ment, also results in a whitened ce. The best example is lacquer ons which before about 1948 ed for themselves a bad name be- e of their rapid gloss loss and whit-

nitrocellulose decomposition ably proceeds as follows: cellulose nitrate, in the presence of is hydrolyzed to cellulose and simultaneously oxidized to liberate cer- gases. This removal of vehicle ex- surface pigment, the resulting surface having less gloss. The NO_2 in the gases evolved, as well as atmospheric oxygen in the presence of light, is capable of oxidizing the cellulose to celluronic acid, the major solid deterioration product identified. As cellulose and celluronic acid are both somewhat water-soluble, the action of rain and dew is to further expose the surface pigment and continually renew the vehicle surface for further deterioration.

This material has been presented in the nature of a preliminary report since further work remains to be done. It is hoped that this information will be of use in the development of finishes which better resist photochemical deterioration. It is also hoped that further papers covering more details of this work will be published.

Acknowledgment:

Suggestions and contributions of members of the General Motors Research Laboratories is hereby gratefully acknowledged.

Photooxidative Degradation of Alkyd Films

By E. B. FitzGerald

The physical effects of degradation in alkyd films have been quantitatively related to the conditions and chemical mechanisms that produce them.

THE foremost objective of the present work was to develop information that would lead to the synthesis of more durable alkyd resins. As a second objective it was expected that methods of measurement and testing would be developed that could be used to estimate the durability of new polymers and finishes in shorter time and more reliably than any of the presently available methods.

The investigation started with a qualitative examination of the gross physical effects that result from exposure of a protective coating to outdoor weather or, in general, to photooxidative conditions. It proceeded with an attempt to measure these effects quantitatively in relation to the conditions that produce them. Finally, an effort was made to establish some of the chemical mechanisms that are involved. The results, which follow, will be presented in this same general order.

Materials and Methods

The resin used in most of the work was a typical automotive alkyd of 50 per cent oil length (6 parts linseed to 1 part tung oil) and an acid number of 18. When used with no modification other than a common drier, this will be referred to as "clear alkyd." Pigment was used in some of the experiments and will be specified where it occurs. Films were also prepared from fatty-acid esters of glycerol and pentaerythritol. These were obtained from the Hormel Institute as part of a cooperative research program sponsored by the Paint and Varnish Production Clubs. Their synthesis has been reported elsewhere (1).[1] Other materials will be described where they occur.

Films were sprayed or doctor bladed on glass slides or steel panels using a solution of the resin in hydrocarbon solvent. Unless otherwise designated, all films were baked at 125 C for 20 min and stored for one month before use. Free films for measurement of mechanical properties were prepared by spraying and baking the clear alkyd on steel panels coated with polytetrafluoroethylene. The films were then lifted from the panels, cut to required dimensions, and stored for one month prior to use.

Four light sources were employed in the work: (1) a 125-w Hanovia quartz mercury vapor lamp; (2) a 360-w Uviarc quartz mercury lamp; (3) a Westinghouse 40-w fluorescent ultraviolet lamp, and (4) a 1000-w water-cooled General Electric AH-6 lamp with Pyrex jacket. The spectral energy distributions from these sources were measured with a quartz monochrometer-thermopile-amplifier arrangement and will be specified where pertinent. Whenever filters were used in combination with one of these sources, their absorption spectra were measured, and the spectral distributions of light actually reaching the specimens were calculated.

Results and Discussion

Gloss Loss.—Deterioration of a finish which is exposed to natural weather can manifest itself in various ways. Cracking, blistering, and peeling, for example, are important aspects of the problem, but in the present work, major attention has been given to the phenomena that result in disappearance of the lustrous surface which characterizes an unexposed finish. An electron microscope view of this effect, popularly known as gloss loss or, in advanced stages, as chalking, is shown in Figs. 1 and 2.

From simple, qualitative observation, it has been concluded that the loss of gloss is concomitant with the appearance of pigment at the surface. This conclusion is borne out by electron diffraction studies of pigmented enamels at various stages of weathering. Thus, a fresh, high gloss surface—shown in Fig. 1—shows no evidence of pigment under electron diffraction, while a chalked surface—shown in Fig. 2—gives a clear, strong pattern characteristic of the pigment. Examination at intermediate stages of weathering has shown that the first perceptible appearance of a pig-

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[1] The boldface numbers in parentheses refer to the list of references appended to this paper.

Fig. 1.—Electronmicrograph of Pigmented Alkyd Film Before Exposure.

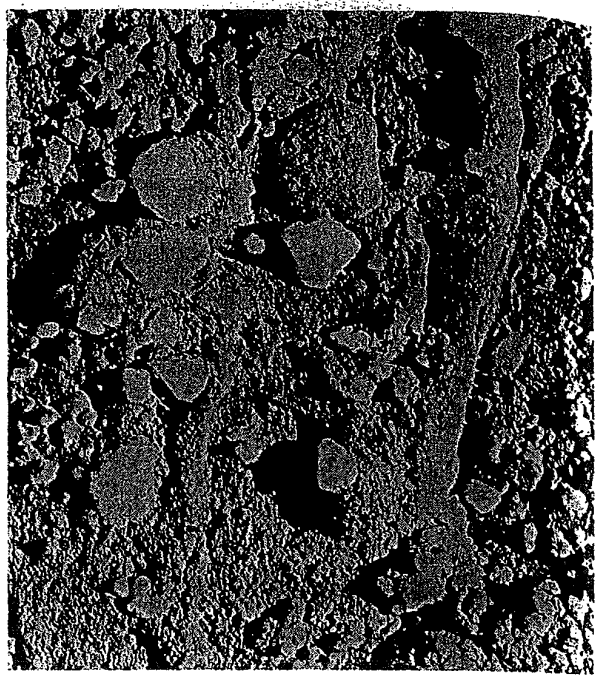


Fig. 2.—Electronmicrograph of Pigmented Alkyd Film After 3 Months in Florida.

ment diffraction pattern occurs before any change can be detected by the unaided eye. These patterns appear at about the same time standard reflection instruments are showing the first perceptible loss in gloss and also about simultaneously with the first appearance of the protrusions seen in the electronmicrograph.

Effect of Light Intensity.—Experience has shown that exposure to light is a necessary condition for the degradation processes that lead to loss of gloss and chalking. Since this clearly implies a photochemical process, it becomes of interest to examine the relationship between the rate of gloss loss and light intensity. A schematic diagram of an experimental arrangement to determine this relationship is shown in Fig. 3. The specimens consisted of 4 by 3-in. steel panels coated with the standard alkyd resin containing 20 per cent rutile pigment by volume. A set of four panels could be exposed simultaneously to radiation from a Uviarc lamp at well-separated levels of intensity; intensity at each level was established by prior measurement using a calibrated photocell device. Water at 25 C was circulated over the panels, since no other way of maintaining a known and constant temperature at the panel surfaces could be devised. Light reflection at the air-water interface was calculated from the Fresnell equation and appropriate corrections were applied. Constancy of lamp performance throughout the experiment was determined by periodic photocell measurements.

The panels were taken from the water periodically and gloss was measured using the du Pont Universal Gloss Meter (2). Results, averaged from several experiments, are shown in Fig. 4. Taking the reciprocals of the times required to reach various levels of gloss loss, it was found that the average rates so obtained were well represented by Eq 1, where R represents gloss units per hour, E is relative incident light intensity and k is a constant. This is shown in Fig. 5.

$$R = kE^{0.83} \quad \ldots\ldots\ldots\ldots (1)$$

It will be shown later that this relationship with light intensity is identical to

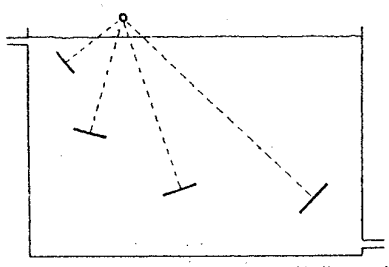


Fig. 3.—Schematic Diagram of Apparatus for Exposing Films to Various Light Intensities.

that obtained for the rate of evolution of volatile decomposition products.

