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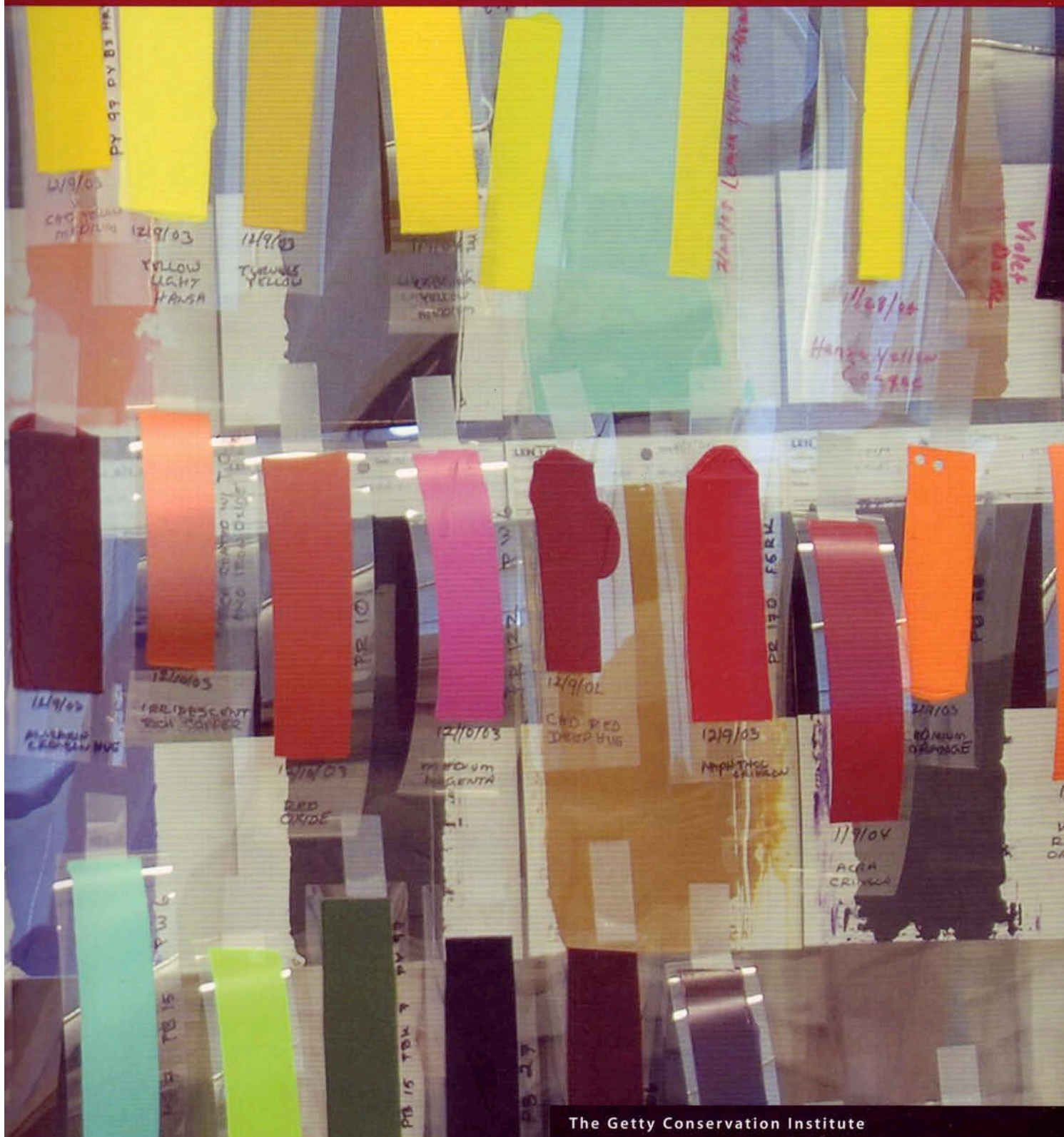
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Tate Modern, London
May 16-19, 2006



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Modern Paints Uncovered
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*Edited by Thomas J. S. Learner, Patricia Smithen,
Jay W. Krueger, and Michael R. Schilling*

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Solvent Action on Dispersion Paint Systems and the Influence on the Morphology—Changes and Destruction of the Latex Microstructure

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Abstract: Binding systems based on aqueous dispersions produce heterogeneous microstructures on film formation. Depending on the system and additives, the original morphology of latex particles can still be recognized after the drying process, despite interdiffusion of the polymer chains. This leads to characteristic physical properties, including a potentially high sensitivity to solvents. The current work tested the action of fifty solvents on three commercially available aqueous dispersion paint systems sold as artists' paint colors. The systems tested are based on acrylic copolymer, acrylic/styrene-copolymer, and polyvinyl acetate/versatate-copolymer components. An immersion-swelling test was applied to quantify the time-dependent swelling capacity. Extractable components were qualified by Fourier transform infrared (FTIR) analysis and quantified by gravimetry. Particular emphasis was given to structural changes within the film as well as surface morphology, documented with scanning electron microscopy (SEM) on cryo-prepared samples. The degree of latex destruction was quantified by a light-scattering technique. Polymer composition and type of additives strongly influence the sensitivity of paint films to solvents. A lot of solvents largely destroy the latex structure, leading to irreversible changes in optical and mechanical properties. Extraction of various mobile components occurs within several discriminate sections along the polarity scale, and thus only specific and narrow windows of selected solvents can be regarded as suitable for conservation treatments. These were evaluated for each of the systems investigated.

Introduction

Acrylic and other dispersion binding systems are widely used in modern paints, and conservators are aware of their high

degree of sensitivity to solvents. The film formation process of these paints has an important influence on their resulting physical and mechanical properties (Provdar, Winnik, and Urban 1996), due to the production of heteromorphic microstructures. Despite the interdiffusion of polymer chains, part of the original latex structure is retained in the dried film, with a continuous network of additives between the compact polymer spheres, and this is primarily responsible for their high sensitivity to solvents. In general, the film properties of latex paints are affected not only by the nature of the polymer, but also by the complex system of binder and additives, as well as film preparation and conditioning. These circumstances generate new demands on techniques for the conservation of acrylic paints (Jablonski et al. 2003). In this context, the action of fifty solvents on aqueous dispersions paint systems was investigated. Focus was given to three types of commercially available artists' paint. Several aspects of the solvent action were investigated, such as swelling capacity, leaching effects, morphological changes in the film core, and modification of the surface structure, as well as the mechanical and physical consequences for paint films treated with solvents.

