Deterioration of Alkyd Resin Films

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THE organic chemistry which is involved in the photooxidative deterioration of an alkyd resin is known to be vastly complex. While much attention is being given to fundamental investigations of oil oxidation by laboratories concerned with the study of edible fats, there are numerous points of interest relating to alkyd resins which may be attacked in a less rigorous manner. One such problem is concerned with determining some of the simple kinetic relationships and over-all physical results of the action of light on an alkyd film. The purpose of the present work, which was carried out as part of a larger investigation, was to determine the rate, the geometrical location or site of attack, its approximate relationship to wave length, and its dependence upon oxygen concentration.

Two very simple and straightforward experimental procedures were used throughout the work—measurements of volatile decomposition products and microinterferometry of the surface.

MEASUREMENT OF VOLATILES

Analysis of volatile decomposition products arising from decomposing linseed oil or alkyd resins is by no means new (*2, 4, 6*). In none of the previous work, however, was any attempt made to use films of precisely known area, weight, and thickness, so that no real estimate of the rate and locus of attack could be made. Further, all of the previous work had been directed toward the very early changes in liquids or wet films. The present effort, on the contrary, is concerned wholly with hard, baked film, and the course of gas evolution is followed up to and beyond the point of easily visible chalking in the case of pigmented films and to corresponding extents of deterioration in the case of clear films.

APPARATUS AND PROCEDURE

The resins to be studied were sprayed on weighed glass panels all 15 × 2 cm. The panels were baked 1 hour at 105° C., aged for from 1 to 3 weeks in the dark, and reweighed. Film thicknesses, in terms of milligrams per square centimeter, or the reciprocal, were calculated from these data; a wide range of thicknesses was prepared, and only perfect panels (smooth even films) were selected for use.

The exposure vessels were quartz tubes, 25 mm. in outside diameter. At one end sealed inlet tubes were connected to a purifying train that removed carbon dioxide and water from the tank gas being fed into the tubes; at the exit end the tubes were equipped with standard-taper openings capable of admitting the specimen panels. A gas absorption train consisting of a pair of Pregl tubes (Dehydrite and Ascarite-Dehydrite), a microcombustion furnace, another pair of Pregl tubes, and a bubble counter was attached to the exit end of the exposure vessels.

A Hanovia Utility lamp—medium pressure quartz mercury vapor—was positioned symmetrically above the horizontal exposure tubes that were always used in pairs. In order to ensure even illumination the lamp was frequently moved a few millimeters in random directions; in this way the effects of hot spots in the lamp and flaws in the quartz exposure tubes were minimized and pigmented panels so exposed gradually acquired an even coat of chalk. The lamp-to-specimen distance was held constant at 10 cm. throughout the work; the total intensity actually received by the panel was estimated from thermopile measurements to be approximately 0.05 watt per sq. cm. In those cases where a borosilicate glass filter was used the energy was about one third of this value. Air was circulated about the tubes by a fan, and thermometers that were placed inside with the specimens stayed at 30° C.

Each run began with the light on but with no specimens in place; gas was passed through the system at 5 cc. per minute until constant weight was obtained in all adsorption tubes. The selected specimens were then inserted; the light was turned off, and gas flow was continued until constant weights were again attained. At this point the light was turned on and weighings of all adsorption tubes were scheduled on a daily basis for usually 7 days. At the end of the run the panels were removed and weighed, and in some cases scrapings were analyzed for carbon and hydrogen.

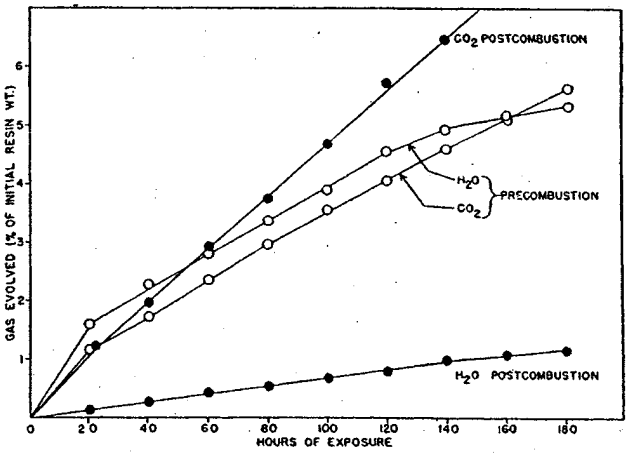


Figure 1. Gases Evolved from Baked Alkyd Film upon Exposure to Ultraviolet Light in Oxygen

The resin used in most experiments was a linseed–chinawood oil alkyd of 50% oil length and an acid number of 18. When used with no modification other than a common drier this is referred to as "clear alkyd." In some experiments this same alkyd was pigmented at 20% by weight with titania, and this is indicated where it occurs in the results.

