REVIEW PAPER

Effects of Acidic Deposition On Painted Wood: A Review

R. Sam Williams
Forest Products Laboratory*

Acidic deposition has captured the attention of many researchers during the last decade and considerable knowledge has been gained in many disciplines including forestry, limnology, atmospheric sciences, and materials science. The study of the degradation of materials by acidic deposition has included the effects on wood, paint, and painted wood. The literature pertinent to the effects of acidic deposition and its precursors on these materials is critically reviewed. The subjects include transport properties of paints and polymers, the reactions of acids with paint components, and the degradation of wood. The research on acidic effects on paint degradation leaves many questions unanswered and the review forms the basis for future research recommendations.

INTRODUCTION

Painted wood is a marriage of two remarkable materials. Paint coatings are thin adherent films of complex mixtures of polymers. pigments. and extenders. with small amounts of uncured monomer. drying agents. surfactants. and other additives. The paint film forms as the solvent evaporates from a polymer solution or suspension and/or as the small molecules react to form a polymer. Wood is an equally complex mixture of polymers and other compounds arranged in an anisotropic, moisture-sensitive, dimensionally unstable material having large variability within a single species and even within a single piece. Given the complexities of these materials and their differences in properties—particularly the moisture induced dimensional changes—one would probably consider such a materials system doomed to failure. But it is not so!

Although wood can decay and both wood and paint coatings are susceptible to photochemical degradation. a properly applied paint system on wood can last a decade, and history offers many examples of properly maintained painted wood lasting for centuries. Even under extreme conditions. such as on wooden boats in water. paints last well. This does not mean that paint problems do not exist, but. almost without exception. they begin with poor design of the structure and are made worse by incorrect application of the paint. Although this review focuses on paint degradation—particularly those systems that degrade too quickly and/or fail catastrophically within a short time – one should not forget the vast amount of properly maintained paint on wood weathering slowly while protecting the substrate for centuries.

Wood finishes vary from highly crosslinked barrier coatings such as catalyzed epoxides to porous low-solids-content stains and wood sealers. This wide variety of finishes is complicated by the range of wood and wood-based composites used as substrates and wide range of uses. Given the broad array of types of paints and finishes. it is interesting that research on painted wood has included only a narrow range of finishes and wood-based substrates that are used outdoors (*Table* 1)[1]. Virtually all acidic deposition-related research on wood finishes has dealt with high-solids-content paint coatings.

The ultimate goal of research on finishes is a cost effective increase in service life. Service life. whether under normal or acidic conditions. represents a significant economic concern. The in-place value of paints that could be at risk to degradation by acidic deposition reaches billions of dollars a year in the United States (*Table* 2).[2] The $24.1 billion calculated for architectural coatings includes coatings on wood. masonry, vinyl. and other materials: finishes on wood substrates comprise by far the major portion of these uses (*Figure* 1). Paints were included in the research sponsored by the National Acid Precipitation Accessment Program (NAPAP) because of the high value of in-place coatings on wood. .Much of the recent research reviewed in this report was completed within this program.

This review includes a critical analysis of the published research on acidic deposition and provides recommendations for future research. The research addressed discolora-

*United States Department of Agriculture, Forest Service, One Gifford Pinchot Dr., Madison, WI53705-2398.

Table 1—Finishing Methods for Exterior Wood Surfaces[1,a]

Type of Exterior Wood Surface	Water-repellent Preservative		Semi-transparent Stains		Paints	
	Suitability	Expected life[b] (yr)	Suitability	Expected life[c] (yr)	Suitability	Expected life[d] (yr)
Siding						
Cedar and redwood	High	1-2	Moderate	2-4	High	4-6
Smooth (vertical-grained)	High	2-3	Excellent	5-8	Moderate	3-5
Roughsawn or weathered						
Pine. fir. spruce. etc.						
Smooth (flat-grained)	High	1-2	Low	2-3	Moderate	3-5
Rough (flat-grained)	High	2-3	High	4-7	Moderate	3-5
Shingles						
Sawn	High	2-3	Excellent	4-8	Moderate	3-5
Split	High	1-2	Excellent	4-8	—	—
Plywood (Douglas-fir and southern pine)						
Sanded	Low	1-2	Moderate	2-4	Moderate	3-5
Textured (smooth)	Low	1-2	Moderate	2-4	Moderate	3-5
Textured (roughsawn,	Low	2-3	High	4-8	Moderate	4-6
Medium-density overlay[e]	—	—	—	—	Excellent	6-8
Plywood (cedar and redwood)						
Sanded	Low	1-2	Moderate	2-4	Moderate	3-5
Textured (smooth)	Low	1-2	Moderate	2-4	Moderate	3-5
Textured (roughsawn)	Low	2-3	Excellent	5-8	Moderate	4-6
Hardboard. medium density[f]						
Smooth						
Unfinished	—	—	—	—	High	4-6
Preprimed	—	—	—	—	High	4-6
Textured						
Unfinished	—	—	—	—	High	4-6
Preprimed	—	—	—	—	High	4-6
Millwork (usually pine)						
Windows, shutters, doors, exterior trim,	High[8]	—	Moderate	2-3	High	3-6
Decking						
New (smooth)	High	1-2	Moderate	2-3	Low	2-3
Weathered (rough)	High	2-3	High	3-6	Low	2-3
Waferboard	—	—	Low	1-3	Moderate	2-4

(a) Data compiled from the observations of many researchers. Expected life predictions are Cor an avenge location in the continental U.S.; expected life will vary in extreme climates or exposure (desert, seashore, deep woods. etc.).
(b) Development of mildew on the surface indicates a need for refinishing.
(c) Smooth, unweathered surfaces are generally finished with only one coat of stain, but roughsawn or weathered surfaces, being more adsorptive, can be finished with two coats. with the second coal applied while the lint coat is still wet.
(d) Expected life of two coats, one primer and one topcoat. Applying a second topcoat (three-coat job) will approximately double the life. Top-quality acrylic latex paints will have the best durability.
(e) Medium-density overlay is generally painted.
(f) Semi-transparent stains are not suitable for hardboard. Solid-color stains (acrylic latex) will perfom like paints. Paint are preferred.
(g) Exterior millwork, such as windows, should be factory treated according to Industry Standard IS4-81. Other trim should he liberally treated by brushing before painting.

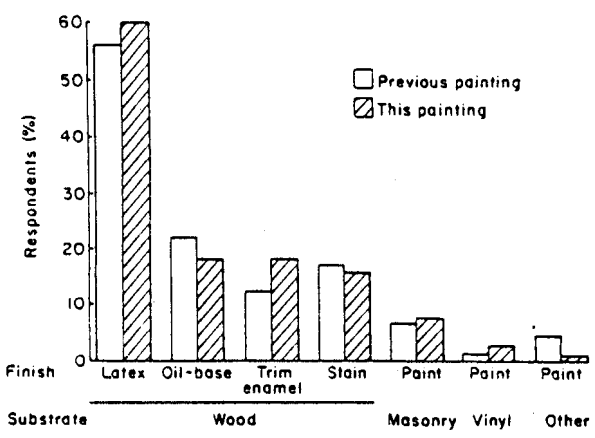

Figure 1—Types of architectural coatings and substrates determined from a 1986 survey[2]

tion of paint by H_2S, formation of bloom. retardation of curing. instability of pigments. effects of SO_2 on the binder. and effects of SO_2 at the paint/wood interface. The research has covered only a small fraction of the wide array of finishes, wood species. and wood-based composites used on wood outdoors (*Table* 1).

SUBSTRATE AND FINISH CHARACTERISTICS

Substrates vary considerably from area to area around the nation and over time. Fifty years ago. solid wood of a few species such as western redcedar (*Thuja plicata*). redwood (*Sequoia sempervirens*). and bald cypress (*Taxodium distichum*) dominated the residential siding market. These have been partially replaced by other species and by wood-composite materials such as plywood. particleboard.

Table 2—1987 Paint Shipments and Associated Coats for the United States[2]

Classification	Shipments (gal. x 10^6)	Factory Cost (x10^6$)	In-Place Value (x10^9$)
Architectural coatings (ext.)			
Oil-based	80	807	9.5
Water-based	123	944	14.6
Automotive finishes			
New vehicles	73	1313	12.0
Refinishing	44	904	22.0
Coil coating	20	303	2.0
Industrial maintenance paints	28	313	2.8
Traffic marking paints	19	95	0.7

flakeboard, medium-density fiberboard. and melamine-formaldehyde-impregnated paper overlays of these materials (*Table* 1). Each species has its own characteristics and wood-composite materials have specific properties that make them distinctly different from their base materials. Finish requirements for different species and different composite materials vary and these properties must be taken into account when formulating finishes.

Wood

Wood properties that are important in finishing are species. moisture content. density and texture. resin and oil content. growth pattern and grain orientation. and defects such as knots. reaction wood, and diseased wood.[3] These properties are characterized by the chemical composition. microstructure. and macrostructure of wood[4,5] [see reference (6), p. 2-11.

Wood is degraded naturally by fungal and bacterial decay and by weathering. Wood-finishing problems caused by decay can be serious but are not included in this review because the growth of wood-decay fungi is insensitive to pH in the range of 4 to 7 [see reference (7), p. 162].

Weathering is the photochemical degradation of the surface of wood and is not to be confused with decay. UV radiation is necessary for weathering to occur. and radiation of these wavelengths can penetrate about 75 µm into the surface of unfinished wood.[8] UV degradation is manifested in an initial color change. followed by the gradual erosion of the wood surface. The radiation causes cleavage of the lignin. particularly in the lignin-rich middle lamella. With a decrease in its molecular weight. segments of the lignin are removed from the surface through the action of moisture. thus causing the wood cells to become less tightly bound. Changes in moisture content cause dimensional changes that accelerate this loosening process. As exposure to radiation continues, the wood cells erode from the surface. In softwoods. the erosion is more rapid in the less dense earlywood than in the latewood, which leads to an uneven surface (*Figure* 2). Surface erosion. however. proceeds very slowly. The erosion rate for solid wood in temperate zones is on the order of 0.3 - 1.2 cm per century and depends mainly on the amount of UV exposure. wood species. and density.[9,11] Other factors affecting the erosion rate include moisture, mechanical abrasion. temperature. and air pollution.

Because weathering of wood is a surface deterioration. it directly affects paint adhesion. The eroded and roughened surface of weathered wood impairs the adhesion of subsequently applied film-forming finish to the substrate,[12-17] Surface degradation occurs if peeled areas are exposed to the weather before refinishing. In the study by Williams,[17] western redcedar boards were weathered outdoors and painted following exposure. Outdoor exposure for as little as four weeks caused significant decrease in paint adhesion; boards exposed for 16 weeks lost about 50% of their paint adhesive strength. This degradation can be slowed or even stopped by wood finishes. The amount of protection the wood surface gets from the finish depends on the finish properties — most notably. the amount and type of pigment in the finish.

Finishes

The modes of paint failure depend. to a large degree, on exposure conditions. the type of finish and substrate. and the interactions among these factors. As a finish system ages, various agents interact with the components of the system to effect change. Effects may vary from one system to another and with the agent causing the change. For example. sunlight and oxygen can effect chemical reactions. and changes in ambient temperature and water can effect physical changes in both the finish and substrate. These are the main factors that cause degradation of painted wood. Other minor factors may include the effects of acidic deposition.