Film Formation of Latex Binder

Latex paints are complex systems containing several additives and processing aids to optimize the film formation process (Wang et al. 1992; Waters 1997; Kittel 1998; Zohorehvand 2001; Jablonski et al. 2003). The principle of film formation of latex binders is not comparable to that of solution systems. According to the literature, the drying and film formation process can be described by a simplified model with three distinct stages (Eckersley and Rudin 1990; Richard 1997; Kittel 1998): In the

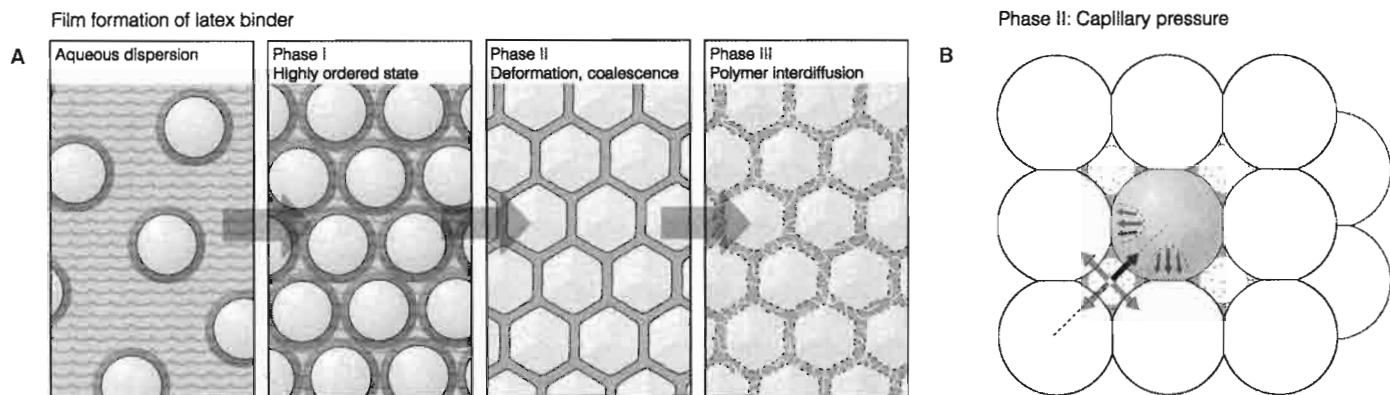


FIGURE 1 (A) In a simplified model, the drying and film formation process can be described by three distinct stages. (B) One of the driving forces is the capillary pressure leading to deformation of the particles and subsequent coalescence. The interdiffusion of polymer chains between particles leads to the stabilization of the system. Based on the film formation process of aqueous dispersions, these binding systems lead to heteromorphic microstructures.

wet state, the solid latex particles are dispersed in water and stabilized by a surrounding layer of surfactants. Electrostatic and steric forces between the charged polymer and the end-chain groups of surfactants keep the spheric particles apart and stabilized in the surrounding aqueous media. These forces are overcome by the evaporation process of the water phase. Film formation is initiated by the coalescence of individual latex particles (Kittel 1998) (fig. 1).

During the first phase of the drying process, water evaporates from the surface, which leads to a concentration and compaction of latex particles. This continues until the polymer fraction has reached about 60–70 percent volume, at which point the particles are in a highly ordered state (Verduyn et al. 2001). The second phase of film formation is initiated by the irreversible coalescence of individual latex particles and accompanied by a distinct reduction of the overall rate of evaporation (Eckersley and Rudin 1996). The drying process during this phase has important consequences on the resulting film, due to the limited time remaining to pack the spherical particles into an ordered structure prior to flocculation.

From then on, compaction continues with particle deformation and the filling of interparticular capillary channels (Dobler and Holl 1996). Different models have been proposed

to describe this process (Dillon, Matheson, and Bradford 1951; Brown 1956; Voyutskii 1958; Bradford and Vanderhoff 1972; Kendall and Padgett 1982), but extended research during the 1980s and 1990s arrived at a combination of different factors (Provdor, Winnik, and Urban 1996). One of the driving forces is the polymer-water interfacial tension, leading to the deformation of particles during the drying process. The coalescence arises from a disequilibrium, whereby the capillary forces must overcome the forces of resistance to deformation (Nicholson and Wasson 1990) (fig. 1B). The capillary force is strongly influenced by the particle size and the surface tension of these lattices (Vanderhoff et al. 1966; Vanderhoff 1970; Armstrong and Wright 1992). In conclusion, the theory of coalescence considers film formation as a process whereby physical forces hold the deformed particles together (Voyutskii 1958, 1963). The third phase is initiated by the formation of a continuous film. This process is dependent on mutual interdiffusion of polymer chains between the particles (Kim and Wool 1983; Chevalier et al. 1992; Zhao and Heckmann 1996). The intermigration is primarily dependent on the nature of the polymer structure and the orientation of the chains (Hahn et al. 1986; Hahn, Ley, and Oberthür 1988; Yoo et al. 1990, 1991). In summary, the sintering or capillary processes, as well as the polymer chain interdiffusion, influence the specific coalescence mechanisms. The participation or dominance of either of those processes consequently depends on various factors.

The development of a homogeneous film from latex is a strongly idealized view. Since the glass transition temperature (T_g) of the polymer is so near room temperature, the interdiffusion of polymer chains is strongly dependent on volatile coalescing aids (Wang and Winnik 1991; Kittel 1998), with other additives effectively working against film formation (Holl et al. 2001). In practice, the resulting polymer film has a heteromor-

phic microstructure, with a continuous network of additives separating the latex particles still retained after film formation (Distler and Kanig 1978; Kast 1985; Zhao and Heckman 1996). This observable fact has important consequences regarding the material properties and the film's behavior on interaction with solvents.

Experimental Setup

Several aspects characterizing the action of fifty solvents on aqueous dispersions paint systems were investigated. Focus was put on three commercially available artists' paint colors based on an acrylic copolymer (Schmincke PRIMAcryl), an acrylic-styrene copolymer (Schmincke Akademie Acryl), and a polyvinyl-versatate copolymer (Lefranc & Bourgeois Flashe) with different proportions of latex to additives (refer to the appendix to this paper for details).