Figure 1 shows the averaged results of three separate runs on the clear alkyd. The term "precombustion" used in the figure refers to gases collected in the adsorption tubes preceding the furnace and immediately following the exposure tubes. The "postcombustion" gases were, of course, collected in the final pair of adsorption tubes. The large ratio of carbon dioxide to water in the postcombustion gases indicates a high proportion of carbon monoxide in the gas entering the furnace.

The decrease in the rate of water evolution in the precombustion gas, which results in an intersection of its curve with that of carbon dioxide, is a typical result, except that in most cases it occurred before 100 hours. Careful examination of the figure reveals that the rate of carbon dioxide evolution is also decreasing, though much more slowly. A few experiments conducted for a longer period of time revealed this decrease more clearly; the total effect is sufficient to denote a drop in the over-all rate of reaction.

It is possible that some contribution to the rate decrease, particularly that observed in the data for precombustion gases at about 20 hours, was due to disappearance of traces of solvent which may have been in the film at the start of the experiment. If this were the case, it must also be concluded that the solvent vapor (all hydrocarbon) was oxidized to carbon dioxide and water while still in the irradiated region. Otherwise it is unlikely that the rate change would have been observed in the precombustion gases; it would, instead, have occurred in the postcombustion data, which are seen to be nearly straight in this region. In any case, traces of solvent, if they exist, may be regarded as no different from any other low molecular weight or easily oxidizable constituent of the film.

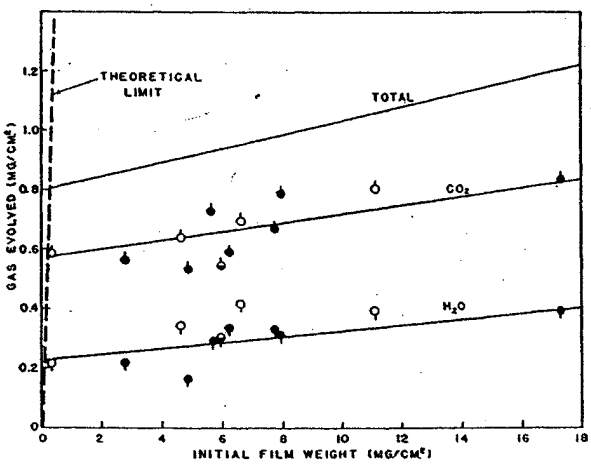


Figure 2. Gases Evolved from Baked Alkyd Film in 100 Hours of Exposure to Ultraviolet Light and Oxygen

○○ Clear alkyd
●● Alkyd and rutile
◐◐ Alkyd and anatase

Unfortunately, there is no way of inferring from these data the true initial products of the photolysis. The slow sweep of gas through the train undoubtedly allows time for the photooxidation of volatile products such as aldehydes and ketones if any occur. While a knowledge of the initial reaction products would be of value in elucidating the chemistry of the process, the lack of this information is not a handicap for the purposes of this investigation.

Figure 2 shows the combined post- and precombustion gas evolution as a function of film thickness. Here the ordinate gives the weight of gas evolved from each square centimeter of film and the abscissa gives the initial weight of pure resin in each square centimeter of film. The equation of the experimental lines is:

$$\frac{w}{\text{sq. cm.}} = A\frac{W}{\text{sq. cm.}} + B \qquad (1)$$

where w is the weight of gas and W is the resin weight. In the case of clears, W is, of course, identical with the film weight, but with pigmented specimens it is equal to 0.8 of that amount.

It is evident from the experimental points that in this test there is no distinguishable difference between clear and pigmented films nor between rutile and anatase pigmentation. Also, it is clear that since a film of zero thickness ($W = 0$) can evolve no gas, the intercepts (B) cannot exist. In fact, the limit of permissible values must be given by the weight of gas which could be evolved upon complete combustion of the film. This theoretical limit is given by the dotted line in Figure 2 and was calculated from the fact that the resin used in these experiments would, upon complete combustion, yield 254% carbon dioxide and 62% water.

Assuming then, that the line representing the total gas intercepts the theoretical limit and follows it down to the origin, the abscissa of the intersection gives an estimate of the depth of film that has been quantitatively eroded from the surface in 100 hours. This amount is found by calculation to be approximately 2 microns.

