

## Colorimetric Method for Measuring Polyester Degradation Due to Weathering

V. E. GRAY and J. R. WRIGHT, *Organic Building Materials Section, National Bureau of Standards, Washington, D.C.*

### Introduction

In general, the methods used to evaluate the degradation of crosslinked polyesters due to weathering are based on changes in (a) visual appearance,<sup>1-4</sup> (b) physical properties, e.g., tensile strength, elongation, and modulus of elasticity,<sup>5-7</sup> (c) gloss, color, and light transmittance,<sup>8-10</sup> (d) yellowness only,<sup>11</sup> and (e) weight.<sup>12</sup> For certain plastics, quantitative instrumental-analytical techniques are used to detect changes in molecular structure caused by chemical reactions (mainly oxidation) which occur during weathering.<sup>13-14</sup>

Unfortunately, instrumental methods based on the absorption of light are not applicable to detect chemical changes caused by weathering in polyester plastics. The presence of the large amounts of strongly absorbing groups in the unexposed plastic and also the glass in the glass fiber-reinforced polyesters make transmittance measurements difficult. Weathering effects, in absence of other methods, have been evaluated by visual observations or changes in physical properties.

The physical properties of polyesters change very slowly, and much time is required to obtain data of significance. Thus a rapid, quantitative test method is needed to evaluate the effects of weathering on polyesters. The present paper describes a colorimetric method for measuring polyester degradation caused by weathering which may in part fulfill this need.

### General Description of the Method

It was found that when polyesters, which had been previously exposed to the elements of weathering, were treated with a diamine, a pronounced color developed. Under the same experimental conditions, however, no color formed with plastics which had not been exposed. The most effective color-producing reagent was *N,N*-dimethyl-*p*-phenylenediamine (DMPDA). A yellow-to-brown reaction product was formed on the surface of polyesters previously exposed to natural or carbon-arc radiant energy. The color changes were very pronounced when observed under visible light, and fluorescent substances were observed under ultraviolet light.

Two different color reactions were used in determining the extent of polyester degradation, and it is important that this distinction be kept

clearly in mind. The first color reaction was produced in the following manner. After weathering for a prescribed time, the plastic test specimen was treated with a known amount of DMPDA in a benzene-methanol solution. A color reaction, which was used as a measure of the degradation of the exposed plastics, took place on the surface of the test specimen. It should be emphasized that this color reaction is probably specific for one type of degradation product and that it would not occur with all degradation products.

The second color reaction made it possible to determine quantitatively the amount of DMPDA reacted with the surface of the weathered test specimen. To do this, an aliquot of the solution used to effect coloration in the exposed plastic was treated with a peroxide to oxidize the unreacted DMPDA. The oxidation reaction produced a brightly colored (pink) solution, the intensity of which was dependent upon DMPDA concentration and could be measured quantitatively by absorption spectroscopy. Thus, by knowing the amount of DMPDA in the reagent solution before treating the exposed plastic and that which remained after reaction, the amount of DMPDA reacted could be calculated by difference. The extent of polyester degradation was related directly to the amount of DMPDA reacted as will be shown in later discussion.

### Materials

Three glass fiber-reinforced polyesters (commercial products) were used and were designated as polyesters A, B, and C, respectively. All were unpigmented panels,  $\frac{1}{16}$  in. thick. A fourth polyester was prepared in the laboratory without glass fiber reinforcement. Like the commercial plastics, this product was clear and approximately  $\frac{1}{16}$  in. thick. *N,N*-dimethyl-*p*-phenylenediamine was obtained as the dihydrochloride salt, reagent grade, and was used without further purification.

### Weathering Conditions

The polyesters were exposed as  $7 \times 15$  cm. panels to both natural and accelerated weathering conditions. At prescribed periods of time, test specimens,  $2 \times 7$  cm., were cut from these panels and the extent of degradation measured. Outdoor exposures were made in Washington, D.C., starting in April, 1961, in weathering racks inclined  $45^\circ$  from the horizontal and facing south. No backing material was used. The weathering racks were located atop a four-story building and were supported 3-5 ft. above an asphalt-gravel roof.

Accelerated weathering was carried out in an Atlas single-arc Weather-Ometer. Exposure to the radiant energy of the enclosed carbon arc was made at  $140 \pm 5^\circ\text{F}$ . The specimens were inverted at the end of each 22-hr. cycle, keeping the same side exposed to the carbon arc. No water spray or thermal shock was used; the exposures were to radiation only.