These factors act in concert to effect various degradation mechanisms but it is often difficult to identify the mechanism responsible for the paint failure. Acidic deposition could affect any of these mechanisms.

LITERATURE REVIEW

Concern about air pollution effects on coatings is not new. Meller and Sisson[18] reported the high economic cost of materials damage caused by industrial pollution. They included paint and other protective coatings as materials at risk and discussed the use of aluminum pigmented primers to protect wood substrates from "acid smoke" and moisture. Since that time. a number of researchers have attempted to determine what part of the cost of coatings maintenance is

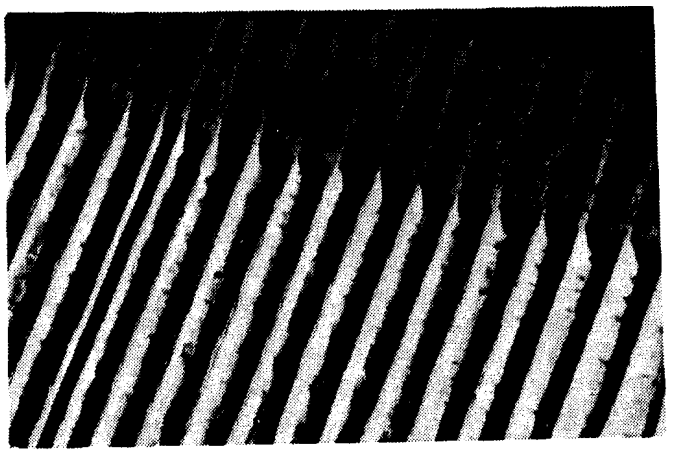

Figure 2—Photograph of a piece of western redcedar (*Thuja plicata*) exposed to the weather for eight years. The unweathered section at the top was protected with a metal strip

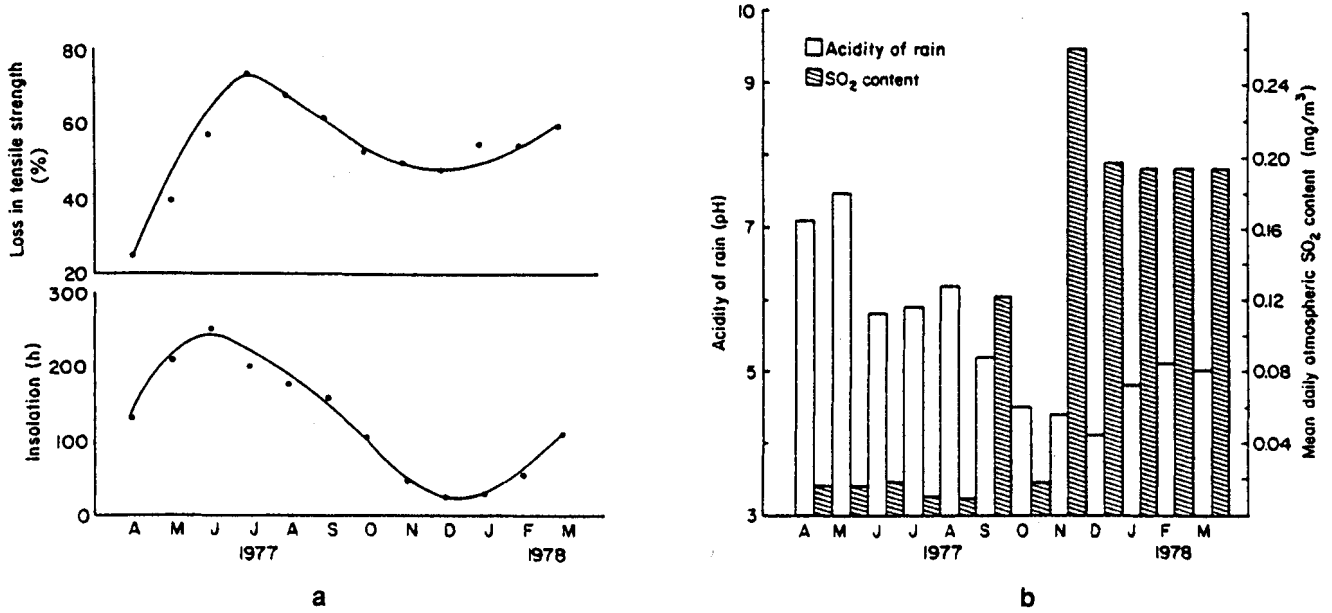

Figure 3—a: Loss of tensile strength of spruce microsections and the mean monthly insolation[21]; b: Mean monthly pH of rain water and sulphur dioxide concentration in the air[21]

attributable to acidic deposition. Studies have included laboratory chamber exposures. outdoor exposures, and consumer and industry surveys. Larson[19] considered SO_2 to be the most serious pollutant threat to paint systems and he mentioned H_2SO_4, HCl, H_2S, and HNO_3 as minor pollutants. He also listed soot and finely divided carbon as contributors to acidic degradation because these particles retain moisture and absorb pollutants.

Gross[20] reviewed the effects of gaseous components such as SO_2, H_2S, NH_3, and O_3, solids such as NaCl, $(NH_4)_2SO_4$, and NH_4Cl, smoke, and volatile organic compounds (VOCs) on paint and paint components. He included methods of investigation. evaluation. and chemical analysis. Information on mechanisms was limited to SO_2. the effect of H_2S on color changes in pigments. and O_3 to binder degradation. Little information was given on the effect of H_2SO_4. NO_2, and VOCs. Gross[20] stated that the field was at an elementary stage. that relationships between concentration of pollutants and mode of action could not be made at that time. and that the cost estimate for degradation was unreliable. He outlined several areas for future research. His list of research needs is still pertinent. No single researcher or team has attempted to evaluate all aspects of the problem. but many have investigated the effects on various components. Given the range of paint and varnish coatings used by various researchers. the interaction among weathering factors and finish components, and the different modes of paint failure. it is useful to organize this discussion by finish component (i.e., binder, pigment. and alkaline components). substrate. and their interface. Agents include sulfuric (H_2SO_4). sulfurous (H_2SO_3), and nitric (HNO_3) acids, hydrogen sulfide (H_2S), sulfur dioxide (SO_2). and ozone (O_3). H_2SO_3/SO_2 are discussed in considerable detail because of their high solubility and permeation in paint coatings and their possible effect on substrates.

Substrate

The wood substrate is an anisotropic material that can change dimension quickly with changes in moisture content. The wood substrate. therefore, subjects the paint coating to these changes. Typical manifestations of substrate change are loss of adhesion (peeling and/or cracking). degradation of the wood surface where the coating has been breached. and penetration of the substrate by chemicals where they have diffused through or circumvented the coating.

Under normal conditions with a two- or three-coat paint system. paint on wood slowly erodes from the surface through the combined action of primarily sunlight and moisture: when the primer coat begins to show, the surface or topcoat can be easily repainted with an additional topcoat. If the paint system fails at the paint/wood interface. the substrate is exposed to weathering. It may not be possible to refinish this unprotected wood for some time. Similarly. wood may be left unfinished while a project is under construction. If wood is more rapidly degraded by acidic deposition during these exposures. it directly affects the paint adhesion when the wood is eventually finished or refinished. The effects on wood and other cellulosic materials of acid rain and the oxides of nitrogen (NO_x) and sulfur (SO_x) have been evaluated.

Raczkowski[21] found that exposing strips of microtomed spruce (*Picea abies*) to outdoor weathering resulted in decreased tensile strength as compared with unexposed controls. The loss in tensile strength along the grain was generally directly related to the amount of sunlight during the summer and fall, but the loss in strength for winter and spring seemed greater than could be accounted for on the basis of sunlight alone (*Figures* 3a and 3b). This greater strength loss was attributed to higher acidity levels. Qualita-

tive inspection of the data indicated that loss of strength was caused by sunlight and was exacerbated by acid, particularly during the winter months. It was not possible to quantify the effect of acid.

Evans and Banks[22] exposed microtomed sections of lime (*Tilia vulgaris*) and Corsican pine (*Pinus nigra*) to dilute sulfuric, sulfurous, nitric, acetic, and formic acids (pH 2.0-6.0) for up to 12 months at 40°C. Specimens showed loss of strength that was pH dependent. The strength loss caused by sulfurous acid was greater than all other acids at similar pHs. They noted that the strength losses may have been caused by a combination of both hydrolytic degradation of the hemicelluloses and a sulfonation reaction of the lignin. Scanning electron microscopy (SEM) data showing failure at the lignin-rich middle lamella further supported the speculation that lignin degradation is partially responsible for the decreases in strength and toughness.

Feist[23] and Williams[24] measured surface degradation of wood surfaces following xenon arc accelerated weathering to determine the efficacy of surface treatments of wood. The degradation of the surface was manifested as erosion and was measured microscopically.[9] These techniques were used to determine the effect of acid treatment on the erosion rate of western redcedar (*Thuja plicata*). Six acid soaks were used: nitric and sulfuric acids at pHs of 3.0, 3.5, and 4.0. Results were similar with both acids and increased the erosion rate 10% over that of the controls.[25]

In subsequent studies, western redcedar specimens were treated with sulfuric, nitric, and sulfurous acids at pHs from 2.0 to 4.0.[26] The erosion rate was dependent on pH and acid type. At a pH of 2.0, sulfurous acid doubled the weathering rate. The effect was slightly less for sulfuric and nitric acids. Statistical analysis of the data showed no significance for any of the acids at pH 3.5 or above.

Deppe and Schmidt[27] evaluated the effect of pH on accelerated weathering of coated and uncoated particleboard. Specimens were soaked in pH 2 sulfuric acid for 72 hours every four weeks during accelerated weathering. With some adhesive systems, particularly melamine/isocyanate-urea/formaldehyde mixed systems, a drop in adhesive strength was observed. Degradation of melamine/formaldehyde (MF)-impregnated paper overlay and a clear MF polymer film were also observed.

Fengel[28] investigated the degradation of spruce (*Picea sp.*) exposed to high concentrations of HCHO, Cl_2, NH_3, and SO_2. Dick and Murphey[29] studied the degradation of wood surfaces by high concentrations of O_3. In a series of three papers, Arndt and Gross[30-32] reported on color and weight changes caused by outdoor exposure and accelerated weathering of wood. No degradation was quantified by any of these investigators using concentrations typical of those found under outdoor exposure conditions.

Interface: Transport Properties Of Wood Finishes

Wood does not allow large amounts of moisture to collect at the paint/substrate interface because of its porous hydrophilic nature, and free water does not exist in wood below its fiber saturation point (approximately 30% by weight). Although it is possible to exceed the fiber saturation point locally at the paint/wood interface under certain conditions—such as a cold paint surface on wood having a high moisture content—moisture is generally wicked away from the interface so that a uniform moisture content is maintained throughout the wood. Liquid water is not likely to form at the paint/wood interface from rain and dew as long as the paint coating is intact. Most liquid water will be shed by the paint coating. Moisture problems occur when the fiber saturation point is exceeded at the paint/wood interface because of improper selection of finish, poor design, and/or marginal application techniques. In situations where the fiber saturation point is not exceeded, the wood substrate undergoes large dimensional change with changes in moisture content. Stresses on the coating system caused by dimensional changes in the paint film and the wood probably increase the risk of failure. These stresses can cause cracking parallel to the wood grain.