The continuing upward slope of the data at greater film thicknesses is a measure of the extent to which the underlying layers of resin are contributing volatiles, possibly including traces of residual solvent, to the total amount collected. It seems likely that this relatively slower process in the depth of the film is due to radiation of longer wave length, which is not filtered by the topmost layer. If this is true, then the decrease in reaction rate that is observed at longer periods of time may be interpreted in two ways:

1. As the surface erosion due to the short-wave ultraviolet proceeds into the film it eventually reaches underlying resin that has been subjected to long wave irradiation for a considerable period of time and as a result has been chemically converted into a more stable form.

2. The other possibility is that the reaction at the surface is not quite quantitative and, as the erosion proceeds, a layer of unreactive debris that acts as a shield is left on the surface.

It is likely that both of these effects occur and that the relative importance of each depends upon whether the film is clear or pigmented. In either case it is reasonable to assume that the rate of initial gas evolution would be decreased if the film were baked an extra-long time prior to starting the ultraviolet exposure. This was tried and found to be the case.

In addition to the experiments using the unfiltered Hanovia lamp with an oxygen atmosphere, a few runs were made using either a borosilate glass filter that excluded short wave lengths, or an atmosphere of purified, dry nitrogen. Results at 100 hours for two typical experiments are:

Pigment	Film Thickness, Mg./Sq. Cm.	Atmosphere	Filter	Total Gas Evolved, Mg./Sq. Cm. CO	H_2O
Rutile	13.8	N_2	None	0.13	0.22
Anatase	6.1	O_2	Borosilicate glass	0.14	0.11

Comparison of these data with those of standard runs shown in Figure 2 reveals that while the reaction is greatly retarded by either a filter of nitrogen, it is by no means negligible in either case.

The rate of chalk development during all of the foregoing experiments in which pigmented films were used was qualitatively observed to be dependent upon the exposure conditions in a most significant way. With the use of unfiltered light and either nitrogen or oxygen atmosphere the first easily perceptible chalk appeared after the evolution of approximately 0.2 mg. of combined gases per sq. cm., while with filtered light no chalk appeared even at higher levels of gas evolution. This seems to confirm the idea that unfiltered ultraviolet gives a highly erosive surface reaction combined with a bulk reaction, while light from which the

TABLE I. HYDROGEN TO CARBON ATOMIC RATIOS AVERAGED FROM SEVERAL SOURCES

Literature Cited	Material Used	Number of Experiments Averaged	H:C Ratio In original material	In off-gases	In residue
(2)	Linseed oil	9	1.76	3.89 ± 0.35	Not given
(6)	Linseed oil	8	1.76	3.22 ± 0.34	1.74[b]
(4)	Trilinolenin	4	1.62	2.01 ± 0.23	Not given
(5)	Linseed oil + ZnO	8	1.76	4.33 ± 0.15	Not given
(3)	Linseed oil + TiO_2	12	1.76	4.60 ± 0.30	Not given
This paper	Alkyd	3[a]	1.20	2.50 ± 0.40	1.20[b]

[a] Data taken from Figure 1 at 140 hours.
[b] Analysis on only one specimen.

short-wave radiation is removed produces chiefly the bulk reaction that leaves the surface relatively intact.

If it is correct, as implied above, that the radiation of longer wave length produces chiefly a bulk reaction, then it follows that thermal oxidation of alkyd films should be solely a bulk reaction. Figure 3 shows the results of a series of thermal oxidation measurements in which panels prepared in the same manner as before were

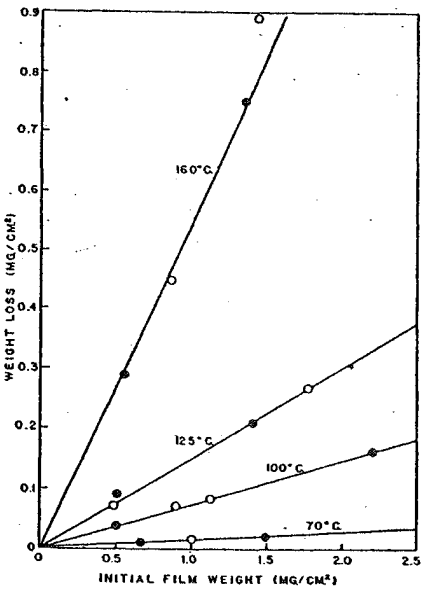


Figure 3. Weight Loss from Clear Alkyd Films in Air Oxidation

○ Glass substrate
● Aluminum substrate

heated in an air oven. This time, however, the volatiles were not caught; instead, the remaining film weight was recorded as a function of time, temperature, and initial thickness. While this method of conducting the experiment is not strictly comparable with that used previously, it clearly indicates the bulk nature of the thermal reaction and lends support to the idea that light in the longer wave lengths produces only a bulk reaction.

