

The Mechanism of Oxidative Degradation of ABS Resin. Part II. The Mechanism of Photooxidative Degradation

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Synopsis

The mechanism of oxidative degradation of ABS resin under ultraviolet irradiation, especially with respect to the wavelength dependencies of the photooxidative rate, has been examined by a spectroweather tester and infrared spectroscopy. The irradiation wave region was 290-800 $m\mu$, and the region was divided into six parts. The changes in each part were examined by infrared spectroscopy. The absorption bands belonging to nitrile and phenyl groups showed no changes, but bands belonging to carbonyl and hydroxyl groups changed markedly, much as in the thermooxidative degradation described in a previous paper. There was a distinct gap between the third and fourth regions, which corresponded to 350 $m\mu$. The graph of the normalized absorbance ratio and the logarithm of the wavelength gave a straight line, and it indicated that the rate of oxidation is proportional to the light intensity and the logarithm of the wavenumber.

INTRODUCTION

ABS resin is vulnerable to ultraviolet irradiation. Generally, the mechanism of photooxidation and of stabilization against it in polymeric materials is not well clarified, and there are not many reports on the subject,¹⁻⁴ especially on the relationship between the UV wavelength and its efficiency in initiating the degradation reaction.⁵ The presence of butadiene in ABS resin makes it difficult to improve the resin's resistance to photooxidation. From this viewpoint an attempt was made to obtain the relation between the photooxidation rate and the wavelength and light intensity and to clarify the mechanism of photooxidation and stabilization.

For the purpose of this work a spectroweather tester was used, and the degraded samples were analyzed by infrared spectroscopy. As a result of the experiments it was concluded that ABS resin has a critical wavelength (350 $m\mu$), above which the irradiation of light has little effect in initiating photooxidation. Below 350 $m\mu$ the rate of photooxidation is proportional to the light intensity and the logarithm of the wavenumber.

EXPERIMENTAL

Commercial ABS resin (butadiene content, 23.2%; acrylonitrile content, 21.7%; styrene content, 55.1%; these were determined by elemental analysis) was purified by dissolving in acetone and precipitating with methanol for removal of the additives, especially the stabilizer. Film specimens were prepared by compression-molding of this resin at 175°C. The sample specimens were subjected to photooxidative degeneration in the spectroweather tester SPW-1 (made by Tōyō-Rika Kōgyō in Japan). The light, produced by a xenon lamp, was divided into monochromatic

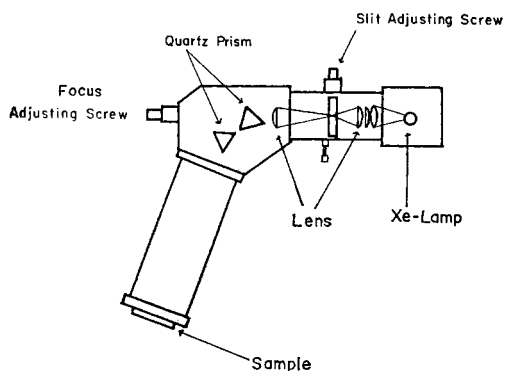


Fig. 1. Spectroweather tester.

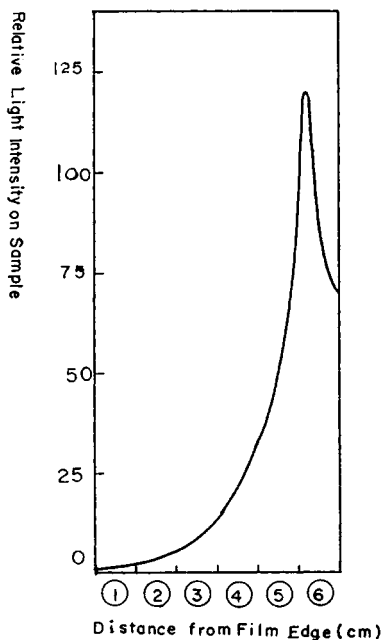


Fig. 2. Intensity of light on sample film.

light (from 290 to 800 $m\mu$) by a quartz prism, and the film specimens were irradiated by continuous monochromatic light; see Figure 1.

