SHRINKAGE STRESSES IN ART AND CONSERVATION COATINGS BASED ON SYNTHETIC POLYMERS

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ABSTRACT—The shrinkage stresses that are created in the application of modern commercial and homemade art and conservation paints, media, and gesso based on synthetic polymers have been measured. Commercial art products tended to dry to essentially stress-free films. Coatings formulated with hard (high T_g or Young's modulus) polymers, however, tended to dry with substantial shrinkage stresses, and those stress levels increased with pigment loading up to the critical pigment volume concentration. In these tests, some films were produced having drying stresses that exceeded the cohesive or adhesive strength of the coating. Even for coatings that remained intact after drying, residual stresses remained in the films, which would leave them at greater risk of subsequent damage from additional applied stresses due to environmental changes or handling. Material analyses to determine the nature of the coating resin or paint binder may provide some means of assessing the likelihood of residual drying stresses being present, although stress measurements on the particular materials found would be needed to estimate the magnitude of those stresses. Treatments to relieve the stresses in coatings may be possible, but extensive testing on the specific material combinations identified on the artifact is necessary to determine the safety and efficacy of the method. Climate control and careful handling, to minimize additional stresses on objects that may be at risk, are the most prudent steps currently available.

TITRE—Les tensions dues au retrait des couches composées de polymères synthétiques et utilisées dans le domaine des arts et de la restauration. RÉSUMÉ—On a mesuré les tensions dues au retrait qui sont créées lors de l'application, dans le domaine des arts et de la restauration, de couches de peinture, liant et gypse composées de polymères synthétiques, et qui ont été préparées commercialement ou artisanalement. Les produits d'art vendus dans le commerce sèchent généralement sans développer de tension. Cependant les couches composées des polymères rigides (ceux avec un coefficient d'élasticité ou une température de transition vitreuse élevée) ont tendance à sécher avec des tensions de retrait considérables. De plus les tensions sont accentuées lors de l'addition de pigments jusqu'à une certaine concentration critique. Lors des tests, certains films produits avaient un niveau de tension supérieur aux forces de cohésion et d'adhérence du polymère utilisé. Même pour les couches demeurées intactes après avoir séché, ces tensions internes augmentent le risque de dommages lorsque des tensions externes sont appliquées, lors de la manipulation des objets ou lors d'un changement des conditions ambiantes. L'analyse des matériaux dont sont composées les couches de résine ou les liants des peintures peut constituer un moyen pour déterminer si des tensions dues au séchage sont présentes. Il n'en reste pas moins que seuls des tests sur la tension des matériaux particuliers peuvent donner une idée exacte de l'ampleur de ces tensions. Des traitements afin de réduire les tensions dans ces films sont possibles, bien que ceux-ci requièrent un nombre considérable de tests sur les couches présentes sur les objets afin de déterminer l'efficacité et la sûreté de la méthode. Le contrôle des conditions ambiantes et le soin lors de la manipulation demeurent les méthodes les plus prudentes afin de minimaliser la création de tensions additionnelles pour les objets dont les couches de surface sont vraisemblablement déjà fragiles.

TITULO—Tensiones de contracción en recubrimientos de arte y conservacion basados en polímeros sintéticos. RESUMEN—Se midieron las tensiones de contracción producidas por la aplicación de pinturas para arte y conservación, ligantes y yesos comerciales y artesanales modernos basados en polímeros sintéticos. Los productos para arte comerciales tienden a secar como películas esencialmente libres de tensión. Recubrimientos formulados con polímeros duros (alto Tg o módulo de Young) no obstante, tienden a secar con tensiones de contracción sustanciales y dichos niveles de tensión se incrementaron con la carga de pigmento hasta la concentración crítica de volumen de pigmento. En estas pruebas, se formaron algunas películas con tensiones de secado que excedieron la tensión cohesiva o adhesiva del recubrimiento. Aún en aquellos recubrimientos que permanecieron intactos luego del secado, permanecieron tensiones residuales que los harían vulnerables a un daño subsecuente por tensiones adicionales aplicadas debidas a cambios ambientales o a su manipulación. El análisis del material para determinar la naturaleza de la resina del recubrimiento o del ligante de la pintura podrían proveer un medio para estimar la probabilidad de la presencia de tensiones de secado residuales, si bien la medición de tensión en los materiales individuales encontrados sería necesaria para estimar la magnitud de dichas tensiones. Es posible realizar tratamientos para aliviar las tensiones en recubrimientos, pero es necesario un amplio control de las combinaciones de materiales identificadas en el artefacto para determinar la seguridad y eficacia del método. Un control del clima y una manipulación cuidadosa para minimizar tensiones adicionales en los objetos en riesgo son los pasos más prudentes de los que corrientemente se dispone.

