

THE NATURAL AND ACCELERATED AGING OF AN ACRYLIC ARTISTS' MEDIUM

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Summary—Changes in appearance and in the chemical and mechanical properties of films of Liquitex acrylic gloss medium, a commercial artists' medium based on an acrylic polymer dispersion, have been studied during natural aging in the dark and in accelerated thermal and light exposure tests. In dark storage at room temperature and humidity, the films acquire a haze and slight yellow discoloration in a few weeks, while the tensile properties stabilize only after film formation has progressed for about 50 days. Crosslinking seems to occur slowly at room temperature, causing the film to become only partially soluble in benzene and butanone, although the extent of this crosslinking does not seem to cause difficulty in film removal even after extended heat aging. The resistance of these films to photochemical degradation by near-ultraviolet light is very high. Exposure of these films to near-ultraviolet light causes very slow scission and oxidation of the polymer, producing a gradual increase in solubility and hardness; severely degraded films suffer a sudden loss of tensile strength.

Introduction

The widespread use of water-based dispersions of acrylic polymers in art and conservation applications justifies a concern about the future performance of these materials. While the particular products which are commonly used in art objects usually contain polymers which are generally regarded as stable, the nature of dispersion formulations provides further reason to investigate the changes that will occur as these materials age. Unlike solvent-based polymers, which form films of relatively unadulterated polymer as the solvent evaporates, dispersions are suspensions of microscopic polymer particles which form solid films by the fusion of those particles. In order to synthesize the polymer in that water-based suspension, and in order to maintain the stability and proper working properties of the fluid dispersion, numerous surfactants, thickeners and stabilizers must be included. The effect of the residues of these additives on the overall aging behavior of the dried films is not well understood. Furthermore, because these films must form by the fusion of the constituent polymer particles, softer polymers, such as acrylates or plasticized polyvinyl acetates (PVA) are often used. The stability of these polymers is not necessarily as high as for the more widely-used solvent-based methacrylate or PVA polymers.

Conventional accelerated aging tests of several commercial acrylic dispersions have been performed in an effort to identify those inappropriate for restoration use because of a tendency to discolor,

become resistant to mild solvents, or develop acidity with age [1–3]. Most of the acrylic dispersions tested showed apparent stability in heat and light exposure tests, although a tendency to discolor in the dark has been noted both in these accelerated aging tests and in more recent studies of naturally aged painting media [4]. As valuable as these studies have been in making judgments about the relative merits of the tested products, the qualitative nature of the analyses and the acknowledged limitations of such standard accelerated aging protocols leave many questions unanswered about the future of these materials.

Consequently a program of research has been started to explore the aging of acrylic dispersions used as painting materials. Rather than attempt to predict the aging behavior of these formulated products through an exhaustive analysis of their composition, we have instead chosen simply to monitor the changes in appearance and in chemical and mechanical properties of the polymer film during aging. While this approach yields the trends in aging behavior, proposed mechanisms by which these changes occur can only be considered speculative, pending a detailed analysis of the product formulation.

The initial study has examined Liquitex acrylic gloss medium, an unpigmented polymer dispersion commonly used as a coating or diluent for acrylic paints. Changes in films of Liquitex acrylic gloss medium under three different types of aging conditions have been studied. Films were monitored during their aging at room temperature and humidity in the absence of light. Oven aging tests were per-

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formed to explore the future development of these chemical changes during dark aging. Exposure of films to various fluorescent light sources also allowed us to probe the photochemical stability of this material and the changes in physical properties which accompany such photodegradation.

Experimental

The acrylic dispersion chosen for this study was Liquitex acrylic gloss medium, which was used without further purification. In its fluid form, the dispersion is alkaline (with a pH of approximately 9) and contains about 40% solids by weight. Prior analysis of the polymer in this material indicated that it contains ethyl acrylate, methyl methacrylate and ethyl methacrylate [1, 5]. The infrared spectrum measured for our cast Liquitex film is identical with the reference spectrum for an ethyl acrylate/methyl methacrylate copolymer [6]. No further attempt was made to define the composition of this material more precisely.

Films of this material were prepared and, using a variety of techniques, their chemical and mechanical properties were tested periodically as they aged. Details of the sample preparation and analytical procedures are given in the Appendix. While most of these analyses were conventional, less common measurements were needed when the films began to develop gel material which resisted dissolution in a range of solvents. First, in addition to the routine 24-hour room-temperature solvent extraction procedure to test solubility, extractions were occasionally performed for extended periods or at high temperatures to ensure that the gel fraction was strictly insoluble and not just slowly soluble due to the high molecular weight of the polymer. Second, when it became apparent that this gel material was an important indicator of the polymer chemistry, a more precise characterization of the gel by its weight fraction and its swell ratio (the volume increase upon immersion in a solvent) was performed routinely. Both of these quantities have been shown to be directly related to the density of crosslinking in the gel network [7, 8].

Films were aged 'naturally' in the dark at room temperature and relative humidity (approximate mean 25°C, 40% RH) or in accelerated heat or light exposure tests. Films for the accelerated aging tests were cast and allowed to age naturally for approximately 60 days in the dark prior to testing. Heat aging was performed in a circulating oven with no humidity control. Three separate light exposure tests were performed using banks of different fluorescent lamps in a controlled environment (23°C, 50% RH). In these tests the films were exposed to

fluorescent lamps emitting UV-B light (peak wavelength approx. 315nm), UV-A light (peak wavelength approx. 350nm), or simulated daylight. Light intensities in the visible and near-ultraviolet (300-400nm) were measured periodically with a radiometer and were relatively constant throughout the exposures. Under the UV-A sources films were exposed to about 25Wm⁻², and under the daylight fluorescent lamps samples were exposed to about 21 000 lux (2 000 footcandles), with ultraviolet intensities of about 1.4Wm⁻². These ultraviolet light intensities can be equated to exposure on display in a museum. One 'museum year' (based on 2 950 hours at 150 lux with 75µWlumen⁻¹ of near-ultraviolet intensity) is equivalent to about one hour under the UV-A sources and to about one day under the daylight fluorescent sources.