### Treatment of Plastic Specimens with DMPDA

Preliminary experiments established three principal conditions necessary for optimum reaction between the exposed polyesters and DMPDA: (a) a solution of methanol-benzene was needed to allow the DMPDA to penetrate the exposed plastic surface; (b) free amine was needed in solution, because the acid salts reacted too slowly; (c) a 2-hr. reaction period permitted the maximum color development between DMPDA and components of the plastic surface.

The DMPDA reagent was prepared for treatment of the exposed plastic surface by dissolving 0.200 g. of *N,N*-dimethyl-*p*-phenylenediamine dihydrochloride in 5.0 ml. of 0.40*N* potassium hydroxide. This solution was diluted in 100 ml. volume with methanol, and subsequently, to 200 ml. volume with benzene. Concentration of diamine salt in the final solution was 1.0 mg./ml.

A polyester test specimen,  $2 \times 7 \times 0.2$  cm., was submerged in 15.0 ml. of the reagent in a specially designed sample tube which afforded maximum contact between the reagent and the plastic. The tube was stoppered to prevent loss of solvent, placed in a wrist-action shaker, and shaken for 2 hr. At the end of this time, a 1.0-ml. aliquot was removed from the tube, and the concentration of the unreacted DMPDA determined by the procedure described in the next section. The plastic test specimen, now a yellow-to-brown color, was removed from the sample tube, washed with methanol and dried. Tristimulus measurements were made on the specimen with the differential colorimeter.

For each polyester evaluated at any given exposure period, duplicates of both exposed and unexposed control specimens were employed. Generally the unexposed specimens caused a very slight decrease in DMPDA concentration, while the exposed specimens caused a much greater decrease. Therefore, the decrease in DMPDA concentration caused by the exposed specimens was always corrected for the decrease, if any, caused by the unexposed or control specimen. This method yielded the amount of DMPDA which reacted with the chemical entities formed during polyester weathering.

### Determination of Unreacted DMPDA

The indirect approach used to determine the amount of DMPDA which reacted with the exposed plastic was described earlier in general terms. Specifically, the procedure was as follows. An aliquot of the DMPDA reagent which had been reacted for 2 hr. with the exposed plastic was added to a 100-ml. volumetric flask containing 50 ml. of reagent-grade methanol and 2.0 ml. of pH 3.0 buffer (hydrochloric acid-potassium acid phthalate). A 1.0-ml. aliquot of benzoyl peroxide solution (1.000 g. of benzoyl peroxide per 100 ml. of methanol-benzene in 90:10 volume ratio) was added and the contents mixed. The volumetric flask was filled to volume with methanol. After mixing the contents by inverting the flask several times, the solution

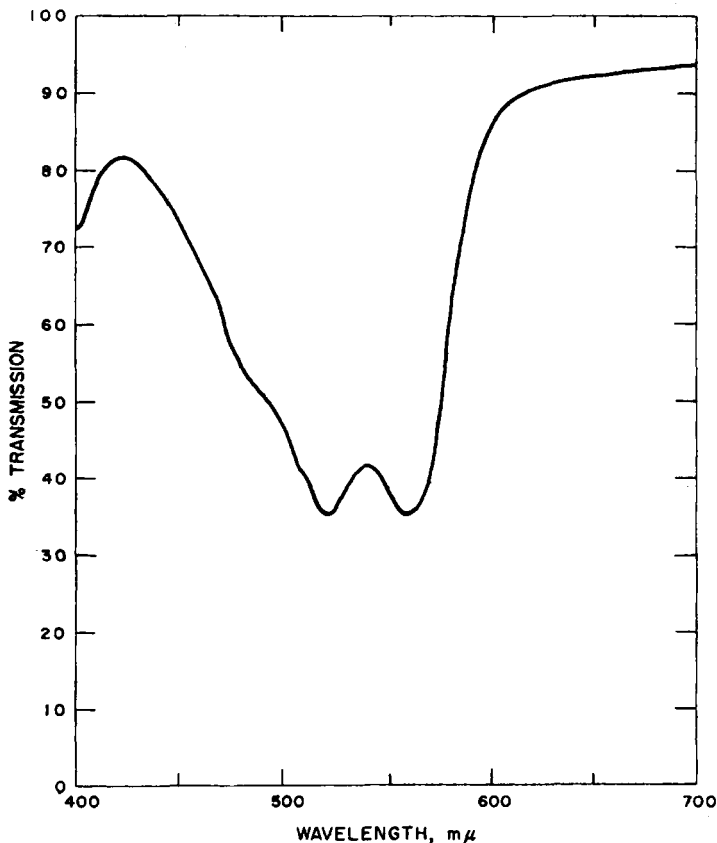


Fig. 1. Transmission spectrum of a methanolic solution (pH 3.0) of DMPDA reacted with excess benzoyl peroxide for 30 min.

was allowed to stand for 20 min., during which time it became highly colored. (Color stability was pH-dependent. The greatest stability was at pH 3.0 or less.)