1. INTRODUCTION

Cracking and flaking are familiar features in old oil or tempera paints and are usually attributed to embrittlement and shrinkage due to oxidative aging of the medium or to damage brought on by external causes such as handling and material responses to temperature and humidity conditions. Such cohesive or adhesive failures in newer coatings formulated with synthetic polymers are less common but are occasionally observed. In such cases it is difficult to attribute the damage exclusively to aging, to extreme environments, or to handling damage, and consequently such a defect may be blamed on "inherent vice," an imprecise term encompassing unspecified problems with materials or manufacturing techniques.

However, it has long been recognized in the coatings industry that films often come primed for physical failure by virtue of their so-called residual internal stress, the stress created in the film during its original application. Such stresses, almost always shrinkage stresses, can arise from several causes, the most common being solvent or additive loss during drying or curing, or release of by-products during condensation reactions to form coatings such as epoxies. These residual internal drying stresses, which are present soon after application of the coating film, are distinct from the internal stresses that develop later as a result of the film's response to temperature or humidity changes, and they are also distinct from the external or applied stresses that occur during mounting or handling. The residual drying stresses themselves can lead to cracking or delamination immediately upon application of the coating, or the film may remain intact but under tension and more prone to failure from additional stresses from handling, environmental responses, or further aging (Hare 1996a; Hare 1996c; Perera 1996).

Over the last 50 years much work has been done to develop a better understanding of the processes leading to stress development in coating films and to examine the influence of paint formulation on the magnitude of the residual drying stresses. In brief, coating films develop shrinkage stress when volatile material is lost during drying, and the polymer molecules, because of strong physical entanglements or because of chemical crosslinks, are unable to move to fill the voids left behind. The amount of void space left in the film and the strength of the forces tending to fill those voids determine the magnitude of the shrinkage stress that the dry film experiences. This same mechanism is well known to cause the shrinkage of solvent-based adhesives, a phenomenon that must be carefully controlled in order to avoid distorting an object or compromising an adhesive join (Newey et al. 1983,102–5).

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Many factors have been found to affect the magnitude of intrinsic shrinkage stresses in coatings (Hare 1996a; Hare 1996b; Sato 1980). Films of polymers having a high glass transition temperature (T_g) or high Young's modulus, whose molecules have a very strong attraction to each other, are prone to developing large internal stresses. Films cast from poor solvents also develop greater stresses than those cast from good solvents.[1] Films cast from rapidly evaporating solvents will generally have more stress than those cast from slowly evaporating ones, presumably because some stress relaxation can occur in the films that are plasticized by the retained solvent. Even films cast from polymer dispersions, especially when they contain volatile additives that will be released, can develop drying stresses (Perera 1984; Perera and Vanden Eynde 1984a). Pigments incorporated into the film increase the internal stresses, probably by stiffening the film and limiting shrinkage to relieve stress accumulation (Croll 1979a; Sato 1980; Perera and Vanden Eynde 1981, 1984b). Other factors, such as the environmental conditions for drying, have been seen to have small effects on the residual stresses of the coatings.

These general trends have by now been well established in the paint industry, so that formulations prone to early failures can be avoided; thus applications of commercial coatings are likely to possess relatively low levels of stress (at least, at the time of application). However, while these trends are known, it remains impossible to predict the magnitudes of stresses in specific coating films and the consequent risk that they face from failure during drying or upon the application of additional stresses. Furthermore, coatings that have been formulated by artists or conservators may have been used without the conscious avoidance of these high-risk materials and combinations, so it is likely that some of these applications will be prone to develop large internal stresses upon drying. To better estimate the magnitudes of drying stresses in coatings likely to be found on art objects, we measured the residual stresses that develop in a number of art and conservation coatings as they dry. In our initial study (Moran and Whitmore 1995), we examined the shrinkage stresses in unpigmented polymer films of acrylics and poly(vinyl acetates) (PVAs), and we verified that the polymers of higher T_g were prone to develop large shrinkage stresses, some of which approached or exceeded the cohesive or adhesive strength of the films. Softer resins such as the poly(vinyl acetates) and Paraloid B-72 formed essentially stress-free films.

