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Project Summary

Analytical Techniques for Measuring the Effects of Acid Deposition on Coatings on Wood

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Preliminary experiments have been carried out to characterize the potential deleterious effects of acidic deposition on three representative paints: an oil alkyd paint and two acrylic latex formulations. The base polymer latex common to both latex paints was also studied individually. Free films of paint have been exposed to relatively high levels of gaseous SO_2 and ultraviolet light, and have been immersed in aqueous SO_2 at pH 2.0. Several analytical techniques have been used to assess the resulting chemical and physical changes in the paint films, including sorption and diffusion measurements, attenuated total reflectance infrared spectroscopy, dynamic mechanical analysis, sol-gel analysis, contact angle measurements, differential scanning calorimetry, and electron spin resonance. All techniques show promise for characterizing the early stages of damage to paint films caused by acidic deposition. The major effects noted in this study include leaching of acid-soluble extender components upon immersion in aqueous SO_2, and enhanced degradation of the base polymer upon exposure to gaseous SO_2 and ultraviolet light.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The objectives of this project are: (1) to study the effects of acid deposition products in combination with near-uv radiation of the micro- and macro-structures of acrylic latex paint coatings, (2) to assess microdamages experienced by acrylic copolymers upon exposure to acid deposition; (3) to determine mechanistic paths that lead to polymer structural changes and microdamage; and, (4) to relate molecular structural changes to macrodamages that affect the service life of exterior coatings used on wood substrates.

The following analytical techniques will be employed: Intrinsic viscosity; Sol/Gel Analyses; Gel Permeation Chromatography; Surface Contact Angles; Differential Scanning Calorimetry (DSC); Dynamic Mechanical Analysis (DMA); Stress-Strain Analysis; Fatigue Tests; Infrared Spectroscopy; Electron Spin Resonance Spectroscopy; ESCA and SIMS; SEM - Fracture Surfaces studies. Changes will be followed in molecular weight, molecular weight distribution, glass transition temperature, changes in bulk properties, the amount of polymer chain scission, crosslinking and oxidation upon exposure of the paint coatings to ultra-violet radiation, SO_2, NO_x and mixtures of the SO_2 and NO_x with air and/or water.

The resulting data will permit determination of the mechanistic paths that result in the degradation of the base polymer in the paint coating and allow

the prediction of useful lifetimes of coatings exposed to acid rain pollutants.

Experimental Procedures

Films of the base and compounded latexes were prepared by the drawdown procedure, using standard draw-down bars, on release paper. They were dried at R.T. for 4 hr, stored in a desiccator oven drierite for 48 hr and then heated at 40°C for 48 hr under vacuum. The films prepared in this manner absorbed negligible amounts of water when stored at R.T. and 64% R.H.

A sample of each film before and after exposure to various environments was obtained and placed in tetrahydrofuran (THF) for 3 days. The soluble portion was separated from the insoluble portion by filtration, the insoluble portion dried and weighed to determine the gel content. The amount of sol was determined by evaporation of the THF.

Intrinsic viscosities were determined at 25°C using modified Cannon-Fenske viscometers.

Thermal analyses were performed with either a Perkin-Elmer DSC-2 or -7, each equipped with a data station.

Samples 1 cm by 6 cm were cut from each film using care to obtain uniform widths. The thicknesses were measured with a micrometer. Dynamic mechanical analyses (DMA) tests were made with an Autovibron DDV-II-C at a frequency of 11 hz and a scanning rate of 2.5°C/min.

The films were exposed to uv light (254 or 350nm) in a Rayonnet U.V. reactor. The samples were mounted in quartz tubes equipped with inlet tubes for SO_2, NO_x, air or various combinations.

Contact angles were measured with an NRL goniometer using distilled water.

The solubility/diffusivity data for gases in polymers is obtained using conventional weight-gain techniques. A sensitive electrobalance system enclosed in a vacuum chamber was constructed for this purpose. Provisions are made for maintaining constant diffusant pressure and temperature. Mass changes (as small as a few micrograms) are monitored as a function of time, and continuously displayed on a chart recorder. A second electrobalance system that can be used in corrosive environments, to be built in the second year, will greatly speed up the data collection process. An Analect FX-6260 FTIR spectrometer equipped with an MCT detector and a flat-plate ATR sampling accessory was used to obtain the infrared spectra. A ZnSe parallelogram crystal with an angle of incidence of 45° was used. All ATR spectra were collected at $4cm^{-1}$ resolution, and 128 scans were accumulated for each sample. The paint films for FTIR Analysis were cast on a clean glass plate surface, dried overnight in air, and transferred to a desiccator containing anhydrous $CaSO_4$ for a minimum of three days. Film thickness was measured using a sensitive micrometer having a precision of ± 1.2 µm. The thickness of the films used in this study was 127 µm (about 5 mils).