The relationships between the light intensity and the wavelength and the length from the edge of the film were obtained and are shown in Figures 2 and 3.

The IR spectra of this film were measured for each part; the film was divided into six parts in 1 cm. steps from the film edge, and the parts were

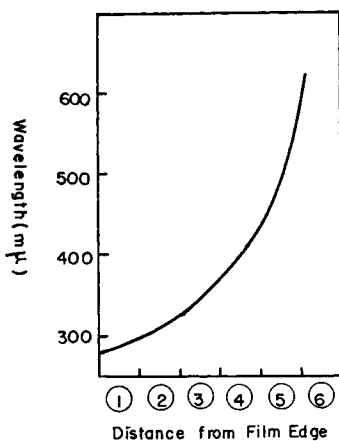


Fig. 3. Wavelength of split light on sample film.

named 1, 2, 3, 4, 5, and 6. The irradiation was carried out at room temperature (20–23°C.) and moderate humidity (60–65% R.H.). When the intensity of split light was weak, the temperature rise of the film specimens under irradiation was negligible. The irradiation area of the specimens was $60 \times 35 \text{ mm.}^2$, and the thickness was $1.5\text{--}1.6 \times 10^{-2} \text{ cm.}$

RESULTS AND DISCUSSION

Ultraviolet (UV) and Visible-Region (VR) Spectra

The UV and VR spectra of ABS resin film were measured with a spectrophotometer QR-50 (made by Shimadzu Seisakusho in Japan). The changes in extinction coefficients with wavelength are shown in Figure 4.

The absorbance at different wavelengths obeyed the Lambert-Beer law, but the line of absorbance versus film thickness did not pass through the original point because of diffused scattering in the film and reflection on the surface. From Figure 4 it is evident that at wavelengths less than 350 $m\mu$ the shorter the irradiation wavelength, the higher the extinction coefficient. Above 350 $m\mu$ the wavelength does not seem to have any effect. This indicates that there is a critical wavelength corresponding to the threshold energy initiating photooxidation. The increase of absorbance is considered to be due to the degradation products, such as carbonyl-containing products.

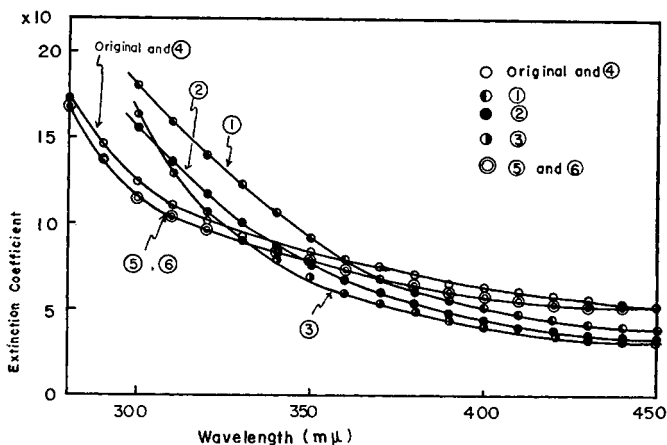


Fig. 4. Ultraviolet and visible-region spectra of degraded film. Numerals in circles signify irradiation wavelength regions according to Fig. 3.

Infrared Spectra: Phenyl and Nitrile Group

The assignment of infrared spectra of ABS resin has been reported in a previous paper.⁶ In the works reported here we examined the 5.1 and 4.45 μ bands that correspond to phenyl and nitrile groups, respectively. The changes in the absorbance of these bands, which were normalized by

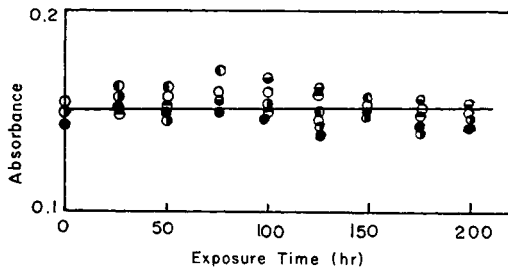


Fig. 5. Change of phenyl group. Parts: (○) 1; (◐) 2; (●) 3; (◑) 4; (◒) 5; (◓) 6.