Under specific conditions the swelling capacity of a material can be an idealized indicator of the degree of solvent interaction. It is therefore a useful tool to describe the solute-specific interactions. Although the assumptions made are not fully adequate for the investigated systems, the swelling behavior still delivers important information to the conservator in practice. In this context, sample films of the three commercial paint media were subjected to immersion, and their swelling capacity was plotted against time. The test applied followed the principle described by Phenix (2002) with minor modifications (Zumbühl 2005). The morphological changes induced by immersion in solvents were visualized by scanning electron microscopy (SEM) on cryo-prepared samples. The freeze-fracture method was chosen to investigate the internal structure of a dried film (Roulstone et al. 1991; Wang et al. 1992), whereby the paint samples were cooled in a liquid nitrogen atmosphere and broken under specific conditions. The uranyl-acetate contrasting method (Kanig and Neff 1975; Distler and Kanig 1978) was applied to selectively mark the additives and make them visible in back-scattered electron (BSE) mode. This approach enabled the investigation of the migration and diffusion of additives into the polymeric material, induced by solvent interaction. The total light scattering (TLS) method was applied to investigate the degree of destruction qualitatively. Furthermore, component extracts of the three paint systems were characterized by Fourier transform infrared (FTIR) spectrometry and quantified by gravimetry. Finally, the influence of solvent action on the morphology and the mechanical behavior of paint films were tested by stress-strain measurements. (Detailed information on the experimental setup is given in the appendix.)

Results

Swelling Capacity

The results from the swelling tests indicate that the swelling capacity of such paint films is enormous, exceeding the swelling capacity of an oil film by a factor of approximately ten (fig. 2A). Over a broad part of the polarity scale, the swelling volume is beyond 100 percent. Normalizing the data, it becomes evident that the investigated paint films document a high sensitivity to solvents over a broad range along the polarity scale, with maximum swelling capacities for solvents inducing strong dispersive interaction, such as chlorinated solvents, as well as polarizable molecules such as aromatics (fig. 2B). The swelling behavior is consistent with the theoretically expected solvent interaction on acrylic polymers. Solvents with minimal swelling action for both acrylic paint types can be found only near the upper and the lower ends of the polarity scale. Highly apolar solvents, such as aliphatic hydrocarbons, as well as very polar solvents, including water, seem to be the least dangerous in this context. Significant differences in the solvent sensitivity were observed for the class of alcohols (fig. 2C). Further investigations on other acrylic paint systems confirmed that the solvent sensitivity regarding alcohols varies considerably among different products, so it is not possible to infer general conclusions about this class of solvents. In contrast to the acrylic latex paint, the matte Flashe-PVAc paint reacts only with highly polar solvents. This material is sensitive to water, formamide, and methanol—all solvents with strongly associated hydrogen bonding. All other solvents, including most of the alcohols, have no swelling action on this paint film (fig. 2D).

The swelling process generally runs extremely fast in acrylics (fig. 3). Swelling begins within the first seconds of immersion, and the largest increase in volume takes place within the next thirty seconds. This behavior is clearly different from that of an oil paint film. Within the first ten seconds of immersion, the increase in volume exceeds 200 percent for the majority of solvents tested. Only the strongly apolar and strongly polar solvents at either end of the scale, including the alcohols, show moderate and slow interaction. The Akademie paint demonstrates this behavior in a much more accentuated way than the PRIMAcryl. Despite the lower swelling capacity overall, the process runs much faster in this system. These results suggest that the film quality after drying strongly influences the penetration of solvents in dried latex paint. Based on the general model of film formation, the penetration is favored in latex structures with limited

