

# Infrared Attenuated Total Reflectance Study of Latex Paint Films Exposed to Aqueous Sulfur Dioxide

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## Synopsis

Fourier-transform infrared/attenuated total reflectance (FTIR-ATR) has been used to investigate the effects of acidic deposition on latex paint films with and without a calcium carbonate extender additive. Paint films approximately 5 mils thick were exposed to aqueous SO<sub>2</sub> (pH 2.0) for various times by simple immersion. Rapid and complete removal of CaCO<sub>3</sub> from the paint film was found to occur, and the kinetics of the removal process were monitored using both weight loss and FTIR-ATR measurements. Both methods revealed Fickian diffusion, with an apparent diffusion coefficient  $D = 1.84 \times 10^{-9} \text{ cm}^2/\text{s}$ . Good agreement was obtained between  $D$  measured via FTIR-ATR and from the weight lost data. The mechanism of removal of CaCO<sub>3</sub> from the latex paint films appears to be controlled by the rate at which water and other components of the aqueous SO<sub>2</sub> solution can diffuse into the film.

## INTRODUCTION

The major purpose of a paint film is to protect the underlying substrate from degradation and deterioration, which may occur upon exposure to the environment. To this end, the paint film itself must remain intact and weather-resistant. Paint films are multicomponent systems, containing in addition to the polymeric latex binder, pigments, extenders, and other additives, some of which are designed to improve weathering characteristics.<sup>1</sup> It is well known that each additive and its concentration relative to the polymeric binder plays an important role in determining the final performance of the paint. Damage to the paint film may result from degradation of the polymeric binder and/or the adverse interaction of other paint components with harmful chemical species in the environment.

In recent years, acid rain has been recognized as a potential source of deterioration of paints,<sup>2,3</sup> although relatively little work has addressed this issue. Jellinek and co-workers<sup>4-7</sup> studied the reactions of acid rain precursor gases SO<sub>2</sub> and NO<sub>2</sub> with various polymers and elastomers. Gutfreund<sup>8</sup> has studied the effects of ozone on the creep behavior of various paint systems, and found evidence for crosslinking and embrittlement. Spence, Haynie, and others<sup>9-12</sup> have assessed the effects of SO<sub>2</sub>, ozone, and nitrogen oxides on paint films, and found increased erosion rates due to leaching of acid-soluble extender components such as CaCO<sub>3</sub>. Edney et al.<sup>13</sup> also found evidence for removal of CaCO<sub>3</sub> in analysis of rain runoff from field-exposed paint samples.

Fourier-transform infrared spectroscopy (FTIR) is a very valuable technique for assessing chemical changes occurring in paint films. The presence of inorganic pigment and extender particles which can scatter and absorb infrared radiation make conventional transmission measurements impossible. However, other sampling techniques, such as attenuated total reflectance (ATR) and photoacoustic detection can be used to good advantage. Both of these are surface techniques, and are expected to be especially sensitive to chemical changes occurring in weathered surface layers in paint. FTIR-ATR surface analysis of photodegraded acrylic lacquers containing 45%  $\text{TiO}_2$  upon UV irradiation has recently been reported.<sup>14</sup> Zhao et al.<sup>15</sup> have used FTIR-ATR to determine the distribution of surfactants in latex films. To date, very little work has been found regarding the use of FTIR-ATR to study acid deposition effects on paint films.

The purpose of the present investigation is to explore the effects of acidic deposition on representative latex paint films through simple immersion exposures to aqueous  $\text{SO}_2$  (pH 2.0), and to evaluate the use of FTIR-ATR for assessing these effects. Two paint formulations were used, one with and one without  $\text{CaCO}_3$  as an extender. The base latex was also included in the study. Changes in the sample weight with exposure time were followed, and these results were correlated with FTIR-ATR spectra to determine the time-dependent changes in chemical composition of the paint.

## EXPERIMENTAL

**Samples.** Two representative flat latex paint formulations were prepared and supplied by Union Carbide Coatings and Emulsions (Cary, NC). In one paint, referred to below as the LC sample,  $\text{CaCO}_3$  (Camel White; Genstar) was added as an extender. The other paint contains no  $\text{CaCO}_3$  and is referred to below as the LO sample. Paint compositions are listed in Table I. The base polymer latex, common to both paints, was also used in this study.