Effect of Wavelength.—Investigation of the relationship between wavelength and degradation is much more difficult than the intensity effect. In the present work, test panels, coated with the same enamel that was used in the intensity measurements, were exposed under various filters to the radiation of a Hanovia lamp. Exposures were carried out, under dry, open air conditions, simultaneously and at uniform distance from the lamp by use of a turntable arrangement. Under these conditions the panels maintained a uniform temperature of about 40 C. Relative values of the light distribution incident upon each panel (Table I), were calculated from the measured output of the lamp and the transmission characteristics of the filters. It was found that spectral output of the lamp changed throughout its lifetime, and the only remedy found for this was to replace the bulb at intervals during the experiment.

Gloss loss of the panels, measured periodically, is shown in Fig. 6. In an effort to unify and correlate these results in the simplest possible manner, it was assumed that if the average rate of gloss loss up to 20 units of loss were to be taken from Fig. 6, then Eq 1 would still hold and the relation including wavelength λ might be represented by some function of $E_\lambda{}^{0.8}/\lambda^n$ summed over

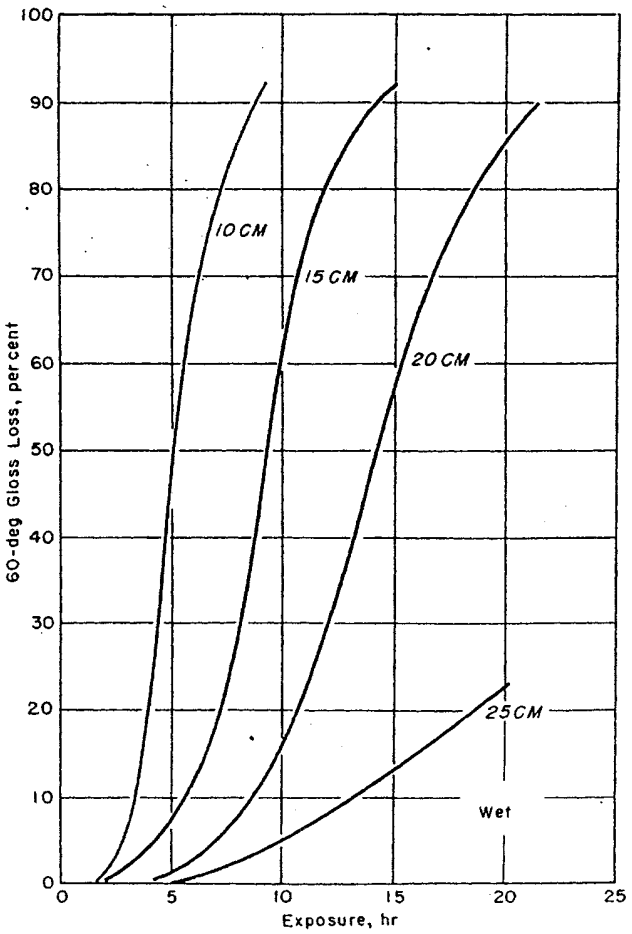


Fig. 4.—Gloss Loss Found at Various Light Intensities.

all wavelengths given in Table I. Accordingly, Eq 2 in which A and B are constants, was found to be in approximate agreement with the data, as shown in Fig. 7.

$$R_{avg} \simeq A \left[\Sigma \frac{E\lambda^{0.8}}{\lambda^4}\right] + B\left[\Sigma \frac{E\lambda^{0.8}}{\lambda^4}\right]^2 \quad \ldots\ldots(2)$$

Equation 2 represents merely an attempt to express empirically the relationship between gloss loss and wavelength. It is nevertheless instructive to compare this equation with one derived for the ultraviolet transmission on a clear film of the same resin. The specific extinction, k, of the clear alkyd is shown in Fig. 8, together with a plot of the relation:

$$k = \frac{1}{d} \log \frac{I_0}{I} = \frac{C}{\lambda^4} + \frac{D}{\lambda^8} \quad \ldots\ldots(3)$$

where d is film thickness and C and D are constants.

Although there appears to be some deviation from Eq 3 in the region of shorter wavelengths, the agreement throughout most of the range is quite reasonable and suggests that the average rate of gloss loss (up to 20 units loss) in monochromatic light is proportional to the specific extinction. This conclusion may be applicable to films other than alkyds, for it is in general agreement with the results given by Long (3), who found that the durability of a variety of films could be correlated with the area under a transmission curve between 3000 and 4000 Å. Exceptions would be found in the case of materials containing structures of very low light transmission and very high resistance to photolysis.

Surface Erosion.—Up to this point, no attempt has been made to define the means by which the chemical processes of photolysis result in the geometrical effects of surface roughness and eventual appearance of pigment particles. It has been implied, however, that matter is being lost by the film through photo-initiated scission reactions that lead ultimately to volatile decomposition products. It would appear simple to detect loss of material as loss in weight, but experiments have shown that, under certain circumstances the weight loss incurred up to the point of chalking may be too slight to measure accurately. For example, if it is assumed that a measurable amount of gloss loss or chalking would be produced by loss through volatilization of the uppermost 0.05 μ of the organic film material, the corresponding weight loss for a reaction confined strictly to the surface, would be 0.2 per cent in a 1-mil film. By the use of interferometry, the disappearance of such small amounts of material can be determined more conveniently and accurately than they can by weighing.

The interferometric method can be applied very simply. In the present work a sharp line of demarcation between an exposed and unexposed film area was produced by laying a double-edged razor blade on the film and positioning an ultraviolet lamp vertically above it. Upon exposure, the unpro-

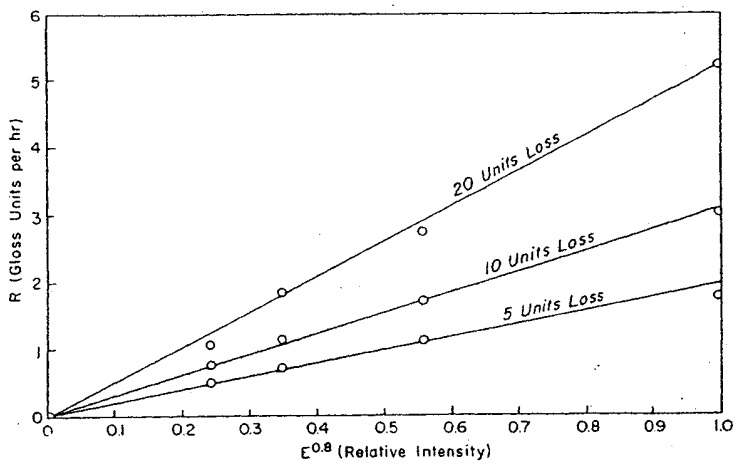


Fig. 5.—Relationship Between Rate of Gloss Loss and Incident Light Intensity.

TABLE I.—RELATIVE ENERGY DISTRIBUTIONS FROM HANOVIA LAMP WITH VARIOUS CORNING FILTERS.

Wavelength, mμ	No Filter	Filter No. 791	Filter No. 986	Filter No. 970	Filter No. 774	Filter No. 733
205	0.15	...	...	...	...	...
215	0.45	0.05	...	...	...	...
225	1.00	0.22	...	...	...	...
235	1.70	0.82	...	...	...	...
245	2.45	1.62	...	...	...	...
255	4.70	3.57	0.15	0.05	...	...
265	5.75	4.77	0.75	0.29	...	...
275	2.40	2.09	0.70	0.38	...	...
285	2.05	1.85	0.98	0.72	...	...
295	5.60	5.10	3.41	3.25	0.22	...
305	7.70	7.10	5.54	5.77	0.84	...
315	9.70	9.04	7.46	8.05	2.32	...
325	0.30	0.28	0.23	0.27	0.12	...
335	1.50	1.39	1.18	1.37	0.79	...
345	0.15	0.14	0.12	0.14	0.10	0.02
355	0.30	0.28	0.23	0.28	0.24	0.20
365	18.60	17.30	14.00	17.10	14.90	12.10
375	0.46	0.43	0.29	0.43	0.38	0.38
390	0.20	0.18	0.07	0.20	0.18	0.18
405	4.30	4.00	...	3.96	3.90	3.90
420	0.20	0.18	...	0.18	0.18	0.18
435	7.05	7.55	...	6.50	7.41	6.41
495	0.25	0.23	...	0.23	0.23	0.23
545	5.12	4.76	...	4.72	4.65	4.65
560	0.15	0.14	...	0.14	0.14	0.14
575	4.00	3.72	...	3.68	3.64	3.64
585 and up	1.30	1.21	...	1.20	1.18	1.18

tected film decreased in thickness relative to the protected part and a step was formed at the boundary; the height of the step was then measured by means of a Tolansky microinterferometer (4, 5, 6). Figure 9 shows typical fringe shifts obtained with the clear alkyd upon exposure to the unfiltered Hanovia lamp and Fig. 10 gives the result of a series of such measurements plotted against time.