In the present study we examine the magnitude of drying stresses in common art and conservation coatings, to identify those materials or combinations that, due to their high residual drying stresses, might be at high risk of damage from additional stress development. In this article we report our measurements of pigmented polymer films, both commercial products as well as paints formulated from polymer solutions containing added pigments. We have also performed tests to verify that the stresses we measure in films applied to flexible substrates are representative of those that develop in films applied to rigid substrates, the more common occurrence on artifacts. Finally we discuss the relevance of these findings to preservation and conservation measures.

2. EXPERIMENTAL APPROACH

As in our previous study, we have used a conventional "beam-bending" method of measuring stresses in coating films. In these tests, coatings are applied to one side of a flexible substrate (in this case, a thin strip of steel sheet), and as the coating dries, it causes the substrate to curl. Precise measurement of the curvature of the substrate, along with the known elastic properties of the substrate material, is used to calculate the stress on the substrate needed to produce the deformation. This calculated stress is inferred to be equivalent to the stress that would be experienced by a film applied to a rigid substrate. In this study we tested this inference by making companion measurements on a coating applied to a substrate that was allowed to flex as the coating dried and shrank (the conventional technique) and on a second sample in which the substrate was held planar until the coating had dried, then released and allowed to deform. The

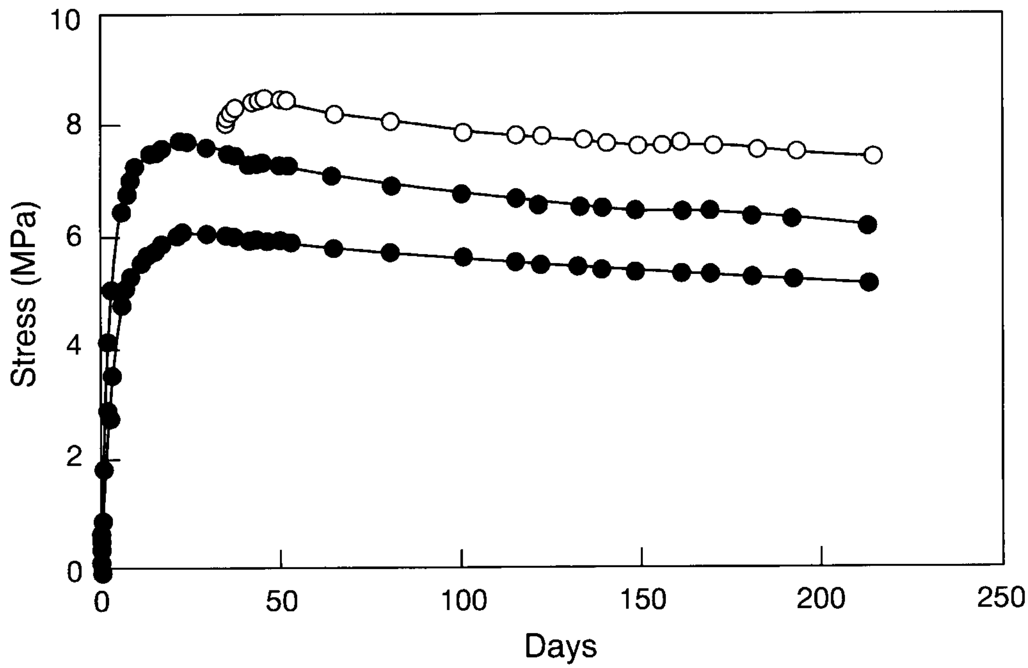

Fig. 1. Stress measured in films of Paraloid B-67 containing 35% PVC titanium dioxide (TiO_2), cast from toluene solution. The lower two curves (solid circles) consist of data from films applied to steel strips that were allowed to curl as the films dried. The upper curve (open circles) represents measured stress in a similar sample in which the steel strip had been held planar for 35 days, then released and allowed to curl.

result for this second sample provided a more direct indication of the stress that was present in the dried coating and allowed a comparison of that quantity to the stress inferred from the conventional test procedure. The device and the measurement procedure are described more fully in the appendix.

