Studies of Latex Paint Films Exposed to Aqueous SO₂: pH Effects

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Synopsis

Latex paint films containing the acid-soluble extender calcium carbonate have been exposed to aqueous SO_2 and other acidic solutions to evaluate the effects of acidic deposition at different pH values on the coatings. $CaCO_3$ is completely removed from these films upon immersion in acidic solutions. The leaching process was monitored with weight loss and infrared measurements. The removal rate was found to be strongly dependent on pH, decreasing with increasing pH. Removal of $CaCO_3$ occurs even for distilled water which has been allowed to equilibrate with atmospheric CO_2 (pH 5.6). The removal rate seems to depend only on $[H^+]$; the identity of the acidic anion is apparently insignificant. An empirical relation between the rate of removal and pH was formulated from the weight loss data. The analyses of the results from both weight loss and infrared methods suggested that the mechanism of removal at pH 2.0 is diffusion controlled, whereas a chemical reaction involving H^+ becomes more important at higher pH values.

INTRODUCTION

Latex paints contain pigments, extenders, and many other additives. The chemical nature of each component and its relative concentration in the paint determine the overall properties of the coating, including its weathering resistance. Earlier studies have shown that accelerated deterioration of paints can be caused by removal of acid-soluble components such as $CaCO_3$ by acidic species in the environment.[1-4] In a recent paper,[5] we found that the $CaCO_3$ extender in latex paint films was totally removed in a few hours upon immersion in an aqueous solution of SO_2 at pH 2.0. Ongoing studies using real-time FTIR–ATR measurement of the leaching process[6] also revealed that as the $CaCO_3$ particles were removed from the film, the molecules of the polymer tend to rearrange to fill up the voids, resulting in thinning of the paint film. In addition, preliminary dynamic mechanical analysis showed that the removal of $CaCO_3$ lowered the elastic modulus of the film above its glass transition temperature ($T_g = 15°C$), meaning that at normal service temperatures the mechanical strength of the paint film would be reduced.

An overall objective of this work is to investigate effects of acid rain on coatings. Typical pH values for acid rain fall between 3.3 and 5.5. The present study was initiated to investigate the rate of $CaCO_3$ removal over this pH range, and to extend the measurements to other acidic solutions. Both weight loss and FTIR–ATR measurements were used to monitor the removal of $CaCO_3$ from the film with exposure time. An empirical equation has been developed to describe the weight loss of the films as a function of immersion time and pH. The mechanism of $CaCO_3$ removal is also discussed.

EXPERIMENTAL

Samples. The $CaCO_3$-containing latex paint for this study was supplied by UCAR Coatings and Emulsions (Cary, NC). The detailed composition of this paint has been described in the previous paper.[5] The approximate composition of the dried paint films is 35% (w/w) TiO_2, 21% $CaCO_3$, 37% polymer, and 7% china clay. The polymer binder was reported to be a copolymer containing a $1:1:1$ mole ratio of vinyl chloride, vinyl acetate, and butyl acrylate, with small amounts (less than 7 mol % total) of methyl acrylate, methyl methacrylate, and acrylic acid.

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 $CaSO_4$ for a minimum of 3 days. Film thickness was measured using a sensitive micrometer (MSC Industrial Supply Co.) having a precision of ± 1.2 μm. The thickness of the films used in this study was determined to be 127 μm for the pH 2 samples and 117 μm for all other samples.