In situations where painted wood is fully exposed to the weather, moisture problems result from the rapid sorption of water through cracks in the paint, joints, nail holes, etc. This type of exposure can quickly give extremely high moisture content at the paint/wood interface. Whether water gets to paint/wood interface by diffusion or through stress-induced cracks in the paint film, it inevitably leads to loss of paint adhesion, subsequent peeling, and often wood decay as well. The exact mechanism for peeling is not very well understood, but it appears that the moisture content at the interface must be above the wood's fiber saturation point before peeling occurs. The stress without water does not seem to result in peeling. Paint peeling is one of the more serious paint degradation mechanisms and may be related to transport properties. Transport properties of paint coatings play a role in determining the risk of degradation to the paint system.

Moisture Transport

In a review of the diffusion and permeation of gases, liquids, and vapors in polymer films, Park[33] found that much of the research on transport properties of paint dealt with moisture, oxygen, and salt (primarily chlorides) transport.

Research on moisture transport properties of paint coatings on wood showed that paints are fairly porous and that it is possible for moisture to diffuse readily into and out of painted wood. It should be emphasized that paint coatings inhibit the loss of moisture more than they do the absorption of moisture and that, under cyclic exposure to high and low

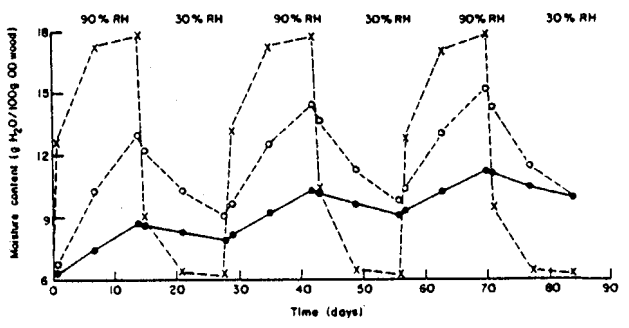

Figure 4—Change in moisture content of ponderosa pine (*Pinus ponderosa*) sapwood finished with one and three coats of aluminum paint when exposed to alternating cycles of 30% and 90% RH at 27°C.[34] x–x—unfinished wood; o—o—aluminum paint, one coat, 25% MEE; and ——aluminum paint, three coats, 65% MEE

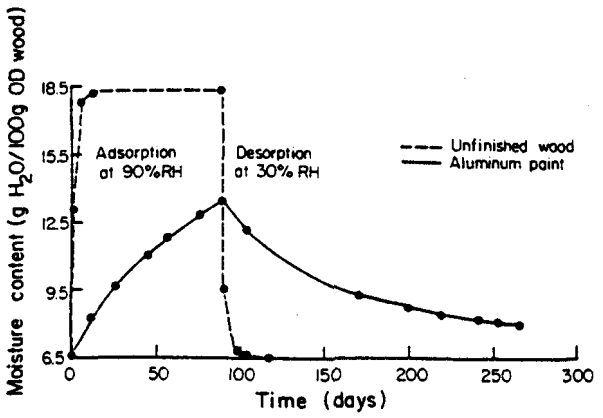

Figure 5—Change in moisture content of ponderosa pine (Pinus ponderosa) sapwood finished with three coats of aluminum paint when exposed to 90% and 30% RH at 27°C compared to unfinished wood[34]

relative humidity. paint traps moisture (Figure 4). This type of cyclic exposure is seldom a problem under most circumstances because sufficient drying time usually passes between periods of high humidity. If wood is subjected to continuous high humidity from either the inside or the outside. loss of adhesion is likely. Kitchens and bathrooms that lack proper moisture barriers and farm buildings that contain livestock subject painted wood to high moisture from the interior.

Feist et al.[34] reported on the moisture transport properties of 91 wood-finish systems. The study evaluated the movement of water vapor through finishes by comparing moisture pick-up in the painted specimens against that of unpainted controls. The ratio gave a moisture-excluding efficiency (MEE) as a percentage of the weight gain of the controls. An MEE of 100% meant the finish was 100% effective in blocking moisture penetration into the finish.

The MEE values for a wide range of finishes are listed (*Table* 3). and typical values for oil-based paints are about 40%. A paint system having one coat of primer and one or two latex-based topcoats provides a lower MEE than would three coats of oil-based primer. For unfinished wood, the moisture absorption-desorption cycles repeat uniformly (*Figure* 4). but for painted specimens, the effectiveness in trapping moisture increases as the MEE increases, as shown by steadily increasing moisture contents. For a single cycle (*Figure* 5). desorption back to an equilibrium moisture content (EMC) of 6.5% requires more than 250 days for a three-coat paint system.

The MEE for water repellents and water-repellent preservatives is about zero for a one-coat system. Absorption-desorption cycles are similar to those of unfinished wood (*Figure* 4). The strength of the water repellents is in their high water-vapor transmission but low liquid-water transmission.

Lindberg.[35] reported similar results with finishes including two-component polyurethane, oil, alkyd, and acrylic latex-based paints.

Ahola[36] showed that moisture transport properties of paint coatings changed with weathering. Some paints became more permeable while others became less permeable. The study included both vapor-phase and liquid-water exposure of latex, oil, alkyd, and polyurethane paints and oil and acrylic latex stains. Perera and Vanden Eynde[37] studied six paints formulated for use on porous materials and showed that water-vapor and liquid-water transport properties and mechanical properties changed as paint film was soaked in water. Water leached out soluble components in' the film. leaving it less permeable to additional water exposure. The film had increased tensile strength and tensile yield stress and decreased elongation after water leaching.

Analysis of leachates showed loss of extenders. The author~~' concluded that values from transport studies with relatively new paint coatings may not be representative of the properties during its service life. Oesterle et al.[38] also reported that changes occur in the structure of paint films with repeated sorption and desorption of moisture.

The permeabilities of free films of polymers and paints have been reported by several researchers.[39-42] The permeabilities depended on the type of polymer. For some polymers. the crosslink density controlled the diffusion rate and this was the primary consideration. For other polymers, the permeability was controlled by the solubility of water in the polymers. It appears that the limiting factor (crosslinking or solubility) in moisture transport in paint films depends on the type of film.

Like water. acid may be absorbed by painted wood either by diffusion through paint or by the flow of acid solutions, vapors, or aerosols through voids in the paint coating.

Sulfur Dioxide Transport

The transport of SO_2 through pigmented and unpigmented polymer films provides an indication of how vulnerable the substrate is to degradation. A wide variety of polymers and paint films has been investigated. Lindner[43] measured the diffusion of SO_2 through free films of chlorinated rubber. linseed oil. nitrocellulose. and epoxide. Davis and Rooney[44] studied the permeation. solubility. and diffusion of SO_2 in polyethylene. poly(w-amino-undecanoic acid) (Nylon 11), and polycarbonate: they reported that no changes occurred in the IR spectra of any of the polymers exposed to SO_2. Jellinek et al.[45] reported no degradation for poly(hexamethylene adipamide) (Nylon 66). In a later study. Davis et al.[46]measured SO_2 permeabilities of several polymers. Polymers included those with good barrier properties such as polyester, polycarbonate, poly(vinyl chloride), and blends of poly(vinylidene chloride) with polypropylene or regenerated cellulose and polymers with poor barrier properties such as high- and low-density polyethylene. and polystyrene. Ranade et al.[47] reported sigmoid-shaped sorption curves for the uptake of SO_2 in diglycidyl ether of bisphenol A (DGEBA) crosslinked with diethylene triamine. They stated that this non-Fickian behavior was typical for polymers in their glassy state. In a later work using polymers in their rubbery state. Ranade et al.[48] reported the diffusion of SO_2 in amine-crosslinked aliphatic epoxide polymer as Fickian over the temperature range 1°-45°C. The diffusion coefficient varied from 7.5 x 10^9 to 28.8 x 10^4 cm^2/s over this range. The polymer had a low glass-transition temperature and was in its rubbery state for all measurements. Diffusion coefficients from the literature were tabulated: values varied from 10,000 × 10^{-10} cm^2/s for vulcanized natural rubber to 1.25 × 10^{-10} cm^2/s for poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-c:4,5-c´]dipyrrole-2,6(1H,3H)-diyl)-1,4-phenyleneoxy-1,4-phenylenel

(Kapton™) polyimide. The kinetics and equilibria of SO_2 in Kapton polyimide were described by Koros et al.[49] and the chemical interactions by Iler et al.[50] Hsieh[51] reported the volumetric diffusion coefficient of SO_2 in ethylcellulose as 530×10^{-10} cm^2/s and nitrocellulose as $7.9 \times 10^{-10} cm^2/s$.

Kuehne and Friedlander[52] investigated the permeation of several polyacrylates and cellulose triacetate membranes to SO_2. Desor and Pauly[53] evaluated a number of solvent- or waterborne paints for barrier properties against CO_2 and SO_2. The permeability of the waterborne dispersion paints was higher than for the solventborne.

Funke and Haagen[54] reviewed the literature on SO_2 permeability of polymer films and paint films and tabulated the results (*Table* 4). They stressed the high solubility of SO_2 in organic coatings and pointed out the need for the development of nontoxic alternatives to lead to scavenge SO_2 in paints. Funke et al.[55] investigated the absorption of anhydrous SO_2 by unpigmented films of alkyd/melamine and epoxide resins. The weight gains following 24-hour exposure were 14 and 11%, respectively, and. upon evacuation. the polymers retained 20-30% of the weight gain. They attributed this retention to the chemical reaction of SO_2 with the resins. These resins were also cast on steel substrates and soaked in 1% aqueous solutions of sulfuric and sulfurous acids. Corrosion of the steel substrate was detected within hours of immersion in the sulfurous acid. whereas the panels in sulfuric acid were corrosion-free for days and even weeks if the coating resisted degradation.

For unpigmented polymer films, it is apparent that the diffusion. solubility. and permeation of SO_2 depend on the polymer type. Diffusion is Fickian for polymers at temperatures above their glass transition (T_g). Although it is slight

Table &Moisture-Excluding Effectiveness (MEE). of Three Coats of Various Finishes on Ponderosa Pine[34]

Effective		Somewhat Effective		Ineffective	
MEE%	Finish Type	MEE%	Finish Type	MEE%	Finish Type
95	Paraffin wax-dipped	14	Polyurethane paint—gloss (2-component)	19	Nitrocellulose lacquer
91	Epoxy finish—clear (2-component)	73	Pigmented shellac house paint	16	Acrylic latex flat
87	Epoxy paint—gloss (2-component)	69	Paraffin wax—brushed	11	Water repellent (1% wax)
84	Aluminum flake-pigmented urethane varnish (oil-modified)	66	Polyurethane finish—clear (2-component) semi-transparent stain)	11	FPL natural finish (linseed oil-based)
82	Aluminum paint (linseed/phenolic/menhaden)	60	Alkyd house primer paint (tall maleic alkyd resin)	10	Latex enamel wall paint (epoxy)
80	Enamel paint—satin (soya/tung)	59	Epoxy paint—gloss (1-component)	4	Acrylic latex house primer paint
		59	Enamel paint—gloss (soya alkyd: interior,	2	Tung oil
		57	Marine enamel—gloss (soya alkyd)	1	Latex pigmented she1lac
		50	Epoxy varnish—gloss (1-component)	0	Semi-transparent oil-based stain
		48	Polysilicone enamel (silicone alkyd)	a	Solid-color latex stain (acrylic resin)
		46	Floor and deck enamel (phenolic alkyd)	0	Alkyd flat wall paint (soya alkyd)
		44	Urethane varnish (oil modified)	0	Latex flat wall paint (vinyl acrylic resin)
		44	Gym seal (linseed oil/phenolic resin/tung oil)	0	Paste furniture wax
		42	Shellac	0	Linseed oil
		42	Solid-color oil-based satin (linseed oil)	0	Linseed oil sealer (50%)
		41	Oil-based house paint (tall/soya alkyds)	0	Unfinished wood (control)
		35	Floor seal I phenolic resin/tung oil)		
		32	Flat latex primer wall paint (butadiene-styrene resin)		
		30	Spar varnish (soya alkyd)		

(a) MEE: 100% = perfect protection or no absorption of water vapor: 0% = no protection as with unfinished wood.

