STUDIES ON THE PHOTOCHEMICAL STABILITY OF SYNTHETIC RESIN-BASED RETOUCHING PAINTS: THE EFFECTS OF WHITE PIGMENTS AND EXTENDERS

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ABSTRACT
The durability of a paint vehicle can be strongly influenced by the pigments which it contains. This report describes an initial investigation of the photochemical degradation of paints formulated with a commercial poly(n-butyl methacrylate) and a variety of white pigments and extenders. Upon exposure to near-ultraviolet light this resin predominantly cross-links, eventually becoming almost completely insoluble. White pigments such as rutile TiO_2 and Green Seal zinc oxide do not alter this tendency but they do slow the cross-linking rate, probably by their ability to absorb UV light. By contrast, a non-absorbing light scatterer like barium sulfate increases the rate of cross-linking, perhaps by increasing the path length of light as it becomes diffused within the paint film. Finally, pigments such as anatase TiO_2 and Kadox 515 zinc oxide not only decrease the overall degradation by screening UV light but also increase the relative importance of chain-breaking chemistries through their photocatalytic properties. Even so, loss of volatile degradation products renders these films as insoluble as the purely cross-linked systems.

1 INTRODUCTION

In order to take advantage of the performance and durability of synthetic resins, many modern art and conservation paints are being formulated with high molecular weight polymers. While some of these paints may have been tested for their durability in a commercial application, few of these vehicles have been examined with a view to predicting their performance in museum environments. At best, the expected long-term stability of these polymeric paint vehicles is extrapolated from studies of the aging of the pure polymer films. This report describes our laboratory's initial investigations into the aging chemistry of pigmented synthetic polymers, specifically examining the effects of pigments on the photochemical degradation of the polymers.

While it may be tempting to assume that a polymer which has proved durable when tested as a pure material will enjoy that same durability when pigments are incorporated into it, such expectations may be unrealistic in light of the many different effects which pigments have been shown to have on polymer properties. These effects can be chemical, such as the reactions of metallic compounds which can alter oil paint polymerization [1], oxidation [2,3], or crystalline salt formation [4], or they can be physical, changing the strength [5] or permeability characteristics [6] of the polymer, for example. Pigments have been found to affect the stability of polymers to light exposure, either increasing their resistance by screening harmful radiation or decreasing their stability by sensitizing photochemical reactions [7,8]. The paint failure known as 'chalking' is probably the most easily recognized of these damaging pigment interactions, and the complexity of the chemistry of chalking is still being explored [9-11].

The experiments described in this report are focussed on the effects of several types of white pigments on the photodegradation of poly(n-butyl methacrylate), a polymer which has seen use as a conservation material and as the vehicle for some retouching paints. This particular resin has been found to undergo predominantly cross-linking chemistry during exposure to near-ultraviolet light and slowly develops insoluble matter as a result [12]. In addition to its conservation use, this resin was also chosen because it is a material of 'intermediate' stability, falling in Feller's Class B of stability [13]. Thus the degradation of the resin may occur at a rate which can be conveniently measured, and the effects of added pigments on these degradation rates can be more easily assessed.

We have examined the changes in this resin degradation chemistry with the addition of three different types of pigments:

a) rutile titanium dioxide and 'Green Seal' French-process zinc oxide, both of which absorb the near-ultraviolet wavelengths responsible for the resin cross-linking [14,15] and yet possess photochemical stability;
b) anatase titanium dioxide and a finer particle size French-process zinc oxide, which also absorb the near-UV but which have been found to 'chalk' other paint vehicles;
c) natural barium sulfate, a common extender pigment which does not absorb light in the near-ultraviolet region [16].

With these pigments incorporated into the methacrylate binder, it has been possible to explore a range of pigment interactions on the photo-assisted aging chemistry of the pure resin.