Materials tested were a representative selection of solvent-based resins used for coatings, solvent-based resins with varying amounts of added pigment, and a selection of various commercial artists' paints, media, and grounds. Many typical acrylic and poly(vinyl acetate) resins were studied in our earlier work (Moran and Whitmore 1995), and only a few of these that are occasionally used as media for retouching paints were included in this study. The samples tested are listed in tables 1 and 2. Details of the material preparation and film application are described in the appendix.

3. RESULTS

3.1 TEST OF ACCURACY OF STRESSES INFERRED FROM MEASUREMENTS MADE ON FLEXIBLE SUBSTRATES

For this evaluation, films of Paraloid B-67 containing 35% pigment volume concentration (PVC) titanium dioxide (TiO_2) were tested. One film was applied to a steel strip that was allowed to flex as it dried. A similar film was applied to a strip that was held planar until the coating had dried, after which the strip was released and allowed to flex as the coating shrank. Stress results for the two types of samples are shown in figure 1. The maximum stresses measured for the pair of treatments differ by less than 25%, which is on the order of the differences observed between replicate films. This finding indicates that the stresses inferred from samples that are allowed to deform upon drying are reasonable estimates of the

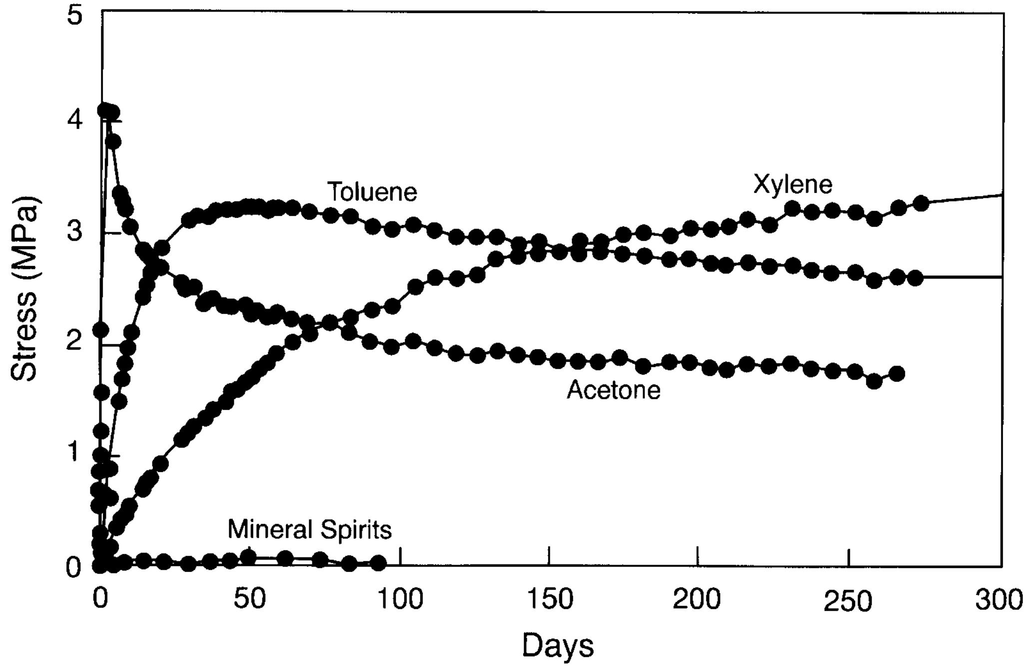

Fig. 2. Stress measured in films of Paraloid B-67 cast from solutions made with different solvents

shrinkage stresses that would remain in films applied to rigid substrates.

3.2 CONSERVATION RESINS AND EFFECT OF SOLVENT TYPE

Of the resins tested here, only Paraloid B-67 (poly[iso-butyl methacrylate]) developed moderately large shrinkage stresses upon drying. The stress in a film of this resin cast from toluene solution is shown in figure 2. For this resin a maximum stress level was reached in 10–20 days of drying, followed by a slow decrease in the measured stress as relaxation processes, either plastic flow or microscopic cohesive or adhesive failures, occurred. It should be noted that the high maximum stress level that developed in a film of this polymer is consistent with its having a glass transition temperature greater than the other resins tested (the T_g for B-67 has been measured in an earlier study to be 59°C, while that of B-72 was 40°C and that of the PVAs around 27°-36°C) (Moran and Whitmore 1995). This approximate correlation of the maximum stress and T_g was observed in that study and also in the earlier work by Stuart Croll (1979b).

