

The Interaction of Hydrogen Sulfide with Lead- and Barium-Cadmium-Zinc-Stabilized Poly(vinyl Chloride)

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Synopsis

Poly(vinyl chloride) polymers stabilized with tribasic lead sulfate discolor upon exposure to hydrogen sulfide gas as a result of lead sulfide formation. The discoloration occurs for samples in both cord and sheet forms and is shown to be a function of total H₂S exposure, reaching a limiting value that is determined by the amount of lead stabilizer used in the polymer formulation. The permeation and diffusion constants for H₂S through PVC stabilized with tribasic lead sulfate and with a liquid Ba-Cd-Zn formulation are found to be $P_{Pb} = (6.0 \pm 0.2) \times 10^{-9}$, $P_{BaCdZn} = (5.2 \pm 0.2) \times 10^{-9}$ (both in cm³ gas-cm film/cm² area-sec-cm Hg), $D_{Pb} = (1.3 \pm 0.2) \times 10^{-7}$ cm²/sec, and $D_{BaCdZn} = (6.4 \pm 0.6) \times 10^{-8}$ cm²/sec, all measured at 21°C. The stabilizing efficiencies of the formulations were assessed by HCl evolution measurements, which show that exposure to H₂S decreases the initial polymer stability for both Pb-stabilized and Ba-Ca-Zn-stabilized formulations. Protection of stabilized PVC formulations from diffusing hydrogen sulfide is thus advisable for long-term stability as well as for color integrity.

INTRODUCTION

Lead compounds are used as stabilizers in a variety of poly(vinyl chloride) (PVC) formulations. These formulations typically demonstrate good process stability and end-product performance characteristics. The color stability of these products during field exposure is less satisfactory, however.

In an earlier paper¹ we reported on laboratory exposures of lead-stabilized PVC to an atmosphere of mixed corrosive gases (H₂S, NO₂, and SO₂). The samples showed significant color degradation and were judged inferior to PVC stabilized with unleaded compounds for applications wherein color stability is important.

In this paper we present the results of experiments designed to explore the color degradation of lead-stabilized PVC in more detail. We first demonstrate that the color changes seen in the mixed-gas exposure test occur when the PVC formulation is exposed to a test atmosphere containing H₂S as the only trace contaminant. We then show that the sulfur uptake in the samples is related to their exposure durations and that the color change is proportional to the sulfur uptake. Permeation measurements and color saturation tests demonstrate that the formulations are highly permeable to H₂S. Finally, we report on measurements of the HCl evolution from exposed and unexposed polymers and comment on the implications of H₂S exposure for the long-term stability of PVC. Some parallel studies with a formulation containing a liquid barium-cadmium-zinc stabilizer are also briefly described.

EXPERIMENTAL

Polymer Formulations

The formulations prepared for these experiments utilized PVC resins, plasticizers, and fillers in proportions identical to those currently in service in telephone retractile cord jacketing. One series of samples contained small amounts of TiO_2 white coloring agent. Four replicate sets of these samples were prepared as cord jackets by standard industrial processing techniques. Two of these sets were stabilized with 2 phr tribasic lead sulfate ($3\text{PbO}\cdot\text{PbSO}_4\cdot\text{H}_2\text{O}$); one of these was covercoated with a polyester formulation. The other two sets were stabilized with 2 phr of a liquid mixture containing a combination of barium-cadmium-zinc octoates and alkyl aryl phosphites (Ba, 5.25%; Cd, 2.25%; Zn, 0.4%; P, 3.2%); one of these sets was also covercoated.

A second series of samples was formulated in sheets of varying thicknesses. These samples were unpigmented and were prepared in three sets which differed only in the amounts of tribasic lead sulfate stabilizer used: 0.5, 2.0, and 5.0 phr. (These formulations represent feasible upper and lower limits for lead stabilizer mixing ratios, together with a sample typical of that in common use.) Sheets ~ 3 mm thick were used for sulfur uptake and color change measurements; sheets ~ 0.5 mm thick were used for permeation tests.

In the preparation of all of these samples, the tribasic lead sulfate was added to the formulations as a needle-like powder with particle dimensions of $\sim 0.5 \mu \times 2 \mu$. While uniformly distributed on a macroscopic scale, it was thus expected to be quite nonhomogeneous on the molecular level.