The exposure to UV-B wavelengths cannot be similarly translated to equivalent doses in museum environments, as the spectral output of these lamps includes wavelengths below 310nm which are encountered outdoors, but not indoors after filtering

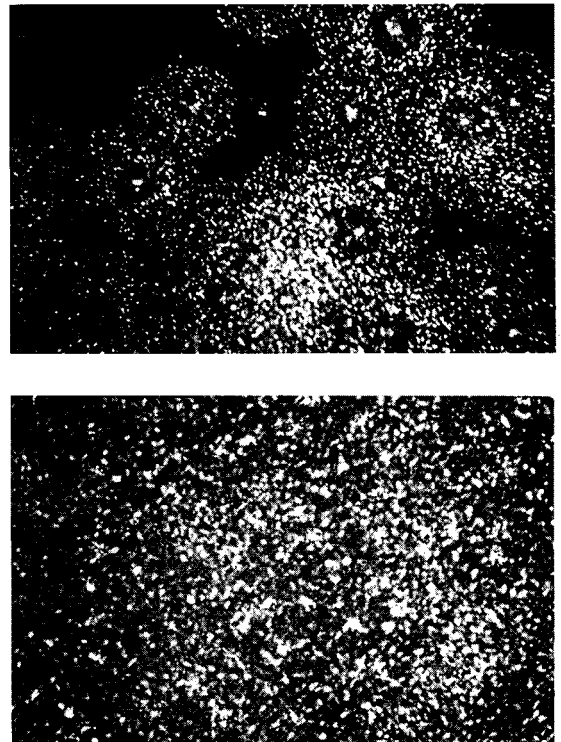


Figure 1 Photomicrographs of films of Liquitex gloss medium after: (above) 27 days and (below) one year. Transmitted light viewed through cross polarizers, magnification 80×. Horizontal full scale is approximately 1.5mm.

the daylight through window glass. Nevertheless, it was decided to explore the photo-degradation under UV-B light for three reasons. First, while perhaps not a common practice, it is still possible that contemporary works of art may be subjected to more stressful environments—higher light levels and unfiltered daylight—than would be found in a typical controlled museum climate. Second, while the photochemistry occurring at UV-B wavelengths may not simulate in detail that which occurs at longer wavelengths, these more severe tests provide the opportunity to explore and characterize the changes leading to the ultimate failure (in this case, the loss of tensile strength) of a relatively stable polymer. By obtaining this picture of the changes which occur over the useful life of the polymer, the authors feel better able to judge how quickly the end of serviceability is approached under less stressful light exposures. Finally, these exposures to UV-B fluorescent lamps were thought to offer a better possibility of separating photochemical changes from the thermal reactions which would certainly accompany exposures to high-intensity arc lamps in conventional weathering test cabinets.

Results

Natural aging

Cast films of Liquitex gloss medium underwent notable alterations in appearance over the first few months of natural aging in the dark. After casting, the milky fluid dispersion dried to a clear film within a few hours. Over the next few weeks, the initially clear films gradually became more highly scattering, first in localized regions, lending a blotchy appearance to the films, then more uniformly, producing the effect of a white haze throughout the films. Microscopic examination of the films during this period showed that the scattering arose from the formation of domains of a different material or phase in the polymer film (Figure 1). Although no further identification of this material or segregation process has been made, the occurrence of such a bloom is typical as surfactants or other residues of the dispersion formulation separate from the polymer matrix during film formation [9]. Alternatively, this separate phase may represent the formation of a complex of the polymer with an ionic salt present in the formulation, such as has been observed in films of poly(ethylene oxide) and polyesters containing various ionic salts [10, 11].

In addition to the haze which develops in these films, initially colorless films acquired a slight yellow coloration during a few months of dark storage

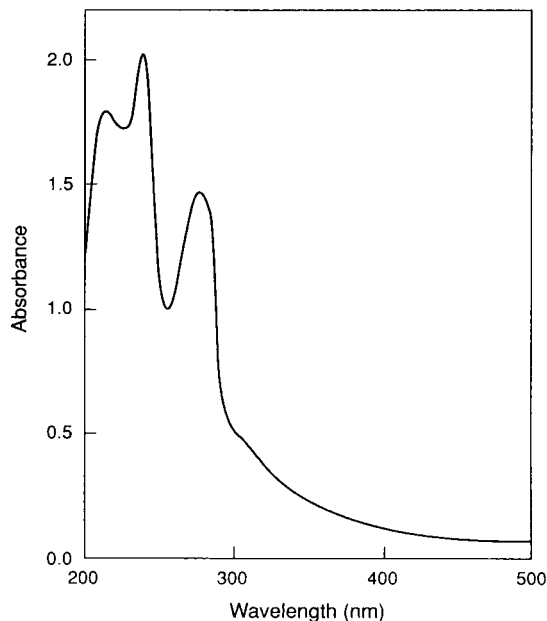


Figure 2 Absorption spectrum of Liquitex film aged for 923 days at room temperature in the dark.

at room temperature. The measured 'degree of yellowing' was only about 0.04 for films aged naturally for 880 days, and this level of discoloration in thin films has been reported to be judged 'acceptable' by a panel of observers [12]. The intensity of the yellow color seemed to depend on the film thickness, with thick films apparently more strongly colored than thin. This trend is consistent with discoloration occurring throughout the film and not just on its surface; indeed, the measured 'degree of yellowing' (i. e., absorbance per unit film thickness) was constant for thick and thin films. Absorption spectra of the yellowed films in the near-ultraviolet and visible wavelength region (Figure 2) were dominated by strong absorptions at 280, 240 and 215nm, all of which were present in the spectra of uncolored films. Yellowed films had increased absorption between 300 and 450nm which probably derived from overlapping absorption peaks in this region of the spectrum, but the presence of these individual absorptions was only indicated by barely perceptible shoulders on the spectrum. Numerical first derivatives calculated for these spectra suggest that shoulders occur at about 300, 325 and 335nm.