In determining the effects of added pigments on resin degradation the approach of Maxim and Kuist [17] has been followed. Using kinetic models developed by others to describe the course of cross-linking and chain-breaking chemistries in linear polymers, the quantitative comparison of these kinetic parameters for pure and pigmented films has been attempted. In this way a more fundamental understanding is sought of the mechanisms by which the observed resin degradation is altered by the incorporated pigments. It should be noted, however, that in these experiments there is no attempt to mimic the exact composition of a restoration paint; instead very small pigment loadings have been used in order to observe chemistry occurring throughout the films. Higher pigment concentrations, such as might be found in a commercial paint, could limit the degradation chemistry to the exposed surface layer of the paint film, and as a result it is difficult to predict from these experiments alone how this inhomogeneous degradation would translate to changes in appearance or reversibility of real paint applications. These practical considerations of the durability of real retouching paints must be the focus of future experiments.

2 EXPERIMENTAL

The polymer used in these experiments was duPont Elvacite 2044, a poly(n-butyl methacrylate) homopolymer. Two different batches of this resin were examined, one which had been recently obtained and one which had been stored in our laboratory for about 17 years. Previous experiments with this polymer indicated that older material becomes insoluble more rapidly than fresh material, and this result was verified in the present tests. In fact, viscosity measurements on the old and new batches of resin show a higher intrinsic viscosity for the older batch, suggesting that some cross-linking may have already begun during the dark storage of the material. Because of these apparent differences in the starting materials, all comparisons of the aging behavior of pigmented and unpigmented resin have been made only between samples formulated with the same batch of resin. It has been found that the pigment effects on the photochemistry are qualitatively the same for both batches of resin.

The pigments used were a rutile TiO_2 (duPont Ti-pure R-900), an anatase TiO_2 (duPont Ti-pure FF), French Green Seal zinc oxide (New Jersey Zinc Co. Florence Green Seal-8), another French-process zinc oxide (New Jersey Zinc Co. Kadox 515), and natural barium sulfate (National Lead Co. Foam

A/Baryta White). Each pigment was ball-milled with a toluene solution of the resin for about 85 hours, and the desired pigment weight concentration was formulated by diluting the milled dispersion with an appropriate quantity of the toluene solution of the pure resin.

The milling operation, in which a ceramic jar containing ceramic balls and the paint ingredients is rotated so that the balls tumble inside the jar, imparts a considerable amount of mechanical energy to the contents of the jar. Over time the ceramic balls slowly abrade, and a small amount of alumina thus becomes entrained in the paint. In addition, the mechanical stress of ball-milling could risk damaging the polymer molecules through chain-breaking [18]. Control experiments have so far failed to reveal any significant loss of viscosity or aging differences after ball-milling the polymer, and the small amount of incorporated alumina has been found to have only a minor effect on the results of the photodegradation experiments.

Films of these paints were cast on aluminum foil with a drawdown blade, dried overnight at 25°C, and oven-dried for 12 hours at 70°C to remove residual solvent. Final dry film thicknesses were determined to be about 25-50μm. The foil-backed samples were cut into pieces whose size and number were suited to the analyses and number of data points desired.

Prepared films were exposed to the output of a bank of Sylvania fluorescent lamps (Q-Panel Co., UV-A 351) in a constant-environment room maintained at 20°C, 50% RH. These lamps emit light in the UV-A region (320-400nm), and the total intensity of ultraviolet light at the sample position (about 9cm from the lamps) was about 3mW/cm^2 as measured with a radiometer (International Light Inc. IL700) equipped with the appropriate cut-off filters. The slow decrease in intensity as the lamps aged was monitored periodically, and because of this variation results are reported in terms of exposure dose (intensity times exposure time) rather than exposure time alone. This use of exposure doses for unequal incident intensities is appropriate only if the reciprocity rule holds. This has been demonstrated to apply to the ultraviolet degradation of a closely related butyl methacrylate copolymer [19].

Three types of measurements were used to monitor the polymer degradation during exposure. Viscosity measurements were made on polymer samples which had been exposed to doses of ultraviolet light small enough so that the entire sample retained its solubility in toluene. Relative viscosities of solutions of these aged polymers, filtered to remove pigment particles, were measured in toluene at 25°C and at various concentrations using a dilution-type capillary viscometer (Cannon-Ubbelohde type) in a thermostatted water bath. From the viscosity vs. concentration data, intrinsic viscosities were calculated by extrapolating the standard Huggins and Kraemer relationships to zero concentration according to ASTM Test Method 2857-70.