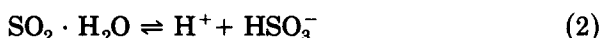
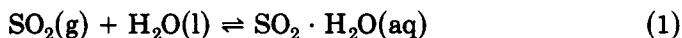
TABLE I  
Acrylic Latex Paint Compositions

Component	Wt %	
	LC	LO
Water	20.5	20.5
UCAR 516 (acrylic terpolymer)	35.0	35.0
RCL 9 $\text{TiO}_2$ (pigment)	21.2	25.4
Genstar camel white ( $\text{CaCO}_3$ extender)	12.7	0.0
Optiwhite P (china clay extender)	4.2	12.7
Aqualon H <sub>4</sub> BR (bioresistant thickener)	0.2	0.2
BYK 155 (dispersant)	0.8	0.8
TKPP (co-dispersant)	0.1	0.1
Triton N101 (nonionic surfactant)	0.2	0.2
Nalco 2315 (foam reduction)	0.3	0.3
Ethylene glycol	2.4	2.4
Texanol (coalescent)	1.4	1.4
Troysan polyphase (biocide)	0.8	0.8
Ammonium hydroxide	0.2	0.2

**Preparation of Paint Films.** The paint films were cast on a clean glass plate surface, dried overnight in air, and transferred to a desiccator containing anhydrous  $\text{CaSO}_4$  for a minimum of three days. Film thickness was measured using a sensitive micrometer (MSC Industrial Supply Co.) having a precision of  $\pm 1.2 \mu\text{m}$ . The thickness of the films used in this study was determined to be  $127 \mu\text{m}$  (about 5 mils).

**Exposure Experiments.** In the exposure experiments, a capped test tube with 45 mL of  $\text{SO}_2$  aqueous solution (sulfurous acid) was placed in a constant temperature bath at  $25^\circ\text{C}$ . A free paint film was then immersed in the test tube for a desired period. After exposure, the film was rinsed with deionized distilled water to wash away the residual acid on the surface. The exposed film was then dried in the desiccator for at least 3 days to constant weight. Sample weights before and after exposure were determined with an analytical balance. The samples weighed about 40–60 mg. The weighing precision is expected to be better than  $\pm 0.5\%$ .

Sulfurous acid was prepared by bubbling  $\text{SO}_2$  gas through deionized distilled water. The pH value of the sulfurous acid was measured using a digital pH meter. The pH value of deionized distilled water stabilizes at about 5.4–5.8, due to the dissolution of  $\text{CO}_2$  and formation of carbonic acid. Sulfur dioxide exists in water as three species: physically dissolved  $\text{SO}_2(\text{SO}_2 \cdot \text{H}_2\text{O})$ , bisulfite ion ( $\text{HSO}_3^-$ ) and sulfite ion ( $\text{SO}_3^{2-}$ )<sup>16</sup>.



It has been reported that there is no clear evidence for the existence of unionized acid  $\text{H}_2\text{SO}_3$ .<sup>17</sup> The ionization constants for  $\text{HSO}_3^-$  and  $\text{SO}_3^{2-}$  are  $1.72 \times 10^{-2}$  and  $6.24 \times 10^{-8}$ , respectively. The major anion present is therefore expected to be bisulfite. The sulfurous acid was prepared with a constant pH value of 2.0, and contained 0.2 g of  $\text{SO}_2$  per 100 g water as determined by weighing.

**FTIR Measurements.** 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  $45^\circ$  was used. All ATR spectra were collected at  $4 \text{ cm}^{-1}$  resolution, and 128 scans were accumulated for each sample. A torque wrench was used to provide uniform clamping force to give a good contact between the sample and the ATR crystal.