Exposure Techniques

Exposure of the cord jacketing material was conducted in the apparatus shown in Figure 1. The corrosive gas monitor is a Houston-Atlas Model 825, which utilizes the reaction of H_2S with lead acetate-impregnated filter tape for detection.² The sensitivity of this instrument to H_2S is ~ 3 ppb. Temperatures were monitored with an Atkins Model 3H51-FX controller using a Type K (Ni-Cr/Ni-Al) thermocouple. Commercial dial hygrometers were used to measure relative humidity. Data were logged at 20-min intervals throughout the exposures.

The apparatus utilized for exposure of the unpigmented sheet samples is shown schematically in Figure 2. The corrosive gas detector is Thermo Electron Corporation Model 43, preceded by a catalytic $\text{H}_2\text{S} \rightarrow \text{SO}_2$ converter. The resultant SO_2 is detected by pulsed fluorescent techniques.³ The sensitivity of this instrument is ~ 1 ppb; the conversion efficiency of $\text{H}_2\text{S} \rightarrow \text{SO}_2$ is $>99\%$.⁴ Temperatures were monitored with a Type K thermocouple, controlled from a Fluke Model 2100A digital thermometer unit. Relative humidity was measured with a LiCl cell (Hydrodynamics Model 15-7012). Data were monitored every 6 min by a data logging system interfaced to digital magnetic tape.

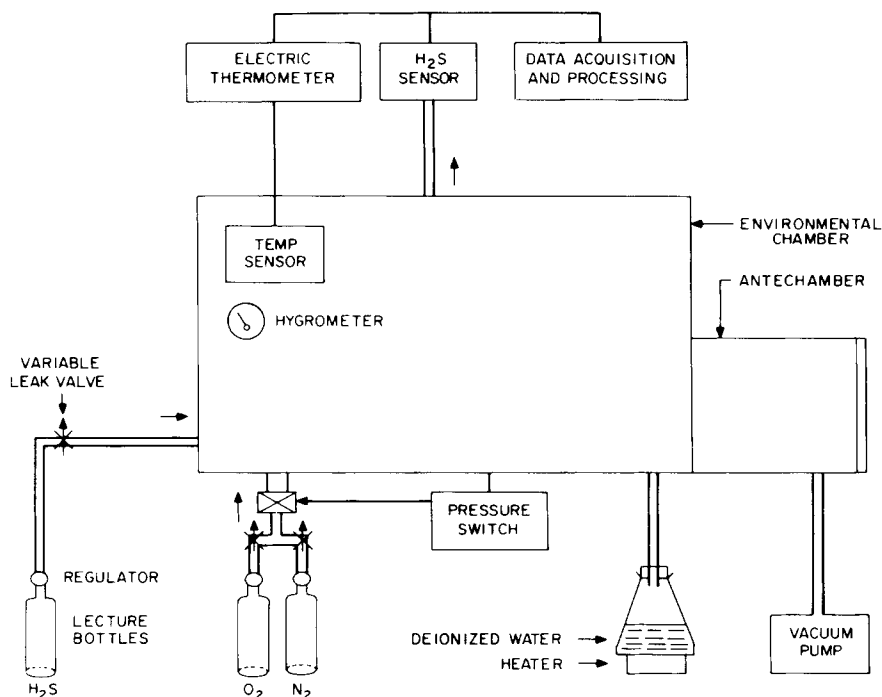


Fig. 1. Schematic diagram of the environmental testing apparatus for the PVC cord jacketing material.

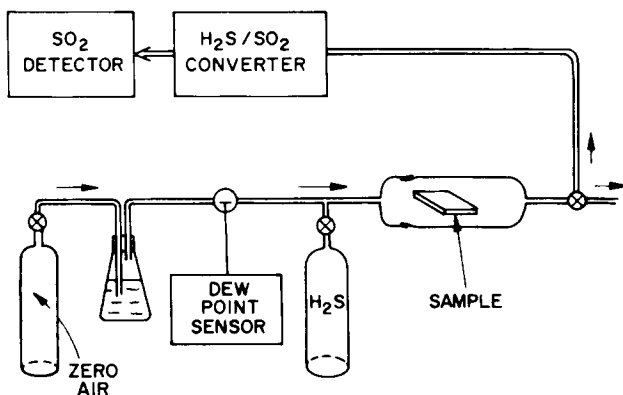


Fig. 2. Schematic diagram of the environmental testing apparatus for the PVC sheet material.