When measurements of this type were carried out on the standard alkyd pigmented with 25 per cent rutile and compared with gloss measurements, it was found that the relationship between decrease in thickness and gloss loss depended upon the wavelength distribution of the light source used for the exposure.

With direct radiation from the Hanovia or Uviarc lamps, the ratio of thickness decrease to gloss loss was smaller than that obtained when the light from these lamps was filtered by a glass, such as Corning No. 970 (Table I), although in the latter case the change took place much more slowly. Decrease in thickness can, of course, result from increase in density, and measurements on the clear alkyd after very drastic exposure indicated that shrinkage up to 3 per cent can be accounted for in this way. It follows that thickness decreases of the magnitude shown in Figs. 9 and 10 could be attributed entirely to change in density unless this change were measured and shown to be negligible or unless the initial film thickness was so small that the decreases upon exposure exceeded the maximum attributable to density effects.

Both of these procedures were applied in the present work and decrease in thickness due to net loss of material was demonstrated. It was concluded that gloss loss and chalking of a pigmented

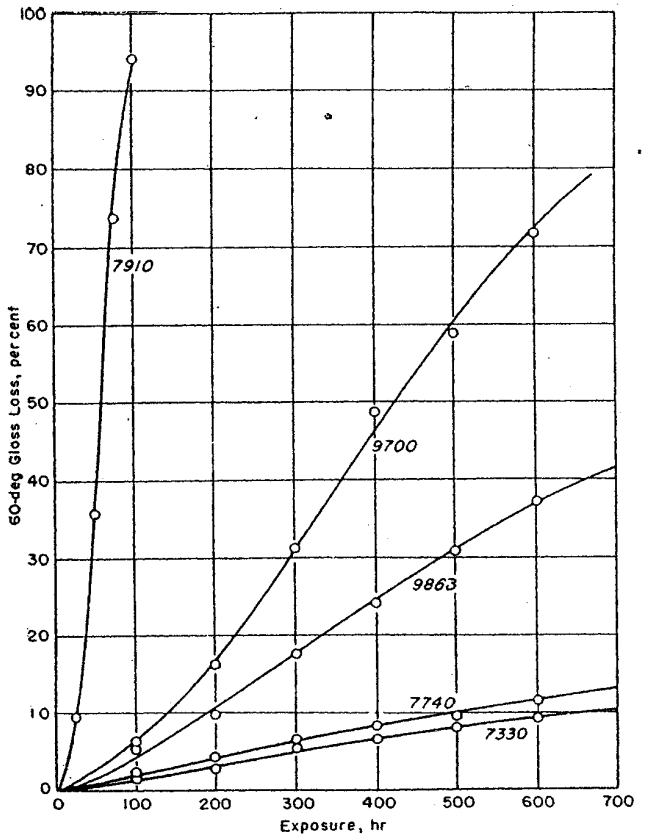


Fig. 6.—Gloss Loss Found with Various Light Distributions.

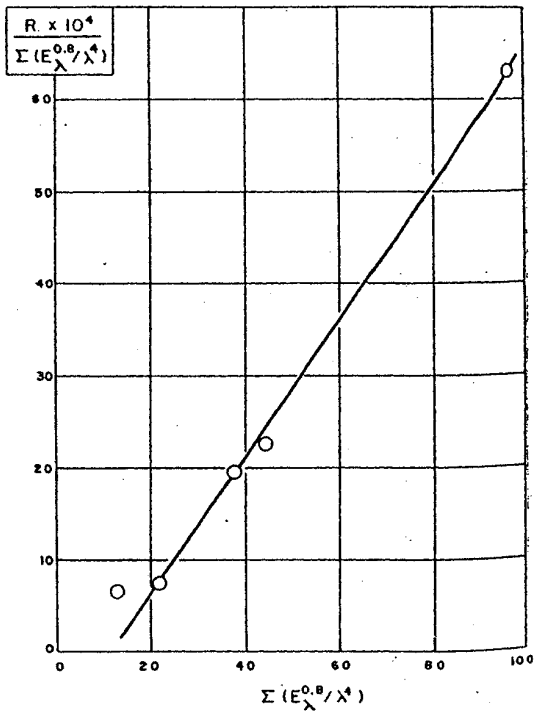


Fig. 7.—Relationship Between Rate of Gloss Loss and Incident Light Distribution.

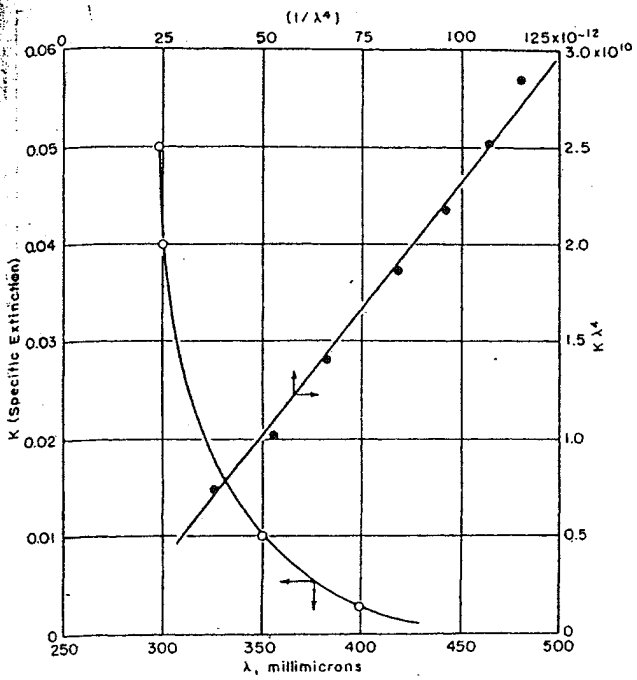


Fig. 8.—Specific Extinction of Alkyd Film.

alkyd result when a sufficient depth of binder has been eroded from the surface by conversion to volatile products. Radiation from the unfiltered Hanovia lamp attacks the surface so rapidly that chalking becomes evident before the bulk of the film has had time to undergo severe degradation. With the filtered Hanovia lamp, attack is slower and, despite the shielding effect of pigment, the radiation penetrates the film sufficiently to cause degradation and loss of volatile products from beneath the surface. Thus, for equal extents of gloss loss, the film exposed to the filtered lamp will have lost more matter in the form of volatiles. The same situation with regard to loss of volatiles obtains for clear film, but the effects penetrate deeper and, although the surface is roughened, true chalking cannot occur.

Analysis of the Film.—The most direct and obvious way of getting information about the chemical nature of degradation is through analysis of the film before and after exposure to photooxidative conditions. No single method is capable of yielding all the necessary information and consequently several techniques were used in this work. One of the most outstanding characteristics of baked alkyd films—their insolubility in all but the most drastic solvents—not only guided the selection of techniques but limited the effectiveness of some that were attempted.

Infrared spectroscopy proved to be one of the most generally informative analytical methods. Films of clear alkyd were cast and baked on rock salt;

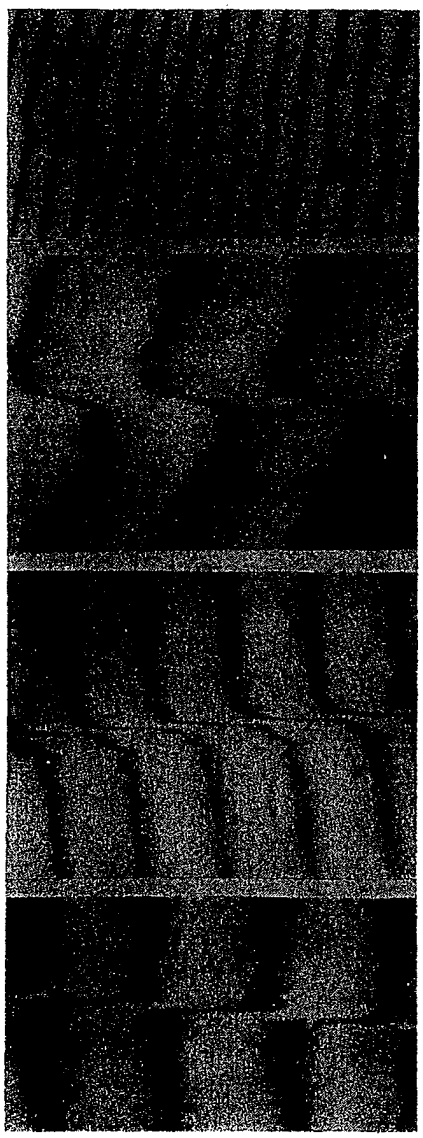


Fig. 9.—Interference Fringe Shifts Produced by Exposure.