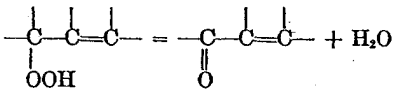
DISCUSSION

Some insight into the chemical nature and mechanism of the processes by which volatile products are evolved may be gained by examining the hydrogen to carbon ratios of the gases as compared with that of the original film. Fortunately, several of the references cited previously (*2–4, 6*) contain data from which these same ratios may be computed. The comparison is given in Table I.

Apparently there is general agreement that the volatile decomposition products are hydrogen-rich compared to the parent material and the hydrogen-carbon ratios of residues are practically unchanged. However, for small-to-moderate amounts of decomposition the hydrogen-carbon ratio of the residue is very insensitive to changes in the composition of the off-gas and no undue importance should be attached to the two values listed in the table.

The hydrogen-carbon ratios of the off-gas are certainly significant and prove clearly that dehydration is an important step both in the mechanism of drying (*2–4, 6*) and in the deterioration of completely dried films as shown here. Corresponding ratios found in the present work using the borosilicate glass-filtered light or nitrogen atmosphere were, in general, higher and averaged between 6.0 and 7.0. This is as it should be, for if the surface reaction initiated by short-wave ultraviolet is nearly quantitative, as postulated above, the gases obtained under such conditions should have more nearly the composition of the whole resin.

Dehydration has also been observed in oxidation studies on pure compounds. For example, Treibs (*8*) found that methyl oleate evolves 1 molecule of water on exposure to air in thin films and methyl linoleate evolves between 1 and 2 moles per mole of ester. One possible mechanism may be that shown in Reaction 1.



(1)

The quantity of carbon dioxide evolved in all experiments except those using the thickest films was far too large to be attributed to simple decarboxylation of free —COOH or to any other single functional group in the molecule. It must be concluded, therefore, that the carbon dioxide (and carbon monoxide) results from chain scission reactions that may originate from hydroperoxide decomposition in the oil and probably also from reactions of complex nature occurring in other parts of the alkyd molecule.

In a study somewhat similar to the present one, except that it was conducted on Buna rubber in vacuo, Postovskaya and Kuz'minskiĭ (*5*) found a quantum yield of 2×10^{-3} for the overall photoreaction evolving volatile products. They interpret this low value as proof that the deterioration is not a chain reaction. Bateman (*1*) likewise found a very low quantum yield (4.0×10^{-4}) for the gas reaction in the photolysis of rubber but did not interpret his result. While the present work was not designed to permit an accurate calculation of the quantum efficiency, a rough estimate may be made with the aid of a few assumptions. Thus, if it is assumed that wave lengths from the lower limit of the lamp (about 2500 A.) to only 3200 A. are effec-

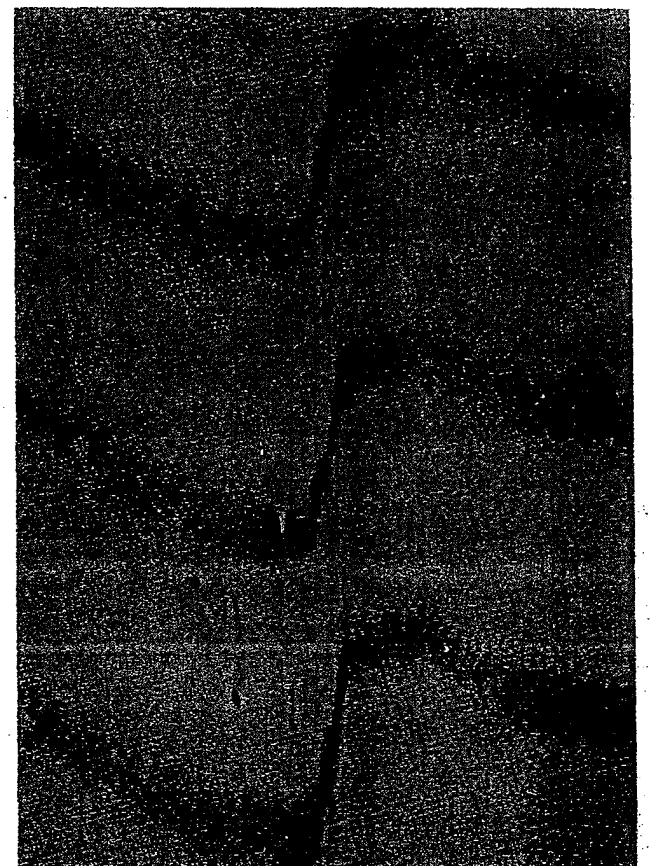


Figure 4. Interference Fringe Shift across Boundary between Irradiated and Unirradiated Areas of Alkyd Films

