

# Photooxidation of Amine Crosslinked Epoxies

## II. Influence of Structure

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### Synopsis

We have studied the photooxidation of networks based on three diepoxides containing isopropylidene or methylene bisphenol structures and three diamines of the dianiline type, with, respectively, methylene (DDM), ether (DDE), or sulfone (DDS) bridges. The results are discussed in terms of photoinitiated radical oxidation mechanisms. The comparison of the different systems shows that the photoinitiating species essentially derive from the phenoxy part, whereas the propagation essentially depends on amine concentration and electron density at the nitrogen atom. The amine structure also plays a very important role in color development.

### INTRODUCTION

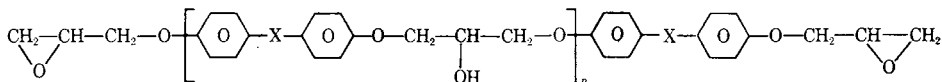
In a preceding paper we have shown some features of the photochemical behavior of an epoxy-amine network based on diglycidyl ether of bisphenol A (DGEBA) and diamino diphenyl methane (DDM). The main photooxidation products are carbonyls and amides, whose yields depend on sample thickness, thermal treatments, and amine concentrations.<sup>1</sup> The aromatic amine structure seems to play an important role in photosensitization and color development.

Little is known in the field of structure-photostability relationships for epoxy networks. Lin et al. compared the photo and thermal oxidations of trimethylboroxine crosslinked systems based on bisphenols containing isopropylidene (DGEBA), phenolphthalein (DGPP), or fluorene (DGEBF) structures. They found that their behavior can be interpreted in terms of autoxidation mechanisms.<sup>2</sup> George et al. pointed out that epoxy novolacs are less photostable than DGEBA systems and that aromatic carbonyl groups resulting from a thermal oxidation during cure treatments can play a photosensitizing role.<sup>3</sup> More recently, Allen et al. studied the electronic spectra of some systems based on DGEBA and aliphatic amines and found two kinds of chromophores: the bisphenol A moiety, which absorbs in the shorter wavelength part of the solar spectrum, and a quinonic structure, responsible for the absorption in the near UV-visible region.<sup>4</sup> In our laboratory, we compared photooxidation rates of DGEBA systems crosslinked by aliphatic (diethylene triamine), cycloaliphatic (isophorone diamine), or heterocyclic (amino ethyl piperazine) amines and found that amide yields are directly related to the initial  $\alpha$ -amino methylene concentration.<sup>5</sup> The same approach will be used in this paper to study the structure-photostability relationships in networks based on bisphenols and amines of the dianiline type.

## EXPERIMENTAL

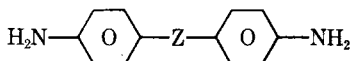
## Materials

Three diepoxides of general formula:



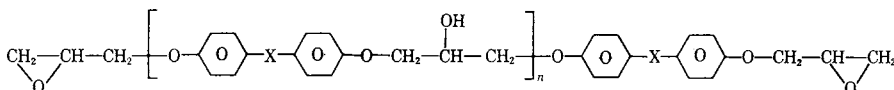
were studied: two of the bisphenol A type differing only by the molecular weight (A and B), whereas C differs from A only by the bridge between aromatic nuclei, the isopropylidene unit being replaced by a methylene.

The diamines under study have the general formula:

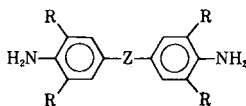


Films of 25–40  $\mu\text{m}$  thickness were prepared by casting and curing on a mercury surface as previously described.<sup>1,5</sup> The following systems were used: diepoxides A and B cured with three hardeners and diepoxide C cured only with diamino diphenylmethane (DDM). In all cases, amine and epoxide concentrations are fixed in stoichiometric ratio, and their thermal treatments are optimized to obtain the maximum value of crosslinking degree. Some data on structures, processing

TABLE I  
Structures, Processing Characteristics and  $T_g$  of Cured Films  
Resins:



Hardeners:



Sample	X	n	Z	R	Epoxide index (mol·kg <sup>-1</sup> )	Gel time $T_g$ (K) with resin A
Resin A	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}- \\   \\ \text{CH}_3 \end{array}$	0.11			5.4	
Resin B	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}- \\   \\ \text{CH}_3 \end{array}$	8.8			0.06	
Resin C	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{C}- \\   \\ \text{CH}_2 \end{array}$	0.03			6.25	
DDM			CH <sub>2</sub>	H		438
DDE			O	H		430
DDS			SO <sub>2</sub>	H		468

TABLE II  
Absorbance per Thickness Unit of the Infrared Peak at  $1885\text{ cm}^{-1}$ , (Absorbance Units- $\text{cm}^{-1}$ )

Sample	$A_{1885}$ ( $\text{cm}^{-1}$ per thickness unit)
A-DDM	$23 \pm 2.6$
A-DDS	$25 \pm 2.0$
A-DDE	$20 \pm 0.75$
B-DDM	$24 \pm 1.3$
B-DDS	$24 \pm 1.3$
B-DDE	$24 \pm 1.3$
C-DDM	$21 \pm 1.8$

characteristics, and  $T_g$  of cured films (measured by DSC) are summarized in Table I.

### Photooxidation and Film Control

For UV irradiation ( $\lambda > 300\text{ nm}$ ), we used the previously described method.<sup>1</sup> The temperature was  $31 \pm 1^\circ\text{C}$  and the intensity  $3.5 \times 10^{15}\text{ photons cm}^{-2}\cdot\text{s}^{-1}$ . The photooxidation was followed by UV and IR spectrophotometry using the infrared peak at  $1885\text{ cm}^{-1}$  as internal standard. The absorbance per thickness unit of this peak is given in Table II. The results are expressed in absorbance units per cm thickness ( $\text{cm}^{-1}$ ).

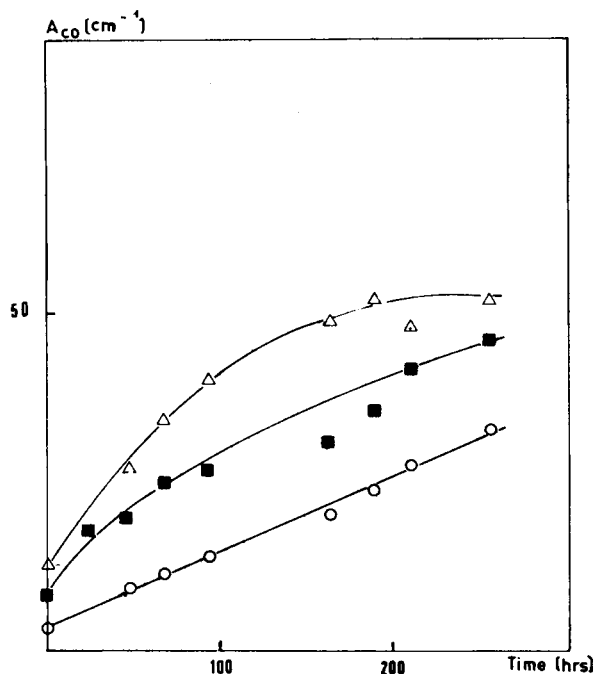


Fig. 1. Carbonyl growth for resin A-DDM (■), resin A-DDS (○), resin A-DDE (△) systems (films of  $30\text{ }\mu\text{m}$  thickness).

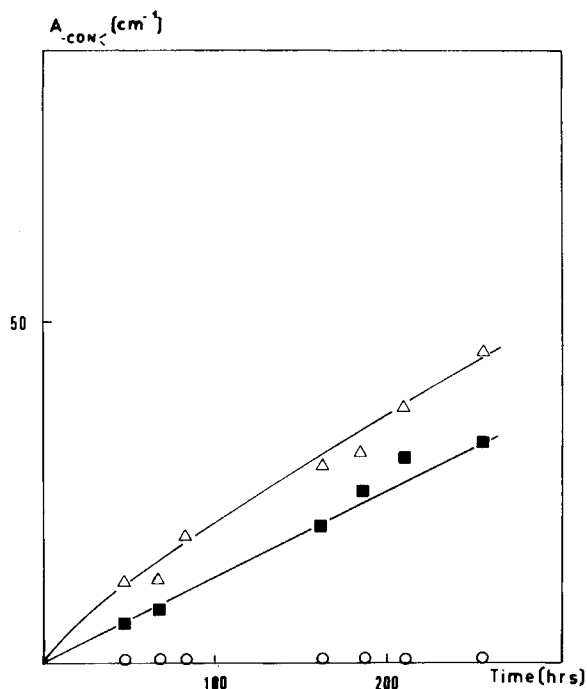


Fig. 2. Amide growth for resin A-DDM (■), resin A-DDS (○), resin A-DDE (△) systems (films of 30  $\mu\text{m}$  thickness).