When the ultraviolet light exposures were sufficiently great to produce insoluble material in the paint films, the amount of this insoluble gel was measured by weight difference after an overnight extraction of the sample in a wire basket having 200μm-diameter holes with 1:1 toluene/acetone at 20°C. It was expected that this extraction would remove a random amount of pigment in addition to the soluble resin fraction, and thus introduce an error into the calculation of gel content. However, visual inspection of the extracts showed them to be free of pigment — nearly all of the pigment had remained trapped in the gel. Calculation of the amount of insoluble polymer material thus assumed that the weight of material remaining after extraction was gel plus pigment; the weight of pigment was subtracted from this value to obtain the weight of the gel fraction. For these analyses duplicate samples were measured and averaged for each exposure dose.

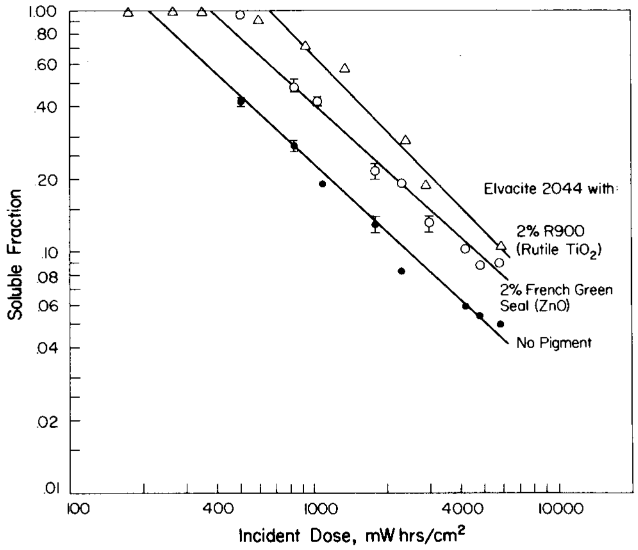

Fig. 1 Fraction of Elvacite 2044-based paints (containing rutile TiO_2 and Green Seal ZnO) remaining soluble in 1:1 toluene/acetone at 25°C, following exposure to near-ultraviolet light.

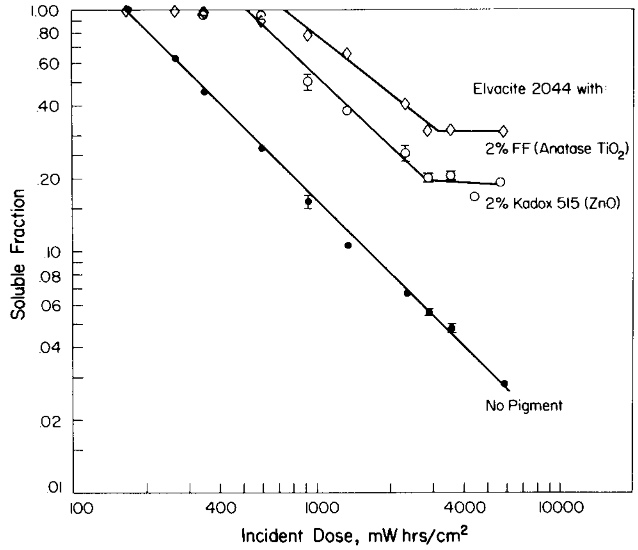

Fig. 2 Fraction of Elvacite 2044-based paints (containing anatase TiO_2 and Kadox 515 ZnO) remaining soluble in 1:1 toluene/acetone at 25°C, following exposure to near-ultraviolet light.

Sample weights were also monitored during the exposures in order to detect oxidation or the loss of volatile products. Soluble fractions, gel fractions and volatile fractions were calculated based on the weight of the resin originally present in the films before exposure.

