated weathering machine.

(2) The poly(vinyl chloride) plastic was found to react with DMPDA after exposure to the radiant energy of the carbon arc. The intensity of the color developed in rigid PVC varied directly with exposure time.

(3) The change in Adams coordinate  $L$  (lightness) showed good agreement with the amount of DMPDA used in reaction with an exposed plastic. When extensive reaction took place, changes in coordinates  $a$  (greenness-redness) and  $b$  (blueness-yellowness) reached maximum values at intermediate exposure periods.

(4) The PVC appeared to undergo photodegradation more rapidly than glass fiber-reinforced polyesters for a given exposure period in the accelerated weathering machine. This statement is based on a more rapid increase in negative  $\Delta L$  values.

(5) The pigmented polyesters were more stable to photooxidation than unpigmented specimens of the corresponding polyester.

(6) The poly(methyl methacrylate) and cellulose acetate-butyrate plastics underwent photochemical degradation to form products which reacted with phenylenediamines to produce colored solutions. DMPDA, *o*-, *m*-, and *p*-phenylenediamine reacted with these plastics in glacial acetic acid.

(7) On the basis of relative intensities of certain absorbance peaks in the visible and ultraviolet regions, it was shown that PMM photooxidation varies directly with the exposure time.

(8) Yellowness was shown to occur in polyesters upon solar irradiation in nitrogen and in the absence of oxygen. The use of yellowness as the index of photochemical oxidative degradation in plastics is questioned.

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### Résumé

On a exposé des échantillons de polyester aux radiations solaires ou aux radiations provenant d'un arc au carbone et on a trouvé qu'il se forme des produits d'oxydation qui, après réaction avec la *N,N'*-diméthyl-*p*-phénylène diamine (DMPDA), donnent des produits de réaction jaune à brun. L'étendue de la réaction a été déterminée de façon directe en mesurant la quantité de diamine qui a réagi, ou de façon indirecte par colorimétrie différentielle. On a étendu les recherches au moyen de cette réaction colorée de façon à développer des tests pour mesurer la dégradation photooxydante des polyesters, du chlorure de polyvinyle rigide, des acryliques et de l'acétate-butyrate de cellulose. La méthode colorimétrique de base a été modifiée pour chacun des types de plastique, en mesurant directement l'absorption de la solution de DMPDA au lieu de mesurer la quantité de DMPDA qui a réagi en employant l'*ortho*-, la *meta*- ou la *paraphénylène*-diamine au lieu de la DMPDA, ou bien en changeant de solvant. On a examiné la reproductibilité de cette disparition de couleur jaune comme indicateur de stabilité photochimique des plastiques.

### Zusammenfassung

Proben von Polyesterkunststoffen bildeten nach Einwirkung von Sonnenoder Kohlebogenstrahlungsenergie Oxydationsprodukte, die bei Reaktion mit *N,N*-Dimethyl-*p*-phenylendiamin gelbe bis braune Reaktionsprodukte bildeten. Das Ausmass der Reaktion wurde direkt durch die Menge des umgesetzten Diamins oder indirekt durch Differentialkolorimetrie bestimmt. Diese Farbreaktion wurde zu einem Test zur Messung des photooxydativen Abbaus von Polyester, starrem Polyvinylechlorid, Acrylaten und Celluloseacetate-Butyrat entwickelt. Die grundlegende kolorimetrische Methode wurde durch direkte Messung des Absorptionsvermögens der DMPDA-Lösung an Stelle der Messung der umgesetzten Menge an DMPDA, durch die Verwendung von *ortho*-, *meta*-, und *para*-Phenylendiaminen als Ersatz für DMPDA in der Farbreaktion oder durch einen Wechsel des Lösungsmittels jedem dieser Plastiktypen angepasst. Die Verlässlichkeit der Gelbfärbung als Indikator der photochemischen Stabilität von Kunststoffen wurde untersucht.

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