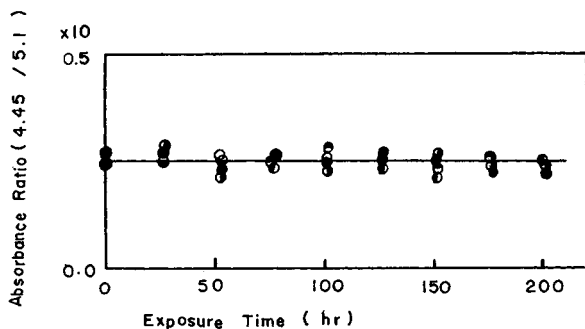


Fig. 6. Change of nitrile group. Parts: (○) 1; (◐) 2; (●) 3; (◑) 4; (◒) 5; (◓) 6.

film thickness, are given in Figures 5 and 6. As in the case of thermooxidative degeneration, there were no marked changes in phenyl and nitrile groups.

The experimental results indicated that no splitting of phenyl or nitrile groups took place during photodegradation.

Infrared Spectra: *trans*-1,4-Butadiene, *cis*-1,2-Butadiene, and Double Bonds

The double bonds corresponding to *trans*-1,4-polybutadiene, the double bonds belonging to *cis*-1,2-polybutadiene, and the terminal double bonds appear at 10.3, 10.9, and 6.3 μ , respectively, as reported in a previous paper.⁶ To show the changes in the double-bond absorbance, the ratios of these peaks to that of the phenyl group (6.9 μ) are plotted against time in Figures 7-9.

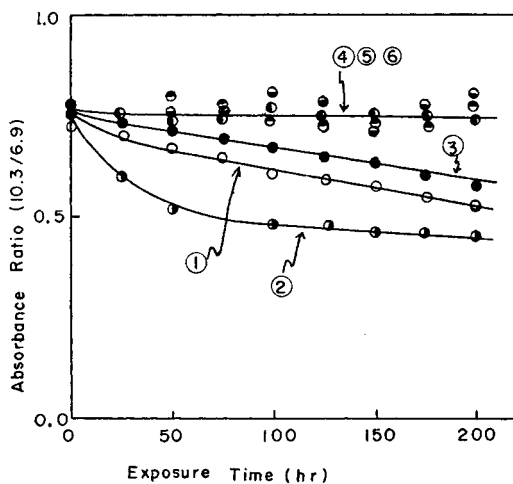


Fig. 7. Change of *trans*-1,4-polybutadiene structure. Parts: (○) 1; (○●) 2; (●) 3; (●●) 4; (●●●) 5; (●●●●) 6. Numerals in circles signify irradiation wavelength regions according to Fig. 3.

A change was observed in *trans*-1,4-polybutadiene, but it was not as large as those due to carbonyl or hydroxyl groups. Though this band overlaps the phenyl group absorption band, the change in it is due only to the *trans*-1,4-polybutadiene, because, as shown earlier, the phenyl group concentration does not change. The absorption bands due to *cis*-1,2-polybutadiene or the terminal double bond showed little change. From Figure 6 it is evident that, concerning the changes of absorbance due to *trans*-1,4-polybutadiene structure with time of irradiation, there is a clear difference between the third and fourth parts. The decrease of *trans*-1,4-polybutadiene structure was considered to be due to the photolysis, which initiates the autooxidation of ABS resin.