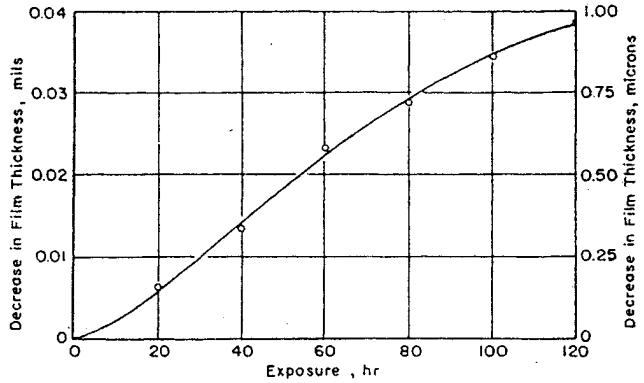


Fig. 10.—Decrease in Film Thickness Resulting from Exposure.

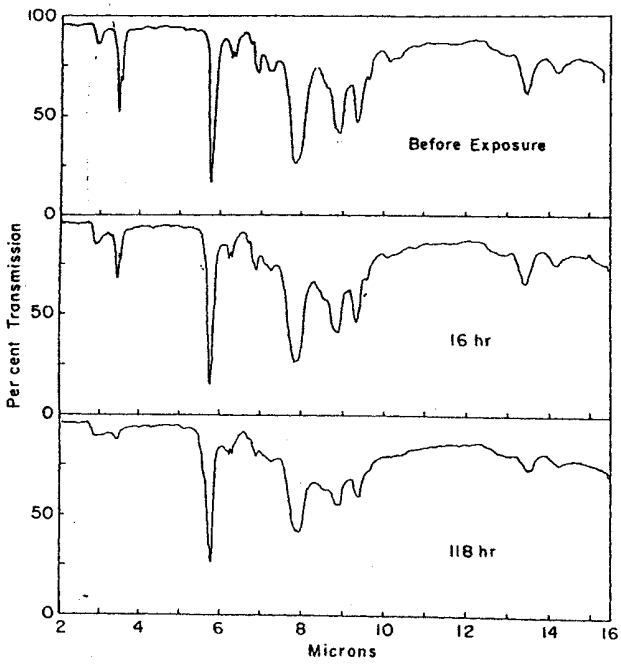


Fig. 11.—Infrared Spectra of Films Before and After Exposure.

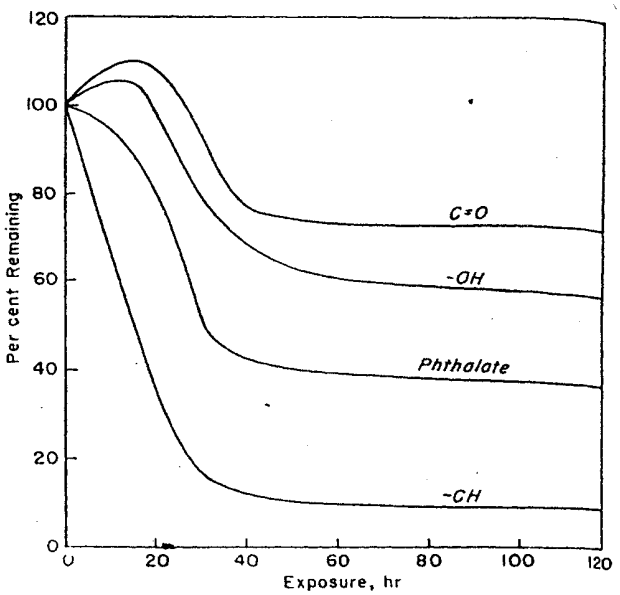


Fig. 12.—Changes in Functional Group Concentrations Resulting from Exposure.

spectra were taken before exposure to photooxidative conditions and at various periods throughout exposure. For the purposes of the present work, only a few of the absorption maxima appearing in the unexposed film (top of Fig. 11) need be identified. The bands at 2.9, 3.4, and 5.8 μ represent hydroxyl groups, aliphatic carbon-hydrogen bonds, and carbonyl groups respectively. The doublet at 6.3 and the bands at 8.9, 9.3, 13.5, and 14.2 μ are characteristic of phthalate esters. The bands at 6.9 and 7.2 are due to $-CH_2-$ and $-CH_3$ respectively, while the deep band at 7.8 arises from carbon-oxygen-carbon links of the ester. There was no evidence of olefinic unsaturation in any of the spectra. The weak bands found from 10 to 10.5 μ also occurred in alkyds modified with pure stearic acid and therefore cannot be attributed to unsaturation.

The changes in composition that were produced by exposure depended upon the nature of the irradiating source, as might have been expected from the work on gloss loss and erosion. Certain qualitative similarities were observed, however, and a typical example produced by exposure to the General Electric AH-6 lamp (intense radiation above 3000 Å) may be seen in the spectra of Fig. 11. Major structural changes evident in these spectra are analyzed quantitatively in Fig. 12. Here, the immediate and rapid decrease in aliphatic carbon-hydrogen content must be attributed to replacement of drying oil hydrogen atoms by hydroxyl, hydroperoxide and carbonyl groups. As the degradation proceeds, and the carbon-hydrogen links become fewer, the rate of decomposition of the new oxygenated groups exceeds the rate of formation and their concentration decreases. Finally, when the carbon-hydrogen content has diminished to about 10 per cent of its original value, the film becomes much more stable.

Formation of oxygenated structures can, of course, take place at sites of original unsaturation in the oil as in reactions I to IV (7):

$$-CH_2CH{=}CH- \xrightarrow{O_2} -CH(OOH)CH{=}CH- \quad \ldots(I)$$

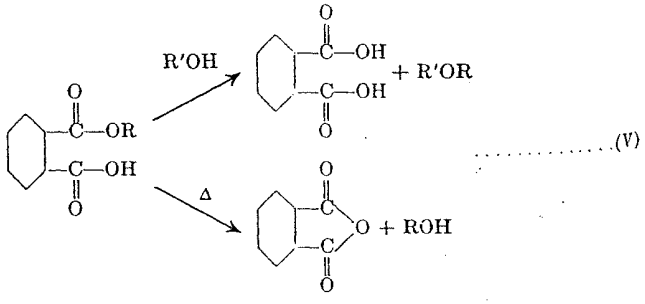
$$-CH(OOH)CH{=}CH- \xrightarrow{-H_2O} -COCH{=}CH- \quad \ldots(II)$$

$$-CH(OOH)CH{=}CH- \rightarrow -CHOH-\underset{\displaystyle O}{CH-CH}- \rightarrow -CHOH\,CO\,CH_2- \quad \ldots(III)$$

$$-CH(OOH)CH{=}CH- \rightarrow -CHO + -CH_2CHO \quad \ldots(IV)$$

Oxidation occurring only at sites of original unsaturation cannot, however, account for the gross changes that are observed. Even if reactions such as III and IV have not eliminated unsaturation during the bake, the decrease in carbon-hydrogen is so extensive that random or repetitive degradation processes capable eventually of attacking any or all of the oil hydrogens must be postulated. This does not imply that the degradation is unrelated to the original unsaturation for, in fact, an alkyd synthetized from pure stearic acid showed practically no change in composition, even after prolonged exposure. Degradation of a drying oil alkyd apparently starts during the bake with the formation of hydroxyls, hydroperoxides, and polyketones at the sites of original unsaturation. Exposure to light results in photolysis of these groups followed by complex oxidation mechanisms in which similar groups are generated and subsequently photolyzed along the remainder of the oil molecule.

