

A NOTE ON THE ORIGIN OF TURBIDITY IN FILMS OF AN ARTISTS' ACRYLIC PAINT MEDIUM

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Summary—Films of *Liquitex gloss medium*, an acrylic dispersion polymer product, have been reported to become turbid slowly due to the formation of microscopic crystalline inclusions. This report describes the analysis of the melting point, morphology, solubility and infrared absorption spectrum of these included crystals and of the crystalline solids extracted from the acrylic films with water. The results of these analyses indicate that the crystals that cause turbidity in these acrylic films are poly(ethane-1,2-diol) [poly(ethylene glycol)] type compounds. A mechanism by which these crystals form in the films is described, and the conditions that favor crystallization are identified. These parameters suggest avenues which might be explored in seeking appropriate treatments to prevent or remedy the turbidity in acrylic media films.

Introduction

In a recent publication the authors reported that films of an acrylic artists' material, *Liquitex gloss medium*, became translucent due to the formation of small crystalline particles within the films [1]. While the formation of that crystalline material in the initially transparent films suggested the phase separation of one ingredient in the formulation, the nature of the particles was not determined. In this note we report the identification of these particles, which impart the slight turbidity to films of *Liquitex gloss medium*.

Results

The particles that form in films of *Liquitex* are shown in Figure 1 in reference [1]. They are needle-shaped, birefringent crystals, with a radial arrangement in some areas that suggests a spherulitic morphology. These crystals begin forming in discrete circular zones, sometimes surrounding larger visible particles; these zones eventually merge to cause the entire film to appear uniformly translucent. The crystals have a waxy texture and are soluble in water, as demonstrated by applying water to a film while observing the crystals through crossed polarizers under a microscope. Water extraction of films of *Liquitex gloss medium* and subsequent drying of the extract yields substantial quantities (about 6% by weight of film) of a waxy material having a melting point of approximately 49°C. Cooled melts of this solid extract contain spherulites which show undulatory 'Maltese cross' extinction patterns when viewed through crossed polarizers under a microscope (Figure 1a).

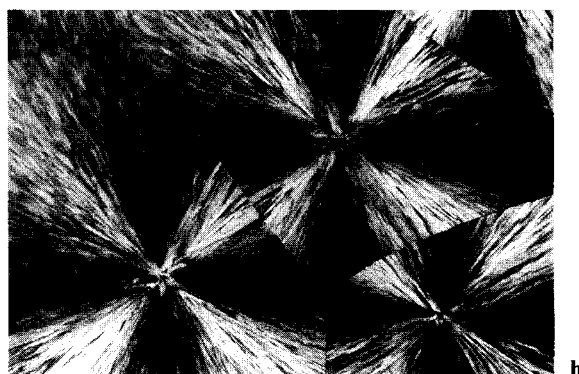
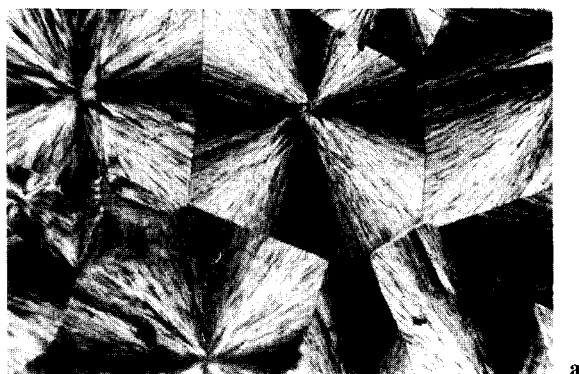


Figure 1 Photomicrographs of (a) water-soluble solids extracted from 70-day-old film of *Liquitex gloss medium* and (b) poly(ethylene glycol), average molecular weight 1500, showing spherulitic crystals displaying undulatory 'Maltese cross' extinction patterns. Transmitted light viewed through crossed polarizers oriented in the horizontal and vertical directions. Magnification $\times 80$.

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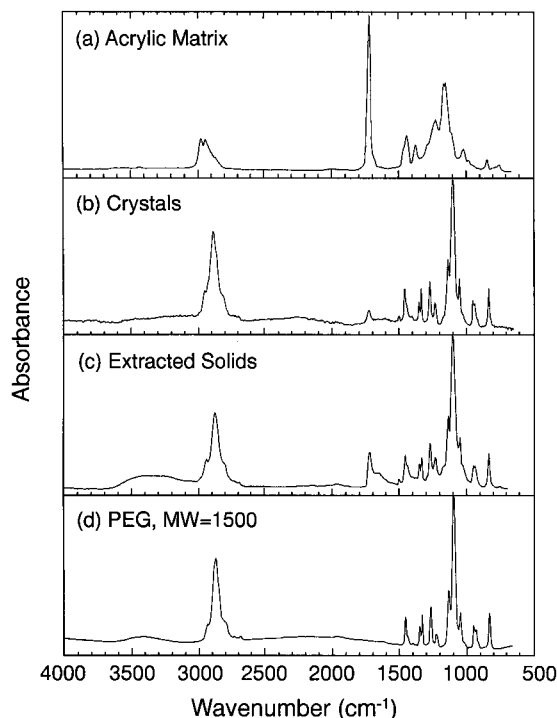