At the end of the 20-min. period, the absorbance of the solution was read at 520  $m\mu$  on a Beckman DU spectrophotometer, 1.0 cm. cells and a methanol blank being used. Absorption maxima were found at both 520 and 560  $m\mu$  and are shown as transmission minima in Fig. 1. The absorbance readings were repeated at 5-min. intervals until the maximum absorbance was reached. This value was used in determining the DMPDA concentration of the solution from a previously established absorbance-concentration curve (Fig. 2). The amount of DMPDA which reacted with the exposed plastic surface was determined by the difference between the quantities reacted with the control and exposed specimens, respectively.

The quantitative aspects of the method are shown by the data in Table I. At an  $\bar{x}$  level of 0.432 absorbance units, the reproducibility was  $\pm 0.001$  absorbance unit. A 0.001 absorbance-unit change is equivalent to a con-

centration change of 0.00152 mg./100 ml. of solution at a concentration level of 0.656 mg./100 ml. of solution. Figure 3 shows the effect of time on the color formed by the DMPDA in benzoyl peroxide. The absorbance of solutions with low concentration of DMPDA appears to be more stable than at higher concentrations. The rapid reaction between amines and

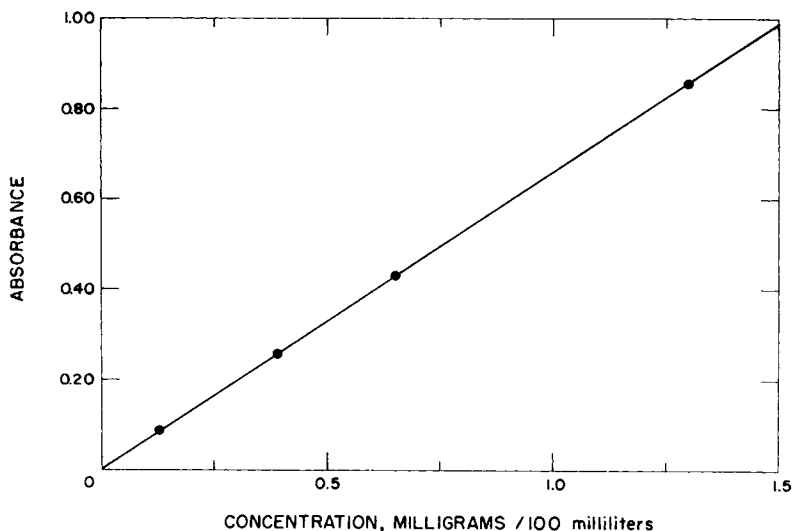


Fig. 2. Maximum absorbance (520  $m\mu$ ) vs. concentration of DMPDA reacted with excess benzoyl peroxide.

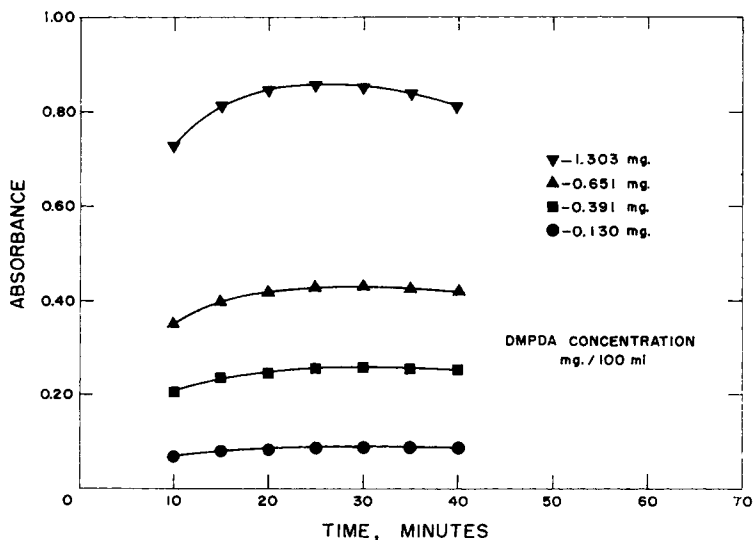


Fig. 3. Absorbance readings (520  $m\mu$ ) of DMPDA-benzoyl peroxide solutions vs. time at four DMPDA concentrations: (▽) 1.303 mg./100 ml.; (▲) 0.651 mg./100 ml.; (■) 0.391 mg./100 ml.; (●) 0.130 mg./100 ml.