During the period of rapid carbon-hydrogen disappearance, the spectra also show a slower decrease in phthalate content of the film. Appearance of phthalic anhydride at the surface of alkyd films or, for that matter, in unopened cans, has been noted under certain circumstances and has been attributed to reactions such as V:



.....(V)

In the present work, evidence in favor of photooxidative loss of phthalate was found in several ways: films exposed to varying degrees of degradation, as indicated by weight losses up to 25 per cent, were analyzed chemically for phthalate ester content using the method of Shreve and Heether (8). In every case, the oxidized film contained the same weight per cent phthalate (within the limits of experimental accuracy) as the original resin. Also, exposures to the direct radiation of a Hanovia lamp were made on films prepared from an alkyd analogous to the standard clear resin, but possessing carbon-14 in the phthalate carboxyl position. Complete elementary analyses were made on these films, and CO_2 obtained from combustion was precipitated as barium carbonate and analyzed. Results of this work (Table II), indicate a small preferential loss of phthalate. It is also apparent that loss of hydrogen during exposure to the Hanovia lamp was accompanied by loss of carbon in nearly the same atomic ratio as existed in the original film. In the dark, however, hydrogen was lost relatively faster than carbon.

It is concluded that oxidation whether photo or thermal initiated, begins in the oil part of the molecule and spreads to the glyceryl and phthalate ester structures such that, on the average, complete alkyd monomeric units are disappearing together. This suggests that phthalate content of the oxidized film may be applied to the infrared analyses as an approximate internal standard. Consequently, replotting the data of Fig. 12 relative to phthalate content should give an indication of the changes in functional group concentrations corrected for decrease in film thickness (Fig. 13).

As mentioned earlier, chemical analysis of the film is greatly handicapped by its insolubility; however, chromatographic analyses of benzene-alcohol extracts of exposed film did reveal the presence of diketones and quinones. Attempts to estimate ethylenic unsaturation by hydrogenation and other means gave erratic results. Qualitative tests, however, were most instructive. For example, films partly exposed to the Hanovia lamp and partly protected, would, upon immersion in aqueous potassium permanganate, acquire a layer of manganese dioxide upon the exposed area, while the unexposed area remained clean. Similarly exposed films immersed briefly in aqueous iodine-potassium iodide and then in a starch solution turned blue on the unexposed area, while the exposed area remained colorless. One possible explanation for the formation of unsaturation during photolysis will be offered in the next section.

TABLE II.—ELEMENTARY ANALYSIS AND RADIOASSAY OF CARBOXYL-TAGGED ALKYD FILMS.

Exposure	Carbon, per cent	Hydrogen, per cent	Oxygen, per cent	Ratio, Hydrogen to Carbon	Relative Activity per Weight Carbon
None	64.00	7.28	28.72	1.37	100
72 hr direct Hanovia ultraviolet	63.75	7.32	28.93	1.37	94.4
72 hr at 120 C in dark	62.76	6.70	30.54	1.28	95.2

Analysis of Volatile Products.—Gravimetric analyses of volatile products were carried out using apparatus similar to that ordinarily employed for semimicro elementary analysis; details and procedure have already been published (4). Alkyd films of known area and weight were placed in a quartz tube and exposed to filtered or unfiltered radiation from a Hanovia lamp in a gentle stream of oxygen or purified nitrogen. The effluent gases were converted to carbon dioxide and water, caught in absorption tubes, and weighed daily for ten days.

One of the most significant conclusions of this work resulted from comparison of the hydrogen-carbon atomic ratio in the off-gases to that in the parent material. When films were exposed to the unfiltered radiation of the Hanovia lamp in oxygen, the hydrogen-carbon ratio in the gases was approximately 2.5 (compared to 1.35 in the film), while use of filtered radiation (Corning No. 970) gave ratios that ranged from 5 to 7, although, of course, the gases were evolved much more slowly. The lower ratios produced by the unfiltered radiation are in agreement with the conclusions obtained from interferometry to the effect that short wavelengths result in total removal of organic material from the film surface. High hydrogen-carbon ratios produced by filtered radiation confirm the infrared and elementary analyses quoted previously by demonstrating that dehydrogenation is one of the important initial effects of photolysis in the bulk of the film.

Another significant result of the gravimetric work was realized by plotting the total weight of gases evolved in a given period of time *versus* the weight of resin per unit area. Such a plot is shown in Fig. 14, which is a composite of results obtained with various light sources. It is important to note, also, that when plotted in this way, data for pigmented and clear films fell on the same lines. The dotted line in Fig. 14 represents the quantity of gases that would be evolved upon total combustion of the film to carbon dioxide and water. Thus, the graph indicates that clear films thinner than about 0.3 mg per sq cm disappear completely in 100 hr of exposure to the unfiltered Hanovia, while with pigmented films, only the pigment remains. Similarly, it is concluded that a thicker film exposed to the unfiltered Hanovia for the same period of time loses approximately 0.3 mg per sq cm from its surface and, in addition, loses material in

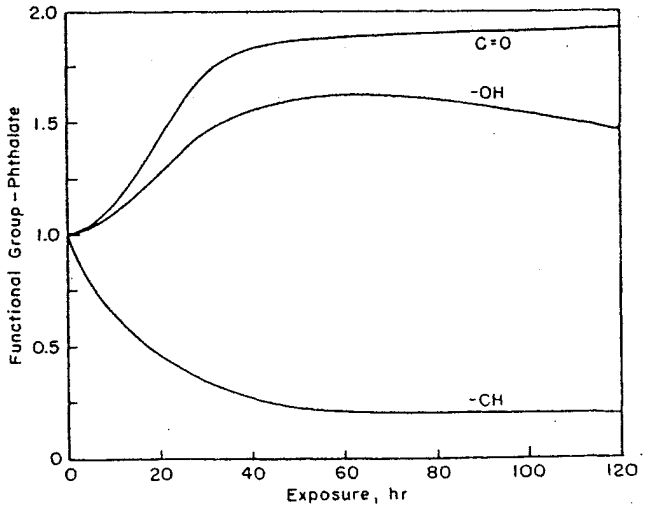


Fig. 13.—Changes in Functional Group Concentrations Relative to Phthalate Content.

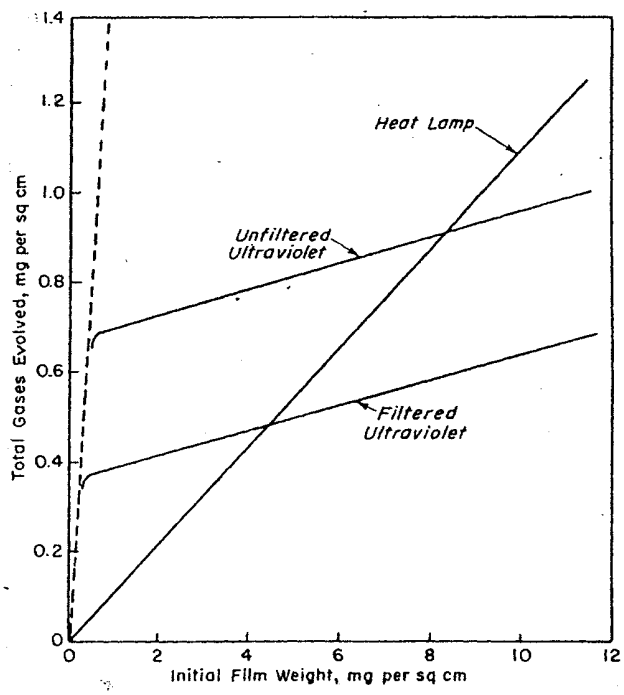


Fig. 14.—Gases Evolved from Alkyd Films During 100 Hr of Exposure to Various Light Sources.

the form of volatiles from beneath its surface.

Figure 14 also shows that a film exposed to radiation from which some of the short wavelengths have been filtered loses a smaller amount of material from its surface, while the loss from beneath the surface is the same as that experienced by a film of identical thickness exposed to the total radiation. Finally, films exposed to a lamp producing intense radiation in the visible and infrared but probably nothing less than 4000 Å evolve volatile degradation products in a manner characteristic of a simple bulk reaction.

The amount of chalking produced from these three exposure conditions was in agreement with that found in the studies of the wavelength effect; films exposed to the unfiltered Hanovia chalked severely in 100 hr, while those exposed to the filtered Hanovia chalked slightly and those exposed to the heat lamp gave no detectable loss in gloss. Changes in thickness calculated from Fig. 14 agreed satisfactorily with results obtained by interferometry.