Analytical Techniques

The color changes that resulted from these exposures were quantitatively determined by analysis with a Diano/Hardy visible light spectrophotometer. This instrument is configured specifically for color measurements; results are presented here in the FMC-II^{5,6} color difference parameter ΔE .

The sulfur content of the exposed samples was determined by x-ray photoelectron spectroscopy, using the $K\alpha$ line of elemental sulfur. The relative amount of sulfur in the samples was determined by reference to measurements of unexposed samples formulated with known amounts of tribasic lead sulfate.

As with the color measurement, this is principally a surface analytical technique; the results refer to the outer $80 \pm 13 \mu\text{m}$ of the sample (as determined by measurements of different thicknesses of identical samples).

HCl evolution was determined by automatic titration with 0.01N NaOH during sample heating under argon.⁸ The titrations were performed with a Sargent Recording pH Stat, Model S-30240.

Permeation experiments involving polymeric materials have traditionally utilized measurement of the pressure increase occurring in an evacuated chamber separated from the pure diffusant by the material under test.⁷ The alternative technique devised for these experiments is shown schematically in Figure 3. The test chamber is constructed of Pyrex; valves are either Teflon or 316 stainless steel. The polymer film forms a barrier between the two chambers, which remain at atmospheric pressure during the experiments. The H_2S concentration in each chamber is initially reduced to <1 ppb (by measurement) by injection of zero air. For polymers with permeation rates $<10^{-8} \text{ cm}^3 \text{ gas}\cdot\text{cm film}/\text{cm}^2 \text{ area}\cdot\text{sec}\cdot\text{cm Hg}$, the source (left) chamber is then filled with H_2S and closed, and the H_2S permeating into the continuously flowing zero gas in the receptor (right) chamber is monitored continuously by the pulsed fluorescent detector. Concentrations are converted to fluxes by utilizing measurements of the flow rate of the receptor chamber carrier gas. For polymer films with high permeation rates ($\geq 10^{-8} \text{ cm}^3 \text{ gas}\cdot\text{cm film}/\text{cm}^2 \text{ area}\cdot\text{sec}\cdot\text{cm Hg}$), flowing mixtures of H_2S with carrier gas are utilized to achieve source concentrations in the range of 1–5 ppm H_2S . The concentrations in both chambers are then monitored alternately during the experiment.

Several advantages accrue from the dynamic gas detection technique for permeation measurement. First, since the actual permeating gas is being monitored, the purity of the gas is not a matter for concern. This characteristic not only eliminates a possible source of experimental error but makes it possible to measure the permeation characteristics of a specific component of a mixture of gases with similar permeation behavior. Secondly, the ability to dilute the

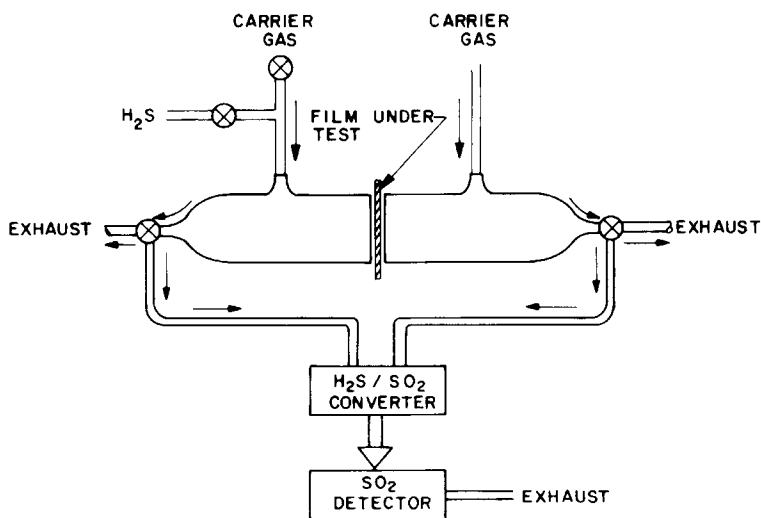


Fig. 3. Schematic diagram of the experimental apparatus used for dynamic gas permeation measurements.