Once the films had become yellow, they exhibited a greenish-yellow fluorescence when illuminated with an ultraviolet source. Fluorescence excitation and emission spectra of the yellow films are shown in Figure 3. The emission spectrum shows that the

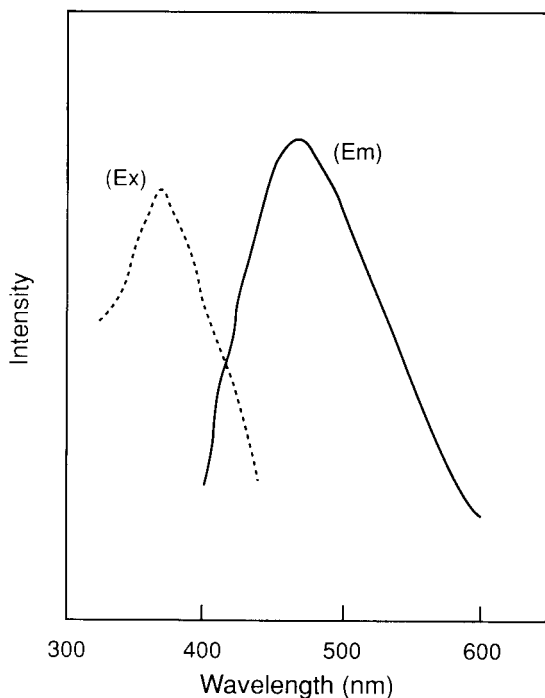


Figure 3 Fluorescence excitation (Ex) and emission (Em) spectra for Liquitex films aged for 1080 days at room temperature in the dark. Excitation spectrum was recorded while monitoring at 475nm, and emission spectrum was recorded while illuminating at 375nm.

fluorescence excited by near-ultraviolet illumination occurs over almost the entire visible spectrum, with a maximum emission between 450 and 500nm. The excitation spectrum shows that excitation of this fluorescence occurs over most of the near-ultraviolet wavelengths accessible to the instrument, with a peak in the excitation spectrum occurring at about 365nm.

At the same time that these changes in appearance occurred, films of Liquitex also underwent rapid changes in their response to solvents. After approximately two weeks of curing at room temperature in the dark, films which had been completely soluble in benzene following a 24-hour extraction at room temperature had become only partially soluble, the remainder forming a highly swollen gel in contact with benzene. From this point on, the film could be characterized by the increasing amount of this gel and by the decreased 'swellability' of the gel in benzene. The solubility and swell ratio during the natural aging of the film are shown in Figure 4.

Although measurement of the material remaining

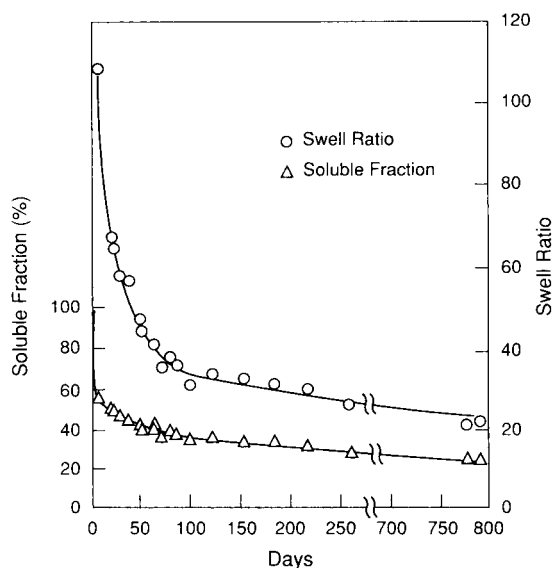


Figure 4 Solubility and swell ratio of Liquitex films during aging at room temperature in the dark.

after a 24-hour solvent extraction showed a monotonic increase in the amount of undissolved residue and a concomitant decrease in 'swellability' of the residue, there occurred a change in the nature of this insoluble gel after about 60 days of natural aging in the dark. Prior to this time, the gel residue remaining after a 24-hour room temperature extraction was still strictly soluble, for it could eventually be put into solution by longer immersion times or by extraction at higher temperature. Viscosity measurements of the soluble polymer indicated that the molecular weight of the polymer remained relatively constant during this early period. After about 60 days, however, the insoluble gel remaining after benzene extraction could not be completely dissolved by more extensive extractions, and solubilities measured by extractions for long periods, at high temperatures, or in different solvents (benzene and butanone) yielded virtually identical results for equivalent films.

In addition to the changes in appearance and chemical properties during the first few weeks following casting, the mechanical properties of the film, its stress at yield and its tensile strength, were also reaching stable values (Figure 5). The films only achieved their ultimate strength and ductility after about 50 days of aging at room temperature in the dark. Once the film had stabilized, the stress-strain response of this material was typical of a tough, ductile polymer. It could be drawn to about three times its length before breaking, and its ten-

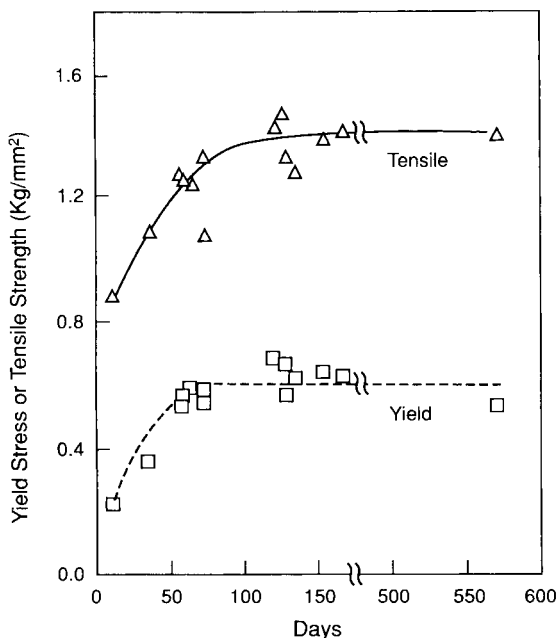


Figure 5 Mechanical properties of Liquitex films during aging at room temperature in the dark.