## RESULTS

### Influence of Hardener Structure in DGEBA Systems

The curves of carbonyl and amide growth for films of  $30 \pm 5 \mu\text{m}$  thickness are given in Figures 1 and 2. The kinetics are more or less autoretarded as previously observed for DGEBA-DDM samples.<sup>1</sup> Concerning the initial rate (Table III), the results call for the following comments: the structural variable Z has a noticeable influence on photooxidation. We found stabilities in decreasing order: sulfone (DDS) > methylene (DDM) > ether (DDE), no amides were found in DDS samples, even after a long time of exposure. UV spectra are given in Figure 3. Before exposure, DDM has its main band (phenyl II-II\* absorption) in the medium UV range ( $\lambda < 300 \text{ nm}$ ), but its long wavelength tail continues until

TABLE III  
Initial Rates of Infrared Peak Growths (Absorbance Units-cm<sup>-1</sup> Thickness-h<sup>-1</sup>)

Sample	Carbonyls	Amides
A-DDM	0.25	0.13
A-DDS	0.13	0
A-DDE	0.30	0.26
B-DDM	0.08	0
B-DDS	0.11	0
B-DDE	0.06	0

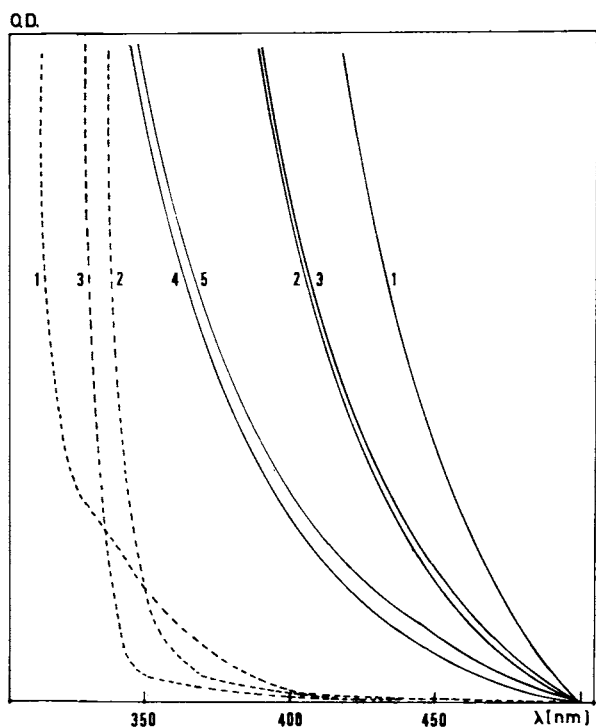


Fig. 3. Ultraviolet spectra of A-DDM (1), A-DDS (2), A-DDE (3), B-DDM (4), and B-DDS (5), before (---) and after (—) irradiation.

450–500 nm. In contrast, ether and sulfone bridges, which give a bathochromic shift of the main band (long wavelength tail at approximately 350 nm), do not display noticeable absorption continuum at higher wavelength. After exposure, we observe the formation of chromophores absorbing in the range 300–500 nm in all systems, which results in the development of a yellow-brown color except

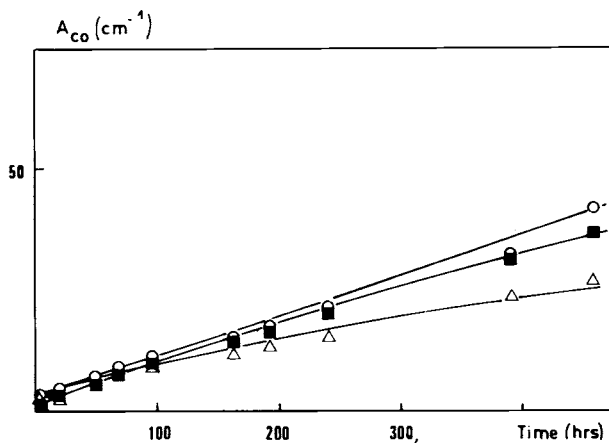


Fig. 4. Carbonyl growth for resin B-DDM (■), resin B-DDS (○), and resin B-DDE (Δ) systems.