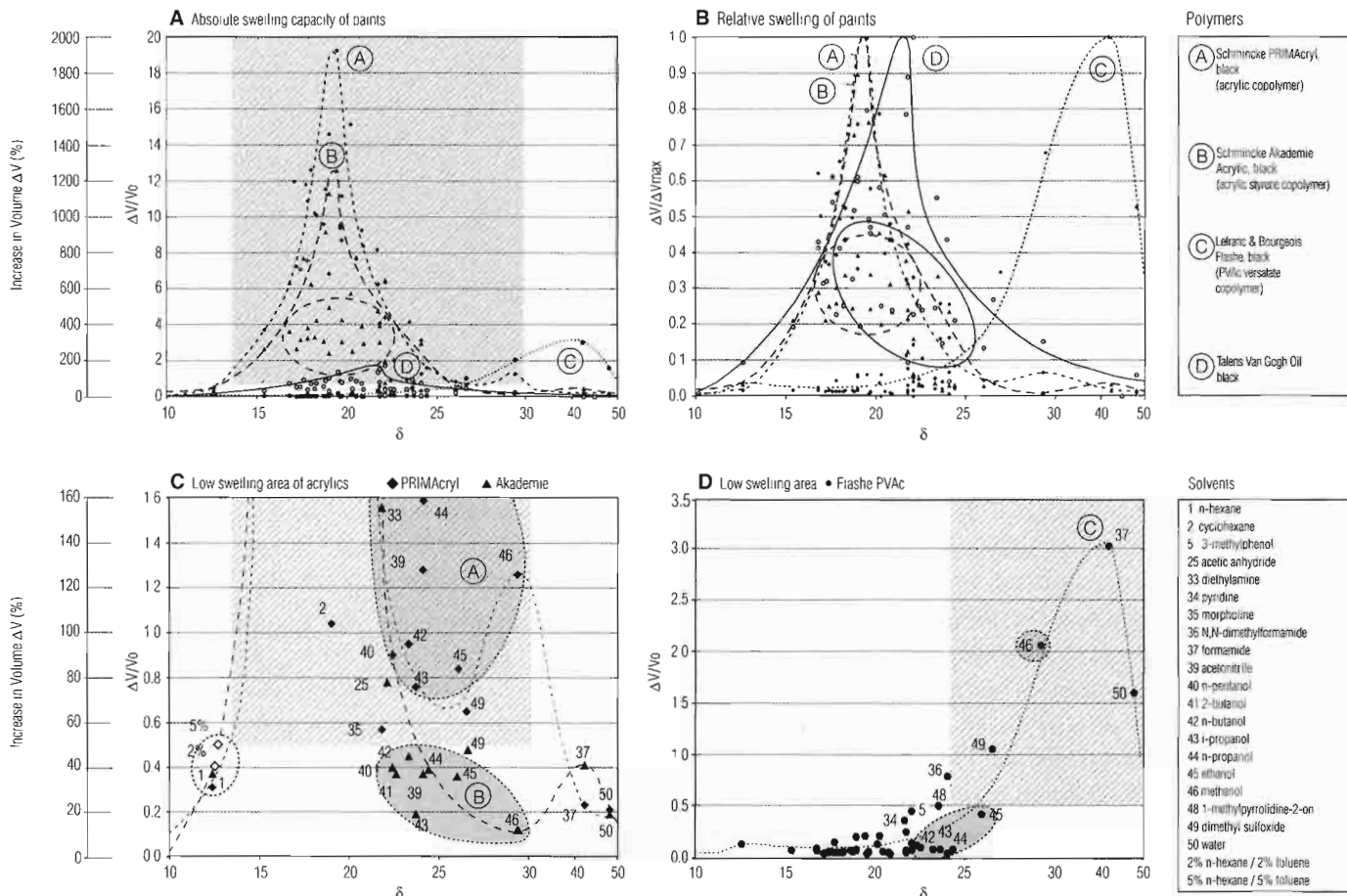


FIGURE 2 (A) The absolute swelling values of latex paint films on immersion in solvents spread along the polarity scale. (B) The relative spectral values show a high sensitivity to solvent interaction over a broad range along the polarity scale, with maximum swelling capacities for solvents inducing strong dispersive interaction. (C) and (D) Enlargement of (A) and (B), respectively, localizing potentially useful solvents with minimal swelling action. Significant differences in the solvent sensitivity were observed for the class of alcohols highlighted in the graphs.

film formation. It is highly facilitated by the interparticular network of incorporated additives, resulting in near-simultaneous swelling action throughout the microstructure. In contrast, in a well-homogenized film, the penetration propagates following a pseudo-Fickian model, similar to the classical penetration of solvents into solid material. The resultant swelling front moves from the surface into the material. There, the

penetration is strongly influenced by the nature of the polymeric material.

Changes in the Latex Microstructure

The solvent action and solvation of polymeric material leads to fundamental changes of the inner microstructure of the latex binder. SEM revealed that coalescence and homogenization are limited under normal film formation conditions, and individual particles are still clearly distinguishable after complete drying (fig. 4A). Solvent treatment by immersion for thirty seconds destroyed the latex morphology to various degrees (figs. 4B–H). In most solvents, the polymeric material of the latex particles is obviously dissolved completely (figs. 4C–G). During the subsequent evaporation process, film formation follows the classic model of dissolved systems, whereby the previous microstructure is irreversibly destroyed. This results in an amorphous and homogeneous film on complete redrying. Solvents with high evaporation pressures and low retention times are less destructive, retaining a still-recognizable

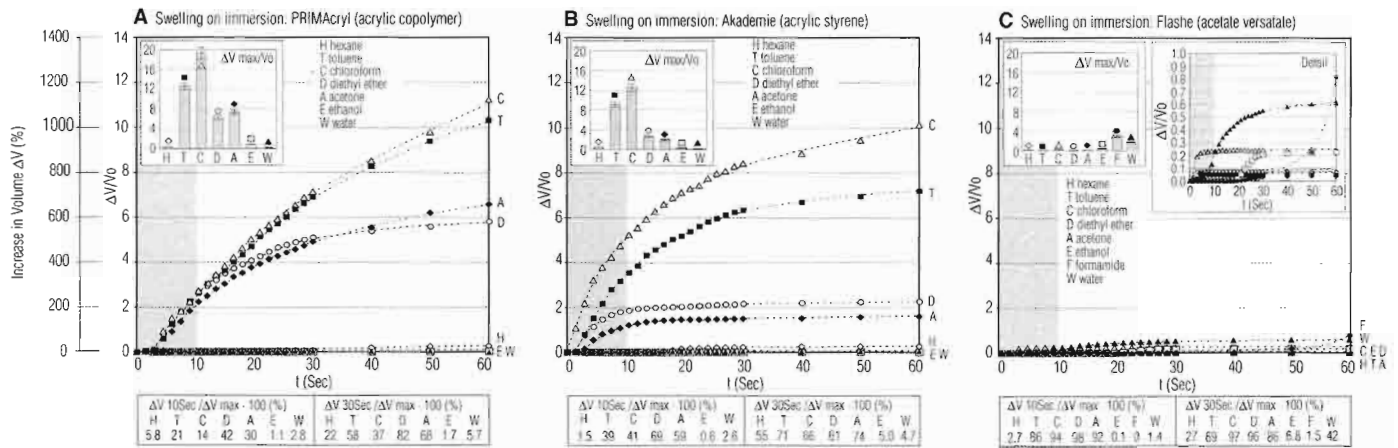


FIGURE 3 Plotting the time-dependent swelling capacity of a selection of seven solvents along the polarity scale reveals the speed of the swelling action. Within the first 5–10 seconds, an enormous swelling power was observed for most solvents.

relic latex structure. Solvent uptake within an equivalent immersion time would thus be relatively low. Nevertheless, the resulting film structure is no longer original, having been more or less destroyed, and is not comparable to the untreated reference.