Exposure Experiments. Dried, free paint films were exposed by immersion in aqueous sulfurous acid, prepared by bubbling SO_2 through deionized distilled water. Sulfurous acid at pH 2 was found to contain 0.2 g of SO_2 per 100 mL water, as determined by weighing. Several paint films could remain immersed in this solution for more than a month without a significant change in the pH. However, at higher pH values (3.0 and 4.0), the pH was found to change during exposure since a large excess of acidic ions was no longer present to react with the $CaCO_3$. For these cases, a simple flow exposure device was used, as sketched in Figure 1. The pH value of the sulfurous acid in the reservoir was kept slightly below the desired pH level. The pH in the exposure chamber was kept constant by controlling the flow rate. pH was monitored with a digital pH meter throughout the exposure period. It was possible to maintain the pH to within ± 0.15 pH units with this system. The temperature was maintained at 25°C with a constant temperature bath. In addition to sulfurous acid exposures at pH 3.0 and 4.0, an exposure was also carried out with deionized distilled water, which was allowed to equilibrate with atmospheric CO_2 to a pH of 5.6.
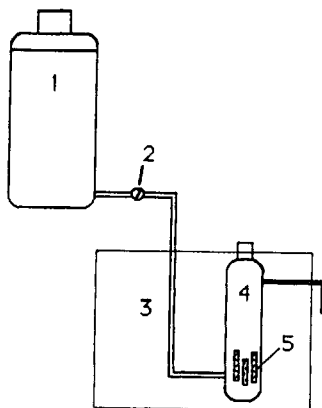

Fig. 1. Illustration of the flow exposure device: (1) reservoir; (2) stopcock; (3) constant temperature bath; (4) immersion chamber; (5) paint films.

After exposure for a desired time, the samples were removed and rinsed with deionized distilled water to wash away residual acid. A different sample was used for each exposure time. Exposed films were dried in a 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 was better than $\pm 0.5\%$.

FTIR Measurements. An Analect FX-6260 Fourier-transform infrared (FTIR) spectrometer, equipped with an MCT detector and a flat-plate attenuated total reflectance (ATR) sampling accessory, was used to obtain the infrared spectra. A ZnSe parallelogram crystal with an angle of incidence of 45°C was used. A torque wrench was used to provide uniform clamping force from sample to sample, and to achieve good contact between the sample and the ATR crystal.

The infrared spectra of the paints is quite complex due to their multicomponent nature and the presence of infrared-absorbing inorganics. However, positive identification of several peaks has been made by comparing paint samples having different compositions.[5] Of interest to this study are the CaCO$_3$ peaks located at 1416 and 875 cm^{-1}, which have been identified as the stretching and wagging vibrations of the CO$_3^=$ group, respectively. The relative amount of CaCO$_3$ removed from the samples can be made through quantitative measurement of the intensities of these peaks as a function of exposure time. Peaks associated with the pigment (TiO$_2$) and china clay (aluminum silicate) are located between 850 and 450 cm^{-1} as a broad band. The peak at 1728 cm^{-1} has been attributed to the C $=$ O stretching mode of the polymer. This peak is well separated from others and was used as a reference for spectral subtraction. All ATR spectra were collected at 4 cm^{-1} resolution, and 128 scans were accumulated for each sample. Spectral subtractions and integration of band intensities were performed by computer.