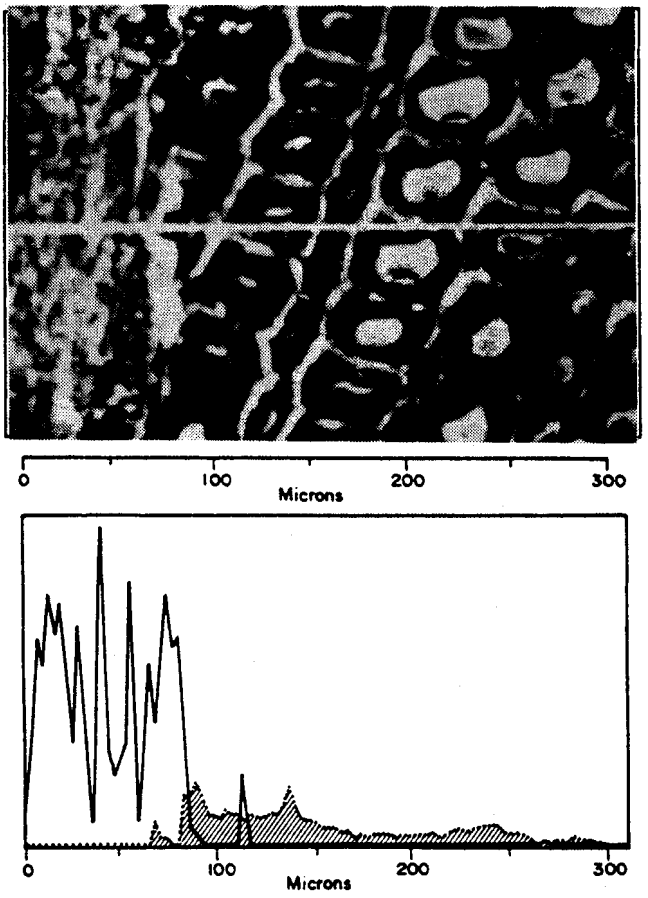

Figure 6—SEM/EDS line scan of sulfurous-acid-treated Southern pine (*Pinus sp*) having one coat of acrylic latex primer and two top coats (Ti =—, S = ---—). Vertical full scale (VFS) = 10,643[63]

for some polymers. they tend to show non-Fickian behavior below their T_g. In addition. the permeability of polymers to SO_2 is rather high compared with other gases; this is caused mainly by the high solubility of SO_2 in many polymers.

From the research reviewed in this section, it is clear that unpigmented polymer films have a large range of permeabilities but that the polymers used in paint formulation generally do not form barriers to SO_2 either in the gaseous state or in solution as sulfurous acid. Although 20% of the absorbed SO_2 was retained in the alkyd/melamine and epoxide films and probably reacted with the polymer. there appears to be little degradation to the polymer itself from SO_2 at low Concentrations. The absorption is inhibited by pigments: furthermore. those pigments that can catalyze the oxidation of SO_2 and scavenge the resultant sulfate ions can limit the penetration even more than can typical pigments.

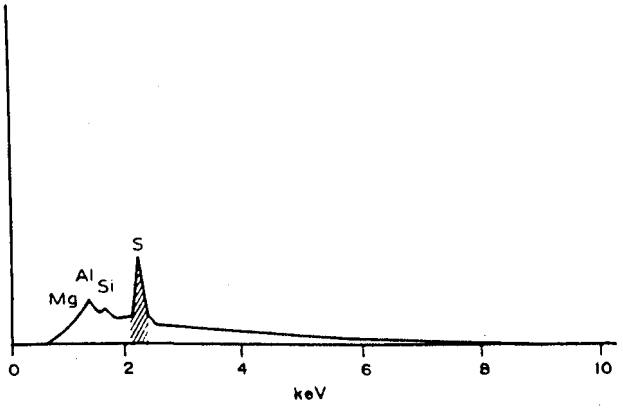

Figure 7—EDS showing the elemental constituents just below paint/wood interface. Vertical full scale (VFS) = 4,096 counts[63]

Svoboda and coworkers[56-59] reported that SO_2 permeated 65% linseed oil-modified pentaerythritol alkyd (naphthenate dryers) free films. The absorption into the film was linear with the square root of time and increased with temperature., At 30°C. the SO_2 penetrated approximately 30 µm into the film after four days. Svoboda et al.[56] also exposed isolated films to dilute sulfuric acid for 37 days. Penetration of sulfuric acid was not detected. The authors attributed the difference in penetration of sulfurous and sulfuric acids to differences in ionic concentrations. The permeation of acids into polymer films depends. to a large extent. on the solubility of the acid in the polymer. Volatile low molecular weight acids such as HF, HCl, HNO_3, and H_2SO_3 dissolve into the polymer in the molecular form.[59] They reported that polymers having low dielectric constants permit the rapid dissolution of undissociated molecular acid into the polymer and that the division between those that dissolve and those that do not, such as sulfuric and phosphoric acids. depends on the energy required to discharge an undissociated molecule from solution at the polymer/solute interface. They reported that SO_2 exists primarily in the molecular form and diffuses into paint in this form whereas sulfuric acid exists in aqueous solutions as hydrated ions. They also reported that the addition of neutral salts such as Na_2SO_4 in H_2SO_4 or NaCl in HCl shifts the equilibrium of the acid dissociation and thus affects the activity of the ions and the ability of the acid to permeate the film. The lack of penetration of sulfuric acid has also been attributed to the repulsion of the negatively charged ions by the polymers.''

The impermeability of the film to sulfuric acid led to the study of films containing a small amount of catalyst. such as Cu, to oxidize sulfite to sulfate. and an additional pigment to scavenge the sulfate. such as $BaCO_3$ or Pb_3O_4[57,58] Pigments such as these decreased the SO_2 penetration into the films to as little as 20% of that into the unpigmented films. A 10% pigment volume concentration (PVC) of ZnO or TiO_2 decreased the SO_2 penetration by 50%. Higher PVC had little further effect on decreasing the penetration. The penetration rate for the pentaerythritol alkyd with 10% PVC TiO_2 was 0.11 $\mu m/min^{1/2}$ and decreased to only 0.10 $\mu m/min^{1/2}$ at 30% PVC.

Sulfur dioxide diffuses readily through paint. A number of studies have documented the high solubility and the ease with which the anhydrous gas permeates paint coatings. Paint can absorb SO_2 and/or HSO_3 from sulfurous acid but it is not clear whether the dissolved SO_2 or the bisulfite ion is the diffusing species. It has been shown that SO_2 reacts with galvanized steel substrates and that the reaction products diffuse back through the paint film and are contained in the run-off from the painted specimens.[60] In a study by Spence et at.[61] that used acrylic latex paint on aluminum substrates. the paint failed because of corrosion of the aluminum substrate and subsequent loss of paint adhesion. Williams et al.[62,63] have also shown that SO_2/HSO_2. in dilute sulfurous acid pemeates acrylic latex paint on wood. In the case of porous

films such as latex paints on reactive substrates, the diffusion of SO_2 through the film was sufficient to bring about catastrophic paint failure.

The high permeability of paint coatings to SO_2/HSO_3 could possibly degrade the wood substrate. It has previously been shown that loss of adhesion can occur if wood weathers before initial painting. It was also shown that acid treatment of specimens during exposure to accelerated weathering increased the rate of surface deterioration: the rate at which wood weathered increased by as much as 50% when wood was exposed to sulfurous. sulfuric. or nitric acids.[25,26] On the basis of the more rapid degradation of wood under acidic conditions. the loss in adhesive strength would probably be higher for boards exposed in areas having acidic deposition than those boards exposed in areas having little acidic deposition.

The SEM/energy dispersive spectroscopy (EDS) analysis was used to detect sulfur in western redcedar (*Thuja plicata*) and southern pine (*Pinus sp.*) wafers painted with alkyd-oil or acrylic latex primer paint following exposure to sulfurous acid. sulfuric acid. and sodium sulfate.[62,63] Sulfur was detected in those specimens exposed to sulfurous acid (Figures 6 and 7) but not in those exposed to sulfuric acid (*Figure* 8) or sodium sulfate solutions. If. therefore. sulfuric acid or the sulfate ion is to affect paint performance. it must reach the wood surface through voids in the paint (Figure 8).

The results clearly show that for both alkyd and acrylic latex paints. sulfur dioxide and/or sulfurous acid readily diffuse to the wood surface. The sulfur compounds accumulate or react with wood at the paint/wood interface of an intact paint system: sulfuric acid does not. It is likely that SO_2/HSO_3^- reacts with the wood at the paint/wood interface. Given the three major constituents of wood—cellulose. hemicellulose. and lignin—it is most likely that the reaction of SO_2 with wood takes place via a substitution at the a-carbon of the phenylpropane unit typical of that found with sulfite pulping (*Figure* 9).[64,65]

The major effect of the SO_2 reaction at the wood/paint interface is probably degradation of lignin: however. small amounts of both cellulose and hemicellulose degradation products also have been recovered from western redcedar soaked in dilute H_2SO_3 or $H2SO_4$.[25] Similar amounts were formed with both acids. but the degradation of the wood was about 40% faster for H_2SO_3 than for H_2SO_4 at pH 2.0. This more rapid degradation by H_2SO_3 was probably caused by the reaction with lignin. The celluloses are more resistant to reaction with H_2SO_4.

Although Raczkowski.[21] Evans and Banks,[22] and Williams[25,26] have shown that H_2SO_3 degrades wood at normal temperatures and low concentrations and evidence exists for this chemical reaction at the paint/wood interface. there is no evidence for a loss of paint adhesion associated with this chemical reaction. With SO_2/HSO_3^-. there may be some effect at the paint/wood interface. but it cannot be quantified. All that can be said with certainty is that. in those areas with high SO_2 emissions. painted wood is susceptible to some added degradation at the paint/wood interface.

The reactions of other acids at the paint/substrate interface are not well established. Several studies on the diffusion of H_2SO_4 through paint have shown that an intact paint coating is impervious to H_2SO_4. Effects of sulfuric acid on painted wood are limited to the paint. and any interface effect is unlikely unless the paint develops cracks or the film integrity is breached. If the coating develops cracks or has voids, some degradation of wood may be possible if the pH is below 3.5. Acidic deposition offers a potential for decreased adhesion. but no effect has been proven.