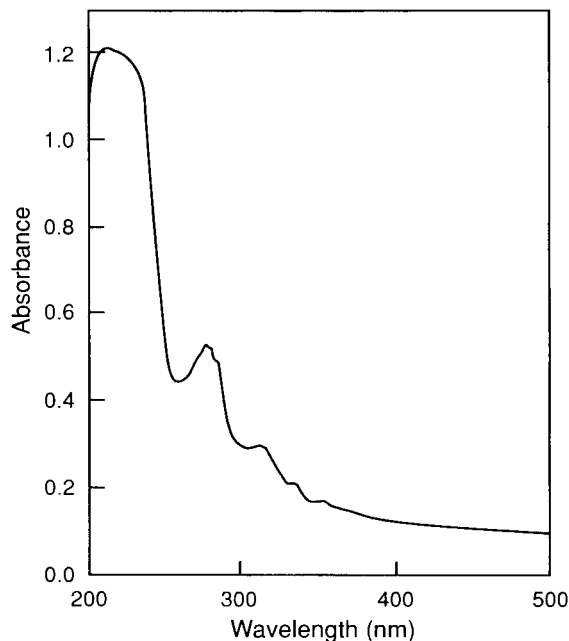


Figure 6 Absorption spectrum of Liquitex film aged at 95°C for 45 days in the dark.

sile strength stabilized at 13MPa (1.3kg mm^{-2}). Its yield strength (the load it can withstand before permanently deforming or 'yielding') of 6MPa (0.6kg mm^{-2}) was about half its tensile strength.

Accelerated aging

Films of Liquitex gloss medium were aged at 75–125°C in order to explore the possible chemical, mechanical and appearance changes which could occur following natural aging for very long times. Because of the rapid evolution of chemical and mechanical properties following casting, the films for these tests and for the light exposure tests were first cured for 60 days at room temperature in the dark before testing. All of the oven tests produced essentially the same changes that had been observed in the naturally aged films: a slight yellow discoloration developed and solubility was lost at rates which increased with oven temperature. In all of these tests, however, the films seemed ultimately to develop only a moderate degree of discoloration and insolubility. For example, prolonged aging at 95°C eventually produced only slightly yellow films (calculated degree of yellowing of 0.1) which were still 10% soluble and could be easily swollen and removed with brief application of mild aromatic solvents. The absorption spectra of these heat-discolored films showed an increase in the peaks at

210, 240 and 280nm, as well as a growth of small, broad absorptions at 310, 335 and 350nm (Figure 6).

The relatively rapid discoloration and solubility loss during dark aging raised some concern about the photochemical stability of this polymeric material. To explore the changes produced by extensive photodegradation, Liquitex films cured at room temperature in the dark for 60 days were exposed to UV-B fluorescent lights (peak wavelength about 315nm). Changes in the solubility and swell of films during this exposure test are shown in Figure 7. Following a very brief period during which yellowing increased slightly and solubility and swell ratio decreased slightly, the films rapidly lost color and regained solubility.*

During the exposure period the films also lost about 8% of their original weight, and the microscopic domains which had caused the optical scattering in the originally hazy films gradually disappeared. No changes in the infrared spectrum of the film were visible after 30 days of exposure.

*This brief initial period was not a heat-induced effect, for oven tests performed at the temperatures that the films experienced under the fluorescent lamps produced no changes. Separate tests on films which had already been oven-aged so that they were discolored and insoluble did not demonstrate this initial effect.

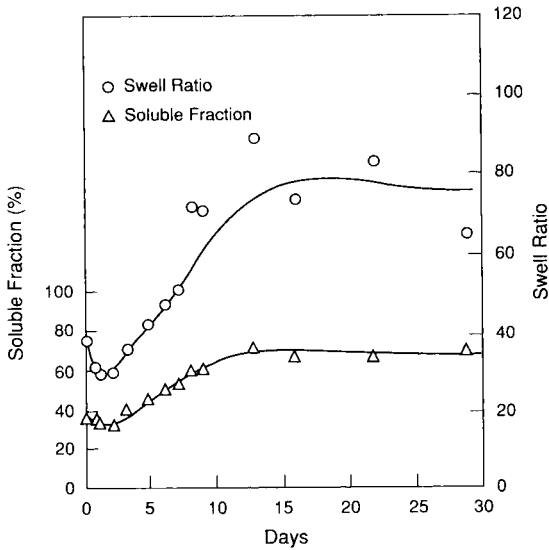


Figure 7 Solubility and swell ratio of Liquitex films during exposure to UV-B lamps.

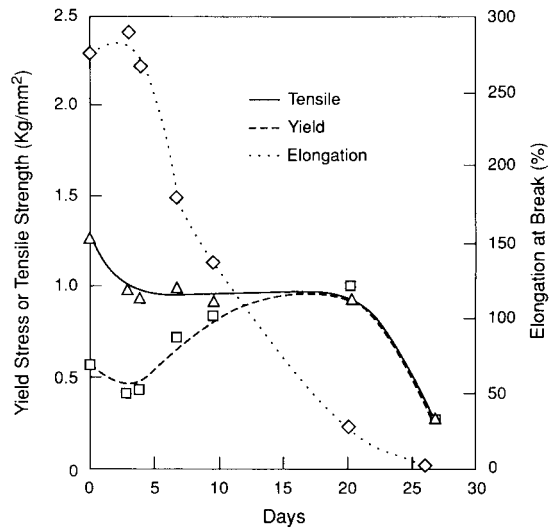


Figure 8 Mechanical properties of Liquitex films during exposure to UV-B lamps.

Concomitant changes in mechanical properties during the UV-B exposures are shown in Figure 8. The tensile strength remained fairly constant during the exposure but was finally lost precipitously after about 30 days of exposure, and this point can be denoted an approximate end of the service life of the film. While the tensile strength was not changing, however, the elongation at break decreased and the yield stress increased steadily during the light exposure. At the same time, pencil (gouge) hardness increased (from softer than a 5B pencil to HB after 19 days of exposure) and the glass transition temperature (T_g) of the polymer rose from 12 to 16°C. These changes all reflect the film becoming progressively less ductile and flexible as it degraded.

Longer wavelength ultraviolet light seemed to cause the same deterioration observed under UV-B illumination, only the degradation occurred much more slowly. Exposure of cured Liquitex films to UV-A fluorescent lights (peak wavelength around 350nm) caused a slow increase in solubility and swell ratio, following a brief initial period when solubility and swell decreased slightly (Figure 9). A decrease in the elongation at break and an increase in the yield stress also suggest that this was a similar degradation as under UV-B illumination, but the changes were occurring much more slowly (Figure 10). Exposure to daylight fluorescent illumination seemed to cause the same slight loss in solubility and swell as were observed at the start of the exposures to the UV-A and UV-B lamps, and these changes occurred so slowly that the increase in sol-

ubility and swell which characterized the advanced stage of photodegradation had not been observed by the end of the 80-day exposure.