A quite different and, in certain respects, more informative means of studying volatile products was accomplished by the use of the infrared spectrograph. Exposure cells were constructed from 10-cm lengths of 5-cm (outside diameter) borosilicate glass tubing equipped with side arms and stopcocks; rock salt windows were cemented to the ends. Films coated on microscope slides were placed inside the cells, where they could be exposed to radiation from a Westinghouse fluorescent ultraviolet lamp through the cell wall without obstructing the infrared beam used for analysis.

A typical result obtained in these experiments is shown in the spectrum (Fig. 15) of gases produced by a dry film of pentaerythritol eleostearate after 5 days' exposure in an oxygen atmosphere. The relationship between light intensity and rate of gas evolution was determined by placing the cells at various distances from the light source, where the relative intensities were measured by a photocell, as in the chalking experiments. The optical density of the carbon dioxide absorption band was determined periodically and converted to pressure by calibration. Rate calculations from these data gave the same functional relationship to intensity (Eq 1) that was obtained for the rate of chalking.

The effect of wavelength distribution was studied by placing filters over the cells; output of the lamp and transmission of the filters are given in Fig. 16.

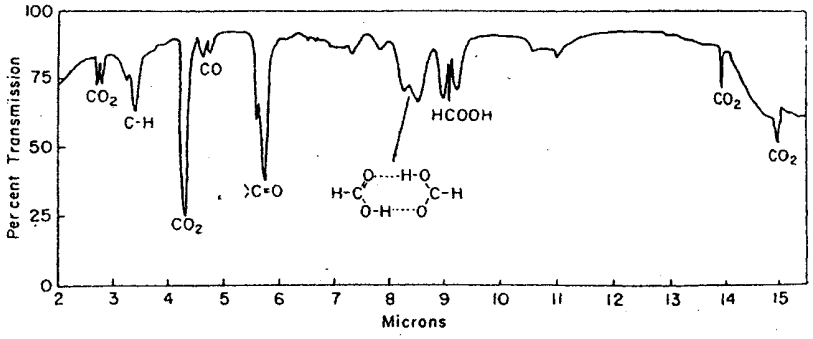


Fig. 15.—Infrared Spectrum of Gases Evolved from Dried Film of Pentaerythritol Eleostearate Upon Exposure to Light.

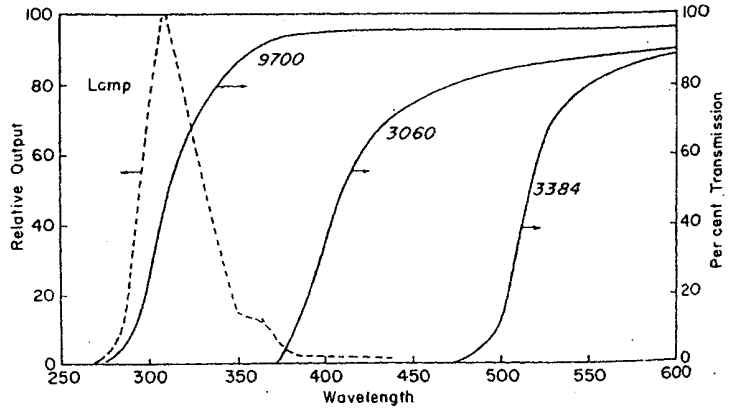


Fig. 16.—Characteristics of Westinghouse Ultraviolet Fluorescent Lamp and Filters Used in Gas Evolution Experiments.

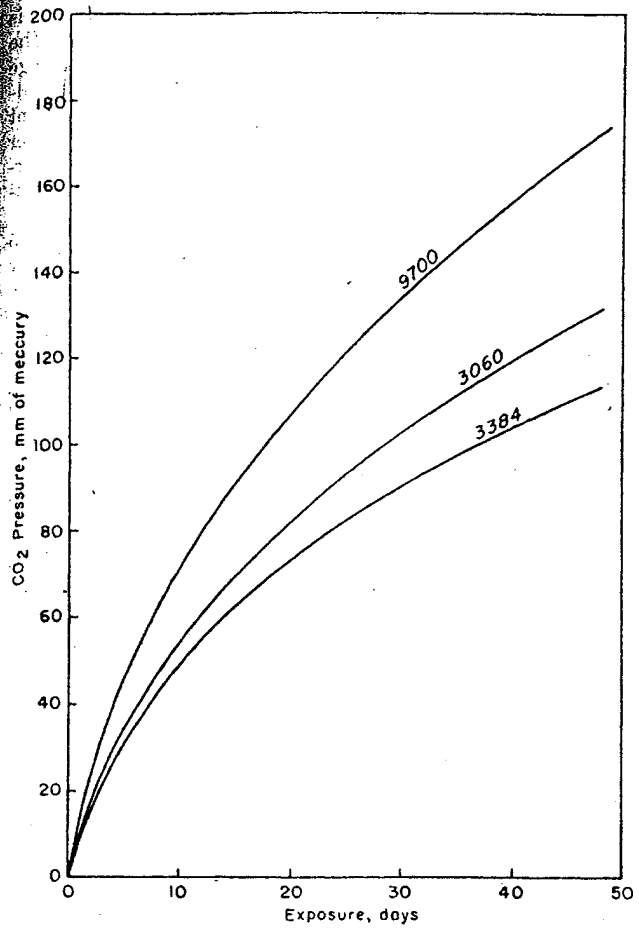


Fig. 17.—Carbon Dioxide Evolution from Dried Film of Pentaerythritol Eleostearate Upon Exposure to Various Light Distributions.

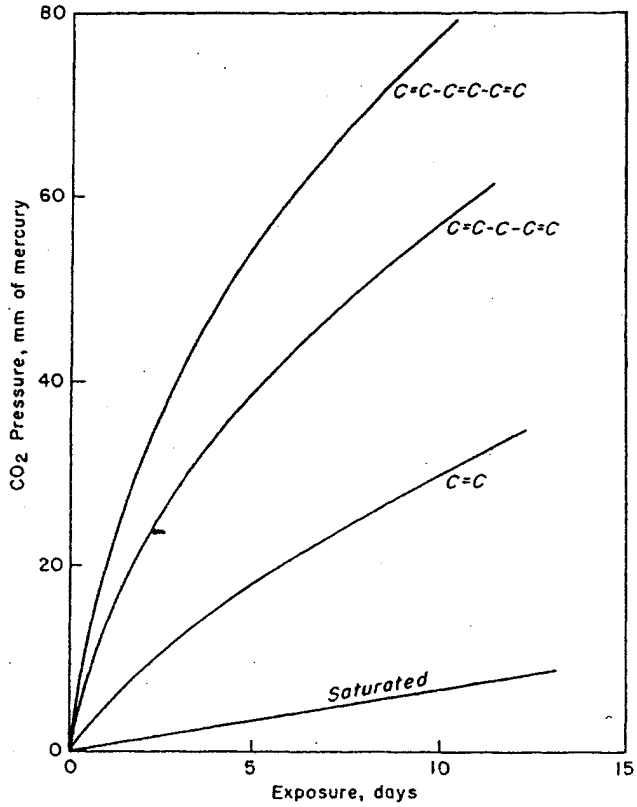


Fig. 18.—Carbon Dioxide Evolution from Dried Films of Drying Oil Esters Upon Exposure to Light.

Results for dried films of clear pentaerythritol eleostearate are given in Fig. 17, which clearly shows the somewhat surprising importance of the reactions due to longer wavelengths. Qualitatively it would appear from Figs. 16 and 17 that the rate of gas evolution from clear films is less dependent upon wavelength than is the rate of chalking in pigmented films. Intuitively, it might be supposed that longer wavelengths are just as effective as the shorter ones in producing volatile products but that their effect is distributed through a greater depth of film. Additional work will be needed to clarify this point and, in particular, the modification that is to be expected from the presence of pigment.

In view of the complexity of alkyd resin films, it is difficult to draw detailed inferences regarding the mechanism of deterioration from experiments on the films themselves. The use of compounds that can serve as models for the various structures present in alkyds provides a means of overcoming this difficulty. For example, it was shown earlier that baked films contain little unsaturation and it was suggested that initial attack by light consists of photolysis of ketones formed during the bake. Further evidence in support of this view was sought by infrared analysis of the volatile degradation products arising from various model compounds during exposure.