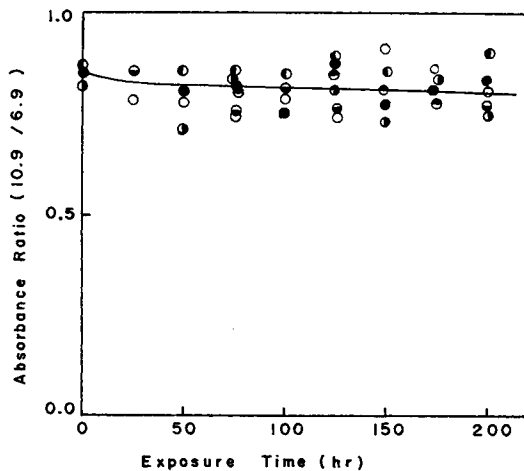


Fig. 8. Change of *cis*-1,2-butadiene structure. Parts: (O) 1; (◐) 2; (●) 3; (◑) 4; (◒) 5; (◓) 6.

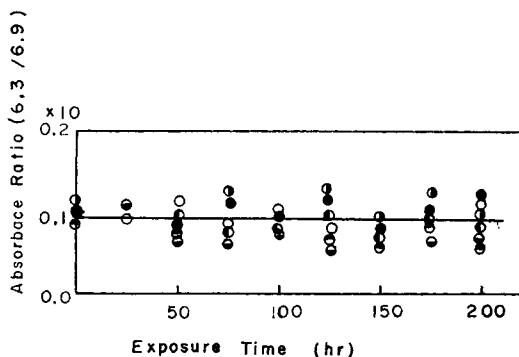


Fig. 9. Change of terminal double-bond structure. Parts: (O) 1; (◐) 2; (●) 3; (◑) 4; (◒) 5; (◓) 6.

Infrared Spectra: Carbonyl and Hydroxyl Groups

To show the changes in —OH and >C=O absorbances with exposure time, the peak ratios of —OH (2.9μ) and >C=O (5.8μ) to the phenyl group (5.1μ) are plotted against time in Figures 10 and 11.

There was a considerable increase in the absorbance of carbonyl and hydroxyl groups at wavelengths below $350 \text{ m}\mu$. The absorbance ratios were normalized by dividing the absorbed light intensity, which was calculated from Figures 2 and 4. The relationship between normalized absorbance ratio and the logarithm of the wavenumber gave a straight line, as shown in Figures 12 and 13. The increase of the tangent of this straight line with elapsed time was due to the increase of the absorbance due to oxidation.

These relationships are expressed as follows:

$$([\text{OH}] \text{ or } [\text{CO}])/I_a = K(t) \log \nu - \log \nu_0 \quad (1)$$

where $[OH]$ or $[CO]$ indicate the concentrations of the hydroxyl and carbonyl groups due to photooxidation, which is proportional to the absorbance ratio, $K(t)$ is the tangent, I_a indicates the absorbed light intensity in the film sample, and ν is the wavenumber. The $K(t) - t$ relation was obtained experimentally; see Figure 14.

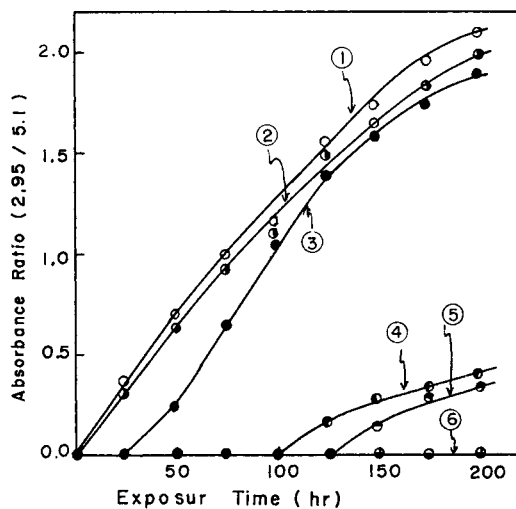


Fig. 10. Change of hydroxyl group. Parts: (○) 1; (◐) 2; (●) 3; (◑) 4; (◒) 5; (◓) 6.