TABLE I  
 Reproducibility of Diamine-Benzoyl Peroxide Reaction  
 Maximum Absorbance (520 m $\mu$ )

Solution	Replicate determinations				Average $\bar{x}$	Standard deviation $s^a$
1	0.431	0.433	0.433	0.434	0.432	0.0011
	0.433	0.434	0.432	0.432		
	0.432	0.431	0.431	0.432		
2	0.433	0.434	0.434	0.435	0.434	0.0008

<sup>a</sup>  $s = \sqrt{\sum(\bar{x} - x)^2/(n - 1)}$ , where  $x$  = value of a single observation,  $n$  = number of observations.

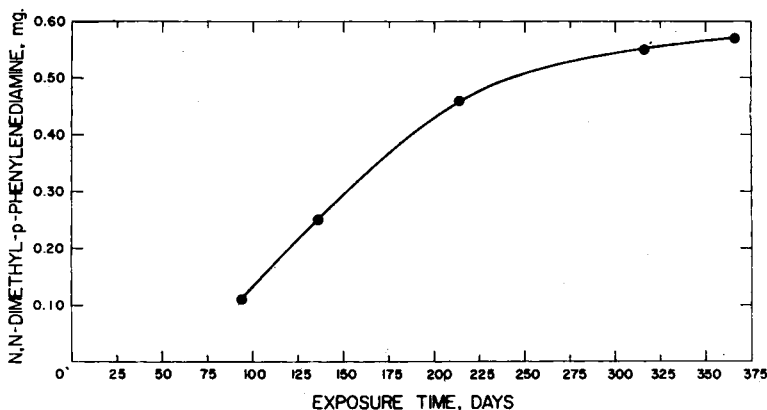


Fig. 4. DMPDA reacted vs. outdoor exposure time for polyester A.

organic peroxides is well known, but not completely understood.<sup>15</sup> Most evidence points to a bimolecular mechanism by which the amine decomposes the peroxide and is changed to another form. This effect, presumably, is the cause of the color change observed in the present work.

#### Color-Change Measurements by Differential Colorimeter

The color produced by DMPDA treatment of the exposed polyesters offered possibilities for an empirical method for correlating degradation and specimen color. While the nonuniformity of the glass-fiber reinforcement in the 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 the color changes which occurred in a given plastic.

A Mecco tristimulus color difference meter using illuminant C (45, 0°) was standardized on the green, red, and blue reflectance values of a white, glass 90% reflectance standard. The DMPDA-treated plastic specimens were placed over the instrument sample port (duplicate specimens taped together to give the largest possible area) with the white 90% reflectance standard placed behind the specimens. A heavy black cloth was used as a

cover to eliminate stray light. The green, red, and blue reflectance values were determined. The plastic samples were rotated 180° about the normal and the reflectance measurements repeated. The average green, red, and blue reflectance values were calculated.

To obtain color values which would most closely relate instrumental and visual color, the reflectance values were corrected to the modified Adams coordinate system described by Glasser and Troy.<sup>16</sup> A more detailed explanation is given in the Appendix below). The Adams coordinates were calculated for the control and the exposed plastic specimens. The color changes ( $\Delta L$ ,  $\Delta a$ ,  $\Delta b$ ) were determined by subtracting the coordinate values of the control specimens from the coordinate values of the exposed specimens.

### Results and Discussion

The results of the first application of the colorimetric method for detecting degradation of plastic A are shown in Table II. Measurements of the amount of DMPDA reacted with the plastic surface after exposure, as well as the changes of the Adams coordinate values  $L$ ,  $a$ , and  $b$  are reported.

Figure 4 was prepared to show the effect of exposure time outdoors as determined by the amount of DMPDA reacted with plastic A. Figure 5 shows the effects produced by exposure to the radiant energy of the carbon arc. In both outdoor and carbon-arc exposures the amount of DMPDA reacting with polyester A was found to increase with the time of exposure. The color of the treated specimen increased with the amount of DMPDA reacted. This change in visual appearance is brought out in Figure 6.

TABLE II  
Effect of Natural and Accelerated Weathering on Plastic A

Exposure time	Changes in Adams Coordinate Values			DMPDA reacted, mg./specimen <sup>a</sup>
	$\Delta L$	$\Delta a$	$\Delta b$	
Natural Weathering				
94 days	-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
Accelerated Weathering <sup>b</sup>				
197 hrs.	-7.89	+2.3	+10.1	0.114
392	-9.27	+5.9	+14.1	0.18
805	-10.87	+8.5	+18.9	0.25
1355	-14.36	+10.7	+18.9	0.32
1601	-18.82	+9.7	+19.5	0.34
2330	-17.36	+11.9	+10.3	0.39

<sup>a</sup> Specimen dimensions were 2 × 7 cm.