Stresses were also measured in films cast from solvents other than toluene. For Paraloid B-72, a resin that developed little measurable stress in films cast from toluene, films cast from other solvents (xylene, diethyl benzene, cellosolve, ethanol) still showed very small stresses (less than 0.25 MPa). For the Paraloid B-67 that showed moderately large stresses, solutions made with other solvents (xylene, acetone, mineral spirits) produced stress levels that were different than in films cast from toluene solution (fig. 2). For the film cast from xylene, approximately the same maximum stress was recorded after the long drying period needed for the release of the slow-evaporating xylene solvent. For the films cast from acetone, an extremely rapid increase to a very high stress was fol-

Table 1. Resin Solutions and Formulated Paints Included in Study

Resin	Solvent	Pigment Added to Toluene Solution	PVC (%)
Paraloid B-67	toluene xylene acetone mineral spirits	titanium dioxide (Ti-Pure R-960)	5,15,25,35,45,55,65
Paraloid B-72	toluene xylene diethyl benzene cellosolve ethanol	titanium dioxide (Ti-Pure R-960)	5,15,25,35,45,55,65
AYAF	toluene	titanium dioxide (Ti-Pure R-960)	5,15,25,35,45,55,65
Laropal K-80	toluene		
Lascaux Acrylic Resin P-550	petroleum benzine (as supplied)		

lowed by a very rapid decrease to a low stress level. This behavior is believed to be evidence of a rapid development of shrinkage stress to levels exceeding the strength of the film, with the consequent cracking of the film manifested in the declining stress level. This trend in behavior is generally consistent with the model behavior outlined by Croll (1979b), in studies cited by Kozo Sato (1980), and in other work done by Dan Perera and D. Vanden Eynde (1983). Films cast from poor or rapidly evaporating solvents developed greater stress than those formed by release of more slowly evaporating solvents (in this case, both the toluene and the xylene evaporated significantly more slowly than acetone).

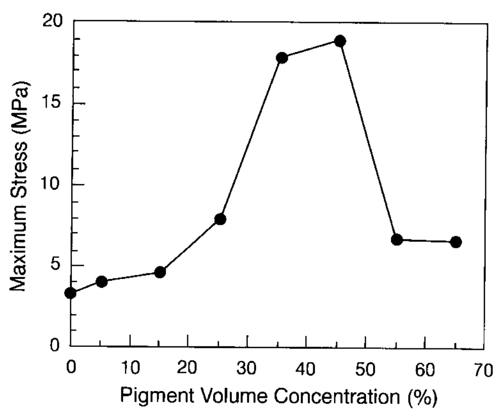

Fig. 3. Maximum stress measured in films of Paraloid B-67 (cast from toluene solution) containing varying amounts of TiO_2

3.3 PIGMENTED RESINS

The maximum stress level was studied for films of Paraloid B-67, Paraloid B-72, and poly(vinyl acetate) AYAF (cast from toluene solution) containing titanium dioxide at varying pigment volume concentrations (shown in table 1). The stress results for Paraloid B-67 paints are shown in figure 3. The maximum stress for the unpigmented resin film is about 3 MPa and increases with greater pigment loading, so that the white paint at 35% PVC experiences a maximum shrinkage stress nearly six times that of the unpigmented film. Because film cracking is observed for some of these films, it is reasonable to infer that the 18 MPa maximum stress approaches the cohesive strength of the paint film. Pigment loadings greater than 35% PVC produced films having smaller maximum stresses, probably because of cohesive/adhesive failure of the films or because the films above the critical PVC can relieve stress by deformation of the

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Table 2. Commercial Art Products Included in Study

Paints	
Winsor & Newton	Griffin Alkyd Titanium White
	Griffin Alkyd London Red
	Acrylic Permanent Rose
Liquitex	Acrylic Titanium White
Magna	Titanium White
LeFranc & Bourgeois	Restoration Color Zinc White
	Restoration Color Titanium Oxide White
Media	
Winsor & Newton	Liquin
	Win-gel
Liquitex	Acrylic Gloss Medium
Grounds	
Liquitex	Acrylic Gesso

porous paint film structure. These findings are in agreement with the general trends reported by others (Perera and Vanden Eynde 1981; 1984b; Croll 1979a).