Table 4—Sulfur Dioxide Permeability of Polymer Film[54]

Polymer Film	Temperature (°C)	Thickness (mm)	Permeability x 10^9 ml (STP) mm / cm^2 sec cm hg
Polyethylene low density	25	230	20.9
high density	25	—	5.68
Polyamide (Nylon 11)	25	61.4	6.58
	25	41	2.16
Polycarbonate (Lexon)	25	131	22.4
	25	25	21.0
Vinylidene chloride-vinyl chloride copolymer	25	—	0.201
Poly(ethylene terephthalate)	22	—	5.27
	25	13	0.201
Poly(methyl methacrylate)	22	—	0.131
Poly(vinyl chloride) (rigid)	25	145	0.116
Teflon	25	—	4.2
Polystryene	25	38	22.0
Cellulose (cellophane)	22	—	52.7
Cellulose nitrate	25	—	176.0
Vulcanized rubber	22	—	1450.0
Silicone rubber	22	—	11800.0

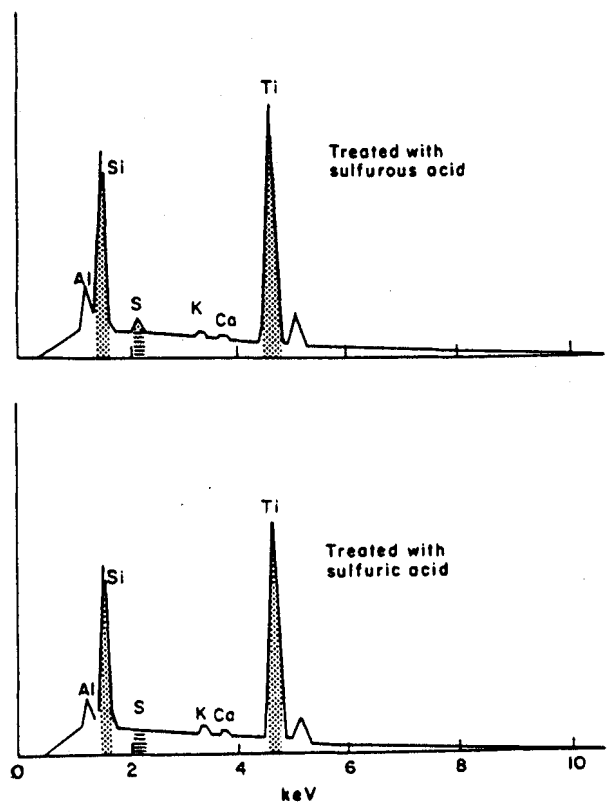

Figure 8—EDS of the paint/wood interface of western redcedar painted with an alkyd primer and topcoat: Top—treated with sulfurous acid. Bottom—treated with sulfuric acid[62]

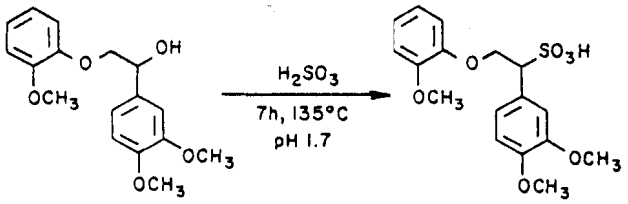

Figure 9—Reaction of SO_2 with lignin[64,65] (courtesy of S. Ralph)

Limiting the acid concentration to that typically found in acidic deposition may not take into account other factors. For example. if acid is absorbed by wood. it is unknown whether the pH of this acid decreases during periods of drying. If the acid is concentrated by the drying of the wood. it is possible that these stronger acids could contribute to hydrolysis of the celluloses: however. this has not been reported. It appears that even if low pH contributed to more rapid degradation in these water-induced failures. the problem would not exist where there weren't already a serious water problem.

Paint Coating

BINDER: The binder in paint is a general term for the polymeric material that forms the paint film either by evaporation of a solvent from a polymer solution or of a carrier from a dispersion or by polymerization of monomers. For film formation by polymerization. drying occurs as the solvent evaporates and polymerization begins. As the polymerization continues. crosslinking of the chains occurs to yield a cured film. The binder acts to bind pigment particles together and to the substrate.

Holbrow's[66] evaluation of oil and oil-alkyd paints and varnishes focused primarily upon the drying of binders and was based on laboratory studies using SO_2, The SO_2 concentrations ranged from 1 to 2 ppm, typical of those measured in Manchester. England, to concentrations in excess of 10,000 ppm. At concentrations of 1-2 ppm, the drying time of linseed. tung. and bodied dehydrated castor oil increased 50-100%. At 7-10 ppm, drying was further retarded. Chemical analysis of the dried paint films revealed that the SO_2 interfered with the autooxidation of the film by reducing the hydroperoxide. At high SO_2 concentrations. drying was completely inhibited, When oil-based paints and varnishes were placed over a solution of 0.2% SO_2 (approximately 16,000 ppm in the atmosphere). the paints and varnishes did not dry: however. when the paints were cured for a few days prior to exposure. these high concentrations of SO_2 seemed to have had no effect.

Exposure of dry but not fully cured films to SO_2 affected the gloss retention of the films, particularly if moisture condensed on the films. Several paints — long-oil pentaerythritol alkyd. linseed stand oil phenolic varnish. long-oil glycerol alkyd. linseed stand oil copal ester varnish. and linseed stand oil — were dried for 24 hours, cooled. placed above a 1.2% sulfurous acid solution for 15 minutes, and exposed to accelerated weathering for seven days. The pentaerythritol alkyd was hardly affected. but the gloss of the linseed stand oil copal ester varnish dropped more than 20% compared to controls. The gloss of the phenolic varnish and the glycerol alkyd dropped about 50%. The greatest effect occurred within the first day or two of cure and the effect was more pronounced under moisture-condensing conditions. The SO_2 exposure during the early stages of oil cure rendered the films moisture-sensitive and they wrinkled under further exposure to moist conditions. All films retained more than 80% gloss if allowed to cure for seven days before exposure. Both warmth and moisture in the weathering chamber were necessary to cause the SO_2-induced loss in gloss.

Many of the paints studied by Holbrow have been replaced by newer formulations and there is no documentation of drying problems with these finishes. In addition. latex paints have replaced alkyds for many architectural uses on wood in the United States. In Europe. alkyds are still popular. There have been no further reports on the curing of oil-based paints following Holbrow's[66] report. It is not known if new oil-based formulations show problems similar to those Holbrow reported in curing of the binder. It does not seem to be a problem at this time. Because latex paints form films by loss of water and concurrent coalescence of the latex particles, ambient SO_2 should not chemically affect their film formation.

Hendricks and Balik[67] studied the effects of SO_2 on free films of paint and the base latex polymer for one of the paints. The base latex polymer used in their research was a terpolymer comprised of approximately equimolecular amounts of vinyl chloride. vinyl acetate. and butyl acrylate and a small amount of methyl methacrylate. Two latex paints were formulated from this polymer: one contained $CaCO_3$ and the other did not. An alkyd gloss paint was also included in their studies. The paint formulations were typical for a mid-priced house paint.

Hendricks and Balik[67] reported the solubility of SO_2 in these paint films and films of the base polymer as bring linear with pressure (Henry's Law behavior) over the range of 50-700 torr with the maximum pick-up for the base polymer of 14% (by weight) (*Figure* 10). The pick-up for the paint film was the same if normalized for the amount of pigment.

Table 5—Solubilty, Diffusion Coefficients, and Permeability of Paint with and without $CaCO_3$ and the Base Polymer[67]

Sample	Solubility (mg SO_2/g sample-torr)	Diffusion Coef. $\times 10^9$ (cm^2/sec)	Permeability $\times 10^9$ [cm3SO_2 (STP) cm^2 / cm^3 sample-cm Hg-sec]
Base Polymer	0.189	14.2	12.1
Latex with $CaCO_3$	0.0622	10.6	4.88
Latex without $CaCO_3$	0.0681	10.9	5.52

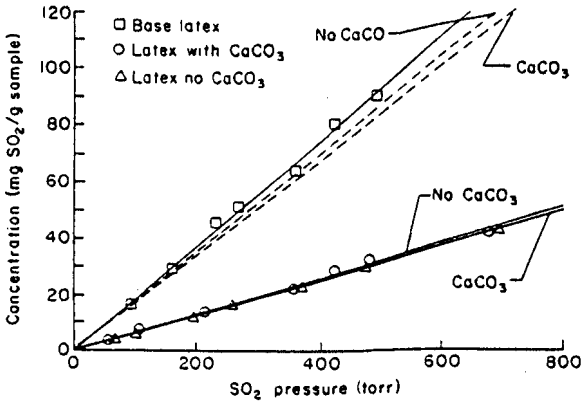

Figure 10—Sorption isotherms of SO_2 in paint specimens at 28°C[67]

They concluded that the pigment did not affect solubility. They also determined diffusion as a function of pressure and extrapolated to zero to obtain the diffusion coefficient (Figure 11). The solubilities. diffusion coefficients. and permeabilities calculated from these measurements were reported (Table 5). The effect of pigment decreases the diffusion coefficient: fillers such as $CaCO_3$ caused the same changes as pigments. As expected, the crosslinked alkyd had a lower value.

Both the base latex polymer and paint made from this polymer desorbed all the SO_2 when a vacuum was applied to the film; the alkyd paint retained approximately 15-20% of the SO_2 absorbed, even after several days at <1 mtorr. Xu and Balik[68-69] concluded that the SO_2 had reacted with the polymer in the paint. They also determined quantitatively the rate of $CaCO_3$ removal from the paints exposed to pH 2, 3, or 4 sulfurous acid or to distilled water (weak carbonic acid, pH 5.6) (*Figure* 12). They reported the complete dissolution of all $CaCO_3$ with all acids and with distilled water. The rates of dissolution were dependent on acid strength. The nominal mass loss was 27%; the reaction was diffusion-controlled at pH 2 and dependent on the acid concentration at pH 3 and above. IR analysis confirmed the loss of $CaCO_3$. The paint without $CaCO_3$ had less than 7% mass loss and showed no change in the IR spectra even after one month's immersion in pH 2 sulfurous acid. They reported similar results with 10 other acids at pH 3.

On the basis of a series of experiments. in which the IR peak intensities were monitored during the exposure of paint to sulfurous acid. Xu and Balik[69] reported that the latex film collapsed as the $CaCO_3$ was removed and the film thickness decreased by 16%. The sorption-desorption experiments were expanded to include thin strips of uncoated wood. Whereas the free films of latex paint lost all SO_2 in the desorption mode. the wood retained 18% (by weight) of the absorbed SO_2.

Fornes, Gilbert, and co-workers determined the effects of SO_2 (both dry and mixed with water vapor) and UV light exposure on free films of paint and base latex.[70,71] The polymer in these films was the same as that used by Hendricks and Balik.[67] They determined the change in gel fraction and the molecular weight distribution of the soluble fraction as the films degraded during exposure. Contact angles were measured and changes in surface morphology were investigated. Dynamic mechanical analysis (DMA) was used to determine the dynamic elastic modulus and T_g. Chemical changes in the gel and solution fractions and surface changes were monitored using ^{13}C nuclear magnetic resonance (NMR). Fourier transform infrared (FTIR) spectroscopy, x-ray photoelectron spectroscopy (XPS), and elemental analysis.