Only low-swelling solvents, such as aliphatic hydrocarbons, caused no visible changes to the inner microstructure, and the character of the spherical latex particles also seems unaffected (fig. 4B). Very polar solvents at the other end of the polarity scale, such as water, do not dissolve the acrylic latex binder, and so the spherical shape of the latex particles also remains intact after aqueous treatment (fig. 4H). The solvent interaction with water is determined by the additives, particularly by the readily soluble surfactants, which include different kinds of wetting agents, stabilizing agents, and thickeners. The latex structure itself remains unaffected with these solvents. And, although the

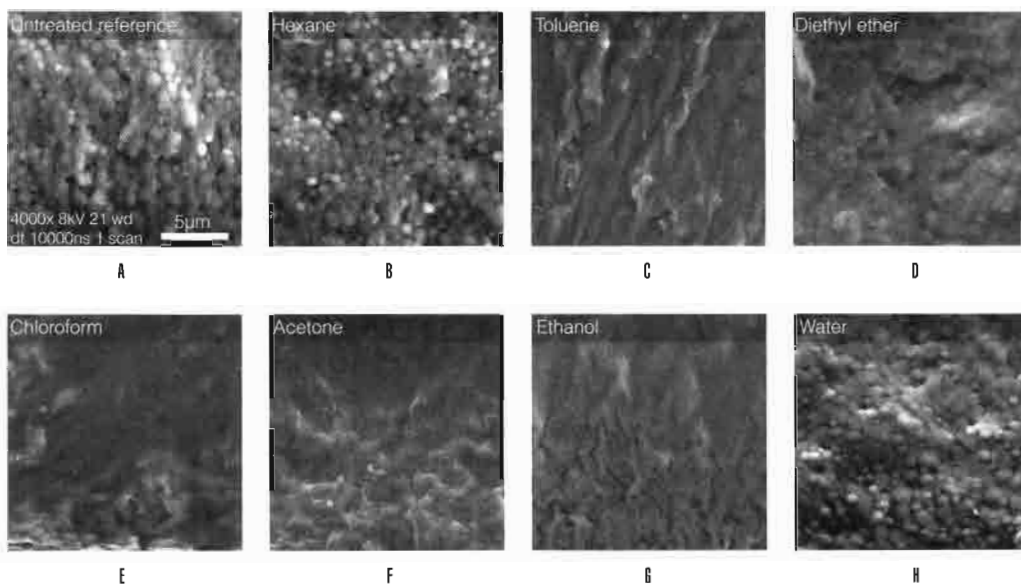


FIGURE 4 SEM images (in secondary electron mode) of freeze-fractured surfaces showing the inner microstructure of an acrylic latex film. The influence of seven solvents spread across the polarity scale is visualized, showing varying degrees of destruction of the morphological structure.

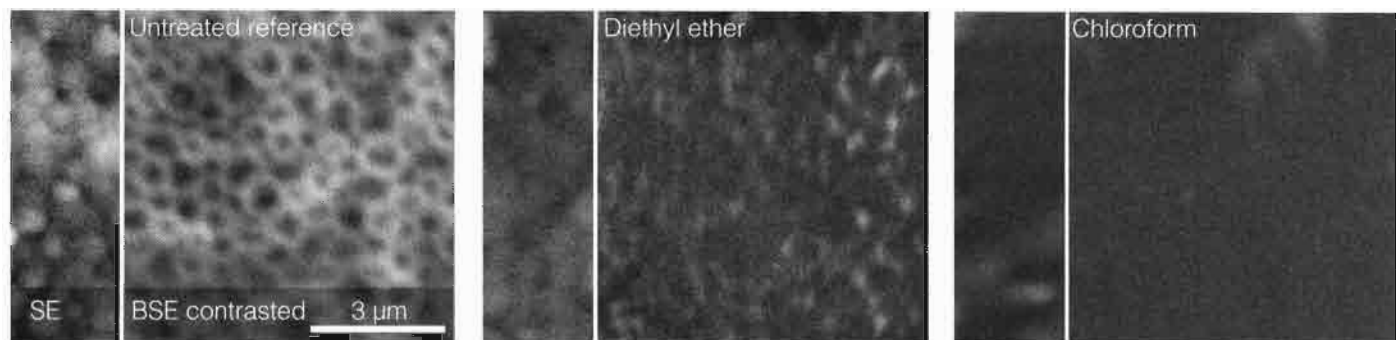


FIGURE 5 SEM-BSE images of sample sections contrasted with the uranyl-acetate method. The additives are selectively marked with uranium and thus become visible through atomic number contrast in BSE mode. In the reference sample, the additives form a continuous network filling the space between distinct and closely packed latex spheres. Diffusion of additives into the dissolved polymer material correlates with the solvating power.

structure seems packed more densely than the reference sample, this is probably the result of the partial leaching of additives that filled the network structure. Films treated with alcohols show varying degrees of destruction, but in all sample cases, the original morphology was modified to some degree.

In samples contrasted with uranyl acetate, the additives are selectively marked and can be made distinctly visible in BSE mode (fig. 5). Looking at the reference sample (no solvent treatment), it is obvious that additives fill the space between distinct latex spheres, forming a polygonal network. When the films are treated with solvents, the additives start to diffuse into the dissolved polymeric material. Depending on the solvating power, additives may become enriched in separated accumulations. Applying moderate solvents having high evaporation pressure leads to various degrees of partial destruction of the original microstructure. Treatment with powerful solvents causes the additives to disperse completely into the polymer matrix. The original structure is totally destroyed through this homogenization process.

These interpretations can be verified by the total light scattering (TLS) method (fig. 6). It is well known that latex binders have a milky appearance when rewetted, becoming transparent again on drying. This event is caused by the existence of separated spherical particles that have a different refractive index than the surrounding liquid phase. Depending on particle size, either Rayleigh or Mie diffraction occurs. TLS delivers qualitative information about the existence of distinct

latex particles within the film structure (i.e., not homogenized). Treatment with solvents, which leads to the dissolution of latex particles, results in films' remaining transparent after rewetting. Of the fifty solvents applied, only the apolar aliphatic hydrocarbon hexane had no influence on the latex structure (fig. 6B). All other solvents were highly destructive, except for some highly polar solvents.

Solvent Extraction

The leaching process in acrylic paint films runs extremely fast. After one minute of immersion time, there was no significant leaching detectable. Over a broad section across the polarity scale, polymeric material was the main constituent of analyzed leachates (fig. 7). But even in solvents with low swelling capacities, several components were leached out in minor quantities. The aliphatic hydrocarbon hexane, for example, dissolved a saturated hydrocarbon component, possibly a colloid stabilizer from the binding system. Water dissolved various additives, such as surfactants, as well as thickeners and processing aids. For the Akademie paint (fig. 7B), similar results can be observed, while the amount of leached components is reduced when compared with the PRIMAcryl results (fig. 7A). Here, ethanol removed a polyethylene oxide derivative and a polyurethane thickener. Most of these components are added during the paint manufacturing procedure.