The depth of penetration  $d_p$ , i.e., the distance at which the electric field amplitude falls to  $1/e$  of its boundary surface value, can be calculated from the equation<sup>18</sup>

$$d_p = \frac{\lambda}{2\pi n_1 (\sin^2 \theta - n_{21}^2)^{1/2}} \quad (4)$$

where  $n_{21} = n_2/n_1$ ,  $\lambda$  is the wavelength of the infrared peak under considera-

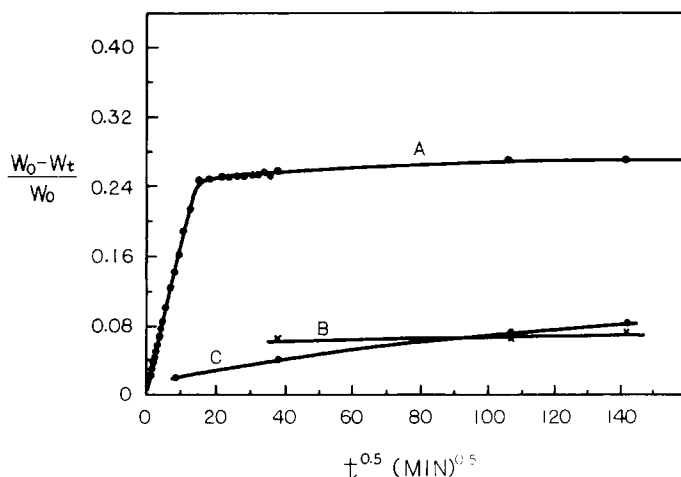


Fig. 1. Weight loss of latex paint film with exposure time: (a) films with  $\text{CaCO}_3$  at pH 2.0; (b) films without  $\text{CaCO}_3$  at pH 2.0; (c) films with  $\text{CaCO}_3$  in deionized distilled water.

tion,  $n_1$  and  $n_2$  are the refractive indexes of the reflecting prism and the sample, respectively, and  $\theta$  is the angle of incidence.

Computer subtractions between spectra were performed using the band at  $1728 \text{ cm}^{-1}$  as a reference, which is the  $\text{C}=\text{O}$  stretching vibration associated with the polymer binder in the paints and does not overlap with other bands.

## RESULTS

Free films of LC and LO latex paints as well as the polymer base were exposed to aqueous  $\text{SO}_2$  (pH 2.0) for periods ranging from 1 min 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. The results are plotted as  $(W_0 - W_t)/W_0$  vs.  $t^{0.5}$  as shown in Figure 1, where  $W_0$  and  $W_t$  are the sample weights before and after the exposure, respectively;  $t$  is the exposure time in minutes. It can be seen that for the latex without the  $\text{CaCO}_3$  extender, only 7.2% of the sample weight is lost after 14 days of exposure. For the latex with  $\text{CaCO}_3$  extender, the weight loss levels off after 4 h, the maximum weight loss being 27% after 14 days. Curve C in Figure 1 shows the weight loss of the LC samples in deionized distilled water (pH 5.4), due to the presence of  $\text{H}_2\text{CO}_3$ ). Only 8.5% of the weight is lost after 14 days. This clearly indicates that the presence of  $\text{SO}_2$  in water accelerates 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, Fig. 1) suggests a Fickian diffusion mechanism for removal of material from the sample. Figure 2 is a replot of these data, using the usual quantities for analysis of diffusion kinetics, viz.,  $M_t/M_\infty$  vs.  $t^{0.5}$ . Here  $M_\infty$  is the mass removed from the film at equilibrium ( $t_\infty = 14$  days), while  $M_t$  is the mass removed at earlier times  $t$ . For Fickian diffusion out of (or into) a thin slab at short times,

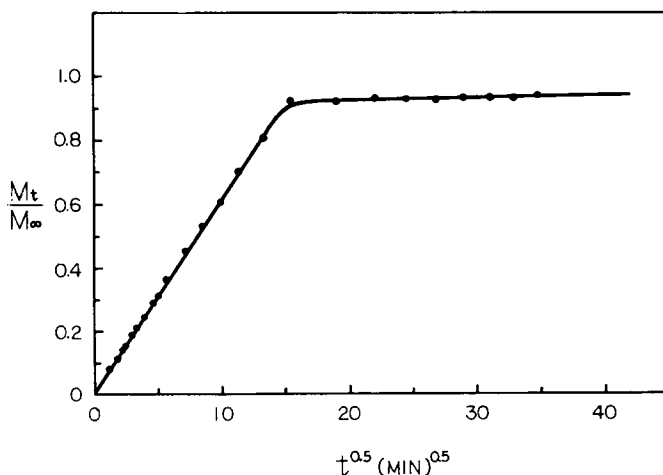


Fig. 2. Kinetics of removal of  $\text{CaCO}_3$  from films exposed to aqueous  $\text{SO}_2$  at pH 2.0.  $M_\infty = 27\%$ ,  $t_\infty = 14$  days.