Figure 2 Infrared spectra of (a) amorphous acrylic polymer matrix in a 3-6-year-old Liquitex film; (b) crystalline inclusions in Liquitex film; (c) water-soluble solids extracted from a 70-day-old Liquitex film; (d) poly(ethylene glycol), average molecular weight 1500. The spectral regions between 2250 and 2450 cm^{-1} have been edited to remove the absorptions of atmospheric carbon dioxide.

For further characterization, the crystalline inclusions, polymer matrix and extracted solids were examined with a Fourier transform infrared microscope. The infrared spectrum of the crystals is shown in Figure 2, along with the spectrum of the acrylic polymer matrix that has been described previously [1]. The infrared spectrum of the solid residue extracted from the film, shown in Figure 2c, closely resembles that of the crystalline inclusions. The spectra of both the crystalline inclusions and the water-soluble extract compare well to the infrared spectrum of a medium molecular weight poly(ethane-1,2-diol) [poly(ethylene glycol) or PEG] (Figure 2d), particularly in the 'fingerprint' region of the spectrum between 700 and 1500 cm^{-1} . Two small absorptions, at 1730 and 1510 cm^{-1} , occur in the spectra of the inclusions and of the extract but not in the reference PEG spectrum. The former can be attributed to a carbonyl absorption and the latter probably derives from a benzene ring structure

[2]. From this analysis alone it is impossible to determine whether these carbonyl and aromatic groups are attached to the PEG chains, whether they reside on other components in a mixture or whether they occur as impurities or degradation products of original formulation ingredients.

This identification of the crystalline inclusions and water-extractable residue as a PEG-type compound is also supported by the solubility, crystallinity and apparent melting temperature of the material. PEGs and substituted PEGs with moderately long PEG chains are easily soluble in water [3], a property shared by the material included in the Liquitex films. These compounds are also semi-crystalline [4], tending to form spherulitic domains (Figure 1b) identical to those observed for the water-soluble residue from the Liquitex films. While this residue is probably not a pure compound, its relatively low melting temperature, 49°C, is consistent with that of a pure PEG of medium molecular weight (the melting point for a PEG of molecular weight 1500 is 50°C), and is below the 75°C limit for the melting point of very high molecular weight poly(ethylene glycol), [poly(ethylene oxide)] [5]. There are many different PEG-type compounds, differing in length of PEG chain and in the groups terminating each end of the molecule. These all display very similar spectral and physical properties, so exact identification of the crystalline inclusions in Liquitex is impossible without more extensive analysis. Nevertheless, the observed crystallinity (particularly the spherulitic morphology), water solubility, melting point and infrared spectrum support our identification of a PEG or PEG derivative as the material that separates from the acrylic polymer matrix, and it is the crystallization of this material that renders Liquitex films turbid.

Discussion

It is reasonable that PEG-type compounds should be found in the solid acrylic medium, as they are often present in the fluid acrylic dispersions, having been used as emulsifiers in the polymer synthesis [6, 7]. When the fluid is cast into a polymer film, PEG-type additives, unlike other types of additive such as ionic surfactants, are not expelled as the polymer particles coalesce during formation of the solid film. Rather, PEG compounds seem to have such a strong affinity for acrylic polymers that they remain in the film after it has dried [8-10].

The precipitation of PEG crystals in Liquitex films is probably not a result of the phase separation of incompatible materials. PEG compounds and acrylic polymers have been found to be thermodynamically compatible, being miscible in

the fluid melt and in solid blends with a low PEG concentration [11–14]. The formation of PEG crystals is instead driven by a combination of two factors: the preferred crystalline morphology of solid PEG compounds, which causes PEG chains that assume a favorable orientation to 'freeze' in position; and the relatively low glass transition temperature (T_g) of the acrylic polymer matrix (measured in earlier work as 12°C [1]). The latter allows both acrylic polymer and PEG chains to be mobile in the solid at room temperature. At room temperature the acrylic matrix is in its rubbery phase, through which the included PEG chains can migrate. When these chains encounter a nucleation site or a spherulitic crystal that has already formed, they can orient in a preferred position to 'grow' a crystal. At the same time, the acrylic chains are mobile enough to accommodate the crystallization of PEG, although the rather poorly formed crystalline domains in Liquitex films (small needles rather than the large spherulites that form in the Liquitex extracts) suggest that some of the acrylic chains may be incorporated into the PEG crystals as they grow.