Despite the very limited swelling, extremely high amounts of material were extracted from the Flashe paint film (fig. 7C). Over a broad range of the polarity scale, polymeric material was leached out. In this particular case, the elimination of components can be understood as a kind of washing-out effect. Very polar solvents such as formamide and water exhibit high dissolution rates of the polyethylene oxide additive. Only for the aliphatic hydrocarbon hexane was no significant extraction of hydrocarbon components observed.

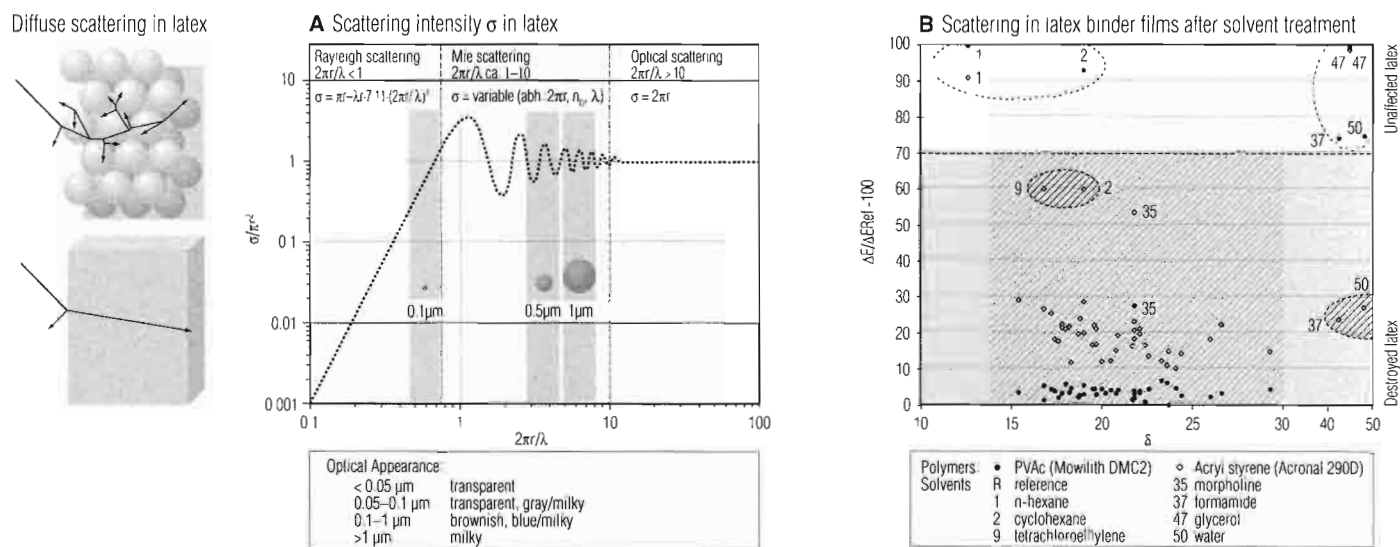


FIGURE 6 (A) The diffuse visible light scattering on rewetted films delivers qualitative information on the existence of distinct latex particles. The light reflection depends on the sphericity of the particles and the refractive index of the material. (B) This graph gives an overview of all results for two binding systems: Mowilith DMC2 and Acronal 290D. On the y-axis, 100% represents the equivalent light scattering in relation to the nontreated reference sample; 0% represents a fully transparent film with minimal water uptake, representing a completely destroyed latex microstructure. The latex particles in Plextol B500 were too small to be differentiated by this method.

Alteration of Mechanical Properties

The solvent treatment of acrylic paint films has a decisive influence on the mechanical properties of the film (fig. 8). The stress-strain measurement of the untreated reference shows a highly elastic and elastoplastic behavior. This characteristic is well known for such binding systems, and is described by the elastic deformability of the latex particles in the film (Distler and Kanig 1978; Rharbi et al. 1996). Differences between the selected products can be explained by the variable nature of the latex material and varying proportions of additives. After paint films were immersed for ten seconds in the solvent and allowed to dry completely, the mechanical properties of the films altered very significantly, becoming much more rigid. This strongly correlates with the swelling capacity. Stiffness increases in parallel with the rate of dissolution, followed by a rapid decrease in the case of extremely powerful solvents. But even films treated with solvents that cause minimal swelling and apparently leave the latex microstructure unaffected are subject to significant

alterations. In contrast to the PRIMAcryl paint (fig. 8A), the Akademie acrylic paint (fig. 8B) shows an extremely heterogeneous behavior and breaks down much faster. This material only retained its homogeneous properties after treatment when low-swelling solvents, such as hexane and water, were used.

The Flashe-PVAc color is different. This paint is much more rigid and has no mechanical strength (fig. 8C). The reference material breaks down after an elongation of only 2%, possibly due to the high level of additives that inhibit full film formation. The extraction of polyethylene oxide additives by polar solvents consequently leads to a somewhat higher elasticity. Immersion treatment with most other solvents leads to the complete loss of any mechanical strength whatsoever. The breaking power is minimal, with films failing at an elongation around 0.5%.

Discussion

The results of this research generate a consistent image of the physical alterations induced by solvent interaction on acrylic latex paint films. The properties of latex paints are strongly dependent on the film formation process. The degree of latex coalescence and polymer interdiffusion is responsible for the latex microstructure. In particular, additives such as thickeners interrupt this process and significantly influence the paint properties. Such materials, for example, display an extremely high sensitivity to solvent interaction. Most of the solvents destroy the microstructure and lead to the formation of a new film. This is comparable to a molecularly dissolved binding system, which results in a film with densely intertwined polymer chains. These irreversible morphological changes lead to a strong increase in