$M_t/M_\infty$  is given by<sup>19</sup>

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left( \frac{Dt}{\pi} \right)^{0.5} \quad (5)$$

where  $D$  is the (concentration-independent) diffusion coefficient and  $l$  is the film thickness.  $D$  has been calculated from the slope of the initial linear region of Figure 2 as  $1.84 \times 10^{-9} \text{ cm}^2/\text{s}$ .

The ATR spectra of the polymer binder and the two latex samples are shown in Figure 3. 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  $400$  and  $1600 \text{ cm}^{-1}$  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  $\text{CaCO}_3$  extender can be observed, as seen by comparing spectra A and B in Figure 3. The two peaks at  $1416$  and  $875 \text{ cm}^{-1}$  are not found in the spectrum of the LO sample, and are identified as the stretching and wagging vibrations of the  $\text{CO}_3^{2-}$  group of  $\text{CaCO}_3$ , respectively.<sup>20,21</sup> The broad band between  $850$  and  $450 \text{ cm}^{-1}$  is absent in the spectrum of the polymer base and therefore has been attributed to the pigment ( $\text{TiO}_2$ ) or the china clay (aluminum silicate) added to the paints. The vibrational frequencies of these additives are located in this region.<sup>21,22</sup> The band at  $1728 \text{ cm}^{-1}$ , due to the  $\text{C}=\text{O}$  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 4, ATR spectra of the LC samples exposed to sulfurous acid for 1, 6, and 30 min are shown. The intensities of the bands at  $1416$  and  $875 \text{ cm}^{-1}$  decrease markedly with increasing exposure time, and are essentially gone after 30 min of exposure, indicating loss of  $\text{CaCO}_3$ . The broad absorbance

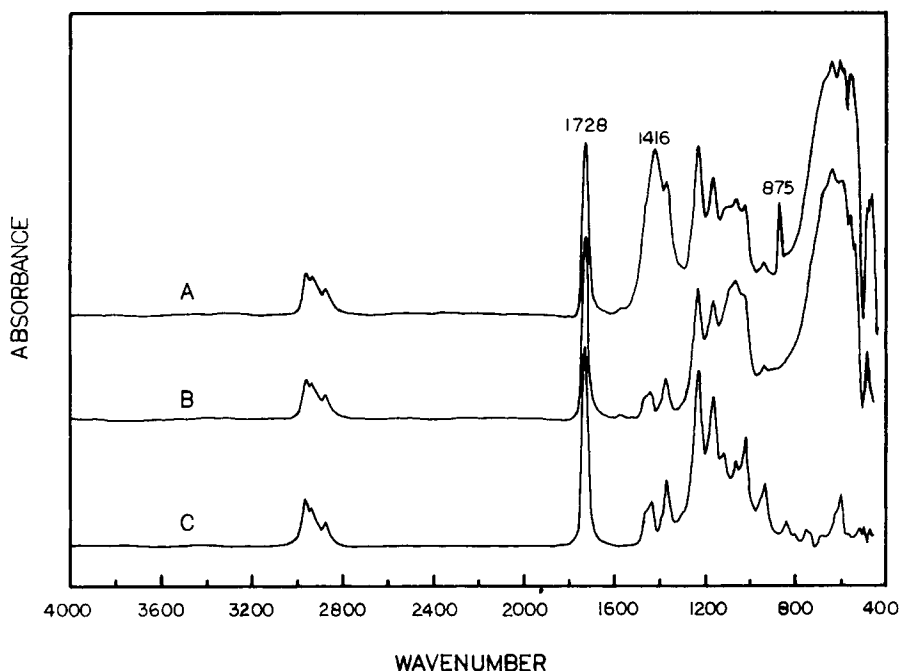


Fig. 3. FTIR-ATR spectra of (a) latex with  $\text{CaCO}_3$ , (b) latex without  $\text{CaCO}_3$ , and (c) base polymer latex.

centered around  $700\text{ cm}^{-1}$  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.