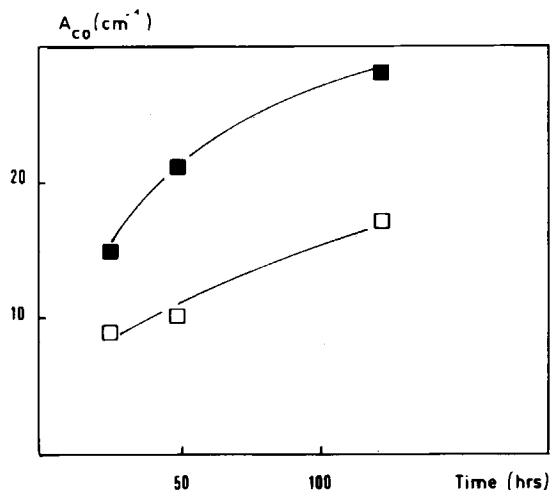


Fig. 5. Carbonyl growth for resin A-DDM (■) and resin C-DDM (□) systems (films of 25  $\mu$ m thickness).

in DDM films, in which a specific photoproduct absorbing at 615 nm is responsible for the green color.<sup>1</sup> The bathochromic and hyperchromic displacement is considerably higher for this latter system than for DDS or DDE for which it is comparable.

### Influence of the Diepoxide Length

The photooxidation of systems based on the diepoxide B is essentially characterized by the following features (Fig. 4 and Table III):

- (a) No amide is found in any system.

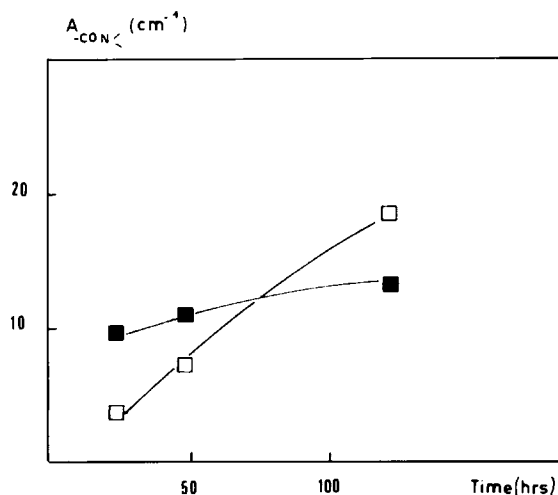


Fig. 6. Amide growth for resin A-DDM (■) and resin C-DDM (□) systems (films of 25  $\mu$ m thickness).

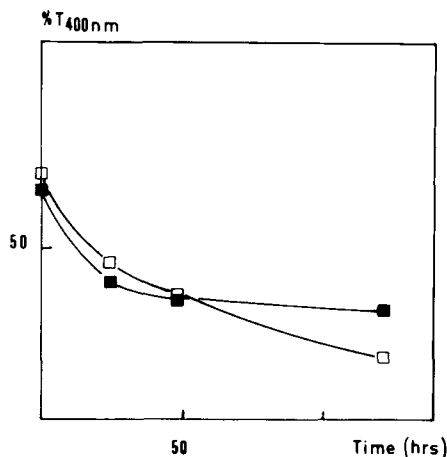


Fig. 7. Evolution of % transmittance at 400 nm vs. irradiation time for resin A-DDM (■) and resin C-DDM (□) systems.

(b) The carbonyl formation is hardly influenced by the hardener structure in contrast with the preceding results.

(c) The rate of the carbonyl buildup is lower than for samples based on the shorter diepoxide (A). However, in DDS systems, only a small difference is found.

(d) The yellowing is significantly less pronounced than for systems based on resin A (Fig. 3).