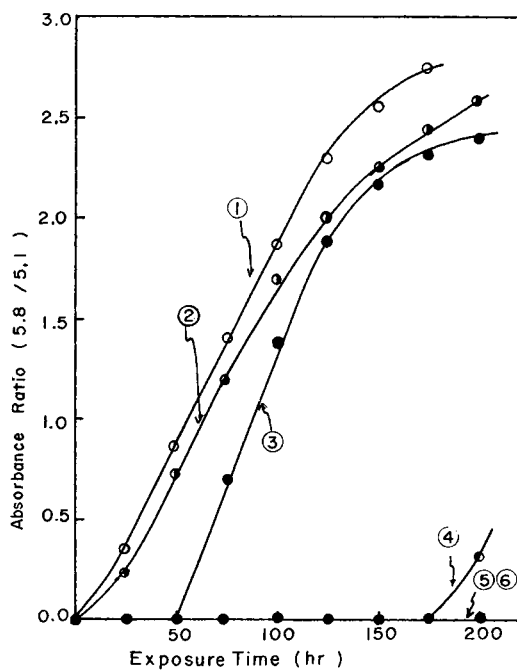


Fig. 11. Change of carbonyl group. Parts: (○) 1; (◐) 2; (●) 3; (◑) 4; (◒) 5; (◓) 6.

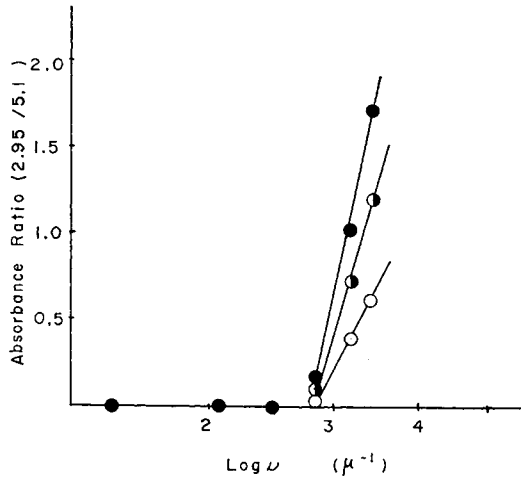


Fig. 12. Absorbance ratio for hydroxyl group versus $\log \lambda$: Time (hr.): (○) 50; (◐) 100; (●) 150.

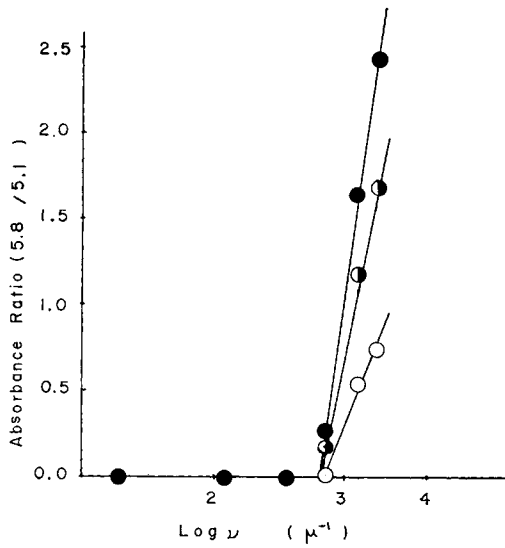


Fig. 13. Absorbance ratio for carbonyl group versus $\log \lambda$: Time (hr.): (○) 50; (◐) 100; (●) 150.

The equations corresponding to various irradiation times are given in Table I.