3 RESULTS

The loss of solubility in 1:1 toluene/acetone of the unpigmented and pigmented 2044 resin during ultraviolet light exposure is shown in Figures 1-3. There was no significant weight gain for the polymer films, suggesting that this loss of solubility is the insoluble gel produced from the cross-linking reaction previously observed in this resin. A substantial exposure dose is required before the onset of insolubility, and it is notable that this dose, called the gel or gelation dose in radiation chemistry, is different for the samples containing pigments. The gel doses for the ultraviolet-absorbing rutile TiO_2 and French Green Seal zinc oxide paints (Fig. 1) are greater than that of the unpigmented resin; that is, it takes a larger UV dose to produce insoluble matter in

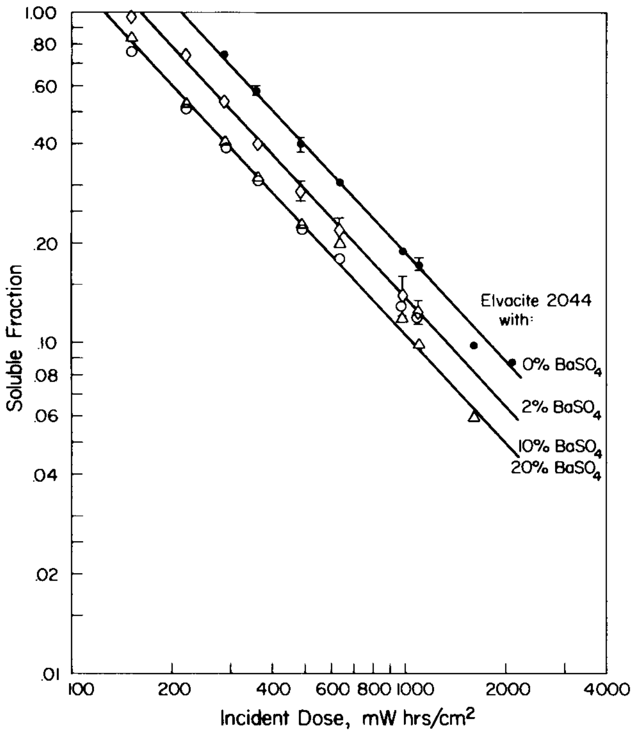

Fig. 3 Fraction of Elvacite 2044/$BaSO_4$ paint remaining soluble in 1:1 toluene/acetone at 25°C, following exposure to near-ultraviolet light.

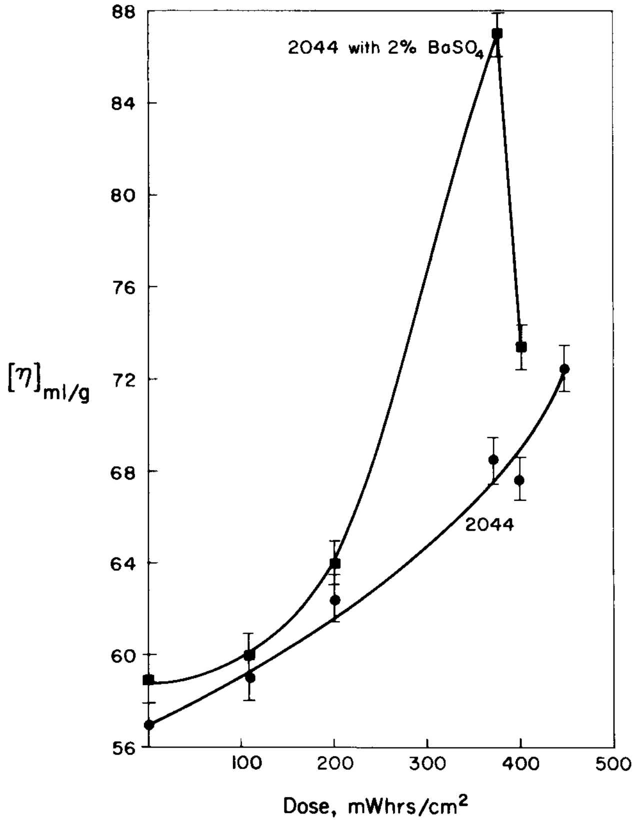

Fig. 4 Intrinsic viscosities of unpigmented and $BaSO_4$-containing Elvacite 2044 following exposure to near-ultraviolet light. Viscosities measured in toluene at 25°C.

these pigmented films. Similarly, the onset of gelation is delayed by the incorporation of the anatase TiO_2 and Kadox 515 zinc oxide pigments (Fig. 2). However, the addition of the inert extender pigment barium sulfate into the resin seems to decrease the time for gelation; the polymer degradation from UV-exposure seems slightly accelerated with the incorporation of barium sulfate (Fig. 3).