### Influence of Diepoxide Structure

The replacement of the isopropylidene unit (resin A) by a methylene (resin C) leads to the following results:

(a) The initial absorption increases, the sample C absorbs approximately 40% more of incident light than the sample A between 340 and 380 nm.

(b) Initial rates of carbonyl and amide buildup are noticeably decreased (Figs. 5 and 6, respectively).

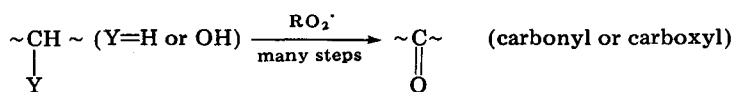
(c) The autoretardation effect is less pronounced as shown by the kinetic curves of amide formation (Fig. 6) and yellowing (Fig. 7).

## DISCUSSION

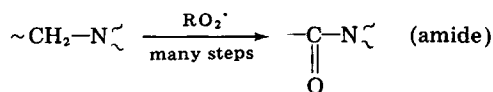
The above results can be discussed on the basis of the previously proposed mechanism,<sup>1</sup> which can be summarized as follows:

Photoinitiation:  $\text{polymer} + h\nu \rightarrow \text{R}\cdot, \text{R}\cdot + \text{O}_2 \rightarrow \text{RO}_2\cdot$

Radical propagation of chain I:



Radical propagation of chain II:



### Influence of the Hardener Bridge on Carbonyl and Amide Formation

The diamine moieties are responsible for the great majority of absorption acts in near UV (Fig. 3 and Ref. 1), so that we could expect that they play an important role in photoinitiation. The carbonyl yields in samples based on resin A seem to be the better criteria for appreciating the efficiency of the chromophores as photoinitiators, because the propagation of chain I is less influenced by the diamine structure than the propagation of chain II, in which inductive effects can modify the methylene reactivity (see below). The comparison of the data obtained in resins A and B (Table III) shows that there is little or no direct influence of the hardener structure on carbonyl formation, the initial rate  $r_{i,\text{CO}}$  remaining constant (DDS) or being divided by a factor of only 3–5 when the hardener concentration is divided by a factor of approximately 100. The photosensitivity seems therefore to be essentially due to chromophores deriving from the phenoxy part, whereas the strongly absorbing chromophores deriving from the diamine part are considerably less efficient in photoinitiation, and can play, in certain cases, a photostabilizing role.

The amide yields display more spectacular differences than carbonyl ones. In systems based on resin B, no amides are found, this is obviously due to the fact that their precursors, the amines, are in very low concentration. Thus, we find, again, a direct relationship between amide yield and initial  $\alpha$ -methylene concentration, as previously shown for DGEBA systems crosslinked by nonaromatic amines.<sup>5</sup>

In systems based on resin A, in which initial amine concentrations are similar, very strong differences in amide yields are found, the reaction rate being zero for the samples A–DDS. We can interpret this behavior in terms of the inductive effect of the bridge Z on the abstractibility of hydrogens on the  $\alpha$ -methylene group (propagation of the chain II). Two reasons speak in favor of this hypothesis:

(a) We found the same differences in amide buildup during thermal oxidation.<sup>6</sup> This is consistent with the fact that hydrogen abstraction by a peroxy radical is a rate determining process in autoxidation.<sup>7</sup>

(b) The initial rate of amide photoformation increases with the electron density at the nitrogen atom determined for the corresponding amines by quantum-mechanical calculations<sup>8</sup> (Table IV).

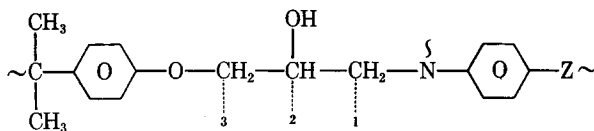
TABLE IV  
Initial Rate of Amide Growth ( $r_{i,\text{CON}}$ ) and Electron Density ( $Q_{\text{NH}_2}$ ) at the Nitrogen Atom for DGEBA Systems

	DGEBA-DDS	DGEBA-DDM	DGEBA-DDE
$r_{i,\text{CON}}$		0.13	0.26
$Q_{\text{NH}_2}$	1.683	1.859	1.882



It is well known that the amine reactivity in polycondensation essentially depends on the electronegativity of the nitrogen atom so that we can expect that the oxidative stability increases when the system becomes more difficult to crosslink.