Discussion

Some of the most dramatic changes in these films, particularly the rapid development of strength, can be attributed to the formation of a continuous film from a polymer dispersion. This film formation takes place in a series of stages that involve the ordering and gradual coalescence of the particles of polymer suspended in the dispersion [13]. While the particles of a dispersion of a soft polymer (the T_g of Liquitex is 12°C) should fuse within a few days [14], the development of ultimate mechanical properties may take longer, as the polymer chains derived from adjacent particles in the film extend and intertwine [15]. As the polymer chains entangle, dissolution by disengaging chains from this solid becomes more difficult, and the ability of a solvent to swell the more tightly knit network of tangled chains decreases. This slowing of the rate of dissolution, through an increase in the *mechanical* resistance to dissolution (the untangling of long chains), has been termed a loss of 'kinetic solubility' [16] and is to be distinguished from a change in solubility parameter, or the *chemical* resistance to dissolution, which is denoted a change of 'thermodynamic solubility'. In other words, for two acrylic polymers differing in molecular weight only, the observed sol-

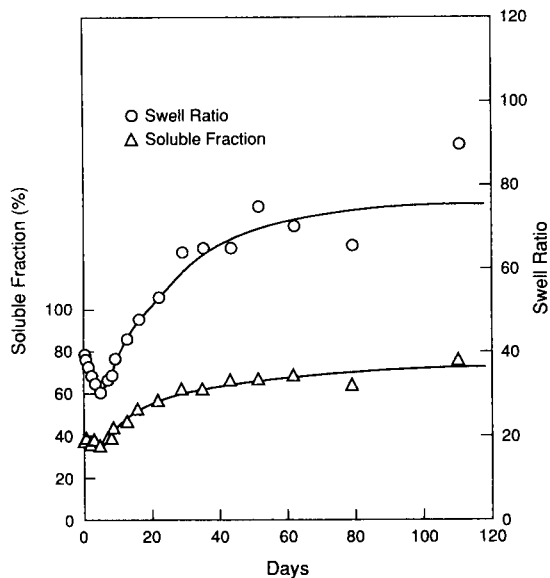


Figure 9 Solubility and swell ratio of Liquitex films during exposure to UV-A lamps.

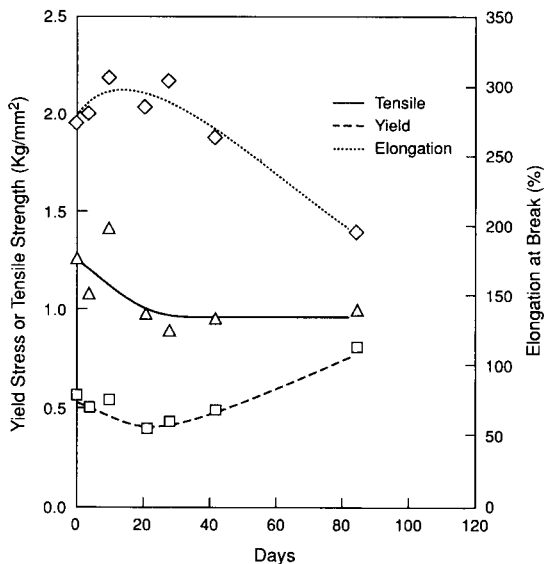


Figure 10 Mechanical properties of Liquitex films during exposure to UV-A lamps.

abilities at any given time may differ not because of different solubility parameters, but simply because shorter polymer chains may be disengaged and put into solution more rapidly than longer chains. Similarly, the observed solubility of a poorly coalesced dispersion-based polymer film can appear greater than that of a well-formed, more completely integrated film of the same polymer.

This process probably accounts for the apparent loss of solubility and the decrease of swell ratio for the gel residue within the first two months after casting, but it is not clear that the further solubility loss beyond the first two months can be attributed solely to further film formation. In particular, the observed persistence of the gel material during rigorous extraction of aged films has hitherto been taken as an indication that chemical crosslinking has occurred, and the production of films which are 90% insoluble suggests the participation of the acrylic polymer in the crosslinks. Although chemical crosslinking is a straightforward interpretation of this gel formation, such rapid crosslinking would be unexpected for this type of acrylic polymer, in which scission would tend to predominate as it slowly degrades. While the presence of crosslinking additives cannot be entirely ruled out, the very low levels of crosslinking which are achieved make it unlikely that significant levels of such an agent have been intentionally added. It is not known whether the dissolution of fully coalesced films of very high molecular weight polymers, an uncommon experi-

ence in conservation practice, can appear indistinguishable from the swelling of chemically cross-linked gel. So, while the possibility cannot be dismissed that this insolubility is a result of the loss of 'kinetic solubility' as the polymer film forms, at this time the insolubility is attributed to the development of low concentrations of chemical crosslinks.

The coincidence between the development of insolubility and color suggests a possible connection between these two changes, and the identity of the chromophores makes this possibility seem more plausible. While the ultraviolet absorption provides only very indistinct evidence of the chromophores which cause the yellow discoloration—the only prominent mid-ultraviolet peak at 280nm may derive not from the discolored polymer but from a non-ionic surfactant containing a benzene ring—the increase of absorption across a broad wavelength region and the evidence of a series of absorption peaks occurring at regular intervals suggest a similarity to the chromophores which are produced in vinyl polymers such as polyvinyl alcohol (PVOH) [17, 18] and polyvinyl chloride (PVC) [19]. In these other polymers, discoloration arises from 'polyene' structures, carbon chains containing conjugated double bonds (alternating single and double carbon-carbon bonds in sequence along the chain). Periodic peaks in the absorption spectra derive from individual members of this family of a particular length, i.e., having a specific number of these double bonds

in the chromophore, and the number of double bonds is used to denote the different members of this polyene class. Other chemical functional groups can occur in these conjugated structures, such as terminal aldehyde, ketone or acid/ester groups. These functional groups tend to shift and broaden the optical absorption spectra of the unsubstituted polyenes, giving rise to separate classes of related 'polyene-type' chromophores [20]. Since the absorption spectra of discolored Liquitex films seem to lack the very sharp, structured peaks produced from the unoxidized polyene chromophores, it is likely that the chromophores produced in Liquitex films are members of the oxidized polyenes having attached aldehyde (polyenal), ketone (polyenone) or acid/ester (polyene acid/ester) groups.