Further evidence of cross-linking is provided by the intrinsic viscosity measurements of the polymer before insoluble matter is formed. These results, shown in Figure 4 for the unpigmented and barium sulfate-containing 2044, demonstrate that the apparent induction time before gelation is not a true period of chemical stability. Rather (for the newer batch of resin) there is a much shorter period during which no viscosity increase is observed, which may be a true induction period, after which the intrinsic viscosity increases monotonically until just before the gelation point occurs. As with the gel point, this viscosity increase seems to occur with smaller ultraviolet light doses for the barium sulfate-containing polymer than for the pure resin film. This intrinsic viscosity is a measure of the degree to which a polymer 'thickens' a liquid, thus restricting its flow through a capillary. This quantity is thus related to the size of a polymer molecule in solution, and the increase observed as the 2044 resin reacts can be interpreted as an increase in molecular size, or in this case an increase in molecular weight due to cross-linking. (The limitations of this interpretation of viscosity changes during polymer aging will be discussed further below.)

The samples which had been formulated with the UV-absorbing, 'chalking' pigments were the only ones which experienced a weight change during light exposure. These films began to lose weight at about the same exposure dose that began to produce gel. The weight loss for these samples, interpreted to be the loss of volatile products of a degradation reaction, is illustrated in Figures 5a and 5b, which also show the relative amount of gel formation during the exposure.

4 DISCUSSION

As shown by Maxim and Kuist [17] and also by Feller and Bailie [20], the kinetics of gel formation in a polymer which degrades predominantly by cross-linking can be used to characterize the relative rates of cross-linking chemistry and chain-breaking processes (if any) which occur simultaneously. Using the model of Charlesby and Pinner [21] to describe these reactions, the ratio of chain-breaking to cross-linking reaction rates can be determined by a plot of $s+\sqrt{s}$ vs. 1/(exposure dose), where s is the weight fraction of the film which remains soluble. From this plot, the chain-breaking to cross-linking ratio (called β/α in Charlesby's notation) is the intercept of the line with the y-axis. A small value of this quantity describes a resin which degrades primarily through cross-linking; a larger value indicates more competition of chain-breaking processes with cross-linking. The value of β/α cannot exceed 2, for then the chain-breaking processes would prevent the formation of any gel and thus there would be no solubility loss to be analyzed. In addition to providing a measure of the different chemistries occurring in the polymer, the value of β/α can also be interpreted as the limiting value of the solubility of the film: a polymer having β/α of zero would eventually become completely insoluble; β/α of about 1.2 means that the film would approach a minimum of 50% solubility with time.

The Charlesby-Pinner plots of the 2044 resin and the films containing barium sulfate, rutile titanium dioxide, and French Green Seal zinc oxide are shown in Figure 6. The intercept of each of the plots is the same, and yields a value of β/α of about 0.2. This value indicates that cross-linking is the predominant degradation path, for about five cross-links occur for every one chain-break. This value also predicts that an infinite dose of ultraviolet light would render the film almost completely insoluble. This value for β/α is comparable to that of 0.12 ± 0.09 determined by Ciabach [22] and to the range of 0-0.5 cited by Feller [23] for a freshly prepared poly(n-butyl methacrylate) aged in a slightly