permeating gas with an inert carrier permits the permeation characteristics of a wide variety of substances with large differences in permeation rates to be investigated. Finally, the active removal of permeant-containing air from the exhaust chamber eliminates the interpretive difficulties of a continuously growing concentration of permeant on the receptor side of the test sample. This last advantage can be demonstrated by a brief consideration of the mathematics of diffusion in a plane polymer film. The basic equation is

$$F = P \frac{dC}{dx} \quad (1)$$

where F is the molecular flux, P is the permeation constant, and dC/dx is the concentration gradient across the film. The integral of F over time is the total flux through the film. It can be readily shown that if the exhaust chamber permeant concentration is maintained at zero, a plot of $Q = \int F$ against time has an intercept given by

$$\tau = \frac{x^2}{6D} \quad (2)$$

where D is the diffusion constant. This equation applies rigorously to the experiments described herein, with the standard provision that chemical binding must be unimportant. If the exhaust chamber is not flushed continuously, however, as is done here, the concentration difference across the film is continually varying, and τ cannot be rigorously determined (although in practice the experimental data are often suitable enough to enable D to be measured with sufficient accuracy).

RESULTS

Exposures of lead-stabilized polymers to hydrogen sulfide produced easily visible color changes, even for relatively low exposures at moderate (< 500 ppb) H₂S concentrations. The off-white PVC (A) was readily changed to tan (B),

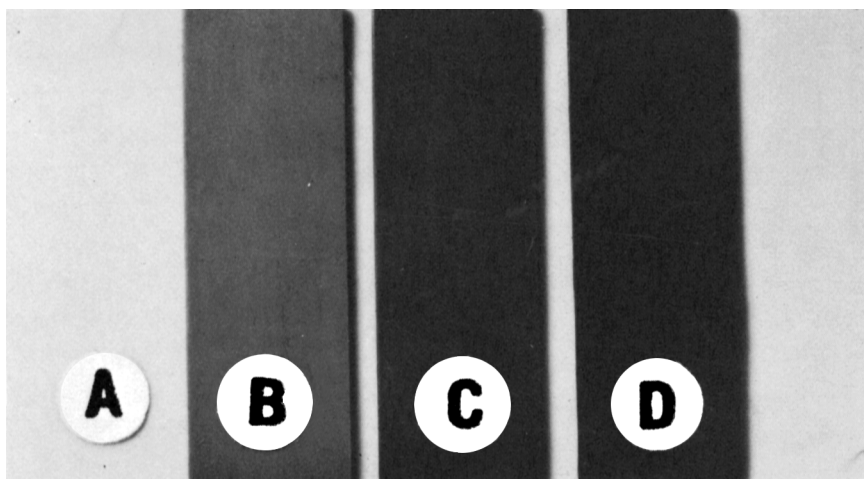


Fig. 4. The visual color spectrum produced by lead-stabilized PVC upon exposure to H₂S: (a) 5.0 phr stabilizer, unexposed; (b) 0.5 phr stabilizer; (c) 2.0 phr stabilizer; (d) 5.0 phr stabilizer. The latter three samples were exposed until no further color change occurred.

brown (C), or black (D) (Fig. 4), the final color depending on the amount of lead stabilizer in the formulation. Through the reflectance properties of the exposed samples the color changes are seen to occur throughout the visible region of the spectrum; an example of such data is shown in Figure 5. The principal compound responsible for the color change is presumably lead sulfide; similar effects have been observed for H_2S exposure of lead-containing paint.⁹

The change in the total color parameter⁶ ΔE as a function of exposure is shown for the sheet samples in Figure 6. It is clear that the amount of lead in the polymer formulation is directly reflected in the rate of color change and in the terminal color that is produced. Color saturation occurs at long exposure times. Similar exposures of cord jacketing and sheet material stabilized with the Ba-Cd-Zn-containing solution produced no detectable discoloration. However, this result does not necessarily rule out the formation of metal sulfides in these experiments. Ba(II) and Zn(II) yield sulfides that are colorless,¹⁰ and it is well known that the formation of yellow-orange CdS can be inhibited (or masked) by the presence of zinc in cadmium-containing formulations.^{11,12}

The relative amounts of gas-phase sulfur taken up by the lead-stabilized PVC can be assessed by x-ray fluorescence studies of the exposed samples. Data for each of the lead-stabilized sheet formulations demonstrate that the color change is proportional to the fluorescence signal from the sulfur $K\alpha$ line, as shown in Figure 7. (The different formulations cannot be compared directly on this figure, since the nearby $M\alpha$ line of lead prevents quantitative background corrections from being made.) It is clear that the amount of sulfur transferred from gas-phase H_2S to localized compounds within the polymer is directly related to the degree of color degradation that results.