Difference spectra between the unexposed LC and LO samples revealed the two  $\text{CaCO}_3$  peaks at  $875$  and  $1416\text{ cm}^{-1}$ . The integrated intensities of these two peaks were followed as a function of exposure time to aqueous  $\text{SO}_2$ . An integrated intensity ratio  $I_t/I_\infty$  can be defined, which should be proportional to  $M_t/M_\infty$ :

$$\frac{I_t}{I_\infty} = \frac{A_{\text{LC}}(0) - A_{\text{LC}}(t)}{A_{\text{LC}}(0) - A_{\text{LO}}(0)} \quad (6)$$

Here the  $A(0)$  and  $A(t)$  terms refer to the integrated absorbances of unexposed samples and samples exposed for time  $t$ , respectively. The subscripts define the sample type. Figures 5(a) and (b) show the plots of  $I_t/I_\infty$  against  $t^{0.5}$  for the two  $\text{CaCO}_3$  peaks. The penetration depth in an ATR experiment is only a few  $\mu\text{m}$ ; therefore the  $\text{CaCO}_3$  will be removed from this thin surface layer in a much shorter time than is required to remove all of the  $\text{CaCO}_3$  from the bulk film (thickness =  $127\text{ }\mu\text{m}$ ). The penetration depths calculated using eq. (4) are  $2.3$  and  $1.4\text{ }\mu\text{m}$  for the  $875$  and  $1416\text{ cm}^{-1}$  peaks, respectively. The very rapid loss of  $\text{CaCO}_3$  from the surface layer is evident in Figures 5(a) and (b).

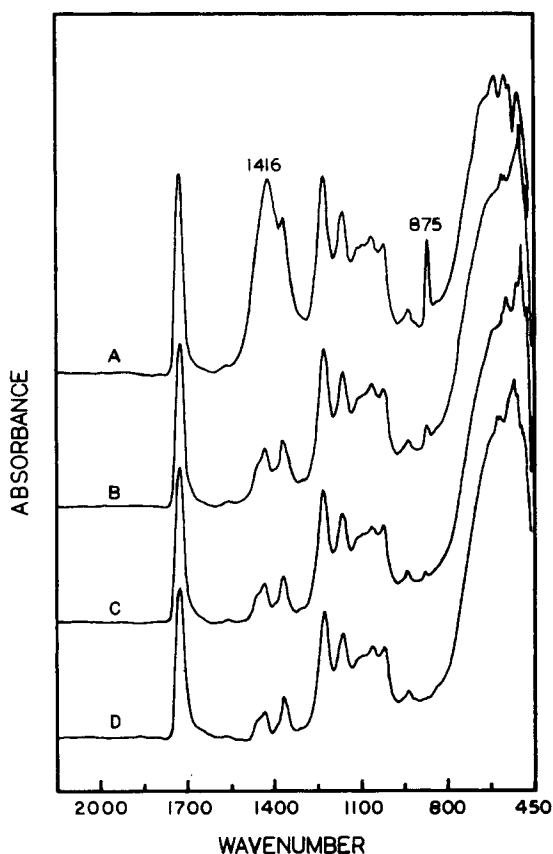


Fig. 4. FTIR-ATR spectra of latex paint containing  $\text{CaCO}_3$  exposed to aqueous  $\text{SO}_2$  (pH 2.0) for: (a) 0 min; (b) 1 min; (c) 6 min; (d) 30 min.

Determination of the diffusion coefficient from the FTIR data is possible, but cannot be carried out in a straightforward manner using an equation similar to (5). Part of the problem is the inability to reproducibly control exposure times below 1 min, thus the (linear) short-time regions of the curves in Figure 5 cannot be obtained. The nonzero intercept of the extrapolated curves in Figure 5 suggests that the linear region has been surpassed. Secondly, there is considerable uncertainty in the assignment of the effective film thickness  $l$ , given that the amplitude of the evanescent wave in an ATR experiment decays exponentially with depth into the sample, and that the concentration profiles of the diffusant remaining in the surface layer are nonlinear.

A detailed analysis has shown that the major contribution to the  $\text{CaCO}_3$  peaks comes from a layer centered around the penetration depth, as calculated from eq. (4), but substantial contribution to the intensity also comes from layers much deeper than this. Details of the determination of the diffusion coefficient from the FTIR data have been presented in a separate paper.<sup>23</sup> The results of this analysis are  $D = 1.77 \times 10^{-9} \text{ cm}^2/\text{s}$  for the  $1416 \text{ cm}^{-1}$  peak, and  $D = 2.25 \times 10^{-9} \text{ cm}^2/\text{s}$  for the  $875 \text{ cm}^{-1}$  peak. Both are in good agreement with the value obtained for  $D$  from the bulk weight loss data.