<sup>b</sup> Exposed in Atlas single-arc Weather-Ometer.

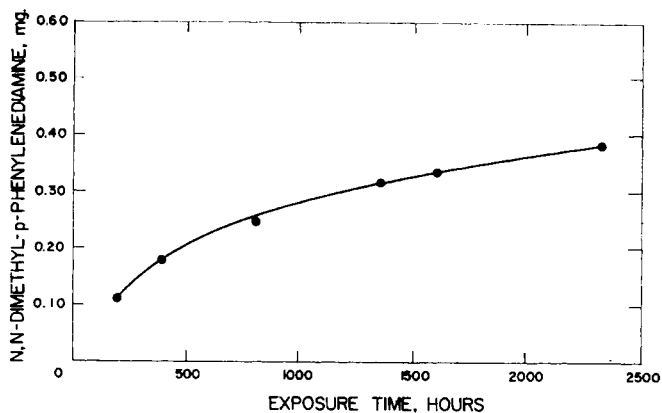


Fig. 5. DMPDA reacted vs. carbon-arc exposure time for polyester A.

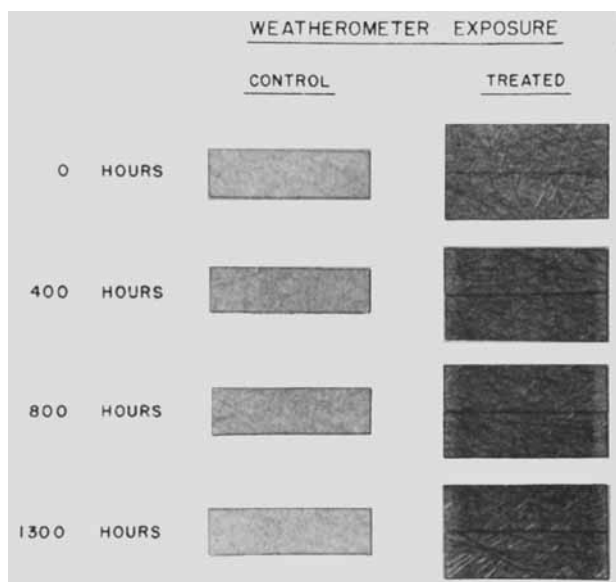


Fig. 6. Formation of color in DMPDA-treated polyester A vs. time of exposure to carbon-arc radiant energy.

The degradation rate, as determined by the DMPDA reacted, varied more in natural weathering than in accelerated weathering. This variation may be due, in part, to the much greater variation of solar radiation as compared with the relatively steady radiation of the carbon arc. However, other factors such as temperature, moisture, atmospheric oxidants, and difference in wavelength of the radiation could have some effect.

The effect of the exposure of plastic A to carbon-arc radiation, as measured by changes in the Adams coordinate  $a$  (redness-greenness), is shown in Figure 7. Comparison of the two methods is also shown in Figure 7. Good correlation between the methods is shown.



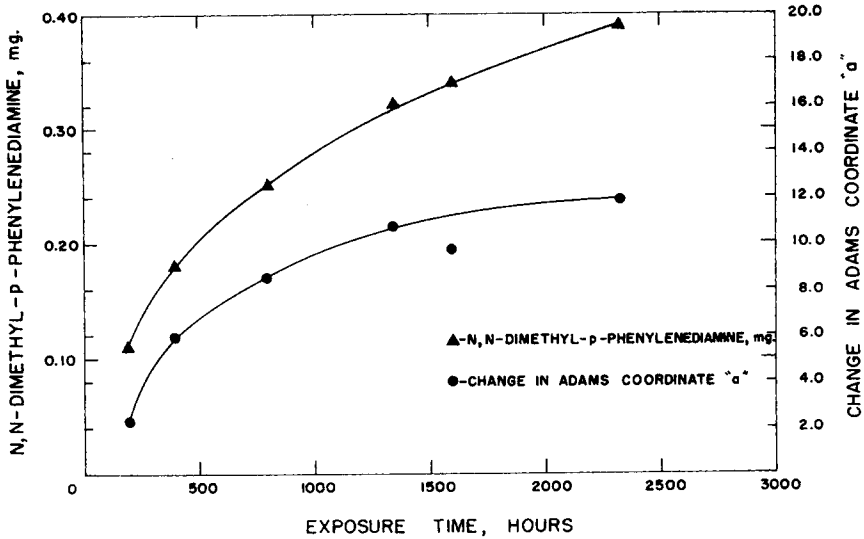


Fig. 7. DMPDA reacted and specimen color vs. carbon-arc exposure time for polyester A: (▲) amount DMPDA reacted; (●) change in Adams coordinate  $a$ .