tive and that all the radiation in this region may be averaged at 2800 A., then the most serious shortcomings are over. The energy emitted by the lamp used in the present work, within the specified range, was estimated from thermopile measurements using cutoff filters, to be about 0.01 watt per sq. cm. at the actual distance used in the experiments. If we neglect surface scattering and assume complete absorption, this amounts to about 1.4×10^{16} quanta per sq. cm. per second. Using the fact that the film thickness in the experiments averaged in Figure 1 was 5 mg. per sq. cm., one may calculate from the data shown there the rate per area evolution of gas molecules of each type. Taking the values at 100 hours and adding the rates for all types of molecules, the result is 1.4×10^{12} molecules per sq. cm. per second. Thus, the estimated quantum efficiency is 1×10^{-4}.

While this result agrees in general order of magnitude with the previously mentioned values for Buna rubber and rubber, it would appear that the situation is too complex to attempt any subtle inferences. It may be safely concluded, however, that in retrospect hardly any other value of quantum efficiency could have been expected from a material which has been used successfully as an exterior protective coating for so many years.

INTERFEROMETRY

Additional information regarding the surface attack of light and oxygen on a hard smooth film may be obtained by well known techniques of interferometry. Optical details may be found in Tolansky (7). Panels were prepared by doctor-blading the resin, clear or pigmented, on plate glass and giving a standard bake. Double-edged razor blades lying on the film were used to give sharp lines of demarcation during irradiation. After the desired exposures had been given, the blades were removed and the entire panel was silvered by vacuum evaporation. Interferographs were made at the boundaries, previously formed by the razor blades, between exposed and unexposed surface. Obviously, if erosion had occurred, a step would be formed whose depth could be determined by measuring the shift in the Fizeau fringes. A series of exposures ranging from 8 to 48 hours was carried out according to this plan, using the unfiltered lamp and air atmosphere. Figure 4 is a typical example of the steps that were found. The height of the steps was estimated from the fact that one full shift of a band corresponds to one half the wave length of light used in making the photograph or about 0.25 micron for the mercury green line that was used here. Results of these measurements showed that the depth of each step was approximately proportional to the time of exposures and that the rate of surface erosion was about 1.5 microns per 100 hours. While this value is somewhat lower than that obtained by the gas analysis method, the agreement seems satisfactory in view of the approximations that had to be made in both methods.

SUMMARY

The decomposition of an alkyd film by light below 3000° A. in a stream of dry oxygen appears to be a nearly quantitative combustion which ultimately yields carbon dioxide, carbon monoxide, water, and small amounts of other volatiles. This reaction occurs in an extremely thin surface layer which disappears as the reaction proceeds and, in the case of pigmented films, produces chalking. The rate of penetration of this surface erosion can be estimated from gas analysis data or microinterferometry.

In addition to the surface reaction there is a bulk reaction that extends throughout the depth of the film and that must be essentially a dehydration or dehydrogenation, since the atomic ratio of hydrogen to carbon in the mixed gases is much higher than it is in the pure resin.

The rate of gas evolution decreases slowly with time, indicating that a new and more stable structure is being formed. The rate with films containing 20% rutile or anatase pigment is about 20% lower than it is with clears, indicating that, to this test, the pigment is an inert space filler.

A similar quantitative surface reaction occurs when the radiation with light below 3000 A. is carried out in a stream of pure, dry nitrogen. The rate of gas evolution in this case is much lower, however, and the oxygen in the carbon dioxide–water mixture comes from oxygenated groups in the resin. With pigmented films, chalking appears at about the same point in the reaction as it does in an oxygen atmosphere as measured by the weight of combined gases evolved, but the atomic ratio of hydrogen to carbon is much greater, and yellowing increases.

When all radiation of wave lengths shorter than 3000 A. is removed from the light, the erosive surface reaction is greatly surpressed while the bulk reaction continues to produce carbon dioxide and water at a slow rate but with a high hydrogen-carbon ratio.

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