A coating device for putting a thin, uniform film of paint on a cylindrical ATR crystal was constructed for FTIR analysis of diffusion kinetics and in-situ analysis of chemical reactions. The associated gas delivery system for these experiments has also been completed. The system will be tested, and should be operational by July 1988.

Experimental Results

Preliminary Mechanical/ Structural Effects of SO₂

The effect of uv light (350 nm) in the absence and presence of SO_2 on the intrinsic viscosity, gel content, contact angle, Tg, and dynamic modulus of the contained polymer in the base latex is shown in Table 1. All the films were from a single casting.

Preliminary Solubility and Diffusivity Data for SO₂

Sorption isotherms at 28°C for SO_2 in the Latex without $CaCO_3$ (LO), Latex with $CaCO_3$ (LC) and polyer base samples have been obtained. The solubility of SO_2 in the samples varies linearly with pressure up to 650 torr (Henry's law behavior) for the two paint samples and the polymer base. The paint sample containing $CaCO_3$ superimposes on the base polymer isotherm, while the sample without $CaCO_3$ has a slightly higher slope. This difference could be due to an inconsistency in the reported amount of polymer in this paint; a value of 35% was used to normalize the data for both paint samples to grams polymer. Reproducibility tests are in progress to check this.

Diffusion coefficients (D) were obtained for SO_2 in each sample at each experimental pressure. D was found to increase with increasing pressure. This trend has been observed before for SO_2 in a polyimide. This is attributed to plasticization of the polymer by the penetrant. The increase in D is most pronounced for the paint sample without $CaCO_3$.

The total flux of SO_2 through these samples is proportional to the permeability, P, which is equal to the product of the diffusivity D and the solubility k_D (Henry's law constant). The pressure-dependent diffusivity translates to a pressure-dependent permeability. The permeabilities of the polymer base and the $CaCO_3$-containing paint are again very comparable, and are in the neighborhood of 10^{-7} cc(STP) cm^2/cm^3 polymer-torr-sec. The permeabilities of the $CaCO_3$-free paint are an order of magnitude higher.

Simple Immersion Tests in Aqueous SO₂

Free films of LC and LO latex paints, as well as the polymer base, were exposed to aqueous SO_2 (pH = 2.0) for periods ranging from 1 minture to 14 days. The polymer base showed no weight loss after 14 days. However, significant weight loss occurred upon exposure to sulfurous acid for the two latex paint samples. For the latex paint without the $CaCO_3$ extender, only 7.2% of the sample weight is lost after 14 days of exposure. For the latex paint with $CaCO_3$ extender, the weight loss levels off after 4 hours; the maximum weight loss being 27% after 14 days. The weight loss of the LC samples in deionized distilled water (pH = 5.4, due to the presence of H_2CO_3) is only 8.5% after 14 days. This clearly indicates that the presence of SO_2 In water accelerated the rate at which materials are leached out of the films. The initial linearity of the weight loss vs. $t^{0.5}$ plot (curve A, Figure 1) suggests a Fickian diffusion mechanism for removal of material from the sample. The diffusion coefficient is 1.84 x 10^{-9} cm^2/sec.