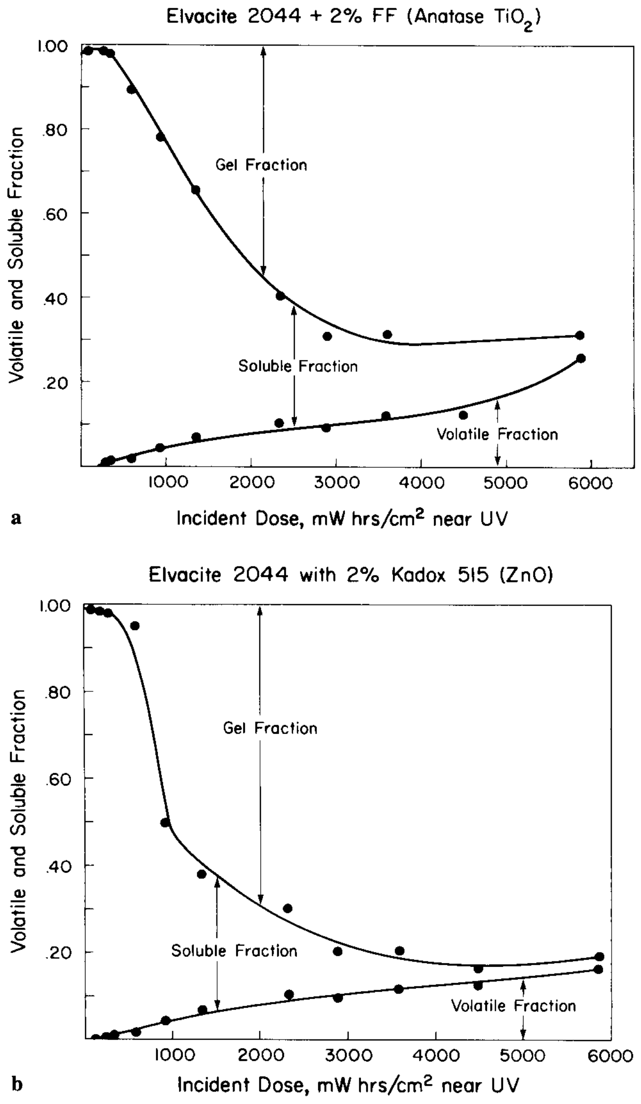

Fig. 5 Soluble (in 1:1 toluene/acetone at 25°C), insoluble, and volatile fractions of Elvacite 2044 containing: (a) anatase TiO_2 and (b) Kadox 515 ZnO, following exposure to near-ultraviolet light.

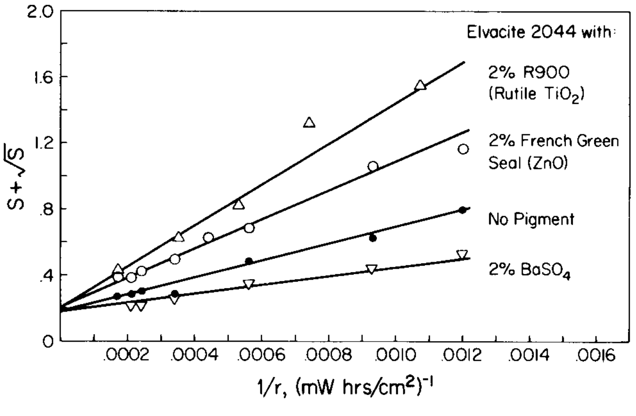

Fig. 6 Charlesby-Pinner plot for illuminated Elvacite 2044 with no pigment, and containing rutile TiO_2, Green Seal ZnO, and $BaSO_4$.