In addition to loss of color integrity, the lead-containing PVC is destabilized to some degree, with respect to loss of HCl, as a result of hydrogen sulfide exposure. To assess the magnitude of this effect, HCl evolution tests were performed on H_2S -exposed and unexposed samples of PVC stabilized with either tribasic lead sulfate or the Ba-Cd-Zn formulation. The HCl evolution curves

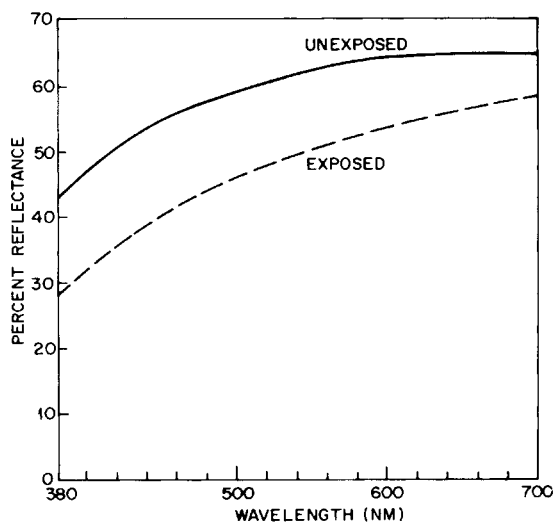


Fig. 5. Reflectance spectra of PVC formulated with 5.0 phr lead stabilizer. The lower spectrum was determined after an H_2S exposure of 27.5 hr at an H_2S concentration of 482 ± 22 ppb.

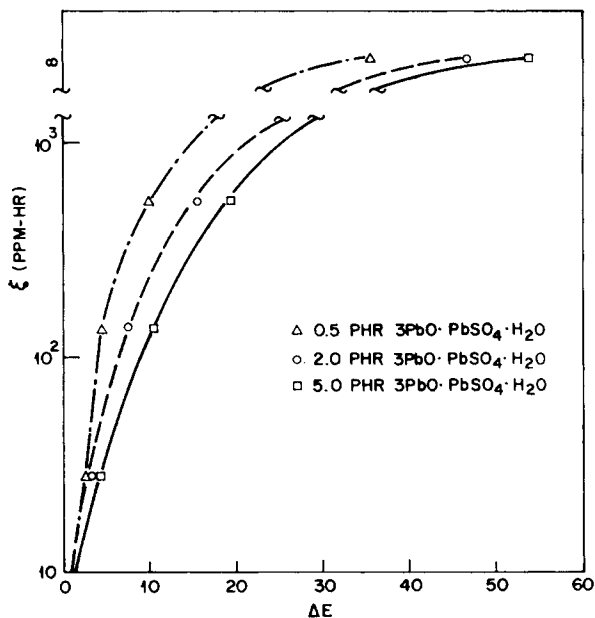


Fig. 6. Relationship between color change and H₂S exposure for sheet samples with differing amounts of lead stabilizer. The estimated experimental errors on this figure and the next are smaller than the areas of the data symbols.

are presented in Figure 8; they show that the unexposed lead-stabilized compound exhibits good stabilization characteristics, despite its failure to show an induction period for the evolution of HCl. After exposure to H₂S, however, the lead-stabilized compound evolves increased quantities of acid upon heating. Treatment with H₂S also affects the stability of the Ba-Cd-Zn-stabilized material, though in a different manner: In this case the stability is first decreased but is then somewhat enhanced at longer heating times (> 5.5 hr).

The results discussed above suggest that the PVC formulations we have examined are poor barrier compounds against H₂S permeation. This supposition is supported by permeation and diffusion studies of the 5.0 phr lead-stabilized PVC and the Ba-Cd-Zn-stabilized PVC. The derived constants are presented in Table I, together with pertinent experimental parameters. These data are best placed in perspective by comparison with other H₂S permeation data, the most comprehensive of which are those of Heilman et al.¹³ The Table I values are among the highest thus far reported for vinyl polymers.