RESULTS

Free films of latex paint containing CaCO$_3$ were exposed to aqueous SO$_2$ at pH 3.0 and 4.0 and to deionized distilled water (pH 5.6, due to the presence of H$_2$CO$_3$) for periods ranging from 1 min to 28 days. In the previous work,[5] we reported that all the CaCO$_3$ was leached out of the film after a 4 h exposure to aqueous SO$_2$ at pH 2.0. At higher pH, the CaCO$_3$ was also completely removed, but the rate of removal was slower. This is evident in both the FTIR–ATR and weight loss data, as shown in Figures 2–4. The FTIR–ATR spectra in Figure 2 represent 1 h exposures at different pH values. The loss of CaCO$_3$ is evident from the disappearance of the CaCO$_3$ bands at 1416 and 875 cm^{-1}. The intensities of these peaks decrease with decreasing pH. The weight loss data are plotted as M_t/M_∞ vs. $t^{0.5}$, as shown in Figure 3. M_t is the mass removed at time t, and M_∞ is the total mass removed from the film at equilibrium. The data for pH 2.0 are taken from the previous report for comparison. In all cases, the total mass loss ($M_t/M_\infty = 1.0$) amounted to 27% of the initial sample weight. This value was reached at approximately 4 h, 3 days, and 20 days of exposure at pH 2.0, 3.0, and 4.0, respectively. CaCO$_3$ and china clay comprise approximately 28% of the weight of the paint films, which suggests that most of these materials are being removed by the acid. This is
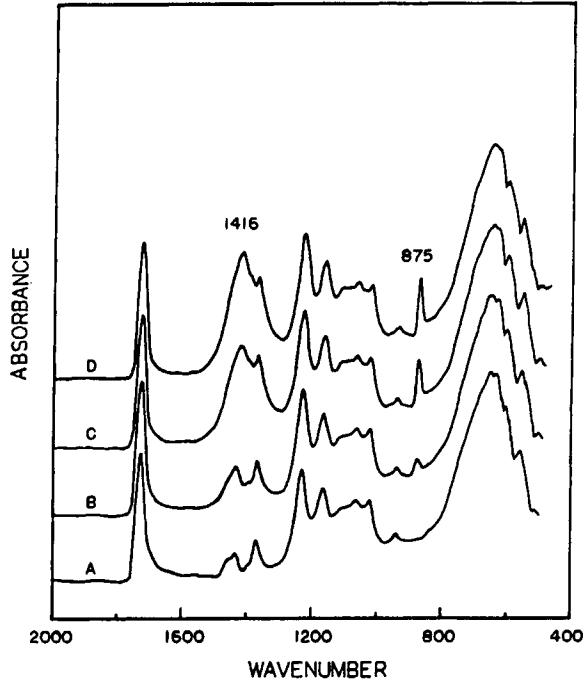
Fig. 2.   FTIR–ATR spectra of paint films exposed to H_2SO_3 at different pH values for 1 h: (a) pH 2.0; (b) pH 3.0; (c) pH 4.0; (d) pH 5.6 (water).
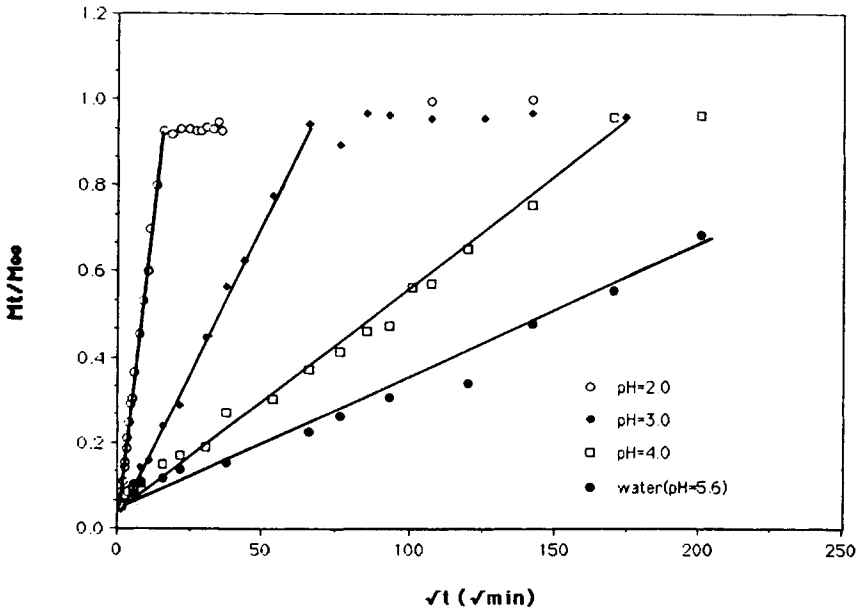