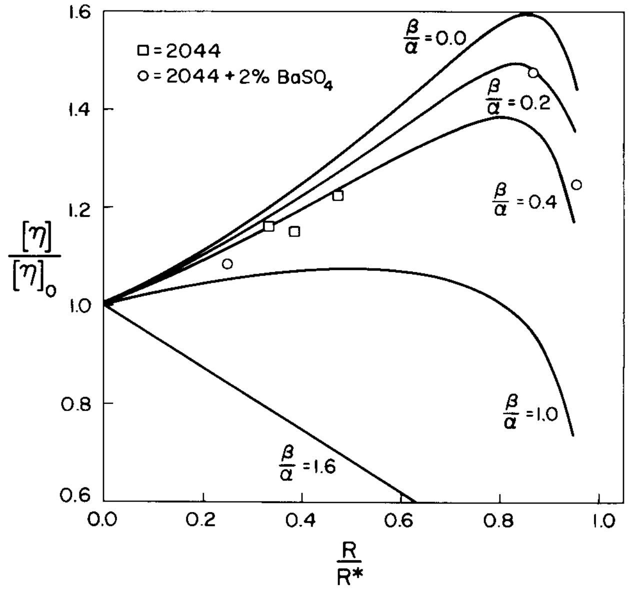

Fig. 7 Intrinsic viscosity change of Elvacite 2044 during exposure to near-ultraviolet light, prior to gel formation. Points are experimental viscosities η (from Fig. 4) for unpigmented and $BaSO_4$-containing resins, normalized to viscosities of unexposed resin (η_0). Dose R relative to gel dose R* determined assuming an induction period of 200mW hrs/cm^2 and gelation dose of 520mW hrs/cm^2 for the unpigmented resin; 130mW hrs/cm^2 induction and 280mW hrs/cm^2 gel dose for the $BaSO_4$-containing resin. Solid curves are calculated from equations in [24], using Mark-Houwink exponent of 0.77 and various ratios of chain-breaking to cross-linking (β/α).

different exposure apparatus.

In addition to providing the relative rates of chain-breaking and cross-linking, the slope of the Charlesby-Pinner plot also gives information about the absolute rate of the cross-linking reaction: the larger the slope, the smaller the reaction rate. An equivalent measure of this rate can be obtained by examining the dose at which gelation begins: for samples which have identical ratios of β/α the gel dose is a quantitative measure of the reaction rate. Although the absolute rate measured in this way will surely depend on details of the samples and aging conditions, the cross-linking rate of the resin containing ultraviolet-absorbing pigments (rutile TiO_2 and French Green Seal zinc oxide) is decreased considerably by a factor of 4-5 from the rate of the unpigmented resin film. By contrast, the resin containing barium sulfate cross-linked faster than the pure resin by a factor of about two.

The intrinsic viscosities of the aging resin films can also be analyzed to derive the value of β/α for the polymer before gelation. (As pointed out by Shultz *et al.* [24], there is no *a priori* reason to expect these ratios to be the same for the linear, pre-gelation polymer molecules and for the highly branched, insoluble gel.) Using the approximate model of Shultz *et al.* [24], one can calculate the expected change in the intrinsic viscosity as gelation is approached for various values of β/α. The curve which best fits the experimental measurements provides an approximate β/α ratio for the pre-gel chemistry. This has been done, giving the calculations and viscosity data shown in Figure 7, for the unpigmented and barium sulfate-containing films. Again the β/α value is small, about 0.2, and is about the same for both pure and pigmented samples.

It should be noted parenthetically that the intrinsic viscosity does not in general increase in cross-linking systems. As illustrated in the calculated curves of Figure 7, for large values of β/α, that is, for materials experiencing substantial chain-breaking in addition to cross-linking, the viscosity can decrease monotonically even though the molecular weight is increasing as gelation is approached. This possibility is cause for caution in interpreting viscosity losses (or, similarly, size exclusion chromatographic changes) in terms of a molecular weight decrease for resins which may also cross-link. Another feature worth noting is the dependence of the observed viscosity change on the exponent of the Mark-Houwink equation, which relates viscosity to molecular weight. For a large exponent, which is the case for poly(n-butyl methacrylate) in toluene, the viscosity increase is relatively large (about 50% of the initial viscosity) as gelation approaches. For polymer-solvent systems having smaller exponents, the viscosity is not a sensitive indicator of molecular weight change. The increase in intrinsic viscosity as a purely cross-linking polymer nears the gel point may only be a few percent.