The ATR spectra of the polymer binder and the two latex paints are shown in Figure 2. Due to the multicomponent nature of the paints and the presence of infrared-absorbing inorganics, assignment of all the bands is difficult, especially in the region between 400 cm^{-1} and 1600 cm^{-1} where overlapping of bands is evident. The polymer binder is a terpolymer of vinyl acetate, vinyl chloride, and butyl acrylate, but the relative composition is not known. Despite these complications, differences between the spectra of samples with and without $CaCO_3$ extender can be observed, as seen by comparing spectra A and B in Figure 2. The two peaks at 1416 cm^{-1} and 875 cm^{-1} are not found
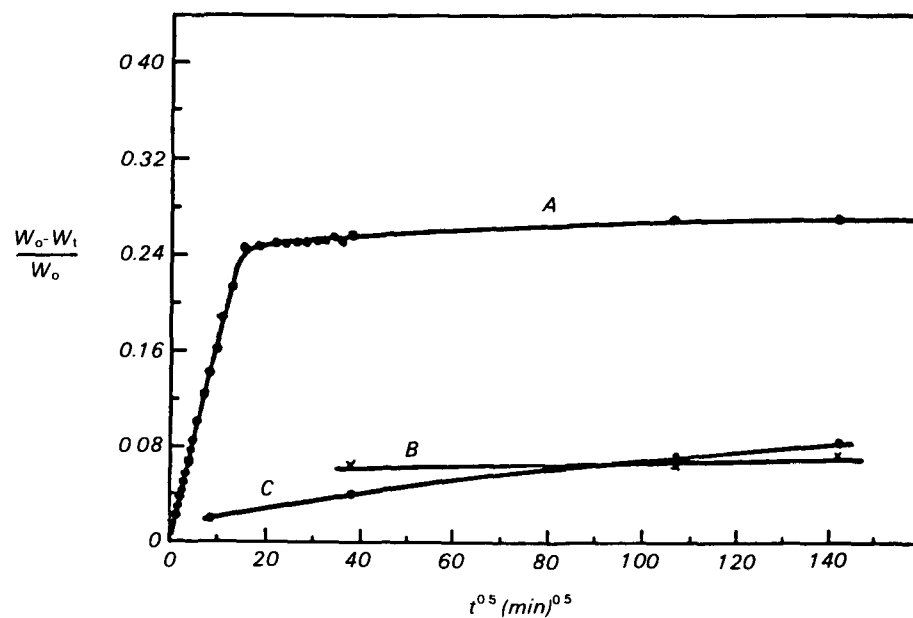
Figure 1. Weight loss of latex paint film with exposure time (a) Films with $CaCO_3$ at pH = 2.0, (b) films without $CaCO_3$ at pH = 2.0; (c) films with $CaCO_3$ in deionized distilled water.
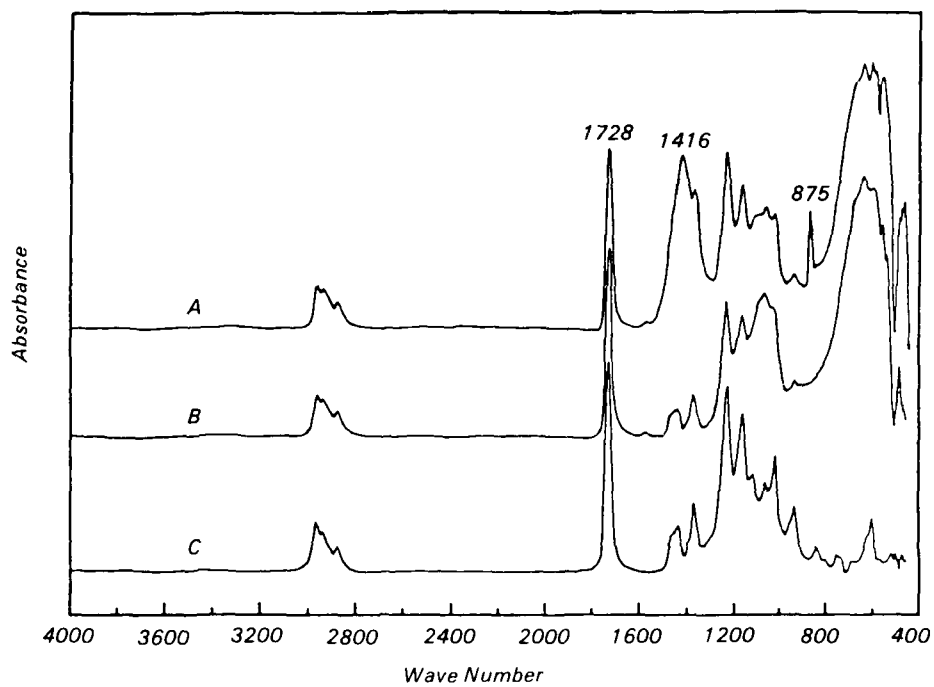
**Figure 2.** FTIR-ATR spectra of (a) latex with $CaCO_3$, (b) latex without $CaCO_3$ (c) base polymer latex.

in the spectrum of the LO sample, and are identified as the stretching and wagging vibrations of the CO_3^{2-} group of CO_3, respectively. The broad band between 850 and 450 cm^{-1} is absent in the spectrum of the polymer base and therefore has been attributed to the pigment (TiO_2) or the china clay (aluminum silicate) added to the paints. The vibrational frequencies of these additives are located in this region. The band at 1728 cm^{-1}, due to the $C=O$ stretching mode of the polymer, is common to all three spectra. This peak is well separated from others and is suitable for use as a reference for spectral subtraction.