Further support for this identification of polyene chromophores is provided by the fluorescence of the discolored Liquitex films. Strong fluorescence of these polyene chromophores has been noted in studies of PVOH [17, 18] and, because of the importance of these polyene structures in biological vision systems, the absorption and fluorescence properties of these compounds have been studied in great detail. It has been found that the fluorescence can only occur in moderate-length chromophores with four to eight double bonds (including the terminal carbonyl) having an unusual ordering of low-lying excited states [21-25]. These studies also clearly demonstrate that the positions of maxima in the absorption, excitation and emission spectra depend on the length of, and terminal function on, the chromophore, on the configuration of the chromophore (i.e., whether the carbon chain is in a *cis* or *trans* configuration at each double bond), and on the solvent environment. Because none of these details can be specified for Liquitex polymer films, it is impossible to assign the absorption/fluorescence in Liquitex to specific chromophores unambiguously. It can be concluded, however, that the fluorescence that occurs in the visible region and which is excited mainly near 365nm is probably due to these moderate-length chromophores having five or six double bonds, including the terminal carbonyl [22, 23, 25]. This visible fluorescence thus derives from the same chromophores which give rise to the near-ultraviolet absorption and the slight yellow color, and this is the reason that the films begin to fluoresce after only slight discoloration has occurred.

Because the detailed composition of Liquitex gloss medium is unknown, it is premature to attribute the production of these polyene chromophores to a specific component or chemistry. These conjugated chromophores may form from elimination of side groups on a long carbon chain or from condensation of smaller species to form the

extended structures. The color development may also depend on the exact nature of the polymer or polymers in this product, since chain defects (particularly C=C-C=O structures) have been found to be initiation sites for the discoloration in PVC [26, p. 85]. It might be significant that the prominent absorption at 215nm in the ultraviolet spectrum of Liquitex films (Figure 2) may arise from this type of defect [18], and growth of this absorption seems to accompany the discoloration.

Additives or residues of the polymer synthesis may also provide the reactants or catalysts for the discoloration chemistry. It is important to note that many acids and alkaline salts have been observed to catalyze the elimination chemistry which produces these chromophores in PVOH [18, 27] and PVC [26, pp. 187-231], and the development of large numbers of long chromophores seems to occur only in films containing catalysts. The incidental addition or generation of such catalysts may be the cause of the exacerbated discoloration of these art products in certain applications [4].

Whatever their origin, the conjugated chromophores may be related to the chemical crosslinks which seem to form in Liquitex films. Just as the unsaturated bonds in drying oils lead to oxidative crosslinking of an oil paint film, the unsaturated bonds in these conjugated chromophores may undergo crosslinking reactions which cause solubility loss during the discoloration of PVC [28; 26, pp. 121-128] and PVOH [29], or they may act as crosslinking agents by reacting with several polymer chains. Alternatively, it is possible that the chemistry which produces these chromophores could cause crosslinks in side reactions, as has also been postulated for the vinyl polymers. While the exact mechanism of this crosslinking is unknown in all of these polymer systems, the acrylic polymer in Liquitex films would seem to be involved in the crosslinking reactions, as up to 90% of the film becomes an insoluble gel.

Following the brief initial period when the exposure to ultraviolet light seems to crosslink the film slightly (perhaps the photoreaction of the unsaturated chromophores rather than of the original polymer), the polymer chains in Liquitex films seem to photodegrade predominantly by oxidative scission, as expected for an ethyl acrylate/methyl methacrylate polymer. This scission breaks down the gel network (increasing its 'swellability') and creates shorter polymer segments that can be extracted from the gel (increasing the solubility of the film). The loss in weight during exposure to ultraviolet light is also consistent with scission of the polymer to produce volatile products. The sudden loss of tensile strength is typical for scission in an amorphous polymer which derives its cohesive

strength from the entangling of the polymer chains. Many studies have demonstrated that ultimate strength properties of a polymer are relatively unaffected by a reduction of molecular weight until chains have become so short that they can no longer effectively entangle with each other and provide cohesive strength to the film [30–32]. Finally, the increased hardness and loss of ductility resulting from ultraviolet light exposure probably arise from the increased attraction between the polymer chains as they incorporate polar groups during oxidative degradation. While this polymer oxidation which must accompany the chain scission may slowly change the solubility parameter of the polymer, it alone cannot increase the solubility of the insoluble gel. Indeed, it was the constant gel fraction measured in a wide variety of solvents that indicated a truly insoluble gel network had formed. For the gel fraction to be taken into solution, the chains must be freed of the crosslinked network by breaking the crosslinks or the chains. Since chain scission is indicated by the weight loss and tensile failure, the solubility and the accompanying swell increases are also attributed to that chain scission.

While films of Liquitex gloss medium did photo-oxidize upon exposure to ultraviolet light, the material generally demonstrated the remarkable photochemical stability associated with this class of acrylic polymers. In comparison to the mechanical property loss under UV-B exposure, tensile strength loss under UV-A lamps would have been observed only after about 200 days, a dose of near-ultraviolet light equivalent to about 5 000 'museum years'. This light resistance can be attributed both to the high stability of acrylate and methacrylate polymers [33] and to the high initial molecular weight of the polymer, which must undergo a large number of scissions before being reduced to the short fragments which cannot contribute to cohesive strength. In terms of polymer photodegradation, this material should thus be considered a member of Feller's 'Class A' of stability [34].

While the tensile strength of this material seems to remain nearly constant over its service life, it has been noted that other properties, notably flexibility, hardness and glass transition temperature, do change as the film oxidizes, and this raises the possibility that these quantities may provide other indications of the progress of oxidative degradation. Of these properties, the loss of flexibility may be the most easily noticed, especially if paintings are routinely rolled for handling, storage or transport. However, it should be noted that, for this material, loss of flexibility may not precede the strength loss, for embrittlement of the film may not be observed until the elongation at break is reduced to only a few percent. In an early study of the relation

between elongation and mandrel testing of flexibility (in which a film on a substrate is rolled around a cylinder of standard diameter), a film which cannot withstand rolling over a 1/8" (3mm) diameter mandrel (a just measurable brittleness in many cases) can still have an elongation at break of 15–35%, depending on the thickness of the substrate [35]. In the present case, then, photodegrading Liquitex films would still be considered flexible until the elongation at break became less than about 25%, which will only occur just prior to tensile strength loss. Thus, although the loss of ductility is an early indicator of photodegradation, the perceptible embrittlement may not significantly precede the tensile failure. If they can be practically monitored, changes in the hardness or glass transition temperature may provide earlier warning of progress toward photo-oxidative strength loss.