Air-dried films of pentaerythritol esters of eleostearic, linolenic, linoleic, oleic, and stearic acids were exposed in the infrared gas cells with an oxygen atmosphere. Area and thickness of the films, distance from the Westinghouse fluorescent lamp, and all other exposure conditions were held constant. Carbon dioxide, carbon monoxide, formic acid, and water were found in every case, and no other products were detected. Also, the relative amounts of the various gases were approximately the same for all the films, but the rates of evolution depended upon the amount of unsaturation originally present in the ester, as shown by the data for the carbon dioxide absorption bands in Fig. 18. When the films were baked prior to exposure, the data corresponding to Fig. 18 were compressed downward (except for the saturated ester which remained constant), but the same relationship between the rates was maintained.

If gas evolution is, in fact, a result of ketone photolysis, then the reaction should proceed—or at least commence—in the absence of oxygen. In order to test this point, two identical dried films of pentaerythritol eleostearate were exposed to the Westinghouse lamp in the infrared cells. One cell was filled with oxygen and the other with nitrogen; both cells were evacuated and refilled with their respective initial atmospheres at approximately two-week intervals, while their contents—between intervals—were monitored by infrared. The results (shown in Fig. 19) suggest that two reactions are involved: (*a*) photolysis of existing oxygenated groups and (*b*) oxidation of residual unsaturation or of unsaturation and free radicals created by the photolysis. Both reactions stopped immediately (so far as could be detected) upon removing the cells from the light.

Exposures of stearic and sorbic acids were carried out as thin layers of powder in the oxygen-filled gas cells. Here, the sorbic acid decomposed rapidly to give carbon dioxide, carbon monoxide, water, formic acid, and acetic acid.

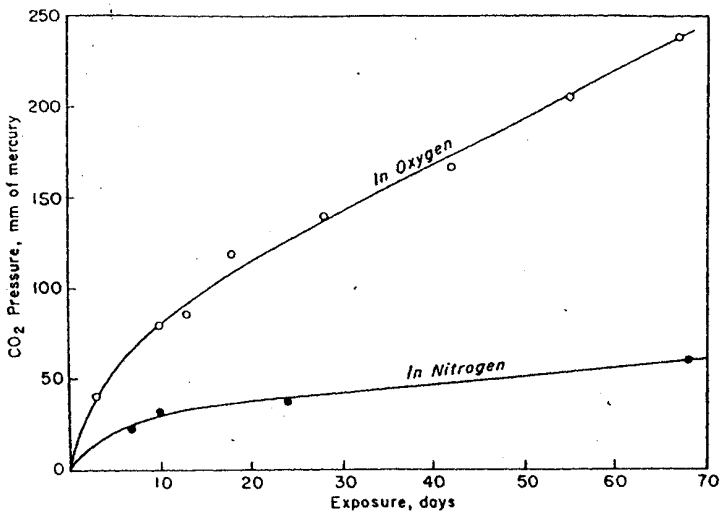


Fig. 19.—Evolution of Carbon Dioxide from Dried Films of Pentaerythritol Eleostearate in Oxygen and Nitrogen.

Also, the residue from the sorbic acid, a viscous, yellow liquid, was found to contain a high concentration of hydroxyl groups. The stearic acid, by contrast, proved to be very resistant to degradation.

From these results, and all of the foregoing, it was concluded that: (*a*) Initial attack by light occurs at ketonic groups that have been formed prior to exposure through hydroperoxidation and rearrangements at the sites of original unsaturation. (*b*) Ketonic or carboxyl carbonyls conjugated with ethylenic unsaturation or with other carbonyls are more readily attacked, particularly by radiation above 3000 Å, than are isolated carbonyls. (*c*) The initial attack does not require the presence of oxygen, but proceeds by the well-known mechanism (9) shown in reactions VI and VII:

$$\left.\begin{matrix}RCOR' \\ RCOCOR'\end{matrix}\right\} \xrightarrow{h\nu} R + R'CO \rightarrow R + R' + CO \quad \text{....(VI)}$$

$$RCH_2CH_2CH_2COR' \xrightarrow{h\nu} RCH{=}CH_2 + CH_3COR' \quad \text{....(VII)}$$

(*d*) In the absence of oxygen, the available carbonyls are eventually consumed and the rate of degradation is drastically reduced. With oxygen present, however, the radicals formed in reaction VI further react to give carbon dioxide, water, and formic acid (9, 10). Furthermore, the lower ketone formed in reaction VII is subject to repetition of both reactions, while the olefin can proceed, via the usual hydroperoxidation, to give more ketone. Radicals formed in reaction VI can also combine with similar radicals on nearby chains to yield new cross-links. It is probable that these radicals are capable of abstracting hydrogen from sensitive points (such as α-methylenes and tertiary hydrogens) and in this way spreading the destruction to parts of the structure not directly susceptible to photolysis. (*e*) The existence of substantial concentration of ketonic carbonyl is the most probable cause of yellowing that is observed in alkyd films upon drying or aging in the dark.

Mechanical Properties.—Up to this point, the major concern has been with attempting to explain the mechanism by which an alkyd film undergoes loss of gloss and chalking upon exposure to photooxidative conditions. Normally, however, degradation is accompanied by other effects, the most important of which is change in mechanical properties. Accordingly, as a conclusion to the present work, a brief study was made in order to relate the observable changes in certain of these properties to the mechanism already postulated.

Clear and pigmented free films 2.5 mils thick were prepared as previously described and cut into strips 1 cm wide. Permanent set measurements were carried out by exposing specimens to radiation from a Hanovia lamp while they were maintained at 10 per cent elongation and 100 C in a quartz-windowed oven. Clamps were applied to the strips at inked reference lines 10 cm apart, and the strips, with their clamps, were placed in the oven for a few minutes prior to attachment to the stretching frame. The oven could be evacuated or maintained with any desired atmosphere during exposure. Lamps were placed 10 cm from the specimens in such a way as to provide uniform illumination. At various intervals, specimens were unclamped and allowed to relax for a few minutes while still in the oven; they were then removed and allowed to relax at room temperature until constant length, as measured by a cathetometer, was obtained. Permanent set was calculated from the equation given by Andrews (12):

$$\text{Permanent set, per cent} = \frac{s - u}{x - u} \times 100$$

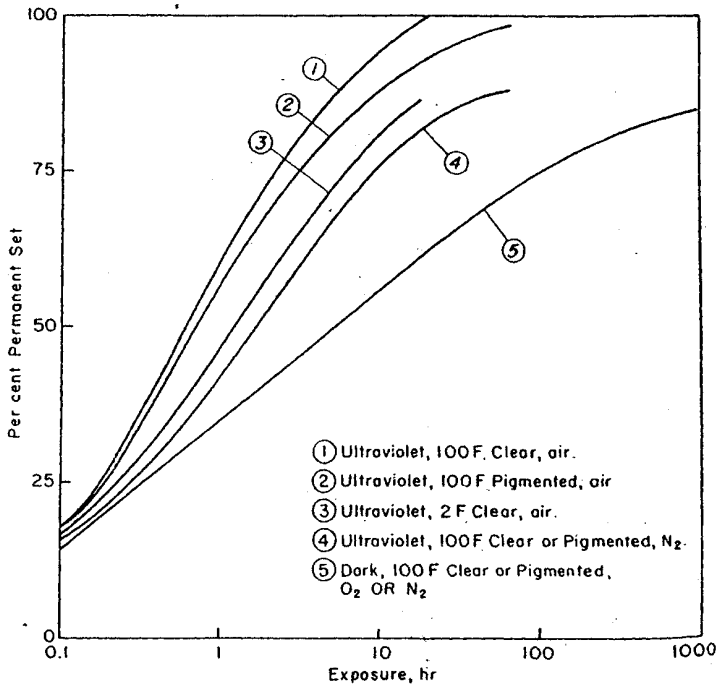


Fig. 20.—Permanent Set Results.