It is interesting to note that the stress-induced failure known as mudcracking (at high PVC) differs in appearance from the cohesive failure that occurred just below the critical PVC. Films having very high PVC (55% and above) show the mudcracking pattern, of wide, jagged cracks, with detaching powdery flakes mainly localized in the thickest areas of the coating. At lower PVC (45%) the failed coating shows instead a distinctive network of very fine cracks, yet the coating remains apparently well adhered to the substrate. The craquelure in the failed coating at 45% PVC can be described as a "mosaic" pattern, in the terminology of the standard test method for assessing coating failure (ASTM 1993), or as a connected network of fine, uniform, smooth, curved cracks forming a random pattern of large islands, according to the descriptive nomenclature of Spike Bucklow (1997). The extensive and random patterning testifies to the isotropic in-plane stress field that caused the failure. (To more easily visualize the different appearance of these failures, see Bucklow [1997, figs. 5, 7], which illustrates the "stress" cracks and mudcracking, respectively, observed in the acrylic paints examined here.) In an old oil paint, such a network of fine cracks might be easily associated with aging changes that presumably develop shrinkage stress from the release of volatile oxidation products from the film, and, in fact, Bucklow terms this pattern in oil paints "aging" cracks. Clearly the essentially new films of acrylic paint created for this study did not fail from the deterioration of the medium but rather from the solvent release during drying. This process is exactly analogous to that which occurs, albeit very much more slowly, to produce stresses in fully cured oil paint films as they continue to oxidize. Thus the creation of identical crack patterns in the stressed acrylic paints and the oxidized oil paints is reasonable. In examining these craquelure patterns, then, one should exercise caution in instinctively attributing such paint failures to extreme age.

The dramatic increase in maximum stress of Paraloid B-67 films with added pigment prompted an examination of the stresses that develop in paints having the softer resins Paraloid B-72 or poly(vinyl acetate) as the medium. The unpigmented films of these resins showed essentially zero shrinkage stresses. Titanium white paint formulated with these resins showed stress levels that were measurable but still very small. The greatest stress maximum found was about 2 MPa for a 45% PVC paint made with Paraloid B-72, and for a paint made with PVA the maximum stress was about 1.5 MPa at 35% PVC. These results suggest that the risk of developing shrinkage stresses in films of these softer resins remains low even when they contain pigment.

3.4 COMMERCIAL PAINTS, MEDIA, AND GESSO

Films of commercial art products were tested to examine the possibility that shrinkage stress would develop in these materials as they are commonly used. Of the range of paints, media, and grounds tested (shown in table 2), none showed evidence of developing significant shrinkage stresses in our studies (i.e., no films showed maximum stresses greater than about 2 MPa). The most nearly comparable art material to our earlier study would be the Magna brand paint, which is formulated with a solvent-based resin and dries by solvent evaporation. Even that material showed no stress in dried films, probably by virtue of its incorporating a very soft resin, poly (n-butyl methacrylate), as the medium. This finding is consistent with our earlier results on pure poly (n-butyl methacrylate) cast from toluene solution, which also dried to an essentially stress-free film (Moran and Whitmore 1995).

4. DISCUSSION

The results of the experiments described here indicate that paintings made with commercial artists' paints and coatings are likely to be at low risk of damage due to intrinsic drying stresses. On the other hand, paints formulated by the artist or conservator may dry to form films that are highly stressed, and thus deliberate choices of materials and formulations should be made to avoid such paints if possible. Use of softer (low T_g) polymers as vehicles, use of good solvents for these polymers, and use of medium-rich paints (to avoid the high PVCs where stress would be greater) are all prudent measures.

For coating applications on existing artifacts, it remains extremely difficult to identify films that may be at risk due to residual drying stresses. Analysis to identify the polymer binder of the paint is an important first step. The type of resin may indicate whether the paint was solvent-based and, if so, whether it is likely to have been commercially prepared. Applications of commercial paint products that have not yet degraded significantly may reasonably be assumed to be at low risk of bearing high stress levels. For applications known or suspected to have been formulated by the artist, those made with high T_g resins may reasonably be assumed to possess some level of shrinkage stress, although the stresses cannot be assumed to be so high as to present significant risk of physical failure. In such a case, study of the stresses to be expected in coatings formulated with these specific materials, in tests such as those described here, would be necessary to assess the magnitude of the drying stresses likely to be present.