By differentiating eq. (1) with respect to time one obtains

$$d([\text{OH}] \text{ or } [\text{CO}])/dt = I_a \log \nu K'(t) \quad (2)$$

From Figure 14 the $K(t) - t$ relation was expressed as follows:

$$K(t) = Ct \quad (3)$$

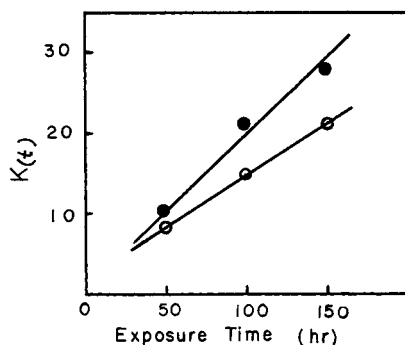


Fig. 14. Tangent of eq. (3): Formation of: (O) hydroxyl; (●) carbonyl.

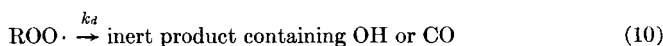
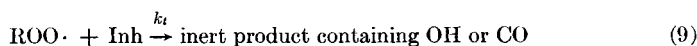
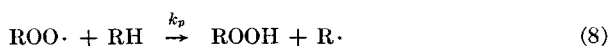
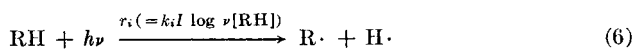
where C is a constant. Therefore $K'(t)$ may be expressed as follows:

$$K'(t) = C \quad (4)$$

By combining eqs. (2) and (4) the rate of carbonyl or hydroxyl group formation may be expressed as follows:

$$d([\text{OH}] \text{ or } [\text{CO}])/dt = I_a C \log \nu \quad (5)$$

From these experimental results it was determined that the rate of oxidation was proportional to the light intensity and $\log \nu$. A photooxidative degradation scheme may be proposed:



The initiating step, eq. (6), could be estimated to be due to the photolysis of the methylene bond of the *trans*-1,4-polybutadiene structure, whose

TABLE I
The Wavelength and Relative Energy of Radiation on the Sample Surface

Part no.	Wavelength at center, $\text{m}\mu$	Wavelength region, $\text{m}\mu$	Energy at center
1	295	290-300	1.0
2	300	300-325	1.6
3	350	325-370	9.0
4	400	370-435	20.5
5	490	435-585	50.0
6	700	585-800	90.0

TABLE II
Parameters of Eq. (1) for the Formation of Hydroxyl Group

Irradiation time, hr.	Parameter $K(t)$	Parameter log	Parameter
50	8.311	3.80	348
100	14.961	6.80	351
150	21.501	9.76	351

TABLE III
Parameter of Eq. (1) for the Formation of Carbonyl Group

Irradiation time, hr.	Parameter $K(t)$	Parameter log	Parameter
50	10.381	4.76	348
100	21.571	9.79	352
150	28.810	12.67	353

bond dissociation energy is 38 kcal./mole, in ABS resin; it corresponds to 817 $m\mu$. From the fact that the rate of oxidation was proportional to the light intensity and not to the square root of the light intensity the termination reaction could be expressed as eq. (9), in which the polymer peroxy radical ($\text{ROO}\cdot$) reacts with an impurity (Inh). A hydroxyl or carbonyl group is formed through decomposition of this reaction product. Another case of hydroxy or carbonyl formation is the decomposition of polymer hydroperoxide (ROOH) into an inert product containing hydroxyl or carbonyl groups; see eq. (10). Since the quantum yield defines $q = a/b$, where a is the number of molecules undergoing a particular process, and b is the number of quanta absorbed by the system, in eq. (1) a is proportional to $[\text{CO}]$ or $[\text{OH}]$, and b is proportional to $I_a/h\nu$, so the q is proportional to $\nu \log \nu$.

There was a linear relationship in the amount of formation of hydroxyl and carbonyl groups, as shown in Figure 15. A similar relationship was obtained for thermooxidation. Therefore the mode of decomposition of ROOH or of an inert product, formed according to eq. (9), in the photooxidation, was similar to that of thermooxidation.