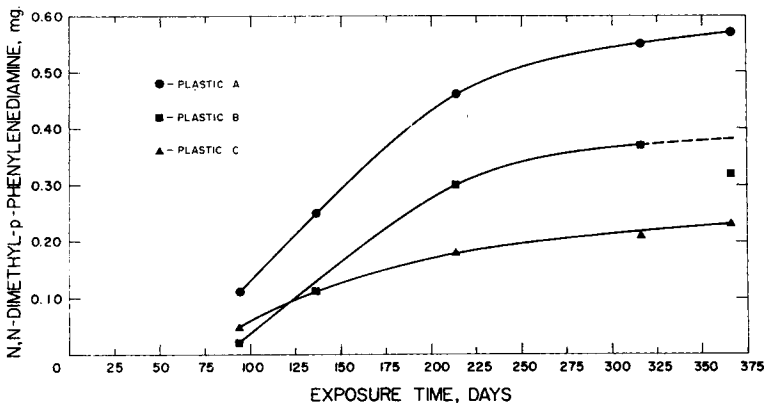


Fig. 8. DMPDA reacted vs. outdoor exposure times for polyesters A, B, and C: (●) plastic A; (■) plastic B; (▲) plastic C.

Exposure results for plastics B and C are shown by the quantitative and empirical methods in Tables III and IV, respectively. The behavior patterns of plastics B and C were, in general, the same as that of plastic A, but the rates of degradation were different for each plastic. The rate effect for outdoor exposure is shown in Figure 8. Polyester C reacted with the least DMPDA, polyester B with slightly more DMPDA, and polyester A with the greatest amount of DMPDA. (See Figure 9 for a visual comparison of this effect in polyesters A and C.) The results were in agreement with visual examinations of the exposed but untreated specimens which re-

TABLE III  
Effect of Natural and Accelerated Weathering on Plastic B

Exposure time	Changes in Adams coordinate values			DMPDA reacted, mg./specimen <sup>a</sup>
	$\Delta L$	$\Delta a$	$\Delta b$	
Natural Weathering				
94 days	-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
Accelerated Weathering <sup>b</sup>				
392 hr.	-3.81	+1.5	+9.6	0.023
512	-7.28	+2.2	+13.3	0.091
805	-5.60	+1.9	+15.0	0.091
1355	-8.90	+3.7	+17.0	0.25
1601	-12.75	+5.1	+22.1	0.18

<sup>a</sup> Specimen dimensions were 2 × 7 cm.

<sup>b</sup> Exposed in Atlas single-arc Weather-Ometer.

TABLE IV  
Effect of Natural and Accelerated Weathering on Plastic C

Exposure time	Changes in Adams coordinate values			DMPDA reacted, mg./specimen <sup>a</sup>
	$\Delta L$	$\Delta a$	$\Delta b$	
Natural Weathering				
94 days	-8.14	+1.3	+9.6	0.046
136	-12.54	+2.9	+13.2	0.011
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
Accelerated Weathering <sup>b</sup>				
392 hr.	-6.45	+1.7	+11.5	0.023
512	-9.12	+2.1	+13.1	0.091
805	-7.30	+2.8	+14.9	0.091
1355	-10.39	+3.9	+18.4	0.18
2230	-12.25	+4.4	+16.7	0.16

<sup>a</sup> Specimen dimensions were 2 × 7 cm.

<sup>b</sup> Exposed in Atlas single-arc Weather-Ometer.

vealed an increasing amount of yellowness in plastics C, B, and A in that order.

A comparison of the colors developed with exposed plastics and DMPDA revealed that the color is related to the radiant energy exposure source as well as to the nature of the polyester being treated. For example,  $\Delta a$  (red-green) coordinate values are higher for plastics exposed to the carbon arc than for outdoor exposure. However,  $\Delta b$  (yellowness) coordinate