DISCUSSION

Although the mechanism of the nonoxidative thermal degradation of PVC is incompletely understood, the overall process is well recognized to involve the formation of colored polyenes via the sequential dehydrochlorination of adjacent monomer units.^{14,15} Metal salt stabilizers for PVC are sufficiently basic to react with the evolving HCl; thus the rate of escape of free HCl from PVC formulations containing such stabilizers is a measure of both the HCl scavenging efficiency of the salts and the intrinsic stability of the polymer. However, free HCl is known to catalyze the dehydrochlorination of PVC,^{14,15} and the reaction of HCl with

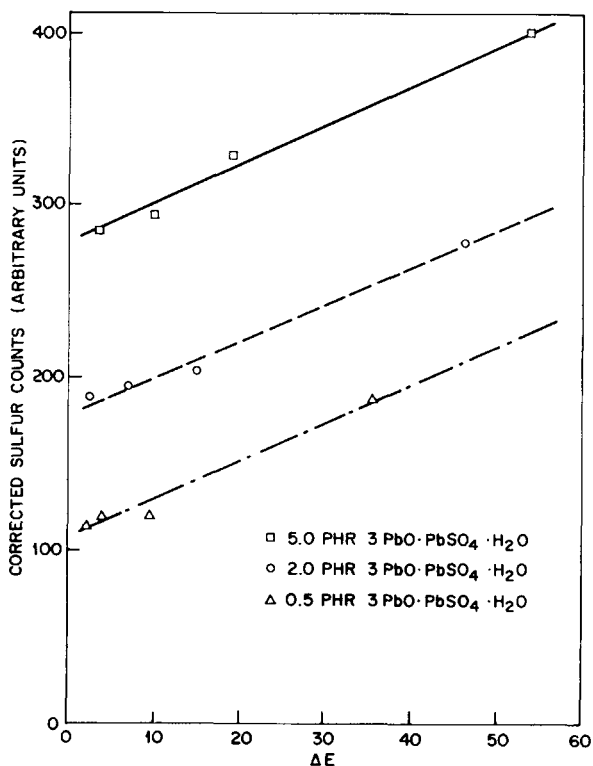


Fig. 7. Relationship between color change and sulfur x-ray fluorescence counts for sheet samples with differing amounts of tribasic lead sulfate stabilizer.

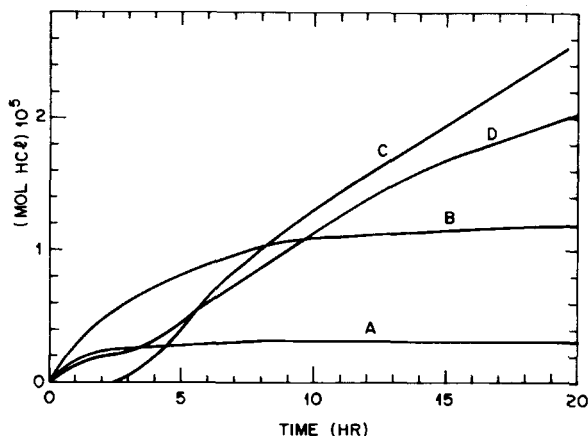


Fig. 8. Rate of HCl evolution measured under argon at $160.5^\circ \pm 0.2^\circ\text{C}$ for 0.300-g samples of PVC formulations before and after 2-hr exposures to 3 ppm H_2S : (a) Pb-stabilized, unexposed; (b) Pb-stabilized, exposed; (c) Ba-Cd-Zn stabilized, unexposed; (d) Ba-Cd-Zn stabilized, exposed.

metal equipment used for processing of the resin would be expected to form metallic chlorides that could also act as dehydrohalogenation catalysts.¹⁴ Metal salt stabilizers that allow the lowest escape rates of HCl are thus frequently found to be the best color stabilizers for the polymer.¹⁶ Moreover, low rates of HCl

TABLE I
Permeation and Diffusion Data for PVC Formulations

	2.0 phr Ba-Cd-Zn-stabilized PVC	5.0 phr Pb-stabilized PVC
Temperature, °C	21.2	21.3
Thickness, mil	5.0 ± 0.5	5.0 ± 0.5
Pressure H ₂ S, torr	760 ± 20	760 ± 20
<i>D</i> , cm ² /sec	(6.4 ± 0.6) × 10 ⁻⁸	(1.3 ± 0.2) × 10 ⁻⁷
<i>P</i> , cm ³ gas-cm film/cm ² area-sec-cm Hg	(5.2 ± 0.2) × 10 ⁻⁹	(6.0 ± 0.2) × 10 ⁻⁹

evolution are important during end-use applications of PVC in which the presence of free HCl can cause corrosion problems. Thus, the HCl escape rate has ordinarily proven to be a useful index of the polymer's technological utility.