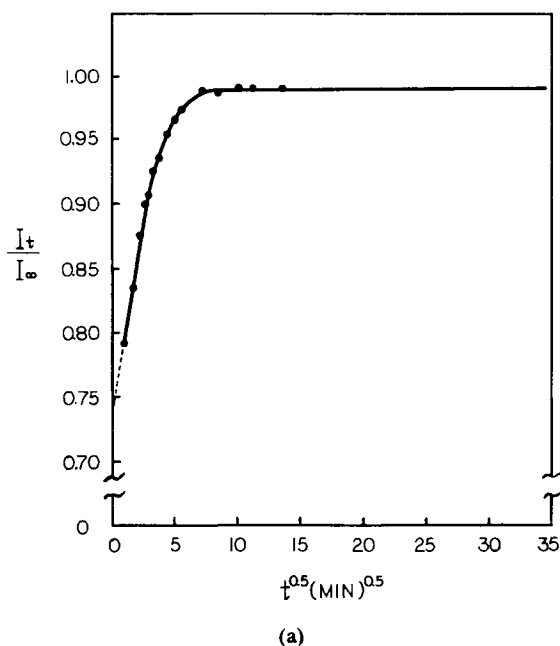


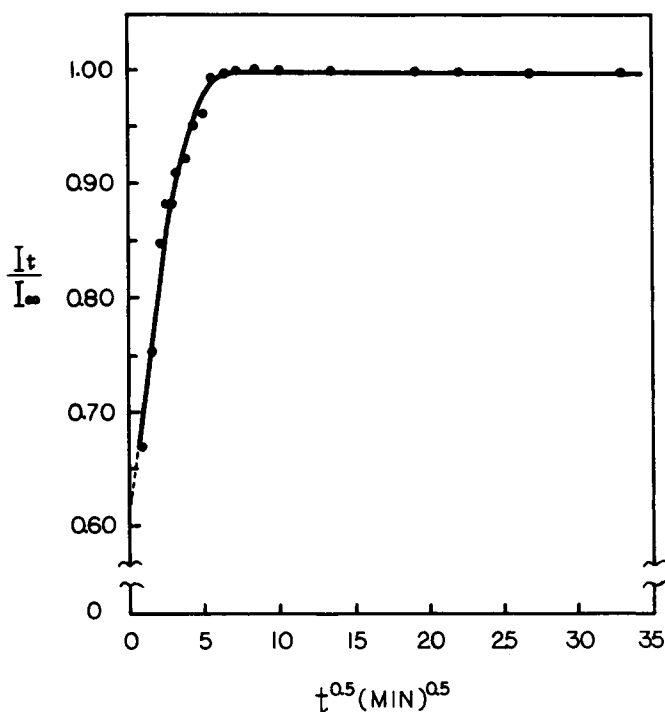
Fig. 5. Kinetics of removal of  $\text{CaCO}_3$  from films exposed to aqueous  $\text{SO}_2$  at pH 2.0, as measured by the integrated intensity ratio from FTIR-ATR spectra: (a) data from  $\text{CaCO}_3$  band at  $1416\text{ cm}^{-1}$ ; (b) data from  $\text{CaCO}_3$  band at  $875\text{ cm}^{-1}$ .

## DISCUSSION

The bulk weight loss data and FTIR spectra clearly suggest that the  $\text{CaCO}_3$  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  $\text{H}_2\text{CO}_3$ , results 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  $\text{CaCO}_3$  is leached out in about 4 h. The approximate composition (in wt %) of the dry LC latex samples is 37% polymer base, 21%  $\text{CaCO}_3$ , 35%  $\text{TiO}_2$ , and 7% china clay. The maximum weight loss is 27%, which is nearly equal to the sum of the weights of  $\text{CaCO}_3$  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  $850\text{ cm}^{-1}$  could be attributed to loss of  $\text{TiO}_2$  rather than china clay, the extremely low solubility of  $\text{TiO}_2$  in acids, relative to china clay, makes this rather unlikely.