If these tests cannot be performed to estimate the stress levels in coatings thought to have drying stresses, monitoring for signs of film failure may be the only means to identify the magnitude of the risk. Cohesive failure will result in widespread cracking of the paint film, while adhesive failure will begin at the edges of the film or along existing cracks, where shear stresses will tend to concentrate (Hess 1969; Croll 1980a; Suhir 1988; Farris et al. 1993). Adhesive failure should also be considered more likely for thick paint films, because while both the tensile forces and the cohesive breaking load of the film increase with thickness (assuming the stress and cohesive strength are constant for the film material), the adhesive breaking load does not (since the adhesive strength is the same for all film thicknesses). Thus the greater tension created in thick films is more likely to overcome the adhesive strength of the bond to the substrate. In fact, for a given stressed coating there exists a critical thickness at which delamination will occur, and this thickness can be used as a measure of the adhesive strength of the interface (Farris et al. 1993). It is also worth noting that the failure due to residual stresses may not occur to the film that is tending to shrink. Rather, shrinkage stresses can be transmitted to other, weaker layers in a composite painting structure (such as a ground layer), and the failure may be observed as cracking in such a weak layer or delamination at a weak interface (Hare 1995). The observation of such physical failures on a painting may be reason to suspect that these coatings, and the other undamaged coatings on that artifact, may have significant residual shrinkage stresses.

For coatings that are considered to have high levels of residual stress, one might consider attempting to treat the object in order to relieve those stressed films. Possible solutions might include mild heat treatment, humidification, or exposure to vapors of "good" solvents. Perera and Vanden Eynde (1987) have shown that heating a coating above its T_g will allow movement of the polymer chains (assuming that they are not crosslinked in the coating) that can relax the tension in the film. Subsequent cooling of the coating, however, can lead to new stresses from the contraction of the different paint materials in a composite painting structure, and the magnitude of the stresses at the end of such a treatment will vary, depending on the nature of the materials and construction of the artifact. Similarly, exposure to high humidity or solvent vapors may prove successful, but it is not possible to make general predictions of the outcome of such approaches. Any such treatment must, of course, be carefully studied for its efficacy and safety for the combination of materials in a specific artifact. While one should certainly approach such stress relief treatments with caution, it is worth noting that routine treatments such as relining with heat-setting adhesives may inadvertently create such thermally annealed paint layers, and the effect of such treatments on the stresses in the paint layers should also be examined in more detail in future work.

Because it is not possible to identify with great certainty the coatings that are at high risk due to residual drying stresses, stabilization to avoid additional stresses becomes an even more important preservation strategy to protect objects that are at risk. Residual stresses can leave a coating very close to its cohesive or adhesive failure level, and additional stresses due to environmental fluctuations (particularly temperature or humidity decreases that will tend to cause materials to shrink) will add to the stresses already present in the coating (Hare 1996a; Hare 1996c; Perera 1996). Stabilization of the environment, as well as avoidance of careless handling, rolling, or mounting of a painting canvas, are prudent measures to prevent the additional stresses that could cause failure of the coatings. Finally, to the extent that it is possible, the aging of such coatings should be slowed, so that stress produced from the release of volatile ingredients or degradation products (a process analogous to the initial solvent release that creates residual drying stress) is minimized (Hare 1996b). All these measures are usually considered prudent preservation steps in any case. However, as institutions decide how best to invest their resources in such measures as climate control, it is important to recognize that some materials are likely to be at greater risk because of their stressed condition. A prudent course would be to identify those coatings that might be at high risk of stress-induced damage and to take special precautions (such as strict climate control and careful handling) to ensure their safety.

5. CONCLUSIONS

The results of the tests reported here are encouraging in that artifacts made with commercial art materials are likely to be at low risk of suffering from inherent shrinkage stresses. Because the coatings manufacturing industry has been aware of these stress-related coating failures for many years, it is likely that essentially all commercial paints have been developed so as to avoid high levels of drying stresses in the dried films. However, the use of commercial art products is hardly universal in the creation of works of contemporary art, and the results reported here reinforce the notion that coatings formulated with high T_g polymers, especially pigmented paints having these resins as binder, are likely to develop high levels of drying stress. Direct measurement of high stress levels in coatings on artifacts remains impossible, and the best method for targeting coatings likely to be at risk is to identify those films containing high T_g polymers. Tests such as those described here could be used to better estimate the magnitude of drying stresses for these specific materials. Remedial treatments to relieve the intrinsic drying stresses must undergo extensive preliminary testing on the specific material combinations found on the objects to ensure their safety and effectiveness. Stabilizing vulnerable artifacts through careful handling and environmental control, to minimize additional stresses on the coatings, is the most sensible preservation step to avoid stress-related failures.