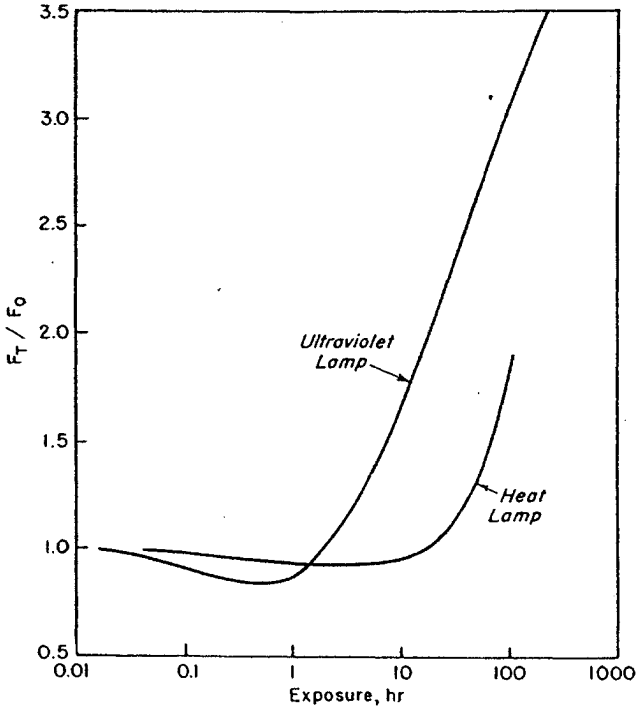


Fig. 21.—Intermittent Stress Relaxation.

where:

u = the original distance between reference marks,
x = the distance when the specimen was stretched on the frame, and
s = the distance after exposure and relaxation.

The results (Fig. 20) give a relative estimate of the number of new, permanent bonds (cross-links) formed by chemical reaction while the specimens were elongated. In the direct comparison between clear films and pigmented films containing 25 per cent by weight of either rutile or anatase, the clear films experienced slightly greater permanent set than did those with pigment, but no difference could be distinguished between the two pigments. This means that the cross-linking reactions penetrated nearly as deeply into the pigmented film as they did into the clear, but it is impossible to infer whether this depth was very slight or comprised nearly the whole film. Exposures in nitrogen resulted in substantially reduced permanent set, and the difference between clear and pigmented specimens could no longer be detected. In the absence of light, no differences due to pigmentation or type of atmosphere could be measured; it is probable that permanent set occurring in the dark results from a simple flow mechanism and does not depend upon the formation of new chemical bonds. The dependence on temperature is shown by one run carried out at 2 C.

According to the mechanisms postulated in reactions VI and VII, chain scission reactions must be occurring simultaneously with cross-linking, but relative rates of the two processes cannot be obtained from permanent set data alone. The net rate of scission and cross-linking can, however, be obtained from intermittent measurements of the modulus of a specimen maintained in a relaxed state during exposure (11, 12). Such measurements were effected by use of a simple electric strain gage apparatus constructed for the purpose. Test strips were cut from the same films and to the same dimensions as those used in the permanent set work; exposures to the unfiltered Hanovia lamp were carried out in air at 25 C. The stress required to elongate the specimens 10 per cent was measured periodically and the ratios of stress at time t to initial stress, F_t/F_o, were plotted against log time. It should be noted that the lamp was turned off a few minutes before each measurement to avoid any possibility that the specimen was above 25 C at the moment of measurement.

Results of this work (Fig. 21) indicate a slight excess of scission processes over cross-linking at an early stage in the exposure but, following this, the rate of cross-linking increases rapidly and finally becomes one of the outstanding features of photooxidative degradation in alkyd films. It was impossible, in this apparatus, to carry out measurements at controlled temperatures above 30 C. However, replacement of the Hanovia lamp by a 375-w Westinghouse infrared bulb gave cross-linking effects qualitatively similar to those obtained with the ultraviolet source. Finally, measurements were made of stress relaxation at constant elongation, but it was found that molecular flow by diffusion was too large to permit the scission reactions to be isolated.

Summary

The initial step in the degradation of drying oil alkyd enamels occurs during the air-drying or baking stages of film formation. Oxygen attacks the unsaturation in the oil and forms hydroperoxides. These hydroperoxides serve either to initiate the α-methylenic chain reaction, which leads ultimately to the formation of useful polymers, or they decompose in side reactions to produce hydroxyl, carbonyl, and other oxygenated groups. The carbonyl groups, especially if they are conjugated with each other or with residual olefinic unsaturation, absorb strongly in the near ultraviolet and significantly at longer wavelengths.

Upon exposure to sunlight, these complex ketones immediately begin to produce carbon monoxide, free radicals, new olefins, and lower ketones. If oxygen is present, the free radicals are oxidized to new photolyzable compounds (which may be volatile); the newly formed olefins are subject to repetition of the hydroperoxidation process and the lower ketones continue to be photolyzed until the chain in which they originally existed is consumed. In addition, the free radicals may attack other parts of the alkyd molecule at random or become stabilized by reaction with other radicals. While all of these reactions start in the oil molecule, their damage spreads by repetition until the glyceryl phthalate ester is attacked and ultimately converted into volatile products.

Long before the film is entirely consumed, the effects of this complex chemical process can be observed as physical changes in the film. Very short wavelengths, as from an ultraviolet lamp, are completely absorbed in a very thin surface layer and repetitive reactions proceed rapidly through complete units of the alkyd structure in this layer. Thus, if the incident light is entirely short wavelengths, the major physical effect is an erosion of the surface, which appears as "chalk" if the film is pigmented or as slight dulling in a clear area; in either case, the freshly exposed surface is hydrophilic, due to its high content of polar, oxygenated groups.

When the film is exposed to polychromatic radiation, such as sunlight,

the longer wavelengths penetrate deeper than the shorter ones and initiate reactions throughout the bulk of the film. Here, the photolytic processes are more gradual, and dehydrogenation with the formation of carbonyl groups and cross-links becomes more important than cleavage. Consequently, hydrogen in the form of water is evolved more rapidly from the bulk of the film than is carbon in the form of its oxides and volatile compounds. As a result, shrinkage, increase in density, embrittlement, and yellowing occur in the bulk of the film. These physical effects are diminished by the screening effect of pigment, but radiation in the longer visible and near infrared part of the sun's spectrum penetrates to the substrate interface in the films of ordinary thickness.

The extent of yellowing is dependent upon the relative rates of formation and destruction of ketone and polyketone structures. Since these rates depend, in turn, upon the wavelength distribution of the incident radiation, various light sources produce characteristic equilibrium levels of yellowing. Thus, a film that has acquired a high level of yellowing through exposure to ordinary indoor illumination, or to heat, may be bleached to a lower level of yellowness in sunlight or to a still lower level by appropriate ultraviolet lamps.

Limited access of oxygen in the bulk of the film undoubtedly has a role in governing the sequence of reactions throughout the film, particularly in the initial stages of drying, but its effects have not been specifically studied. Water vapor appears to have little influence on the degradation processes, but liquid water accelerates chalking by the physical effects of swelling and solution and possibly by chemical interaction as well.

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Acid Contamination as a Source of Error in Boiling Nitric Acid Test for Corrosion-Resistant Steels

By Robert J. Bendure

THE boiling nitric acid test, ASTM Recommended Practice A 262,[1] has been found useful for measuring the quality of stainless steels with respect to their ability to resist attack by nitric acid and as an indication of the effectiveness of heat treatments that may have been employed or of adjustments of composition that may have been made to accommodate otherwise damaging heat treatments. Excellent reproducibility between duplicates is normally obtained, except in those instances where the penetration rates are quite high. In such cases it is not unusual for duplicate specimens to show marked variation in corrosion rates.

High and erratic penetration rates were obtained when the testing area inadvertently contained hydrofluoric acid fumes.

This test has been used in our research laboratories for a number of years, the testing being carried out in a laboratory in which chemical analyses are also made. The heating apparatus used consists of two multiple burner gas-fired hot plates placed side by side so that twenty-four 1000-ml wide mouth Erlenmeyer flasks can be accommodated simultaneously. Each flask is equipped with a finger-type condenser, the cooling water being taken from a manifold-type distributor.

For most types of material the rate of attack follows a similar pattern—the first period rate may sometimes be slightly higher than the second period rate, following which each of the succeeding three periods will have rates as

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[1] Tentative Recommended Practice for Boiling Nitric Acid Test for Corrosion-Resisting Steels (A 262 – 52 T)‡ 1952 Book of ASTM Standards, Part 1, p. 998.

[2] R. J. Bendure, "Contamination of Nitric Acid as a Source of Error in the Huey Boiling Nitric Acid Test," *Corrosion*, Vol. 10, p. 7 (1954).