The removal of  $\text{CaCO}_3$  from paints by acids has also been reported by other researchers. In a controlled field study on effects of acid deposition on paints, Edney et al.<sup>13</sup> collected and analyzed the rain runoff from panels coated with an acrylic latex paint containing  $\text{CaCO}_3$ . Control samples were covered during rain events and sprayed with an equivalent amount of deionized water. Calcium was detected in the runoff from all samples, the calcium flux being higher when the rain was more acidic. Removal of calcium from the control samples was accelerated when acid-producing pollutants (e.g.,  $\text{SO}_2$ ) deposited on the surface (dry deposition) and subsequently reacted with the deionized spray to produce sulfurous acid. Campbell et al.<sup>9</sup> reported that acidic deposi-



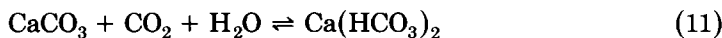
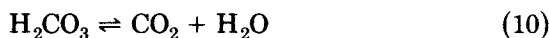
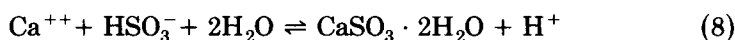


(b)

Fig. 5. (Continued from the previous page.)

tion resulting from the reaction of  $\text{SO}_2$  with water increased erosion rates of latex paints by removing acid-soluble extender components such as  $\text{CaCO}_3$ .

$\text{CaCO}_3$  is commonly used to remove  $\text{SO}_2$  from industrial waste gases. Slack<sup>24</sup> has listed the relevant chemical reactions that take place during this process. The leaching of  $\text{CaCO}_3$  from latex paints by aqueous  $\text{SO}_2$  may well be controlled by the same reactions. These might include<sup>24</sup>



No detectable evidence for sulfite or bisulfite ion was found in the FTIR spectra of exposed films. This suggests that if reactions (8) or (12) occur, they must occur in the bulk solution, not in the paint film, or else the sulfite-containing products diffuse out of the film before it is removed and analyzed. If

reactions (10)–(12) occur, dissolved  $\text{CO}_2$  could play a role in the  $\text{CaCO}_3$  removal process. However, in our work, the amount of  $\text{CO}_2$  in solution is small compared to the amount of dissolved  $\text{SO}_2$  at pH 2. Reactions (11) and (12) are therefore unlikely to produce very much calcium sulfite. We believe that the removal of  $\text{CaCO}_3$  from the sample is controlled primarily by the amount of bisulfite ion present [reaction (8)], which is in turn controlled by the concentration of  $\text{SO}_2$  [reactions (1)–(3)]. In our experiments, the molar ratio of  $\text{SO}_2$  to  $\text{CaCO}_3$  (assuming all of the  $\text{CaCO}_3$  is leached out) was always greater than 10:1. Since the dissociation of  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and  $\text{HSO}_3^-$  is very rapid, equilibrium is established instantaneously,<sup>25</sup> and bisulfite ion will be available as long as an excess of  $\text{SO}_2$  exists.

The mechanism of removal of  $\text{CaCO}_3$  from the latex film must involve three steps: (1) diffusion of the components of the  $\text{SO}_2$  aqueous solution into the film, (2) reaction and/or dissolution of  $\text{CaCO}_3$ , and (3) diffusion of  $\text{CaCO}_3$  (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  $\text{CaCO}_3$  (or its ions) out of a water-swollen film could occur much faster than the initial diffusion of water,  $\text{SO}_2$ , and ions into a dry, unswollen film. Final resolution of this issue must await additional work. In this regard, independent measurement of the diffusion coefficient of water (as a vapor) into these latex films, as well as additional immersion experiments at different pH values should be of help. These experiments are currently in progress in this laboratory.

## CONCLUSIONS

Simple immersion experiments of latex paint films in aqueous  $\text{SO}_2$  solution at pH 2.0 have resulted in loss of acid-soluble components such as calcium carbonate and china clay. The FTIR spectra indicate that the polymer base remains chemically stable after 14 days of exposure. The removal of these components is well described by Fickian diffusion process. The effective diffusion coefficient for the removal of material from the paint has been measured both by weight loss and FTIR-ATR methods, with good agreement between the two. Although the FTIR-ATR spectra come from only a thin surface layer, the data so obtained seem to be representative of the bulk sample in this case.

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