The crystallization of one polymer component in a blend with an amorphous polymer has been shown to be strongly dependent on temperature [15, 16]. Spherulite growth will occur only below the melting temperature of the crystalline component (so that the solid phase will form) and above the glass transition temperature of the amorphous component, so that migration of the crystallizing material and expulsion of the amorphous material from the growing crystals can occur. The growth rate for the crystals peaks between these limits, which for the PEG compounds in the Liquitex acrylic films occurs between 12°C (the T_g of the acrylic) and 50°C (the melting point for the PEG). The size and perfection of the crystals should increase with temperature, as the crystalline phase is more ordered when expulsion of the amorphous phase from the growing crystal is easier.

These considerations suggest two possible routes to minimize the disfiguring turbidity of clear coatings of such acrylic media. For films having already developed PEG crystals, raising the temperature of the films could melt the crystals and redissolve the PEG into the acrylic matrix. Exploratory tests have shown that heating of turbid Liquitex films to 60°C can restore much of the clarity to the films. However, since this treatment only mixes the PEG back into the acrylic matrix, leaving the conditions which drove the original PEG crystallization unaltered, the recurrence of the crystal formation over time seems likely. For films that have not yet become turbid but are expected to be prone to such changes (including those that have already been

heated to clarify existing turbidity), cold temperature storage might offer hope of postponing the formation of the PEG crystals. Lowering the temperature to near or below the glass transition temperature of the acrylic film should slow the migration of PEG chains as well as prevent the formation of large PEG crystals. The success of this procedure in postponing the haze development has not yet been demonstrated, and the embrittlement of the polymer film when cooled to below its glass transition temperature carries associated risks of physical damage. Both of these potential treatments are merely starting points for future study to determine the efficacy and risks associated with such courses of action. While more research is necessary before undertaking such interventions, understanding the nature of the crystalline inclusions as well as the process driving their formation can only aid efforts to find treatments to reverse or prevent the development of turbidity in acrylic dispersion media films.

While the most obvious consequence of residual PEG compounds is the development of turbidity as they crystallize, other film properties may also be affected by the presence of PEG crystals or PEG compounds dissolved in the acrylic matrix. The dissolution of PEG surfactants has been reported to plasticize methacrylate polymers [8, 9], but precipitation of large amounts of polyethers caused films of poly(methyl methacrylate) to become weak, probably due to the formation of large crystals that have low strength and serve as failure initiation sites [12]. Our examination of the physical properties of Liquitex films during the precipitation of crystalline inclusions showed no evidence of such a weakening effect; indeed the strength of the films increased while the PEG crystals were forming, due to the concomitant polymer entanglement during film formation [1]. The intimate blending of a PEG compound and the solid acrylic polymer could also have important consequences for the stability and aging behavior of the film. At present these possible chemical interactions are unknown, and their investigation is beyond the scope of this note. Whether the presence of a PEG compound contributes to the slight but rapid yellowing of Liquitex gloss medium, or whether its interaction with the acrylic matrix causes the unusually rapid crosslinking observed in these films, is the subject of further research.

Conclusions

In summary, the water-soluble crystalline inclusions causing the turbid appearance of films of Liquitex gloss medium are identified as residual PEG

compounds. These materials remain within the polymer during film formation, due to their affinity for the acrylic matrix. Because of their strong mutual attraction, PEG chains migrate through the acrylic to accrete slowly into crystalline domains. Films of other acrylic dispersion polymer products containing these types of compound are also expected to become turbid. Potential treatments to remedy or prevent the turbidity by heating or cooling of the films must be tested thoroughly in future work. Other consequences of the retained PEG compounds on the physical and chemical properties of the acrylic film are not yet known.

Appendix: experimental procedure

The Liquitex gloss medium studied came from two batches, manufactured in 1990 and 1994. Films were drawn down on glass plates and allowed to dry at ambient conditions in the dark. Crystalline inclusions were examined after the films had become turbid. For analysis of the water-extractable components, samples of dried films were removed from the glass plates, weighed, and placed in jars containing small amounts of water. After shaking these containers overnight, the solutions were transferred to glass Petri dishes and allowed to evaporate to dryness at room temperature. Weight fractions of solid extracts were calculated from the difference between the original weight of the film and the weight of the residue after extraction and drying to constant weight. The waxy solid poly(ethylene glycol) sample (with an average molecular weight of 1500) was analyzed as provided. The melting point of the extract was measured by differential scanning calorimetry using a modified version of the standard test method [17]. A 4mg sample was heated once from 10 to 90°C at 20°C per minute while purging with nitrogen. The water sensitivity of the crystalline inclusions in the Liquitex films was observed by examining the film during water immersion under a microscope, using cross-polarized illumination to highlight the birefringent inclusions.