Patil et al.[70] reported that certain combinations of SO_2/H_2O/UV light had detrimental effects on the polymer in paint films (*Table* 6). In these exposures. high levels of SO_2 were used to evaluate various techniques for measuring film degradation. The base polymer had a multi-modal molecular weight distribution and an initial gel content of approximately 22%. After a 24-hour exposure to SO_2 and UV light (under both wet and dry conditions), the gel content increased to about 60-65% and the viscosity of the soluble fraction decreased. They interpreted this as an indication of chain scission (decrease in viscosity) and crosslinking (increase in gel percent) but that the mechanical properties were dominated by a crosslinking. DMA showed a dramatic increase in T_g. Sulfur dioxide alone caused essentially no change under dry conditions. After 96 hours, the contact angle was 0° and the T_g increased from 23°C to 87°C. The viscosity also decreased. Under wet conditions, chain scission was even greater: the viscosity dropped from 1.0 to 0.08 dl/g and the crosslinking was less. They reported that DMA clearly showed increased T_g, with the modulus remaining high, and they interpreted this as significant crosslinking.

On the basis of the ^{13}C NMR results, Sankar et al.[71] reported that the polymer exposed to SO_2/UV light had a decrease in carbonyl signal associated with the acrylate group. whereas UV light alone did not. It was also reported that HCl and acetic acid were formed during exposure by the decomposition of polyvinyl chloride and polyvinyl acetate and the formation of unsaturated carbon-carbon bonds. The formation of sulfur-carbon bonds was reported. They also suggested that slow attack of the butyl acrylate group occurs. They reported a synergistic effect on polymer degradation between UV light and SO_2 under both wet and dry conditions.

The degradation reactions of the binder. however. have been proven for high concentrations of SO_2/HSO_3^-. They are more rapid when moisture is present and are synergistic with UV light. Degradation includes both crosslinking and chain

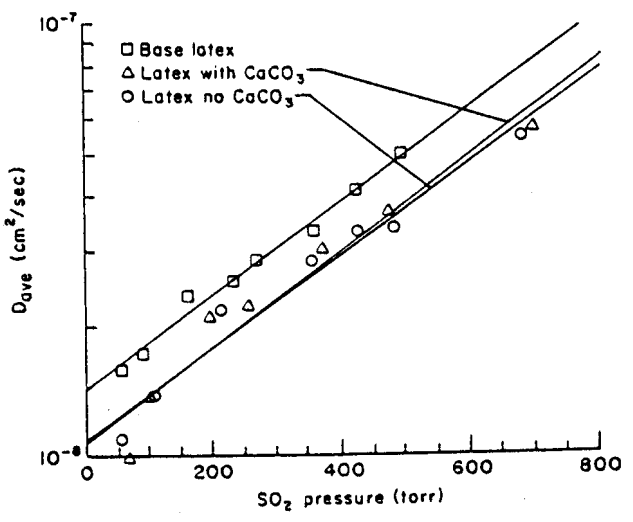

Figure 11—Diffusivities of SO_2 in paint specimens at 28°C[67]

Table 6—Properties of the Base Polymer of a Latex Paint upon Exposure to SO_2/H_2O/UV Light Combinations[70]

Exposure Conditions					Properties			
Time (hrs)	UV Light (350 nm)	Air	SO_2	H_2O	[n] (dl/g)	Gel (%)	Contact angle (deg)	T_g (°C)
0				-	1.00	22	77	23
24	+	+	-	-	0.98	78	77	15
48	+	+	-	-	0.83	29	78	16
96	+	+	-	-	0.55	36	78	16
48	-	-	+	-	1.00	22	74	25
96	-	-	+	-	1.00	21	76	23
24	+	-	+	-	0.15	65	45	—
48	+	-	+	-	0.13	64	50	78
96	+	-	+	-	0.12	65	—[a]	87
24	+	+	-	+	1.00	19	78	—
48	+	+	-	+	1.00	21	72	—
96	+	+	-	+	0.90	23	83	—
21	+	-	+	+	0.19	61	45	—
48	+	-	+	+	0.05	60	40	49
96	+	-	+	+	.08	58	—[a]	60

(a) Drop spread immediately

scission. However, no concentration-degradation relationship has been established at high concentrations. nor has degradation at low concentrations been established. It is unclear whether the degradation of paint coatings by SO_2 also occurs at levels typical of those found in the environment.

There are only a few published reports on the effect of acids other than SO_2/H_2SO_3 on the binder in paint coatings. The only documented case of finish degradation with dilute H_2SO_4 (pH 2) was the report by Deppe and Schmidt[27] on the degradation of melamine-formaldehyde coatings on particleboard: there was no quantification of the degradation. In other studies of acid effects. the acid strengths were considerably stronger than found in the environment. Other than as reported by Deppe and Schmidt,[27] no deterioration of clear coatings was noted at pHs typical of those found in the environment.

Strong acids and high concentrations of O_3 have been used to accelerate the degradation of paint coatings. Tsingarelli and Orzhakhovskii[72] reported the effects of formic and acetic acid vapors. NO_2, and nitric. formic. and acetic acid solutions on the durability of unpigmented coatings as measured by anticorrosive protection or loss of electrical insulating capacity. Gutfreund[73] used O_3 to deteriorate paint in accelerated testing and correlated the results with outdoor testing.

PIGMENTS, EXTENDERS, AND DRIERS: Pigments, extenders, and driers comprise the solids in the paint film held in place by the binder. The pigments give paint its opacity and may be colored or uncolored. As with pigments. extenders are generally inorganic in nature and are used to help control rheology and increase the solids content of the paint. Driers catalyze the curing of polymers and are often organometallic compounds such as cobalt naphthenate.

Ward[74] investigated soiling of exterior house paint for a variety of paint formulations with and without lead pigments and driers. The lead pigments and driers caused blackening of paints in industrial areas. Hoffmann[75] developed a method for maintaining extremely low concentrations of H_2S for laboratory studies and later reported the effects of these low concentrations on paint.[76] In investigating the sulfide staining of flat and gloss alkyd paints. he found that staining resulted from the reaction of H_2S with small amounts of lead naphthenate driers in the paint. Staining did not occur in paints containing cobalt naphthenate driers. Watson." however, reported that H_2S could cause sulfide staining of paints containing cobalt driers.

Sulfide staining can also occur if paint containing phenylmercury mildewcides is exposed to H_2S.[78] Wohlers and Feldstein[79] reported that H_2S concentrations above 0.05 ppm for several hours under optimum conditions could darken

Table 7—Paint Formulations Used by Spence et al.[61]

	Alykd		Latex	
Ingredients	Subtotal (%)	Components (%)	Subtotal (%)	Components (%)
Pigments	35.3		36	
Titanium dioxide		22.6		23.8
Magnesium silicate		7.1		—
Silica		3.I		11.0
Tetrachloromethyl sulfonyl pyridine		—		0.8
Mildew-resistant agent NTC		1.2		—
Silicate		1.0		0.4
Vehicle	64.7		64	
Polyester resin		—		4.4
Acrylic		—		14.5
Water		—		45.1
Raw linseed oil		7.6		—
Soya alkyd resin		24.4		—
Mineral spirits and driers		32.7		—

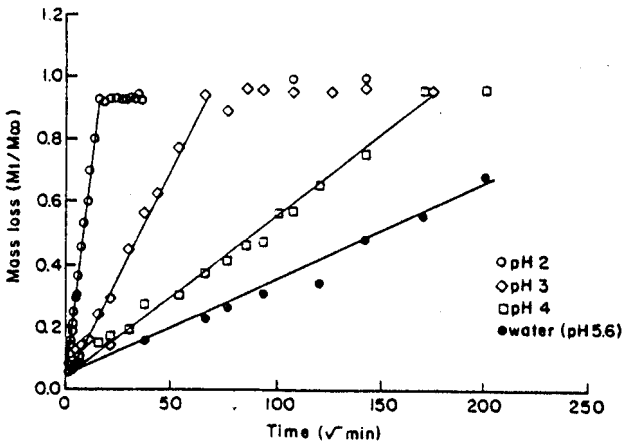

Figure 12—Mass loss of $CaCO_3$ from latex paint specimens exposed to sulfurous acid[68]

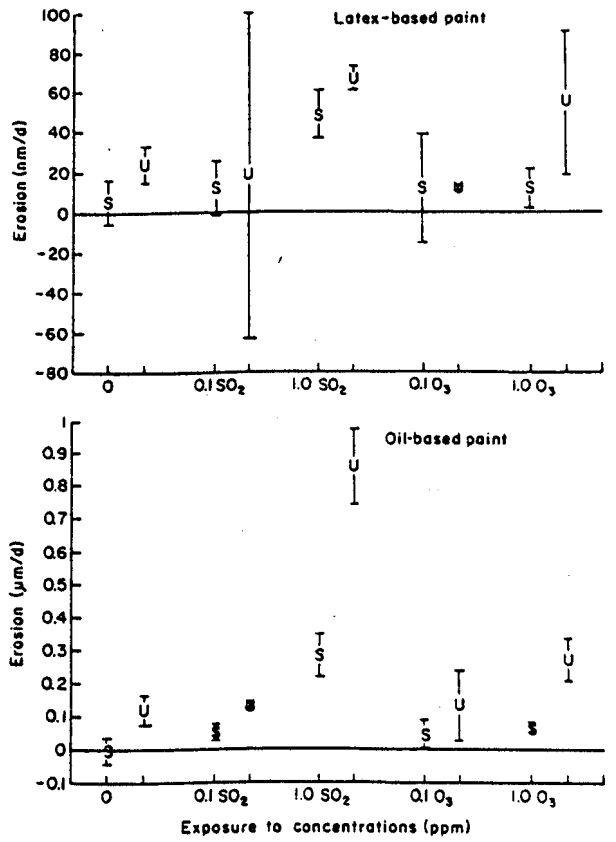

Figure 13—Erosion of shaded, s, and unshaded, u, panels painted with latex or oil-based paints exposed to SO_2 or O_3 in a laboratory chamber.[86] The bars represent the 95% confidence limits for these slopes

paint. When the darkening was not severe. the original color returned within several days after the H_2S had abated as a result of air oxidation. In cases of severe darkening, as much as six months was required for paint to revert to its original color.

The staining intensity of lead and mercury sulfides depends on the distribution of the metal salts in the paint film and the H_2S concentration in the atmosphere.[80] Macdonald[81] reported similar results. Merz[82] reviewed building materials at risk to environmental pollution and cautioned against using red lead. white lead. chrome yellow, chrome orange. or chrome green in exterior paints used in environments having high H_2S pollution. The degradation of paint by H_2S is a local effect. and it affects only a few pigments. In areas where H_2S is common. care in selecting paint should eliminate potential problems.

Holbrow[66] reported that some pigments could be discolored by SO_2. Paints containing Brunswick green were sensitive to 0.2 ppm concentrations of SO_2 for the first few hours after painting and to higher concentrations (200 ppm) for several days. The color change was caused by the bleaching of the lead chromate ($PbCrO_4$). Several other pigments were sensitive to sulfur compounds. Boxall and von Fraunhofer[83] found that red lead (PbO_2 2PbO) darkened on exposure to sulfur compounds: basic lead sulfate ($2PbSO_4$ PbO) discolored: and ultramarine blue ($3Na_2O_3$ Al_2O_3 $6SiO_2$ $2Na_2S$) rapidly decomposed when exposed to dilute acid.