From the kinetic analysis of eqs. (6)–(10) and for a stationary state the rate of formation of carbonyl or hydroxyl groups may be expressed as follows:

$$d([\text{OH}] \text{ or } [\text{CO}])/dt = K_i[\text{ROO}\cdot][\text{Inh}] + K \cdot [\text{ROOH}] \\ = r_i - r_i[\text{RH}]/[\text{Inh}](k_u/k_t)(\exp \{-k_{at}\} - 1) \quad (11)$$

By making the assumption that the second term of eq. (11) may be neglected at an early stage of photooxidation this equation may be transformed as follows:

$$d([\text{OH}] \text{ or } [\text{CO}])/dt = r_i = k_i I \log \nu [\text{RH}] \quad (12)$$

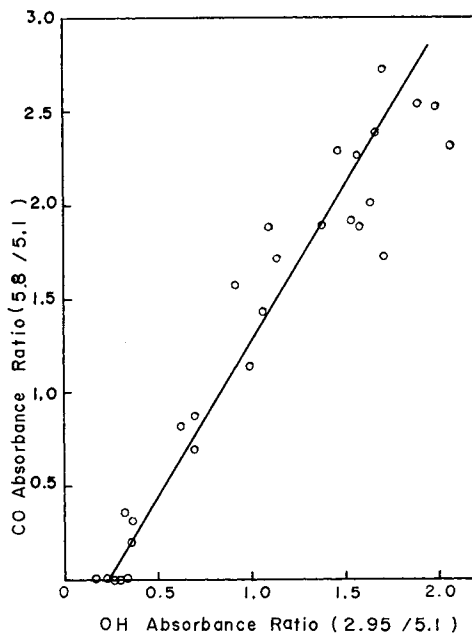


Fig. 15. Relation between CO and OH groups formed by degradation.

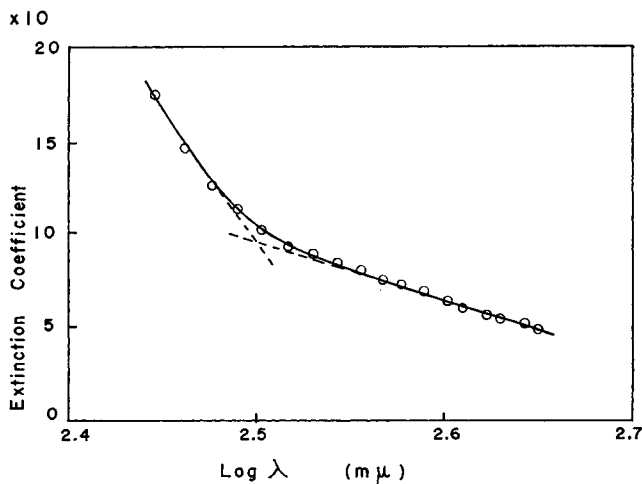


Fig. 16. Relation between absorbance and $\log \lambda$ of original ABS film.

Since r_t and $[RH]$ may be regarded as constant, this equation well fits eq. (5), which was derived experimentally.

The critical wavelength may be elucidated as follows. As in the case of polyethylene,¹ it is a necessary condition for the photolysis of ABS resin, but not an always sufficient one, that the irradiation energy must be greater than the bond dissociation energy of the methylene bond of a

trans-1,4-polybutadiene structure, 38 kcal., corresponding to 817 m μ . To meet the requirement it is necessary in the photooxidation of ABS resin that the resin be irradiated in the region of wavelengths shorter than 340 m μ . This is shown in Figure 16, where the increase of absorbance is proportional to log ν and resembles the form of eq. (1).

CONCLUSION

By using the spectroweather tester it was found that there is a critical wavelength in the photooxidation of ABS resin. The critical wavelength was determined from the intersection on the x axis of the absorbance of OH versus log ν straight line. The critical wavelength (350 m μ) corresponds to the point below which absorption of ABS resin increases markedly. The photooxidation rate of ABS resin is proportional to the light intensity and log ν . A reaction scheme is proposed for elucidating these relationships, and it is suggested that the photooxidation of ABS resin takes place by photolysis of the methylene bond in the *trans*-1,4-polybutadiene structure in ABS resin.

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