Fig. 3.   Data points: weight loss of latex paint films exposed to H_2SO_3 at different pH values: (—) fits to $M_t/M_\infty = Rt^5$. pH: (○) 2.0; (◆) 3.0; (□) 4.0; (●) water (pH 5.6).
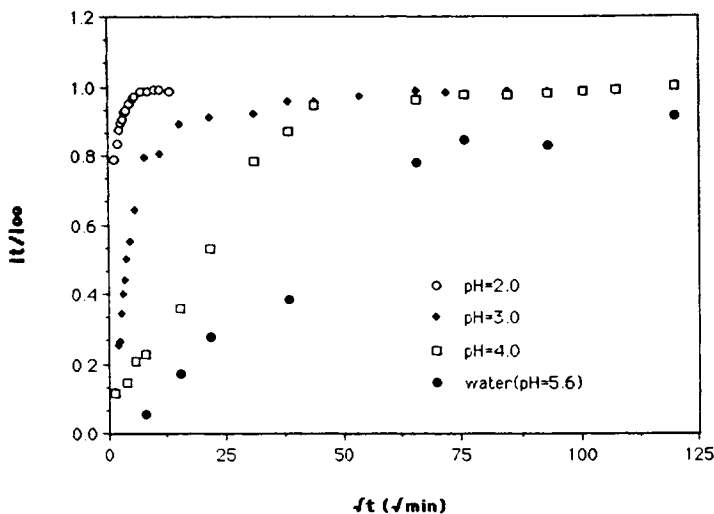
Fig. 4. Relative intensity of the CaCO$_3$ peak at 1416 cm^{-1} vs. time for films exposed at different pH values: (○) 2.0; (◆) 3.0; (□) 4.0; (●) water (pH 5.6).

also supported by the infrared data. It is clear that the lower concentration of acidic ions at higher pH results in a slower leaching rate. This suggests that a chemical reaction involving H$^+$ ions controls the kinetics of the leaching process at higher pH. In contrast, the data for the pH 2.0 exposure show good initial linearity with t,[5] suggesting diffusion-controlled kinetics. This change in mechanism is further reinforced by comparison of the weight loss data with the FTIR data.

Figure 4 shows the plots of the integrated intensity ratio I_t/I_∞ for the 1416 cm^{-1} CACO$_3$ peak as a function of exposure time at each pH. I_t/I_∞ should be proportional to M_t/M_∞, and is defined as

$$\frac{I_t}{I_\infty} = \frac{A(0) - A(t)}{A(0) - A(\infty)} \tag{1}$$

where $A(t)$ refers to the integrated absorbance of the 1416 cm^{-1} peak at exposure time t. $t = 0$ represents an unexposed sample, and $t = \infty$ represents a sample with no CaCO$_3$. The 1416 cm^{-1} peak was used for these calculations instead of the 875 cm^{-1} peak because the integrated absorbance is higher, and the data are less noisy. The diffusion coefficient calculated from this peak was also found to agree more closely with the value obtained from the bulk weight loss data at pH 2.0.[5]

Although the FTIR–ATR data is qualitatively similar to the weight loss data shown in Figure 3, it should be recognized that the depth which can be probed in an ATR experiment is only a few micrometers. The calculated penetration depths d_p are 2.3 and 1.4 μm for the 875 and 1416 cm^{-1} peaks, respectively.[7] The degree to which the data from this thin surface layer is representative of the bulk sample must be tested. A numerical method has been developed to obtain a diffusion coefficient from FTIR–ATR data such as in Figure 4.[8] It is based on the assumption that the concentration profiles of

TABLE I
D Values[a] Obtained from Weight Loss and FTIR–ATR Data

H_2SO_3 solution $\Rightarrow$	pH 2.0	pH 3.0	pH 4.0	pH 5.6
D from weight loss	184	8.61	1.12	0.381
D from FTIR–ATR				
(1416 cm^{-1} peak)	183	1.32	0.125	0.0225
D (wt loss)/D (FTIR–ATR)	1.0	6.5	9.0	17

[a]Units: cm^2/s $\times 10^{11}$.

CaCO$_3$ remaining in the film are Fickian. Very good agreement has been obtained between this method and the weight loss results for the effective diffusion coefficient (D) for CaCO$_3$ removal by aqueous SO$_2$ at pH 2.0. However, the diffusivities obtained from the two methods do not compare well at higher pH. The disagreement becomes more significant as pH increases. Table I shows the results of these calculations. The D values from weight loss measurements have been calculated from the initial slopes of each curve in Figure 3, using the following equation for diffusion out of a thin film, applicable at short times:

$$\frac{M_t}{M_\infty} = \frac{4}{l} \left(\frac{Dt}{\pi} \right)^{0.5} \qquad (2)$$

where l is the film thickness. The good agreement obtained between these two independent methods for measuring D at pH 2.0 strongly supports the assumption of a diffusion-controlled mechanism for CaCO$_3$ removal at this pH. The FTIR–ATR data from the surface can be considered representative of the bulk sample at pH 2.0. The failure of the assumption of diffusion control at higher pH, as evidenced by the divergence of D values in Table I, is suggestive of a change in the mechanism of CaCO$_3$ removal.