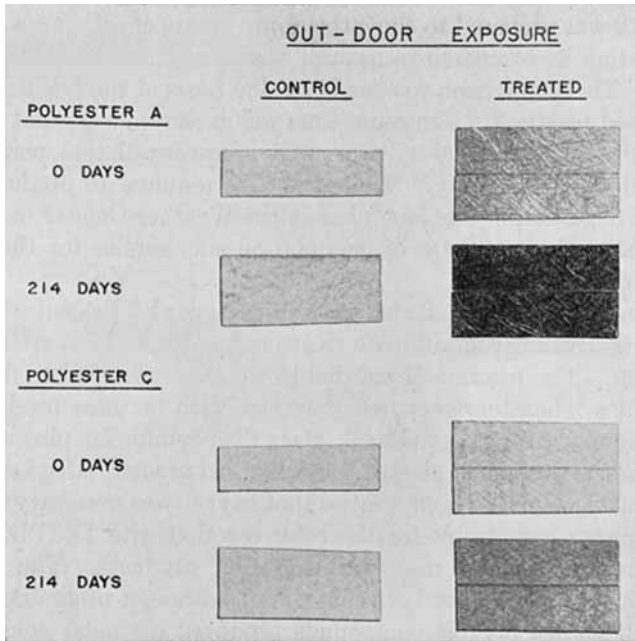


Fig. 9. A comparison of the color formed in the DMPDA-treated polyesters A and C, due to natural weathering.

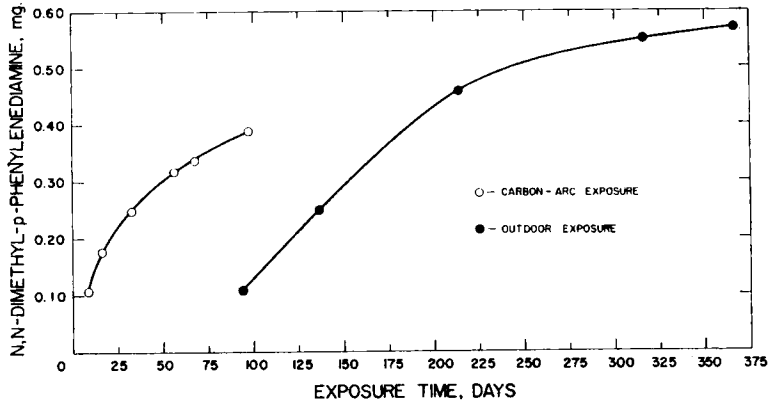


Fig. 10. DMPDA reacted with outdoor and carbon-arc exposed specimens vs. exposure time for plastic A: (O) carbon arc exposure; (●) outdoor exposure.

values increase for all three plastics under carbon-arc exposure, but the  $\Delta a$  coordinate values increase appreciably for plastics A and B only, and not for plastic C. These color changes which appear to vary with the radiant energy exposure source and with a given polyester could be caused by different chemical structures formed during exposure and by chemical differences in the commercial materials.

Figure 10 was prepared to show the approximate effectiveness of carbon-arc irradiation as compared to natural weathering in causing plastics degradation. The comparison was made on the basis of the DMPDA reacted with exposed plastic A. Exposure time was based on a normal 24-hr. day for natural weathering and a 24-hr. carbon-arc irradiation period for an accelerated weathering day. While the time required to produce a given amount of degradation was much less in the Weather-Ometer, it was interesting to note that the rate of degradation was similar for the exposure periods employed.

The nature of the chemical changes taking place at the plastic surface and subsequently causing coloration on treatment with DMPDA are not known at this time. The reaction is not due to the presence of glass fiber. The exposure of a laboratory-prepared polyester with no glass produced color reactions similar to the commercial, glass fiber-reinforced plastics. Separate experiments in which plastic A was exposed to solar radiation in atmospheres of nitrogen and oxygen, proved that oxygen was necessary to produce the components responsible for the color reaction with DMPDA. Thus, the colorimetric method measures oxidation products. The nature of these products has not yet been elucidated, although preliminary experiments with known organic compounds produced a similar color reaction with benzaldehyde and *p*-aminobenzaldehyde.

### Summary and Conclusions

From the investigation described herein, it has been shown that a colorimetric method, in which an exposed polyester surface is treated with *N,N*-dimethyl-*p*-phenylenediamine, can be used to follow the degradation of polyesters to natural and accelerated weathering. Three commercial, glass fiber-reinforced polyesters were evaluated. In all three, the color formation caused by the DMPDA varied directly with the time of exposure. All plastics degraded at different rates under the same exposure conditions. The extent of the reaction between the amine and the surface of the exposed plastics was measured by the changes of the Adams coordinates and by the amount of amine reacted with good correlation between the two methods.

The colorimetric method appears to have considerable potential as a rapid, accurate method for evaluating the stability of plastics to weathering. However, much remains to be done in elucidating its applications and limitations. The nature of the chemical reactions responsible for color formation in the exposed plastics should be understood. Application of the method should be extended to many polyesters and to other types of plastic materials which are exposed to and degrade from weathering. A correlation should be established between degradation as measured colorimetrically and by conventional methods such as changes in physical properties. Long-term exposure data are needed to establish the reliability of the degradation curves obtained colorimetrically. Once validated for other plastics, the colorimetric method should be quite useful in comparing the relative stability of these materials.