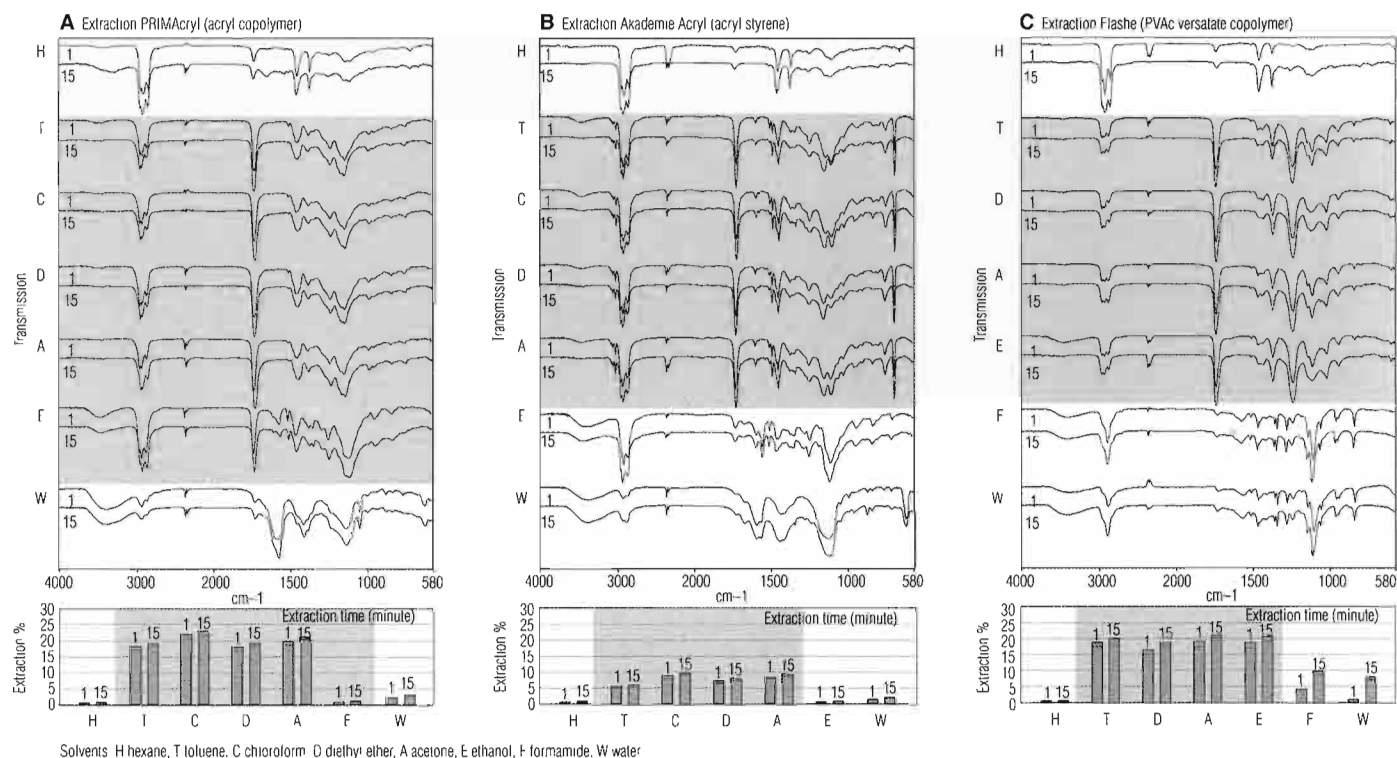


FIGURE 7 This graph shows the leached components after 1 minute and 15 minutes of extraction time for each of the three paint systems: (A) PRIMAcryl, (B) Akademie, (C) Flashe. Extracts were characterized by FTIR and quantified by gravimetry. Varying amounts of different components were leached along the polarity scale. The marked area highlights leaching of polymeric binder material.

stiffness of these paint films. In highly swollen systems, diffusion processes are facilitated, and an accumulation of binding material along the surface was observed. This segregation phenomenon leads to a further decrease in mechanical strength, as well as visible changes in the optical appearance. The homogenization is disturbed by a large volume of additives, such as thickeners. The resulting material properties are therefore strongly influenced by these components. In this context, the Flashe paint color is an extreme case, since film formation is inhibited by the enormous volume of polyethylene oxide additive. The binder is therefore easily washed out by solvent interaction, which results in powdery films without any mechanical strength whatsoever, even with highly polar solvents.

Overall, only aliphatic hydrocarbons and highly polar solvents, such as water and, in some cases, alcohols, left the latex microstructure unaffected. While inducing minimal mor-

phological alterations, treatment with hexane or water does affect the mechanical properties. However, a quite different mechanism seems responsible for the structural changes: these solvents are not able to dissolve the acrylic polymer, but they penetrate the core shell of the latex particles and locally act as a plasticizer (Sullivan 1975; Vezin and Florence 1981; Wang and Winnik 1991, 1993; Baumstark and Schwartz 2001). Interaction with water has a similar effect (Sperry et al. 1994; Kast 1985; Levine and Slade 1985). This kind of effect is well known from the action of film formation aids. For example, lowering the glass transition temperature enhances polymer interdiffusion and leads to an optimized interparticular stability (Hoy 1973; Richard 1996; Juhué and Lang 1994). In the case of water, repetitive treatments have the same effect (Schwartz and Kossmann 1997). The accompanying leaching of additives leads to a further enhancement of this process. After the hydrophilic additives are leached out, the water affinity is reduced (Snuparek 1996; Steward et al. 1996). The extent of structural changes caused by treatment with water is thus not comparable to the dissolved systems described above. A similar effect regarding structural modifications was observed by an increase in temperature (List and Kassis 1982; Hahn et al. 1986; Hahn, Ley, and Oberthür 1988; Eckersley and Rudin 1993). An optimized interdiffusion also leads to greater stiffness of the material.