One of the exposure runs was carried out in deionized distilled water (pH 5.6), where the only acidic species present is carbonic acid, formed by the dissolution of atmospheric CO$_2$ into the water. The acidic ion concentration is quite low ($[H^+] \approx 2.5 \times 10^{-6} M$) at pH 5.6. However, a 28-day exposure of a paint film to this solution results in loss of 70% of the CaCO$_3$ from the sample. Longer exposure times (estimated at 40 days) should result in removal of all of the CaCO$_3$. This indicates that leaching of CaCO$_3$ from the paint can be caused by acidic species other than H$_2$SO$_3$.

For the purpose of making practical estimates of the amount of CaCO$_3$ removed from the paint at various (acid rain) pH values, an overall weight loss rate R was obtained from a fit of each curve in Figure 3 to $M_t/M_\infty = Rt.^5$ R is plotted against pH in Figure 5. The solid curve in Figure 5 is described by the following relationship, which can be used to estimate R over the pH range 2.0–5.6:

$$\log R = -0.1928 - 1.174x + 0.1065x^2 \qquad (3)$$

where x is the pH value. The time required for complete removal of CaCO$_3$
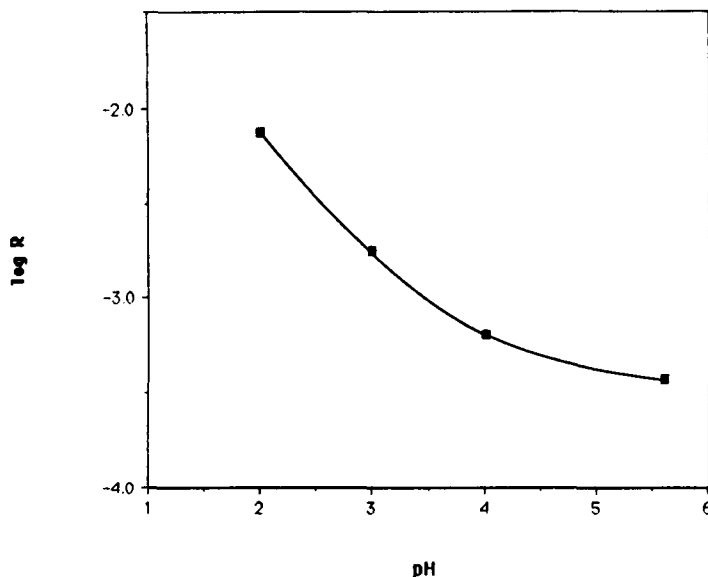
Fig. 5.   Data points: overall removal rate (R) of $CaCO_3$ from paint films from weight loss data in Figure 3: (—) eq. (3).

(t_∞) can be estimated from the fact that $M_t/M_\infty = 1.0$ at t_∞. This simple model assumes that the weight loss rate remains constant up to t_∞, and then immediately becomes zero. Although this is clearly an approximation, the resulting error in t_∞ should be fairly insignificant for practical estimates of weight loss. Since diffusion processes are not rate-controlling at typical acid rain values (3–5.6), the removal rate should be independent of film thickness. Scaling of R for different thicknesses should not be necessary over this pH range.

TABLE II
Weight Loss of Latex Films After 3-day Exposure to Various Acids

Solution	Initial pH	Final pH	Weight loss (%)
H_2SO_3[a]	3.0	3.3	23.5[b]
H_2SO_3 + 1 mL Na_2SO_3[c]	3.0	3.3	23.0
H_2SO_3 + 3 mL Na_2SO_3	3.1	3.4	22.2
H_2SO_3 + 6 mL Na_2SO_3	3.1	3.5	22.7
H_2SO_3 + 3 mL Na_2SO_3	3.0	3.3	25.5
HCl	3.0	3.5	22.5[a]
HNO_3	3.0	3.5	20.6[a]
H_2SO_4	3.0	3.5	24.1[a]
50% H_2SO_3 + 50% HNO_3	3.0	3.5	21.4[a]
50% H_2SO_3 + 25% H_2SO_4 + 25% HNO_3	3.0	3.5	22.2[a]
Water + 3 mL Na_2SO_3	9.0	8.3	4.4
Water	5.6	8.1	5.0

[a] $[H_2SO_3] = .0032M$, 200 mL solution used for 40 mg sample.
[b] Average of at least two measurements.
[c] $[Na_2SO_3] = 0.1M$.