We can now return to the problem of differences in carbonyl rates between samples based on resin A: For this system,



In our hypothesis, the carbonyl group could have at least two sources: chain I, which is common to all systems, and chain II, in which peroxy radicals formed at  $C_1$  abstract hydrogen atoms in  $C_2$  or  $C_3$ . In other words, the methylene in  $C_3$  and the sec alcohol serves as a transfer agent for chain II. The high values of carbonyl yield in systems A-DDM and A-DDE are therefore not surprising, if we consider such a mechanism.

### Influence of the Diepoxide Bridge on Carbonyl and Amide Formation

The significant difference observed between photooxidation rates of the systems based on resins A and C containing the same concentration of the same hardener (DDM) is a confirmation of the great importance of the diepoxide part in photoinitiation. Theoretically, we cannot expect any photoreactivity of the regular structural unit in the solar UV range, because the phenyl  $\Pi-\Pi^*$  absorption of nonconjugated aromatic compounds is found below 280 nm. This is confirmed by the UV spectra of the resins A and C before crosslinking (Fig. 8). The photosensitization is therefore due to impurities or structural irregularities, depending on synthesis modes and thermal history. The DGEBA

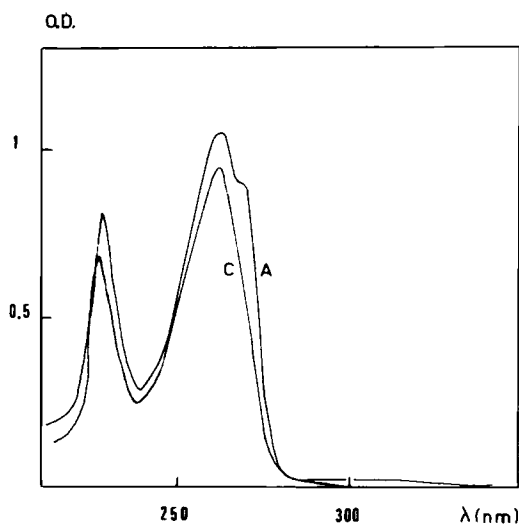


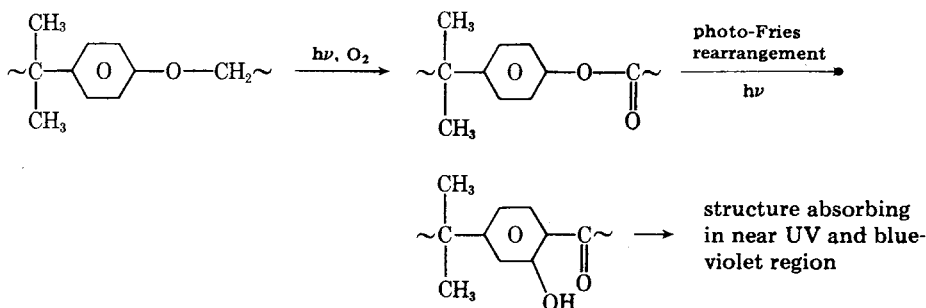
Fig. 8. UV spectra of resin A and resin C before crosslinking.

spectrum reveals, for instance, the presence of a near UV absorbing impurity (weak band between 280 and 340 nm in Fig. 8), which could be a photoreactive compound. Such small intensity bands are completely masked in cured samples by the strong absorption of the amine oxidation products so that UV spectra of films cannot give relevant information on their photosensitivities.

### Color Development

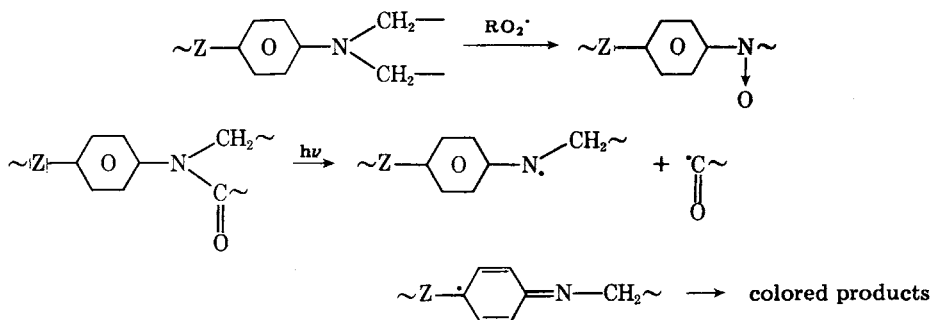
At least four kinds of chromophores can contribute to the color development during photooxidation:

(a) Products resulting from the oxidation of the phenoxy part: Their contribution is relatively small, as shown by results obtained from samples based on resin B. However, they cannot be neglected. Primary photochemical reactions are not expected in this part, in the solar UV range, so that the more probable mechanism could involve an oxidative attack of the glycidyl part:



The occurrence of a photo-Fries rearrangement is now well established in polycarbonates, which contain very similar structures.<sup>9</sup> The resulting *o*-hydroxy phenone could play a role in the autostabilizing behavior.<sup>1</sup>

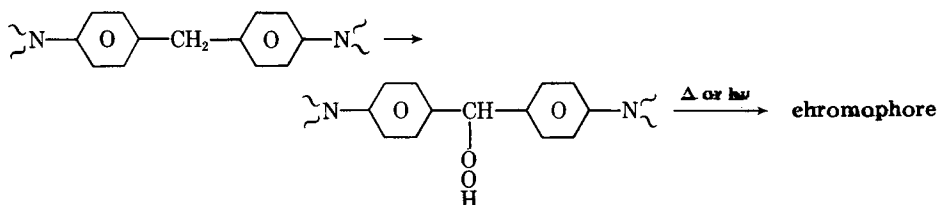
(b) Products resulting from the oxidation of the amine part, independent of diamine structure:



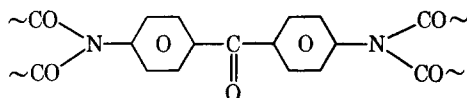
The color development in amine antioxidants containing similar structures is well known by practitioners and the mechanisms are probably very complicated.<sup>10</sup>

(c) Oxidation products depending on the hardener structure: It is interesting to consider the curing of DDM systems, which undergo the strongest yellowing among all systems under consideration, and which are characterized by the

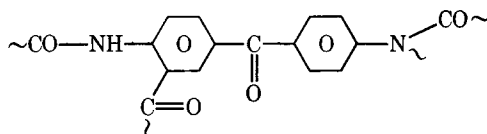
formation of a specific chromophore absorbing at 615 nm. Our previous results showed that this structure derives from the thermal decomposition of an hydroperoxide, and we proposed the following mechanism:



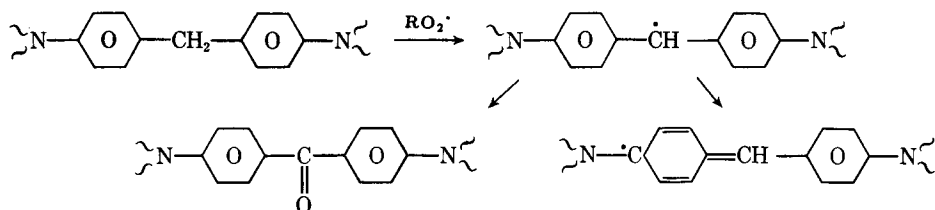
The sequence of oxidation acts could lead to highly conjugated structures such as



and probably their photoproducts deriving, for instance, from photo-Fries rearrangements<sup>11</sup>



Whichever mechanisms are operative, stronger colorations are expected with DDM than with other hardeners, because only the methylene bridge is able to undergo chemical transformation, leading to a highly conjugated structure involving the two nuclei of the hardener:



In conclusion, the photochemical behavior of amine crosslinked epoxies containing the bisphenol moiety can be summarized as follows:

(a) The main structural changes can be discussed in terms of radical oxidation initiated by photoreactions.

(b) The more important loci of photoinitiation derive probably from the phenoxy part of the polymer and could be impurities or oxidation products, initially present in the epoxy resin.

(c) The amide formation depends on initial amine concentration and nitrogen atom electron density.

(d) Color development is essentially linked to the amine structure, and the specific behavior of DDM systems can be explained by the oxidative attack of the methylene bridge, allowing the formation of highly conjugated structures.

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