## Appendix

### Conversion of Tristimulus Values to a Uniform Color Space by Use of Modified Adams Coordinates

The C.I.E. tristimulus values are the most easily computed from instrumental measurements from either tristimulus colorimeters or spectrophotometers.<sup>17a</sup>

The C.I.E. tristimulus values represent the proportions of three standard primary colors which upon additive mixing will match the color being measured. Visual color differences, however, do not vary linearly with differences measured in C.I.E. coordinates.<sup>17b</sup>

Several methods for correcting C.I.E. tristimulus values into a visually uniform system have been proposed. A system based on one proposed by Adams offers the most satisfactory compromise between visual uniformity and ease of computation.<sup>16</sup> In this system, the tristimulus reflectance values are converted to three other dimensions which are used as the rectangular coordinates of a visually uniform color space. The lightness coordinate,  $L$ , plotted on the vertical axis corresponds to the value in the Munsell color system. The other two coordinates,  $a$  and  $b$ , are a measure of redness-greenness and blueness-yellowness, respectively. Positive (+) values of  $a$  signify redness; negative (-) values signify greenness; positive values of  $b$  signify yellowness, negative values signify blueness. The plane designated by the coordinates,  $a$  and  $b$  for a given value of  $L$  is described in the Munsell color system by the polar coordinates, hue and chroma. The units of the dimensions,  $L$ ,  $a$ , and  $b$  have been so adjusted that visually equal differences in any dimension correspond to equal numerical differences. The unit used is approximately equal to the N.B.S. unit of color difference whose magnitude was originally chosen to be equal to the smallest color difference of commercial significance.<sup>17</sup> The smallest difference that can be seen by a trained observer under ideal lighting conditions is approximately 0.3 N.B.S. unit.

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### Synopsis

Chemical changes occurring in thermoset polyesters during exposure to solar and carbon-arc radiant energy were determined quantitatively by a color reaction with a diamine, *N,N*-dimethyl-*p*-phenylenediamine, in a methanol-benzene solution. The amount of diamine reacting with a specimen and the color change of the treated specimen, as measured by differential reflectance, varied directly with exposure time. Three commercial polyesters (glass fiber-reinforced) exposed under identical conditions showed widely different degradation rates as measured by the amount of *N,N*-dimethyl-*p*-phenylenediamine used per specimen. The relative stability of the three materials was independent of irradiation source. The color of the treated specimen was dependent on exposure time.

### Résumé

Les variations chimiques dans les polyesters thermodurcissables provoquées par l'exposition au soleil et à l'énergie d'irradiation d'un arc de carbone, furent déterminées quantitativement par une réaction de coloration avec la *N,N*-diméthyl-*p*-phénylènediamine en solution dans un mélange méthanol-benzène. La quantité de diamine réagissant avec un échantillon et la variation de coloration de l'échantillon traité, telle qu'elle a été mesurée par réflexion différentielle, est directement proportionnelle au temps d'exposition. Trois polyesters commerciaux (renforcés par de la fibre de verre) exposés dans des conditions identiques, montrent des vitesses de dégradation nettement différente, celle-ci étant mesurées par la quantité de *N,N*-diméthyl-*p*-phénylènediamine ayant réagi avec chaque échantillon. La stabilité relative des trois matériaux était indépendante de la source d'irradiation. La coloration de l'échantillon traité était fonction du temps d'exposition.

### Zusammenfassung

Die in wärmehärtenden Polyestern während Sonnen- oder Kohlebogenbestrahlung auftretenden Veränderungen werden quantitative durch eine Farbreaktion mit einem Diamin, *N,N*-Dimethyl-*p*-phenyldiamin, in Methanol-Benzollösung bestimmt. Die Menge des mit einer Probe reagierenden Diamins und die durch Differentialreflexion gemessene Farbänderung der behandelten Probe waren der Bestrahlungsdauer direkt proportional. Drei handelsübliche Polyester (verstärktes "Fiberglas") zeigten unter gleichen Belichtungsbedingungen, gemessen an der Menge des pro Probe verbrauchten *N,N*-Dimethyl-*p*-phenyldiamins, weitgehend verschiedene Abbaugeschwindigkeit. Die relative Stabilität der drei Stoffe war von der Strahlungsquelle unabhängig. Die Farbe der behandelten Proben hing von der Bestrahlungsdauer ab.

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