In Figure 3, ATR spectra of the LC samples exposed to sulfurous acid for 1, 6, and 30 minutes are shown. The intensities of the bands at 1416 cm^{-1} and 875 cm^{-1} decrease markedly with increasing exposure time, and are essentially gone after 30 minutes of exposure, indicating a loss of $CaCO_3$. The broad absorbance centered around 700 cm^{-1} becomes sharper with increasing exposure. This result is also found for the spectra of exposed LO samples. In contrast, the spectra of the polymer base show essentially no change after 14 days of exposure. Subtraction of the spectrum of the polymer base exposed for 14 days from

the spectrum of an unexposed sample resulted in a flat line across the entire spectral range.

Determination of D from the FTIR-ATR Data

Difference spectra between the unexposed LC and LO samples revealed the two $CaCO_3$ peaks at 875 and 1416 cm^{-1}. The integrated intensities of these two peaks were followed as a function of exposure time to aqueous SO_2. The penetration depth in an ATR experiment is only a few μm, therefore the $CaCO_3$ will be removed from this thin surface layer in a much shorter time than is required to remove all of the $CaCO_3$ from
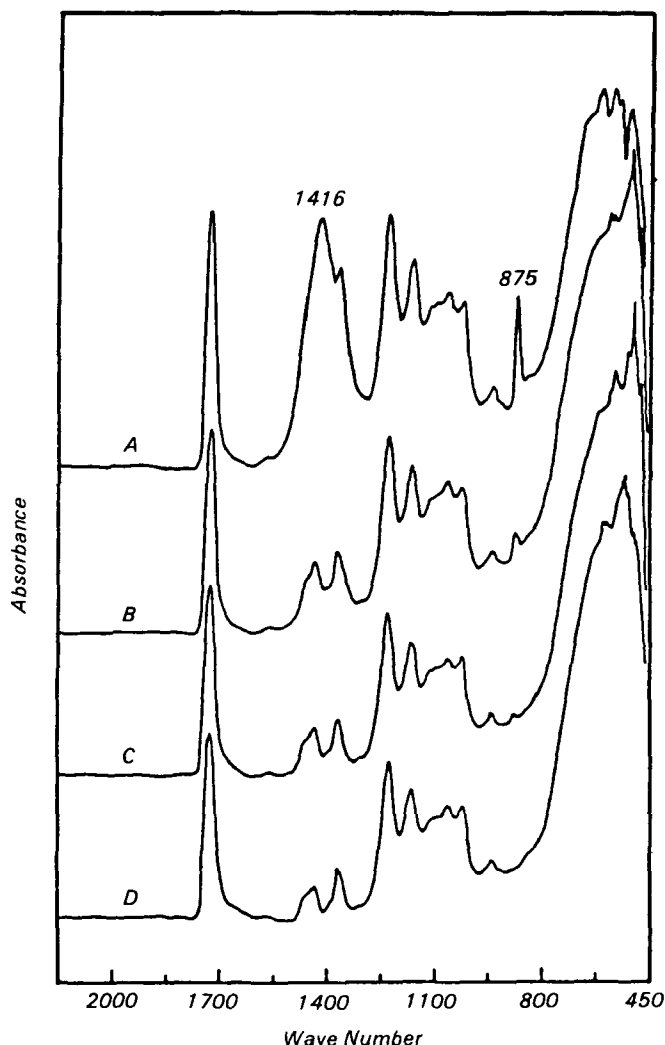
Figure 3. FTIR-ATR spectra of latex paint containing $CaCO_3$ exposed to aqueous SO_2 (pH = 2.0) for (a) 0 min ; (b) 1 min.; (c) 6 min., (d) 30 min

the bulk film. The penetration depths are 2.3 and 1.4 µm for the 875 and 1416 cm^{-1} peaks respectively. The very rapid loss of $CaCO_3$ from the surface layer is evident in Figures 4-(a) and (b).

The diffusion coefficient cannot be obtained from Figures 4-(a) and (b) in a straightforward manner. Exposure times below 1 minute could not be reproducibly controlled, thus the (linear) short-time regions of the curves could not be obtained. Secondly, there is considerable uncertainty in the assignment of the effective film thickness f, given that the amplitude of the evanescent wave in an ATR experiment decays exponentially with depth into the sample, and that the concentration profile of the diffusant remaining in the surface layer are nonlinear.