Infrared spectra were measured using a Fourier transform infrared spectrometer with a microscope accessory. The spectrometer was purged with dry air and controlled with software running on a Macintosh IICi computer. Samples were mounted on a diamond window, and the areas for analysis were isolated with variable-sized apertures while observing under the microscope using crossed polarizers. The spectra were the sum of 200 scans collected with 8cm⁻¹ resolution in the range 625–4000cm⁻¹; the spectra were baseline-corrected

and edited to remove the small absorption peaks around 2350cm⁻¹ due to atmospheric CO₂. Preliminary identifications of the film inclusions and extracts were made by comparison with the spectral library of materials in the Rutherford John Gettens collection in the Straus Conservation Center at the Harvard University Art Museums.

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Materials and suppliers

- Liquitex acrylic gloss medium and varnish: Binney and Smith, Inc., PO Box 431, 1100 Church Lane, Easton, PA 18044-0431, USA.
- Poly(ethylene glycol), average molecular weight 1500 (Cat. no. 20,243-6): Aldrich Chemical Company, Inc., 1001 West Saint Paul Avenue, Milwaukee, WI 53233, USA.
- Fourier transform infrared spectrophotometer (Model 510M): Nicolet Analytical, Inc., 5225 Verona Road, PO Box 4451, Madison, WI 53744-4451, USA.
- Infrared microscope (IR-Plan): Spectra-Tech, Inc., 2 Research Drive, PO Box 869, Shelton, CT 06484-0869, USA.
- Differential scanning calorimeter (Model DSC-6): Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859, USA.

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Résumé—On reproche aux films de Liquitex gloss medium, un polymère en dispersion acrylique, de se troubler lentement par la formation d'inclusions cristallines microscopiques. Ce papier décrit l'analyse du point de fusion, la forme, la solubilité et le spectre d'absorption infrarouge de ces cristaux inclus et des solides cristallins extraits par l'eau des films acryliques. Les résultats de ces analyses montrent que les cristaux qui causent l'aspect trouble dans ces films acryliques sont des composés du type poly(éthane-1,2-diol)[poly(éthylène glycol)]. On décrit un processus par lequel se forment ces cristaux dans le film, et les conditions qui favorisent la cristallisation. Ces paramètres suggèrent des voies de recherche des traitements appropriés, afin de prévenir ou d'apporter un remède à l'aspect trouble des films de liant acrylique.

Zusammenfassung—Liquitex, eine polymere Acrylharzdispersion, findet Verwendung als synthetisches Medium zur Herstellung glänzender Überzüge. Berichten zufolge entwickeln mit Liquitex aufgetragene Filme eine Tendenz zur Trübung, die auf die Ausbildung mikroskopischer kristalliner Einschlüsse zurückzuführen ist. Der vorliegende Bericht präsentiert Untersuchungen zu Schmelzpunkt, Morphologie, Löslichkeit und dem Absorptionsspektrum im Infrarot dieser eingeschlossenen Kristalle und der mit Wasser extrahierten kristallinen Feststoffe. Die Ergebnisse dieser Analysen deuten darauf hin, daß die Trübungen von Poly(ethan-1,2-diol)[poly(ethylenglykol)]-Bestandteilen ausgelöst werden. Mechanismen und Vorzugsbedingungen für die beschriebene Kristallbildung innerhalb der Acrylharzfilme werden beschrieben. Mit Hilfe dieser Parameter zeigen die Verfasser des Artikels eine Methodik auf, die zur erfolgreichen Behandlung oder sogar zur Verhinderung der Trübungen von Acrylharzfilmen führen könnte.

Resumen—Han sido ya tratado y mencionado el hecho de que las películas de medium brillante de Liquitex, un producto basado en una dispersión de polímero acrílico, se vuelven progresivamente turbias debido a la formación de inclusiones microscópicas cristalinas. Este artículo describe el análisis del punto de fusión, morfología, solubilidad y espectroscopia de absorción de estos cristales incluidos y de los sólidos cristalinos extraídos con agua de estas películas acrílicas. Los resultados de estos análisis indican que los cristales que causan la turbidez son compuestos del tipo poli(etano-1,2-diol)[poli(etilenglicol)]. Se describe un mecanismo por el cual estos cristales podrían formarse, y se identifican las condiciones que favorecen esta cristalización. Estos parámetros sugieren factores que deberían ser explorados en busca de tratamientos apropiados para prevenir o remediar la turbidez en películas de medium acrílico.