Torlaschi et al.[84] studied the effect of SO_2 on anatase and rutile titanium dioxide (TiO_2), zinc oxide (ZnO), iron oxide-yellow (FeO OH). iron oxide-red (Fe_2O_3), chrome oxide (Cr_2O_3), cadmium yellow (CdS), cadmium red (CdS(Se)), lithopone (ZnS + $BaSO_4$), ultramarine ($(Na,Ca)_8(Al_6Si_6O_{24})S$), Prussian blue (KFe $Fe(CN)_6$ xH_2O), chrome yellow ($Pb(Cr,S)O_4$), molybdate red ($Pb(Cr,S,Mo)O_4$), and zinc chromate ($K_2Zn_3(CrO_4)_4$ $Zn(OH)_2$ $2H_2O$) pigments. At 0.67% SO_2 in air, zinc oxide and zinc chromate reacted to form water-soluble salts. which leached from the film. Chrome yellow and molybdate red were reduced to chromium sulfate. The degradation was less if the formulation also included TiO_2 pigment. The other pigments were stable at this concentration. but the authors reported that; at higher concentrations. some of the pigments exhibited incipient degradation. particularly if drops of condensed acid were allowed to evaporate. Merz[82] identified several pigments sensitive to sulfuric acid·(white lead, red lead, zinc oxide, zinc white, zinc yellow, zinc green, lithopone, ultramarine blue, and Schweinfurt green). He also cautioned against using $CaCO_3$ extenders.

The discoloration of pigments occurs in limited areas and is of a temporary nature and. even if data were available. it would not be appropriate to use it as a measure of paint degradation. The phenomenon merits mention. however. because of the relative aesthetic value of pigments in paint coatings exposed to the environment. Painted wood is often refinished because of discoloration. particularly surface deposits such as mildew, but it is not possible to assess the magnitude of this problem. In addition, discoloration is often accompanied by other forms of degradation and the interactions among these degradation modes is also difficult to assess.

Many paint components sensitive to color change are no longer extensively used in house paint because of environmental concerns. This is particularly true for lead-containing pigments and driers.

Alkaline components of paints. which serve as extenders and colorants and affect flow characteristics of paint, can neutralize acid, $CaCO_3$ and ZnO are alkaline components of many paints. Acids and their precursors such as SO_2, at concentrations typical of those found in the environment.

Table 8—Accumulated Run-off Concentrations for Laboratory Chamber Experiments[60]

Sample	Condition	Vol. (ml)[a]	Concentration (nmoles/cm²) of H^+	Ca^{++}	Zn^{++}	$HCOO^-$	NO_3^-	HSO_3^-	SO_4^{--}	HCHO
Latex	Dew	1.89	4.6	2.4	74.9	47.5	108.3	12.7	32.5	53.7
	Dry	0.00	18.2	2.6	31.6	2.3	129.8	0.0	4.8	—
Latex-c[b]	Dew	2.06	13.8	357.0	59.6	23.6	161.1	368.6	86.8	533.6
	Dry	0.00	3.0	255.5	30.8	7.0	497.8	0.0	7.3	—
Oil	Dew	1.57	144.4	3.2	37.2	55.2	120.1	0.0	96.8	164.9
	Dry	0.00	4.9	0.8	9.4	2.7	22.6	0.0	4.4	—
Oil-c,z[c]	Dew	4.26	38.6	109.6	171.2	105.7	306.6	13.4	100.7	259.7
	Dry	0.00	4.3	40.6	50.0	4.0	147.2	0.0	5.2	—
G-steel[d]	Dew	5.99	21.2	1.7	2277.6	704.I	517.2	2235.6	692.0	3668.I
	Dry	0.00	2.I	0.9	425.3	7.7	764.1	0.0	46.1	—

(a) Total volume of dew collected.
(b) E = Contains $CaCO_3$
(c) z = contains ZnO.
(d) Galvanized steel.

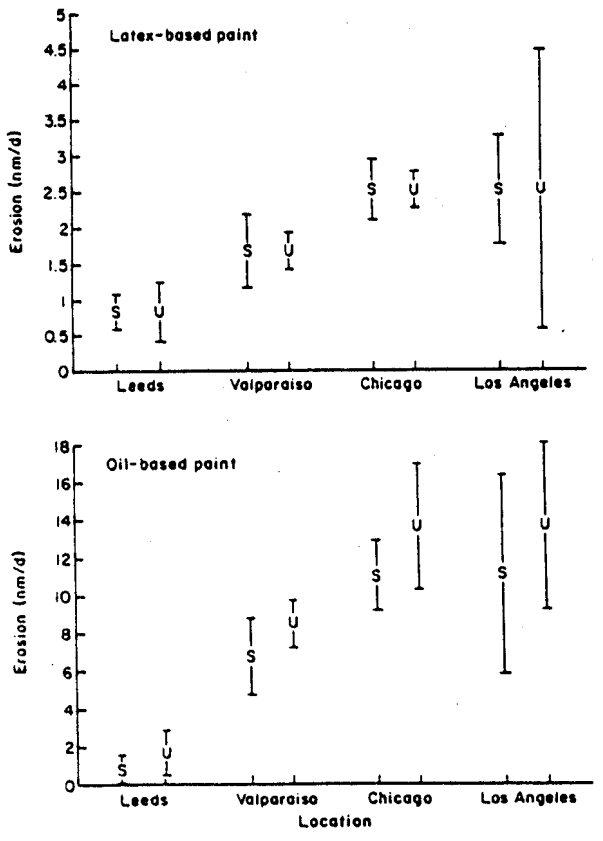

Figure 14—Erosion of shaded, s, and unshaded. u. panels painted with latex or oil-based paints exposed to outdoor weathering at four sites." The bars represent the 95% confidence limits for these slopes

can react with these components. The rate of dissolution is a function of acid strength. and laboratory studies have shown that dissolution occurs with dilute mineral acids, such as sulfuric. as well as with weak acids. such as carbonic and sulfurous acid.[69] At pHs typical of those found in the environment. the loss of $CaCO_3$ can be measured gravimetrically. In studies using gaseous SO_2, degradations occurred more rapidly during periods when the surface was wet. They showed that binder morphology changed as $CaCO_3$ dissolved. and it seems that paint binder has some effect on the dissolution rate of alkaline components exposed to sulfurous acid. It is certain that paints having these components will lose weight when exposed to acid but the phenomenon is complicated by other factors.

Spence and collaborators[85,86] exposed both oil-based and latex house paints to laboratory and field tests (*Table* 7). The oil-based paint contained calcium carbonate and magnesium silicate extender pigments whereas the acrylic latex-based paint contained only aluminum/sodium/potassium silicate extenders. Although these finishes were formulated for use on wood, they were applied to stainless steel substrates because the objective of the study was to evaluate film-surface deterioration, not the film-substrate interface. All specimens were exposed to SO_2 and O_3, and some to UV light (unshaded) while others were shaded. Exposure to 0.1 ppm SO_2 had no effect (*Figure* 13). The rates for the latex coatings increased to about 60 nm/day when exposed to 1.0 ppm SO_2. The difference between the shaded and unshaded remained about the same. The greatest increase in erosion rate (about 0.3 µm/day and 0.9 µm/day for shaded and unshaded. respectively) occurred with oil-based house paint having $CaCO_3$ extender pigments exposed to 1.0 ppm SO_2.

In most cases the effect of light and SO_2 appeared consistent except for the oil-based house paint. In that case, the erosion of the unshaded specimens was more than twice as fast as the erosion of the shaded specimens. The data indicate a synergism between these two effects with the oil-based house paint. but not with the latex house paint. It should be noted, however, that the oil-based paint contained $CaCO_3$ whereas the latex paint did not and oil-based paints are more susceptible to UV degradation than acrylic latex paints. The

synergism may be an isolated effect caused by combining a highly UV-sensitive binder with $CaCO_3$ extender pigments. The surface erosion was confirmed using attenuated total reflectance-infrared (ATR-IR) spectroscopy and scanning electron microscopy.

The results with O_3 were less clear although the oil-based paint was more severely affected than the latex paint. The degradation with O_3 appeared to have been primarily a photochemical degradation. The relative difference between the control and the specimens exposed to O_3 was the same at both concentrations under shaded conditions but increased when unshaded (*Figure* 13).

The data from field exposures[86] showed significant differences in erosion of paint coatings for specimens from a clean site and three dirty sites (*Figure* 14). It was not possible to establish a cause and effect relationship because no pollutant concentration data were obtained for these sites. The ATR-IR and SEM analyses were similar to the results from the chamber study and showed greater binder degradation for the alkyd. The highest erosion rate occurred for coatings with acid-sensitive extender pigments (mainly $CaCO_3$) in areas of high pollution.

In a later study,[61] a controlled environment chamber was used to identify direct and possible synergistic effects of SO_2, NO_2, and O_3 on an oil-based house paint and an acrylic latex house paint (*Figure* 15). The paints were applied to aluminum panels and exposed to all combinations of low- and high-concentration conditions: 0.03 or 0.5 ppm SO_2, 0.05 or 0.5 ppm NO_2, 0.08 or 0.5 ppm O_3. and 50 or 90% relative humidity. The surface erosion as determined by mass loss 'was measured at 250, 500, and 1000 hours of accelerated weathering (Figure 15). Variables in chamber conditions included temperature. relative humidity, pollutants (SO_2, NO_2, and O_3), dew, and light. The chamber was constructed such that the paint surfaces were subjected to moisture-condensing conditions. The results of the study, based only on mass loss, indicated that oil-based house paints having magnesium silicate extenders were affected by SO_2 and relative humidity. This can easily be seen by plotting the data in decreasing order of erosion and arbitrarily separating the data into three groups (Figure 15). The highest erosion generally occurred on specimens exposed to high SO_2 (S) and high relative humidity (H). The lowest erosion rate occurred on specimens exposed to low SO_2 (s) and low relative humidity (h). The high and low levels of nitrogen dioxide (N,n) and ozone (O,o) appeared to have no effect.