Exposure of yellowed Liquitex films to the light sources in these tests generally caused the discoloration to bleach. While these results are consistent with the photobleaching studies of discolored PVOH [36] and PVC [37], these other studies also suggest potential problems with light bleaching. It was found that conjugated chromophores of different lengths had different reactivities upon light exposure: very long chromophores (absorption maxima >400nm) seemed to bleach much more slowly. Attempts at bleaching may thus cause a hue shift as the short chromophores are preferentially bleached. Simultaneously with the bleaching reactions, light exposure may also create more chromophores or their precursors, and in PVC a maximum bleaching effect was followed by discoloration upon further light exposure. Finally, light bleaching may disrupt long conjugated chromophores by inducing crosslinking reactions, and solubility loss may accompany bleaching. Future studies will test the relevance of these findings to the light bleaching of Liquitex films.

Conclusions

In the dark, films of Liquitex gloss medium tend to discolor and apparently crosslink rapidly but slightly: even after prolonged oven aging, the discoloration in thin Liquitex films was barely perceptible and the crosslinked material remained easily swollen and removable with brief application of mild aromatic solvents. The yellowing is attributed to the formation of conjugated 'polyene' structures, and the production of moderate length chromophores (having five or six double bonds) also causes the films to fluoresce under ultraviolet illumination. The crosslinking may derive from reactions of the unsaturated bonds in these chromophore structures

or from the reactions which created the chromophores.

There is an intuitive association between discoloration and solubility change, since both are often conspicuous signs of chemical deterioration. Indeed, for many polymers discoloration accompanies the loss of desirable chemical and physical properties as the material degrades. By contrast, during the dark aging of Liquitex gloss medium the discoloration which occurs does not appear to be associated with a rapid oxidative deterioration of the polymer: besides the solubility change which seems to occur from slight crosslinking, there is no evidence for concomitant reactions which degrade the other chemical and physical properties of the polymer. In this case, then, the polymer seems to demonstrate two widely different degrees of 'stability', depending on whether that stability is measured by the appearance of the material or by the retention of the original chemical and physical attributes of the polymer.

While dark aging at room temperature did not produce greatly discolored or crosslinked films after two years, the ultimate level of yellowing during dark aging may depend on both the rate of formation (catalyst concentration and production from other degradation) and the rate of consumption (from light exposure, oxidation, reaction with pollutants, etc.) of these chromophores. Different applications or aging conditions which alter the rates of either of these types of chemistry may produce ultimate levels of discoloration and crosslinking which differ from those observed in this study. Consequently, it is not known whether the mild discoloration and crosslinking produced in the oven aging tests accurately simulate the future of this material after prolonged natural aging.

The resistance of this polymer material to photochemical degradation by near-ultraviolet light is very high. In its photochemical stability and retention of mechanical properties, it can be considered a 'Feller Class A' polymer material, and this probably derives both from the intrinsic stability of the acrylic polymer and from its high original molecular weight. In the present study, light exposure also seemed to bleach the discoloration in the films but, in view of the reported photochemistry of these same chromophores in other polymers, the effectiveness and side effects of this treatment should be questioned.

Appendix

Films of Liquitex gloss medium were prepared as 'draw-downs' on glass plates using an applicator blade having a 254 μ m clearance. The thickness of

each dried film was measured with a micrometer and was in the range of 50–100 μ m. The variation in film thickness probably resulted from inability to control the exact solids content and fluidity of the dispersion during film preparation. To the extent that it was possible, groups of samples having comparable dimensions were used for the various tests. After preparation the films were stored in a clean dark box.

Conventional molecular weight measurements by analysis of the dissolved polymer could only be performed on the whole film within the two weeks following casting, because the films gradually became only partially soluble in a wide variety of organic solvents, including benzene, methylbenzene (toluene), methanol, propanone (acetone), butanone (methyl ethyl ketone) and tetrahydrofuran. When the films were completely soluble, molecular weights were monitored by measuring the intrinsic viscosity of benzene solutions at 25°C using Cannon Ubbelohde Series 25 or 50 viscometers according to a standard method [38].

Because accurate molecular weight measurements became impossible once the film began to form insoluble gel, indirect measures were adopted in order to monitor the course of the polymer chemistry. Weight changes were followed by periodic measurement of the films on an analytical balance. The nature of the polymer solid was probed by measuring the sol fraction and volume swell ratio of the insoluble gel following a 24-hour extraction in benzene at 25°C. Occasionally extractions with benzene or butanone were also performed for extended times or at higher temperatures in order to verify the persistent nature of the gel residue. Values of the soluble fractions and swell ratios are the average of two to four determinations on samples taken from replicate films. The gel weights were corrected for the weight of soluble polymer which was retained in the swollen gels, based on the solvent content of the gel and soluble fraction of the film.

In order to correlate the changes in chemical properties with the changes in physical properties of the polymer films, tensile measurements were made on separate samples of films prepared identically to those which had been analyzed chemically. Rectangular samples (80–90 × 12mm) were cut from the aged films. The film thickness was measured with a micrometer, and an average of three measurements was calculated. Samples were conditioned at 23°C, 50% RH for 24 hours in a controlled environment room in which the tensile measurements were also made. Tensile stress-strain measurements were performed according to a standard method [39], using a gauge distance of 50mm and draw speed of 300mm minute⁻¹. Strips of blot-

ter paper were used on each grip surface to prevent slippage of the sample during testing. Yield stress, elongation at break and tensile stress at break were calculated from the stress-strain profiles and the initial film cross-sectional area, and the resulting values from measurements on a minimum of four replicate film samples were averaged.