Several exposure experiments were performed at pH 3.0 for a fixed period of time (3 days) using a series of several different acidic solutions and mixtures. The amount of solution used was adjusted so as to maintain a large excess of acidic ions relative to the amount of $CaCO_3$ contained in the paint samples (about 6 : 1 mole ratio), except for two solutions which had an initial pH other than 3.0. Weight loss results are listed in Table II. The final weight loss is nearly the same for each solution at pH 3.0, regardless of the identity of the acidic anion present. Mixtures of anions from different acids also showed no significant effect on the amount of $CaCO_3$ removed. The weight loss was much smaller, however, for the solution at pH 9.0 containing $SO_3^=$ but very little H^+, and for deionized distilled water at pH 5.6. The weight loss appears to be dependent only on the concentration of H^+.

DISCUSSION

These results clearly indicate that the presence of SO_2 in the water accelerates the rate at which $CaCO_3$ and clay are leached out of the paint film. In addition, the concentration of SO_2, which determines the equilibrium concentration of H^+ ions, greatly affects the rate of removal. The removal process is believed to involve at least three kinetic steps[5]: (1) diffusion of water and ions into the film, (2) reaction and/or dissolution of $CaCO_3$ inside the film, and (3) diffusion of $CaCO_3$ or its reaction products out of the water-swollen film. For exposures carried out at pH 2.0, the initial linearity of the weight loss data with t suggests that the rate-limiting step is controlled by Fickian diffusion. The rate of chemical reaction must be much faster at pH 2.0. This is further supported by the FTIR–ATR data, which is also consistent with the assumption of a diffusion controlled process at pH 2.0.[8] Independent measurements of diffusion of water into these paint films indicate that step (1) occurs very quickly, and is not rate-controlling.

For the exposures carried out at higher pH values, the agreement between the two methods for calculating D becomes discordant as shown in Table I. Apparently, at pH 3.0 and above, the kinetics are no longer controlled by a diffusion process. In spite of this, the data in Figure 3 are still approximately linear with $t^{.5}$ although there is more scatter than in the pH 2.0 case. The diffusing medium for $CaCO_3$ removal, being essentially a water-swollen paint film, does not change significantly with pH. Therefore, it is expected that the time required for the reaction/dissolution products of $CaCO_3$ to diffuse out of the film, *once they are formed*, should be relatively independent of pH. The fact that this is *not* the case further reinforces a change in mechanism at pH 3.0.

Two models for describing the data at pH 3.0 and above were tried, both based on a chemical reaction involving $CaCO_3$ and H^+. Since pH was held constant during the leaching process, $[H^+]$ was assumed to be constant in each model. In one model, the rate for $CaCO_3$ removal was assumed to depend on the surface area A of the $CaCO_3$ particles:
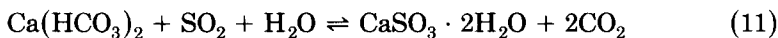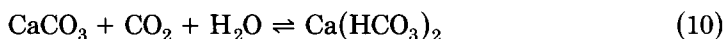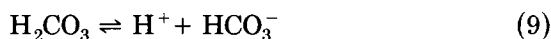
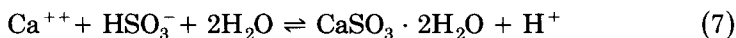$$-\frac{dm}{dt} = k_1'A[H^+] = k_1 A \qquad (4)$$

where m is the mass of $CaCO_3$ remaining in the paint film and k_1 is the rate constant, which is dependent on pH. A was expressed as a function of m, which led to a linear relation between $(1 - y)^{1/3}$ and t, where $y = M_t/M_\infty$. The other model involved standard first-order kinetics, and the removal rate was expressed as

$$-\frac{dm}{dt} = k_2'm[\mathrm{H^+}] = k_2m \qquad (5)$$

where again the rate constant k_2 is pH dependent. This model led to a linear relation between $\ln[1/(1 - y)]$ and t.