APPENDIX: EXPERIMENTAL

For these tests, films of resin solutions and paints were applied at 0.25 mm wet film thickness to thin, flexible, stainless steel strips. The resin solutions were made at 30–40% (w/v) concentration, with the exception of the resins dissolved in poor solvents, which were made at the highest concentration possible. Paints were formulated by ball-milling pigment-resin solutions at 65% pigment volume concentration (PVC), then adding varying quantities of pure resin solution and pure solvent to achieve the desired solids content and PVC for the final paint. The substrates were stainless steel feeler gauge stock, strips measuring 13 mm wide, 140 mm long, and 0.13 mm thick. The thicknesses of the coated strips were measured with a magnetic thickness gauge, and the thicknesses of the coatings were then determined by difference. Dry coating thicknesses ranged from 0.02 mm to 0.08 mm. The samples that were meant to probe the stresses that develop on rigid substrates were prepared in the same manner, only the steel strips were held on a magnetic plate while the paint was applied and as the coatings dried over the next 35 days. After that time the strips were released from the plate and measured in the same manner as the other samples.

Upon being coated on one side, the steel strips curled due to the stresses derived from the drying of the paint. A relationship originally developed by Stoney (1909) and further refined by Corcoran (1969) allows the stress in the coating to be inferred from the amount of curvature and the geometric and elastic properties of the substrate. The curvature of the coated steel strip was measured with an instrument made after the design of Croll (1980b), using a capacitative transducer to sense the displacement of the strip from a planar position. The details of the measurement technique and the formulas for determining the elastic constants of the strips and the stresses in the coatings are described in a prior publication (Moran and Whitmore 1995).

Because the stresses in the coating films vary with environmental conditions, the coated strips were stored and the stresses were measured in a glove box maintained at 25°C and 50% RH. The airflow into the box was filtered with activated charcoal and Purafil to remove pollutants and split into two metered flows. One airstream was dried by passing it through a bed of Drierite, and the other was saturated with water vapor by bubbling it through water. The streams were temperature-conditioned in a water bath and mixed in the proportion that achieved the desired conditions in the glove box. The flow rate through the box was 1 liter per minute, selected to allow control of the interior conditions and to provide efficient venting of the solvent vapors released from the films as they dried. Stress measurements were made at frequent intervals (every 30 minutes) during the initial drying period, and at less frequent intervals as the stress began to change more slowly. Each data point was an average of two to three measurements on each sample.

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NOTE

1. In this context, the term "poor" solvent refers to a solvent that, while able to dissolve a polymer completely, has a relatively lower solvent power for the polymer than so-called "good" solvents. The relative "goodness" of the solvent for a particular polymer may be measured by the polymer's solubility in the solvent, the time for complete dissolution, the conformation of the polymer chains when dissolved in the solvent, or the properties of the dried film cast from the solvent.

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SOURCES OF MATERIALS

Capacitative transducer (Model No. 3101-SP-BNC with HPT-150 probe)
Capacitec
P.O. Box 819
87 Fitchburg Rd.
Ayer, Mass. 01432

Steel strips (301 stainless steel, 13 mm x 140 mm x 0.13 mm)
Precision Brand Products
2250 Curtiss St.
Downers Grove, Ill. 60515

Thickness gauge (Positector Model No. 6000-F3)
DeFelsko Corp.
802 Proctor Ave.
Ogdensburg, N.Y. 13669

Temperature and humidity sensor (HMI32 with HMP32UT probe)
Vaisala
100 Commerce Way
Woburn, Mass. 01801-1068

Drierite
A. Hammond Drierite Co.
P. O. Box 460
Xenia, Ohio 45385

Activated charcoal and Purafil
Purafil
P. O. Box 80434
Atlanta, Ga. 30366

Resins (Rohm and Haas Paraloid B-67, Paraloid B-72, Union Carbide AYAF, Laropal K-80 and Lascaux P-550 solutions)
Conservation Materials Ltd.

1165 Marietta Way
Sparks, Nev. 89431

Pigments (Ti-Pure R-960)
DuPont Co.
White Pigment and Mineral Products
1007 Market St.
Wilmington, Del. 19898

Solvents
Available from various chemical supply houses.

Art supplies
Available from various retail outlets.

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