In addition to these analyses, which were performed at frequent intervals during the aging, other analyses were made occasionally on separate films which had received similar aging treatments. Infrared spectra were taken of thin (approximately 5µm) free films on a Fourier transform infrared spectrophotometer with a spectral resolution of 4cm⁻¹. Glass transition temperatures were determined by differential scanning calorimetry with a programmed sequence of two heating cycles from -30 to 70°C at 10°C minute⁻¹. Pencil hardness of the films was determined as specified in the standard test method [40]. Absorption spectra of films were determined from the transmittance in the 190–700nm wavelength region (4nm resolution). Numerical derivatives of these spectra were calculated using the computer software provided with this instrument in order to detect and locate poorly resolved spectral features. 'Degrees of yellowness' were calculated from the absorbances at 380 and 600nm according to the method of Down [12]. This measure normalizes the absorbance at 380nm to the film thickness so that the yellowing per unit film thickness can be quantified. Fluorescence excitation and emission spectra were recorded (2nm wavelength resolution for excitation, 6nm for collected emission) for aged samples which displayed visible fluorescence when illuminated with a near-ultraviolet 'blacklight'. Fluorescence from the illuminated surfaces of solid films was collected at about 20° from the surface normal. These data were automatically corrected for varying lamp output, optics transmission and detector sensitivity across the spectrum.

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Suppliers

- Liquitex acrylic gloss medium and varnish: Binney and Smith, Inc., PO Box 431, 1100 Church Lane, Easton, PA 18044-0431, USA.
- Analytical balance (Model AE 163): Mettler Instrument Corp., PO Box 71, Hightstown, NJ 08520, USA.
- Tensile tester (Model TM-M): Instron Corp., 100 Royall Street, Canton, MA 02021, USA.
- Fourier transform infrared spectrometer (Model 5DXB with a 1280 processor): Nicolet Instrument Corp., 5225-1 Verona Road, Madison, WI 53711, USA.
- Differential scanning calorimeter (Model DSC 220C): Seiko Instruments Inc., 2990 West Lomita Blvd, Torrance, CA 90505, USA.
- UV-visible spectrophotometer (Lambda 6, with Labtech integrating sphere and UVDM software): Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859, USA.
- Fluorescence spectrometer (Fluorolog): Spex Industries, 3880 Park Avenue, Edison, NJ 08820, USA.
- UV-A and UV-B fluorescent lamps (UVB-313 and UVA-351): Q-Panel Corp., 26200 First Street, Cleveland, OH 44145, USA.
- Daylight fluorescent lamps (F48t13): Sylvania, PO Box 9544, 450 Butler Street, Pittsburgh, PA 15223, USA.
- Radiometer (Model IL700): International Light, 17 Graf Road, Newburyport, ME 01950, USA.

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Résumé—On a étudié les changements d'apparence et de propriétés aussi bien chimiques que mécaniques des films de médium à base de vernis acrylique Liquitex (un médium du commerce employé par les artistes qui a pour base la dispersion d'un polymère acrylique) durant le vieillissement naturel dans le noir, et une exposition accélérée à la chaleur et à la lumière. Dans le noir, et à la température et à l'humidité ambiante, les films deviennent brumeux et présentent une légère coloration jaune en quelques semaines, tandis que l'élasticité ne se stabilise seulement qu'après 50 jours environ. Le crosslinking semble à faire lentement à la température ambiante, rendant le film seulement partiellement soluble dans le benzène et la butanone, bien que l'étendue de ce crosslinking ne rende pas l'enlèvement du film plus difficile, même après un vieillissement à la chaleur. La résistance de ce matériau polymère à la dégradation photochimique par le proche ultraviolet est très élevée. L'exposition de ces films en proche ultraviolet cause une scission très lente et une oxydation du polymère entraînant une solubilité et un durcissement accrus. Plusieurs films dégradés présentent une perte soudaine d'élasticité.

Zusammenfassung—Gegenstand der Untersuchung sind physikalische und chemische Eigenschaften von Aufstrichen des Acrylmediums Liquitex, einen kommerziellen Künstlermalmittel auf der Basis einer Acrylharzdispersion. Die Kunstharzfilme wurden natürlichen Alterungsversuchen unter Lichtausschluß und beschleunigten Temperatur- und Lichttests ausgesetzt. Bei Dunkelheit sowie Raumtemperatur und -feuchte entwickeln die Filme innerhalb einiger Wochen eine Trübung und leichte gelbliche Verfärbungen. Die dehnungseigenschaften stabilisieren sich erst nach einer Filmbildungsdauer von etwa 50 Tagen. Bei Raumtemperatur

scheint sich eine Vernetzung nur langsam einzustellen, die eine nur noch teilweise Löslichkeit des Films in Benzol und Butanon zur Folge hat. Das Ausmaß dieser Vernetzung erschwert aber die Entfernbarekeit des Filmes auch bei anhaltender Alterung unter Wärmeeinfluß nicht nachhaltig. Die Resistenz des Polymers gegen photochemischen Abbau durch UV-Strahlung ist sehr groß. Die Exponierung der Kunstharzfilme im nahen UV Bereich verursacht eine sehr langsame Spaltung und Oxidation des Kunststoffes. In der Folge erhöhen sich Löslichkeit und Härte nur graduell; stärker zersetzte Filme zeigen einen plötzlichen Verlust an Zugfestigkeit.

Resumen—*Se estudiaron los cambios visibles y químicos y las características mecánicas de películas del medium acrílico brillante de Liquitex (un medium comercial para artistas basado en una dispersión de polímero acrílico) durante un proceso de envejecimiento a oscuras y en pruebas de aceleración térmica y de exposición a la luz. Después de unas semanas en condiciones de temperatura y humedad de ambiente, y con la exclusión de luz, las películas manifiestan un pasmado y una ligera descoloración amarillenta. Las características de su capacidad de tensión se estabilizan solamente cuando la formación de la película haya durado unos 50 días. A la temperatura de ambiente, cross-linking parece ocurrir lentamente, haciendo que la película se queda solamente parcialmente soluble en benceno y butanona. Sin embargo, no parece que el grado de cross-linking dificulta más la eliminación de la película, inclusive después del envejecimiento con calor. Este material polimérico muestra una elevada resistencia a la degradación fotoquímica de luz ultravioleta cercana. La exposición de estas películas a la luz ultravioleta cercana ocasiona un proceso de corte y oxidación muy lentos del polímero, produciendo un aumento gradual de solubilidad y dureza. Las películas que estan severamente degradadas sufren una repentina pérdida de su capacidad de tensión.*