In general, both models fit the pH 3.0, 4.0, and 5.6 weight-loss data equally well at longer times, but slight deviations were noted at shorter times (up to about 1 h). These deviations can be explained as a result of the additional contribution from diffusion at short times. However, neither model was considered completely satisfactory, because the rate constants k_1 and k_2 failed to scale quantitatively with pH. This may be a result of the local concentration of H^+ ions in the paint film being different than the H^+ concentration in the surrounding solution. Thus, while a simple reaction rate model does not completely account for the data above pH 2.0, the trends with pH indicate that a chemical reaction involving H^+ is an important contributor to the leaching process at these pH values.

Possible reactions of $CaCO_3$ with SO_2 and CO_2 in aqueous solution have been listed by Slack as[9]

$$\mathrm{H^+} + CaCO_3 \rightleftharpoons Ca^{++} + HCO_3^- \qquad (6)$$

$$Ca^{++} + HSO_3^- + 2H_2O \rightleftharpoons CaSO_3 \cdot 2H_2O + H^+ \qquad (7)$$

$$Ca^{++} + SO_3^= \rightleftharpoons CaSO_3 \qquad (8)$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (9)$$

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2 \qquad (10)$$

$$Ca(HCO_3)_2 + SO_2 + H_2O \rightleftharpoons CaSO_3 \cdot 2H_2O + 2CO_2 \qquad (11)$$

The results of the exposures to different acid solutions shown in Table II lead to the following conclusions regarding the significance of these reactions in the leaching process. (1) Reaction 8, in which $SO_3^=$ ions react with Ca^{++} ions, is not likely to occur, since addition of large amounts of SO_3^- (as Na_2SO_3) to the solution did not change the amount of $CaCO_3$ removed. (2) When H_2CO_3 was the only acid species in the solution (as in the pH 5.6 case), reactions 9 and 10 apparently occur, because some $CaCO_3$ was removed from the film, although the rate was slow. These reactions would become negligible if H_2SO_3 or other stronger acids exist, since the presence of H^+ from dissociation of H_2SO_3 will hinder the ionization of H_2CO_3 in (9). (3) H^+ plays a major role in the $CaCO_3$ removal process, as already discussed. The key reaction in this process should therefore be (6), followed by the reaction of Ca^{++} ion with bisulfite ion (7).

Between pH 3 and 6, bisulfite ion is known to be the most abundant sulfur species in water/SO_2 solutions.[10-12] The reaction product in (7), $CaSO_3$, has about triple the solubility in water as $CaCO_3$,[13] which would make (6) and (7) a more likely route to production of $CaSO_3$ than (10) and (11).

For the purpose of studying the effects of acid deposition of coatings, it is now clear that basic fillers such as $CaCO_3$ added to latex paints used on exterior surfaces are eventually completely removed by normal rain (pH 5.6). This process is accelerated in the presence of any pollutant which can form an acidic species upon reaction with water. This leaching process causes changes in the mechanical properties of the coating, and may eventually have an adverse effect on the lifetime of the coating.

CONCLUSIONS

The rate of loss of acid-soluble fillers such as $CaCO_3$ in a representative latex paint through simple immersion in aqueous SO_2 solution has been found to be pH-dependent. The concentration of H^+ ion in the acidic solution governs the rate of reaction with $CaCO_3$, regardless of the identity of the acidic anion. At pH 2.0, the removal process appears to be diffusion-controlled. Between pH 3 and 5.6, the rate at which $CaCO_3$ reacts with H^+ becomes more important. Simple chemical reaction rate models have not been completely successful in describing the leaching kinetics quantitatively above pH 2.0. An empirical relationship has been developed to describe the weight loss as a function of time and pH.

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