The curves of Figure 8 show that H₂S exposure decreased the initial stability (i.e., increased the initial rates of HCl evolution) obtained with both of the metallic stabilizers used in the present study. On the other hand, at long dehydrochlorination times, the stability of the Ba-Cd-Zn-stabilized formulation was actually somewhat improved by prior exposure to H₂S. However, from the standpoint of technological practicality, this result is probably less significant than the destabilization observed at the outset of the run. The shapes of the curves obtained with the Ba-Cd-Zn system are similar to those ordinarily found for PVC containing metal soaps,¹⁷ whereas the curves obtained with the lead-containing system are of an unexpected variety.

Neither the curve shapes nor the destabilizing effects of H₂S can be quantitatively rationalized at this time, particularly since the situation is complicated by the presence, in the formulations, of several other constituents in addition to the stabilizers themselves. Nevertheless, one can think of a number of factors that may have been responsible, qualitatively, for the stabilization phenomena that were found. These include, inter alia, a relatively low reactivity of metal sulfides toward the liberated HCl, a hypothesis requiring experimental verification; the relatively low scavenging efficiency of tribasic lead sulfate itself, as noted by several previous workers¹⁸⁻²²; and changes in the scavenging efficiency of this insoluble stabilizer compound (see below) due to morphological alterations¹⁸ caused by the interaction with H₂S.

Color changes were also observed during all of the experiments of Figure 8; viz., white → brown (Ba-Cd-Zn system, H₂S exposed or unexposed), brown → dark brown (Pb system, H₂S exposed), and white → brown (Pb system, unexposed). These changes occurred in a gradual manner, and no attempt was made to correlate them quantitatively with the HCl evolution rates.

One of the most interesting aspects of the data of Figure 8 is the very pronounced reduction in rates of HCl evolution observed with both of the lead-containing samples at longer heating times. This result suggests that, in the earlier stages of these runs, the lead stabilizer may have increased the intrinsic stability of the polymer by destroying labile defect sites.⁸ To our knowledge, tribasic lead sulfate has never been previously shown to function in this manner. However, the literature does contain some evidence to indicate that this stabilizer forms complexes with conjugated double bonds,^{19,23,24} and one can therefore entertain the possibility that such complexation might have inhibited the



Fig. 9. Scanning electron micrograph of tribasic lead sulfate needles (5.0 phr) in the PVC formulation.

dehydrochlorination of polyenyl chlorides in the degrading PVC. In any event, our observations suggest that further study of the mechanism of stabilization by tribasic lead sulfate (before and after H_2S exposure) would clearly be worthwhile.

As a first step in such an endeavor, it is obviously important to know the state of dispersion of the stabilizer in the polymer formulation before exposure to H_2S . For this purpose a $650 \pm 150 \text{ \AA}$ carbon film was vacuum deposited on a sheet sample containing 5 phr of tribasic lead sulfate, and back-scatter SEM images, used to probe the sample in depth, were then recorded. A typical example of the resulting images is shown in Figure 9. The needle-like structures were inferred to be the stabilizer because of their size and shape; this surmise was confirmed by elemental analysis with the SEM nondispersive x-ray detector. In view of the poor dispersion of the tribasic lead sulfate observed in the present work, the low initial HCl-trapping efficiency of this stabilizer (cf. Fig. 8) is certainly not surprising.

The dramatic changes in color that are seen on exposure of the lead-stabilized PVC to hydrogen sulfide make it of interest to relate these exposures to atmospheric conditions. Ambient hydrogen sulfide concentrations are seldom measured, but current information indicates that the most severe of the long-term average field exposure concentrations is $\sim 10 \text{ ppb}^{25}$; typical values are in the range of 0.1 to 1.0 ppb. Much higher levels of H_2S ($\leq 20 \text{ ppm}$) are occasionally found in tunnels and manholes.²⁶ Since definite color changes are seen at integrated exposures of as little as 1 ppm-hr, loss of color integrity can occur on time scales of minutes to days in many field locations. This suggests that polymeric materials that may encounter reactive atmospheric gases in field use should be formulated to minimize any adverse effects that would thereby be produced. In addition to H_2S and the well-known O_3 , other atmospheric trace species of potential concern are CH_3SH , CH_3SCH_3 , NO_2 , and SO_2 .

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