The results of this analysis for the data in Figure 4 are D = 1.77 x 10^{-9} cm^2/sec for the 1416 cm^{-1} peak, and 2.25 x 10^{-9} cm^2/sec for the 875 cm^{-1} peak. Both are in very good agreement with the value of 1.84 x 10^{-9} cm^2/sec obtained from the bulk weight loss data. The solid lines in Figure 4 were obtained by fixing these values for D and back-calculating the expected values of I_t/I_∞.

Discussion

Mechanism of UV/SO$_2$ Effects

The data in Table 1 demonstrate that exposure to uv causes both chain
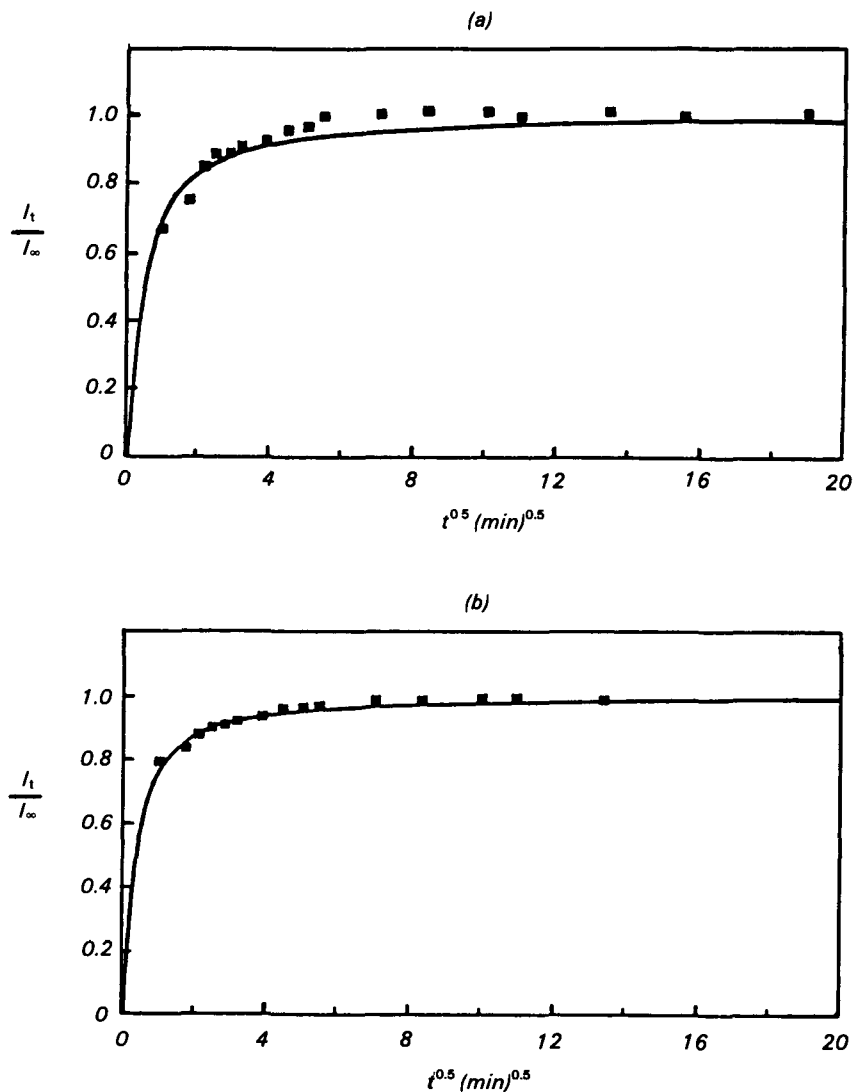
Figure 4. Data points: removal of $CaCO_3$ from LC paint films exposed to sulfurous acid as measured by the integrated intensity ratio of (a) the $CaCO_3$ band at 875 cm^{-1}; (b) the $CaCO_3$ band at 1416 cm^{-1}. Solid lines: calculated variation of the integrated intensity ratio with $t^{0.5}$.