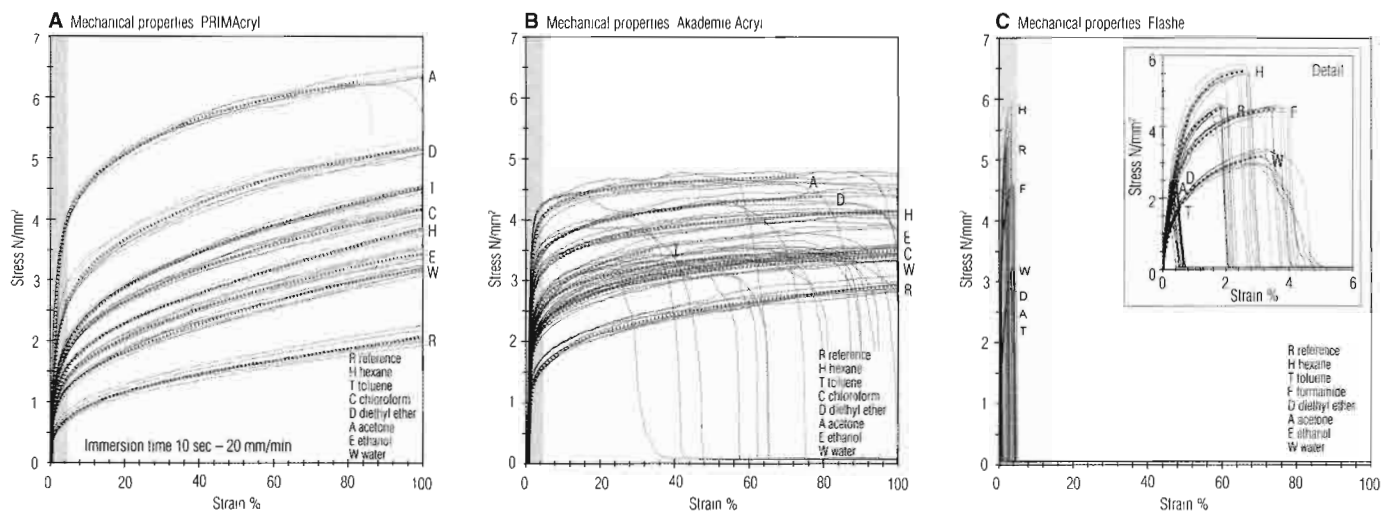


FIGURE 8 After paint films are immersed for 10 seconds in solvent and then completely dried, the mechanical properties of the films are subject to significant alterations. After treatment with solvents, all films were much more rigid, with some samples exhibiting heterogeneous mechanical behavior. This effect strongly correlates with the swelling capacity.

Conclusions

These findings suggest that the composition of latex paint systems has a major influence on film formation and the resulting morphological microstructure, as well as the physical properties of these films. Overall, latex paints are extremely sensitive to solvent interaction. The specific effect not only depends on the nature of the polymer but is strongly influenced by the morphological microstructure. Interaction with solvents leads to variable modifications of this structure and, in many cases, to its total destruction. Only very apolar solvents seem to leave the microstructure more or less unaffected. Thus, only a very small selection of solvents may be considered as suitable for conservation treatments.

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Appendix

Materials

- Schmincke PRIMAcryl professional—pigment: PBk11 PBk7; acrylic copolymer; additive content: 2% (thickener: 1%); pigment volume concentration (PVC): 60%; minimal film formation temperature (MFT): 13° C
- Schmincke Akademie Acryl—pigment: PBk11, PBk7; acrylic-styrene copolymer; additive content: 4% (thickener: 2%); PVC: 50%; MFT: 19° C
- Lefranc & Bourgeois Flasche—PVAc versatate (Veova) copolymer; pigment: PBk 11, PBk 7; additive content: 5%–10%; MFT: 18° C
- Plextol B500 (Rohm)—acrylic copolymer
- Acronal 290D (BASF)—acrylic-styrene copolymer
- Mowilith DMC2 (Höchst)—PVAc maleinic acid dibutyl ester copolymer
- Solvents—All solvents supplied by Merck apart from 1,1-dichloroethane and 2-ethoxyethanol (Grogg Chemie) and dichloromethane, 1,2-dimethoxyethane, 4-hydroxy-4-methyl-2-pentanone, and acetophenone (Fluka)

Instrumentation and Preparation

The immersion-swelling test (modified from Phenix 2002) was carried out on free films (300 μm thick, 14 mm wide) prepared with an Erichsen GmbH preparation tool. Films were allowed to dry for 92 days. Segments (1 mm wide) were then fixed in a circular glass holder (inner diameter 4 mm), designed to inhibit lateral deformation (Zumbühl 2005).

The swelling power of solvents was documented using a Wild M5 microscope + Nikon Coolpix 5000 camera mounted on a ProMicron ocular adapter. Timed sequential images were controlled with a Nikon Remote Cord MC-EU1. Swelling power was quantified by ImageJ image-processing software. The scanning electron microscope (SEM), secondary electron (SE), backscattered electron (BSE) images, and X-ray maps were produced on a CamScan 4 (Cambridge). Samples were carbon coated using a Baltec Med 020 (C-thread, flash mode). Samples for SE images were prepared by the freeze-fracture method described in Roulstone et al. (1991). Samples were left for 21 days after solvent treatment.

SE images were collected at 8 kV, 21 mm working distance, 4000 \times magnification, 10,000 ns dwell time. Samples for BSE imaging were cut using a Diatome diamond blade under cryogenic cooling and treated with uranyl acetate (Kanig and Neff 1975; Distler and Kanig 1978). A 5% solution of uranyl acetate (Merck) was filtered with a Millipore Millex-GV hydrophilic PVDF 0.22 μm filter. A drop was put on a Parafilm sheet. After immersion for 60–120 seconds, samples were rinsed twice with distilled water. BSE images were collected at 20 kV; 21 mm WD, 10,000 \times magnification; 10,000 ns dwell time, and one to three averaged frames.

The total light scattering procedure was used, as described in Bohren and Huffman (2004) and Van Tent and te Nijenhuis (1992a, 1992b). Latex binder films were immersed for 60 seconds. VIS light reflection was measured with photo spectrometer Minolta CM-2022 (d8/SCI). Samples were dried for 19 days after solvent treatment. Leaching was measured by infrared spectrometry and quantified by gravimetry. Paint film samples (500 mg) were immersed in 50 ml of solvent for 1 minute and 15 minutes. Samples then dried for 7 days after solvent evaporation. Measurements were carried out on μ -FTIR Perkin Elmer System 2000 with a Cassegrain-microscope, with samples leveled onto a CVD diamond window. Settings used were transmittance mode, 32 averaged scans with 2 cm^{-1} resolution. For quantitative analysis, two spectra with less than 4% deviation were collected.

Stress-strain measurements were carried out on Zwick tensile tester Z2.5/TN1S in controlled room conditions of 54%–56% relative humidity (RH) and 17°–18° C. Free paint films (14 mm wide, 100 mm effective length) were made by brushing paint onto Teflon-coated foil. Samples were immersed in solvent for 10 seconds, dried for 23–24 days, and then removed from the foil. Seven replicates per paint type were tested. Zwick settings were elongation speed, 20%/minute; maximum elongation, 100%.

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