To summarize the results for these pigments, the presence of both ultraviolet-absorbing and non-absorbing pigments does not seem to affect the overall degradation pathways for the 2044 resin. The rates for these photochemical reactions are affected, however, being slowed by the ultraviolet absorbers and accelerated by the supposedly inert scatterer, barium sulfate. Both these effects can be attributed to the optical properties of these types of pigments. By absorbing the ultraviolet light which could otherwise be absorbed by the resin and cause degradation to proceed, the rutile TiO_2 and Green Seal zinc oxide decrease the amount of light which penetrates the polymer film per unit incident dose. In contrast, the barium sulfate does not absorb these wavelengths of light and cannot protect the resin by screening it from the incident light. Instead of merely offering no protection, however, the presence of this pigment exacerbates the photodegradation of the resin by scattering the light inside the film. Light which enters a scattering film does not pass directly through it, as it would through an unpigmented film. Instead, the light scatters many times from pigment particles and from the surfaces of the film. This optical process in effect increases the path length of the light in the film, and the chance for absorption of the light by the polymer is thus greater. As a result, more resin degradation can occur for the same incident light flux. A detailed description of this optical phenomenon is complex [25-27], but this enhanced absorption in scattering systems has been observed in other experiments [28,29] and may also be at work in systems where scattering pigments accompany unusual resin or pigment degradation [30,31].

The anatase TiO_2 and Kadox 515 zinc oxide both seem to act as UV-absorbing pigments in delaying the onset of gel formation in 2044. Unlike the other pigments, however, ultraviolet light exposure causes substantial weight loss in the films containing these pigments. This can most easily be attributed to the chalking tendency of these particular materials. The mechanism of chalking is fairly well established for these pigments and is believed to begin with radical formation by photo-assisted oxidation of water at the surface of the pigment particle [11]. UV exposure creates large numbers of these radicals in the vicinity of the pigment surface which then attack the polymer, causing chain scissions and eventually producing small, volatile molecules.

It is notable that those radicals generated in the chalking 2044 films do not seem to accelerate the cross-linking chemistry, which might have been considered the preferred degradation path for this polymer. If the tendency for pure 2044 to cross-link stems from a propensity to form radicals on the butyl side-chains of the polymer, radical attack, which would have much less specificity toward the side-chains, might increase the probability for chain-breaking. Another possible reason for the increased importance of chain scission processes in these systems is that attack on the side-chain would be more likely to lead to cleavage (and low molecular weight, volatile products) than to cross-linkages. Without more detailed product analyses for these systems, all such mechanisms remain speculative.

Even though the degradation path for the polymer seems to shift from predominantly cross-linking to predominantly chain-breaking in these chalking films, the data in Figures 5a and 5b suggest that the development of insolubility may nevertheless be the most troublesome long-term change in the polymer film. Because the volatile products of degradation are lost from the film, the remaining material becomes almost all cross-linked gel. Clearly the details of a particular paint application which might affect the rate at which volatile degradation products are lost may determine the actual properties of the aged film. By the same reasoning it might be expected that analyses of naturally aged paints might give a distorted view of the actual degradation routes, if some reaction products have been lost from the film.

5 CONCLUSIONS

During the course of these experiments we have demonstrated again the methods for extracting information about the various processes by which a polymer can degrade. Using the formalisms of Charlesby and of Shultz, Elvacite 2044 is shown predominantly to cross-link with ultraviolet light exposure. Competition from chain-breaking chemistries is minor, with only about one chain-break occurring for each five cross-links. The pure resin films would become nearly completely insoluble at infinite doses.

The majority of pigments tested here did not alter the degradation chemistry of the polymer. The UV-absorbing pigments did slow the overall degradation rate by decreasing the intensity of light reaching the polymer. The scattering, non-absorbing barium sulfate accelerated the resin degradation by a factor of about two in these films, probably increasing the effective light interaction by scattering and diffusing the light once inside the film. Finally, the chalking pigments delayed the onset of degradation by absorbing the ultraviolet light but, once begun, the degradation produced large amounts of volatile products. The loss of these materials over very long exposures again renders the remainder of the film almost completely insoluble.

MATERIALS

Elvacite 2044: E.I. duPont de Nemours and Co., Inc., Wilmington, DE 19898, USA.

Ti-pure R-900, FF: E.I. duPont de Nemours and Co., Inc.

Florence Green Seal-8, Kadox 515: New Jersey Zinc Co., Inc., Palmerton, PA 18071, USA.

Foam A Baryta White: deLore Division of National Lead Co., St Louis, MO 63111, USA.

UV-A 351 lamps: The Q-Panel Co., 26200 First St, Cleveland, OH 44145, USA.

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