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Sample Reference No.	Exposure Time UV (350nm)	(Hr) SO_2 (ml/min)	[η] (dl/gm)	Gel Content (%)	Contact Angle (θ)	Tg (°C)	$E1X10^{10}$ dynes/cm² (at -30°C)
1-75-BL	0	0	1.00	22	78	22	2.50
1-77-BL1	48	0	0.82	32	71	22	2.50
						24	2.16
1-78-BL2	96	0	0.50	60	65	35	2.72
						33	2.40
						34	1.90
						34	1.90
1-79-BL3	48	2	0.17	66	52	—	1.24
						83	1.27
1-80-BL4	96	2	0.11	68	*	97	4.54
						100	2.29
						80	1.49
1-81-BL5	0	2 (48 hr)	1.00	22	63	35	1.64
						25	2.44
1-81-BL6	0	2 (96 hr)	1.00	22	67	24	1.25
						24	2.07

*Water drop spread immediately

scission and crosslinking of the polymer. The intrinsic viscosity decreases and the gel content increases with uv exposure time. The higher molecular weight species will be preferentially converted to gel (crosslinked polymer) increasing the fraction of low molecular weight species in the soluble portion and resulting in a decrease in intrinsic viscosity. However, the decrease in contact angle indicates an increase in the carbonyl group content which must result from chain scission. The small increase in Tg confirms crosslinking has occurred. Exposure to SO_2 alone has relatively little effect. However, the combination of uv and SO_2 results in rapid polymer microstructural changes. The intrinsic viscosity decreases by nearly an order of magnitude, the gel content triples and the Tg increases markedly. For example, the Tg increases from approximately 22°C for the unexposed base latex to about 75-80°C for samples exposed for 48 hrs to both uv and SO_2. The polarity of the surface also significantly increases. This indicates that uv and SO_2 in combination cause rapid microstructural polymer changes, namely chain scission and crosslinking.

Mechanism of $CaCO_3$ Removal

The bulk weight loss data and FTIR spectra clearly suggest that the $CaCO_3$ extender added to the latex paint is removed when the film is exposed to solutions containing acidic ions. Exposure to deionized distilled water, in which the acidic species come from H_2CO_3, rsults in loss of less than 10% of the sample weight in 14 days. However, upon exposure to pH = 2.0 sulfurous acid, essentially all of the $CaCO_3$ is leached out in about 4 hours. The approximate composition (in weight %) of the dry LC latex samples is 37% polymer base, 21% $CaCO_3$, 35% TiO_2, and 7% china clay. The maximum weight loss is 27%, which is nearly equal to the sum of the weights of $CaCO_3$ and china clay. The changes in the infrared spectra also support the loss of these two components. Although the sharpening of the broad band between 450 and 850 cm^{-1} could be attributed to loss of TiO_2 rather than china clay, the extremely low solubility of TiO_2 in acids, relative to china clay makes this rather unlikely. No detectable evidence for sulfite or bisulfite ion was found in the FTIR spectra of exposed films.

The mechanism of removal of $CaCO_3$ from the latex film must involve three steps: (1) diffusion of the components of the SO_2 aqueous solution into the film, (2) reaction and/or dissolution of $CaCO_3$, and (3) diffusion of $CaCO_3$ (or its ions) out of the water-swollen film. Given the Fickian kinetics for the overall removal of material from the film, the rate limiting step must be diffusion controlled. Therefore, if any of the above chemical reactions do occur, they must be very rapid in comparison. It is not possible to distinguish between steps (1) and (3) with the present data, although one of these processes should be much faster than the other, otherwise, Fickian kinetics would not be observed. Thus, the diffusion coefficient measured in these experiments represents either step (1) or step (3) in the mechanism proposed above, but not a combination of the two. It would seem that diffusion of $CaCO_3$ (or its ions) out of a water-swollen film could occur much faster than the initial diffusion of water, SO_2, and ions into a dry, unswollen film.

Summary

During the first year of this project preliminary studies were conducted to determine the best techniques to identify chemical and physical effects on polymeric coatings used on wood due to wet and dry acid deposition. The following techniques were employed Fourier transform IR, gravimetric measurements to obtain diffusivities and solubilities, dynamic mechanical analysis (DMA), sol-gel analyses, intrinsic viscosities (IV), differential scanning calorimetry (DSC), contact angle and electron spin resonance (ESR). Emphasis during the initial phase of our investigations has been on free films of latex paint. Some preliminary work has begun on alkyd paint films and coatings on wood substrates.

Preliminary exposure studies show that the techniques employed are well suited to follow changes in the microstructure of latex films as a function of exposure to acid deposition.

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J. W. Spence is the EPA Project Officer (see below).

The complete report, entitled "Analytical Techniques for Measuring the Effects of Acid Deposition on Coatings on Wood," (Order No. PB 89-127 518/AS; Cost: $15.95, subject to change) will be available only from:

  National Technical Information Service
  5285 Port Royal Road
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