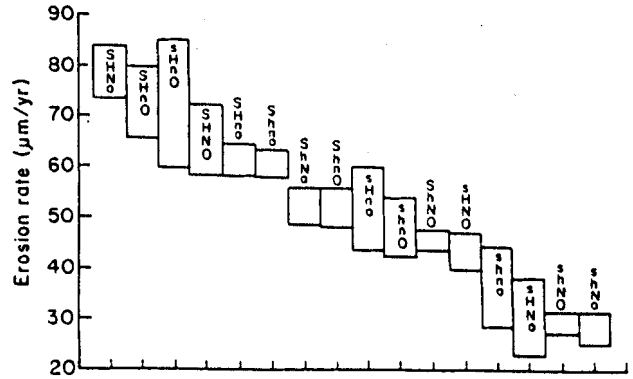

Figure 15—Effect of RH, SO_2, NO_2, and O_3 on the erosion rate of oil-based paint coating. R and r, S and s, N and n, and 0 and o designate high and low concentrations of moisture (RH), SO_2, NO_2, and O_3, respectively. From data by Spence et al[61]

Table 9—Average ion Concentrations of Run-Off from Panels Exposed at Raleigh, NC or Steubenville, OH [60]

Sample	Condition	Concentration (nmoles/cm²) of H^+	Na^+	K^+	Ca^{++}	Zn^{++}	$HCOO^-$	Cl^-	NO_3^-	SO_4^{--}
					RALEIGH, NC					
Latex	DI	0.28	2.09	1.14	0.59	—	0.24	0.35	1.22	1.22
	Ambient	4.18	3.02	1.78	2.12	—	0.98	7.29	5.73	5.17
Latex-c[4]	DI	0.13	1.67	0.74	4.25	—	0.29	4.36	1.80	1.46
	Ambient	1.29	3.36	2.11	11.75	—	0.9'4	10.17	6.91	6.45
Oil	DI	0.49	0.44	0.17	0.63	—	0.06	1.0	10.79	0.59
	Ambient	4.16	0.85	0.93	0.83	—	0.46	1.6	82.22	2.70
Oil-c,z[b]	DI	0.88	0.35	0.87	1.19	0.64	1.42	1.2	31.04	0.52
	Ambient	1.32	0.69	0.34	3.63	1.98	0.44	2.7	04.19	3.37
					STEUBENVILLE, OH					
Latex	DI	0.10	3.43	0.73	5.18	—	1.41	6.38	1.06	4.22
	Ambient	5.40	0.78	0.90	15.15	—	0.07	6.67	11.02	19.15
Latex-c[a]	DI	0.08	1.23	0.85	6.94	—	1.17	6.36	1.22	4.73
	Ambient	1.91	0.85	1.03	23.14	—	0.07	8.50	13.01	24.31
Oil	DI	0.25	5.11	0.68	3.36	—	1.78	7.42	0.80	3.34
	Ambient	3.50	0.60	0.69	13.69	—	0.07	4.55	9.60	15.38
Oil-c,z[b]	DI	0.14	2.42	0.33	3.24	0.99	1.17	1.36	0.76	2.90
	Ambient	1.59	0.87	0.76	19.96	3.47	0.09	5.47	11.46	20.50

(a) c = contains $CaCO_3$.
(b) z = contains ZnO

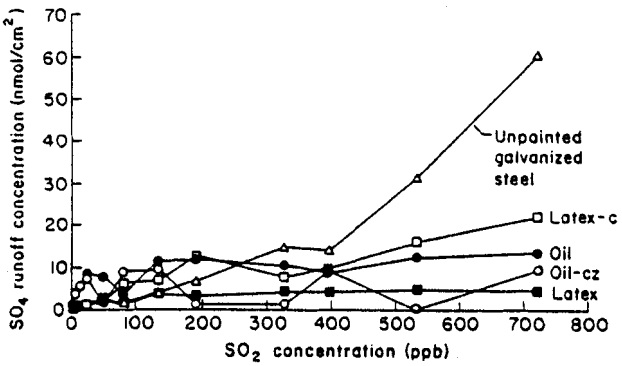

Figure 16—Sulfate ion runoff concentration as a function of SO_2[60]

In a more recent report. Haynie and Spence[87] evaluated two house paints that were exposed for up to 30 months at nine locations in the area of St. Louis, Missouri. At each of these locations. the ambient pollution levels and weather conditions were monitored. Measurements included SO_2, NO_2, and O_3 concentrations, sunlight, and time of wetness. The paints were formulated without $CaCO_3$, applied to stainless steel substrates. and placed both in northern and southern exposures at each site. After the 30-month exposure. the mass loss of the specimens was evaluated with respect to the various combinations of the environmental conditions. The only statistically significant result obtained was for exposure to NO_2 and time of wetness: NO_2, in combination with moisture. caused a gain in mass. Results for SO_2 were not significant.

The results from these experiments should be viewed with some caution because of possible complications in using mass-loss measurements to calculate film erosion. Addition- or condensation-type reactions of pollutants with paint components, diffusion of pollutants into the film. outgassing of the paint. and accumulation of dirt (particularly in the field exposures) can all adversely affect the mass-loss measurements.

With these concerns in mind. the evaluation of erosion by mass loss in paints that are resistant to erosion is likely to be lost in experimental error. whereas paints containing $CaCO_3$ or silicates show measurable losses. These losses completely overshadow the other degradative processes that may be occurring in the paint during the exposure. It is not surprising. therefore. that significant effects were found. in the preceding experiments. only for paint containing $CaCO_3$ or silicates. Evaluating the other effects requires an understanding of the process involved in the degradation and can only be achieved by other techniques including laboratory and field exposure experiments.

The laboratory studies did not take into account the different permeabilities of polymers and acids. the effects of UV light. or the dry deposition of other alkaline materials. Since the permeation of SO_2 in paint is high. alkaline components can readily react. In exposure to other acids that do not penetrate polymer films as well as SO_2, it is not clear how UV degradation of the polymer affects the results. It may be necessary for the polymer to undergo UV degradation to expose the pigment to the acid. UV degradation is further complicated by the unknown effects of low concentrations of acid. Either $CaCO_3$ reaction or photochemical degradation of the binder may be the rate-determining factor in the erosion of paint coatings. If the dissolution of $CaCO_3$ is slower than the photodegradation of the binder, then the loss of $CaCO_3$ commensurate with erosion should not be considered a function of the acid. Only those Factors that affect the rate-determining step for a particular failure mode should be considered for determining the accelerating effect. For example. if acidic deposition increased the rate of erosion of the surface but the paint failed by peeling. there is not a clear link between the acidic deposition and the damage function for this mode of failure.

Edney[60] and coworkers[88,89] reported the chemical composition of run-off from painted western redcedar panels coated with latex and alkyd paints formulated with and without $CaCO_3$. The panels were exposed outdoors at Raleigh, North Carolina (suburban), and Steubenville, Ohio (industrial) and were compared with painted galvanized steel panels exposed in a chamber. In the chamber study, painted galvanized steel panels were exposed to a complex gas mixture containing steady-state concentrations of 230 ppb 0_3, 180 ppb NO_x, 380 ppb HCHO. 7 ppb HNO_3, and SO_2. The SO_2 concentration was varied from 0 to 722 ppb for each of the exposures and the SO_4^{-2} concentration of the runoff was measured for the various SO_2 concentrations (*Figure* 16).

The run-off data from the chamber study (*Table* 8) showed that acidic gases such as SO_2 and HNO_3 dissolved the alkaline ($CaCO_3$ and ZnO) components in the paint. Those finishes high in $CaCO_3$ had ZnO and high Ca^{+2} and Zn^{+2} run-off. A substantial amount of zinc was leached from all painted galvanized steel, whereas the specimens painted on western redcedar exposed outdoors had no detectable zinc. unless the paint contained ZnO pigment. This substantiates the transparency of paint to SO_2 and shows that the substrate can be degraded. particularly under wet (dew) conditions.

Edney reported that leaching of ZnO (the mildewstat) might harm the paint, but he could not link the loss of $CaCO_3$ to a decrease in service life. He indicated that degradation of polymers would likely cause harm to film integrity but found no evidence for polymer degradation.

Higher bisulfite salt (HSO_3^-) concentrations were found in runoff samples collected from specimens containing alkaline components exposed under moist conditions. The SO_2 was absorbed into the water on the surface and reacted with the alkaline components. is forming bisulfite salts. In specimens with less accessible alkaline components. such as $CaCO_3$ in oil-based paint. the reaction was slower than with more accessible $CaCO_3$ in latex paint (*Table* 8). The acid concentrations confirm this reaction and were lower in the runoff from the specimens having high HSO_3^- concentration.

Edney[60] compared the calcium run-off from specimens exposed at Steubenville and Raleigh (*Table* 9). The difference for latex paint with and without $CaCO_3$ at Raleigh was about 9 nmole/cm^2 day (11.75 minus 2.12) and at Steubenville, about 9 nmole/cm^2 day (24.14 minus 15.150). For oil paint at Raleigh. the difference was about 3 nmole/cm^2 day (3.63 minus 0.83) and at Steubenville, about 6 nmole/cm^2 day (19.96 minus 13.69). From this data. it appears that the ambient conditions in Steubenville as compared with Raleigh have no effect on the amount of $CaCO_3$ leached from latex paint and only a little effect on oil paint. Soluble calcium salts were, for the most part, caused by calcium salt precipitation and not from dissolution of $CaCO_3$. The almost identical values

for the dry deposition (DI) support this conclusion, although the lower values are somewhat puzzling.

Surface Deposits

Surface deposits such as soiling and salt formation are most often problems in protected areas such as under eaves and soffits. The formation of water-soluble crystals of ammonium sulfate "blooming" on the surface of paint is an example of salt formation.

Ames and Gourley[90] investigated the formation of bloom on varnish prepared from pentaerythritol alkyd resins. They identified $(NH_4)_2SO_4$ as the compound responsible for the deposit but did not determine whether it was deposited as $(NH_4)_2SO_4$ or formed in place by the reaction of SO_2 with NH_3 under moist conditions. Others who have also investigated bloom formation[66,91,92] have reported that it requires moisture and is dependent on the type of paint. The formation was more severe on the pentaerythritol alkyd than on glycerol alkyd. Hill[93] reported that crystalline bloom could form on paint through a thermal precipitation mechanism. He found that moisture was unnecessary for bloom formation and reported $(NH_4)_2SO_4$ particle sizes of less than 2 µm diameter deposited under dry conditions. Giese[94] reported that bloom on latex house paint occurred mainly on protected areas of structures and was caused mainly by SO_2. The problem was worse for paint containing $CaCO_3$.

Strauch et al.[95] reviewed bloom formation on paint coatings and summarized the data to show six causes for this effect. Deposits of atmospheric pollutants and acid-catalyzed degradation of the paint components were two of the causes; others were extraction of soluble components of the film such as wetting and dispersing agents. diffusion of pretreatments through the paint, diffusion of soluble salts from the substrate. and combinations of these five causes. In their investigations to verify these causes, they exposed emulsion paints to acid in the 4-4.5 pH range for two years. Paints with and without $CaCO_3$ showed no bloom formation. They did not rule out possible degradation at higher pHs over longer time but described the degradation as chalking. They did verify the formation of sulfates from atmospheric pollution under moist conditions. On wood substrates. pretreatments with alkaline stripper caused bloom formation if the stripper was not neutralized and thoroughly washed from the surface. The residue consisted of sodium and calcium carbonates.

Schurr and Van Loo[96] and Campbell et al.[86] investigated the cause of intercoat peeling of house paints on under-eaves and found that. under certain weather conditions common to the Great Lakes area of the United States. paints containing zinc salts or barium metaborate caused the formation of a residue on the surface of paint. When the eaves subsequently were repainted. this residue caused catastrophic intercoat failure. The residue was shown to contain sulfates. but no mechanism was proposed for the formation of these sulfates. They could have formed by direct dry deposition of sulfate particles or by the reaction of SO_2 or sulfuric acid aerosols with the paint. They reported that the problem could have been eliminated by washing the under-eave area prior to repainting.

Holbrow[66,97] reported that soiling of paint by particulates — including sulfates and chlorides of iron. calcium. and zinc — in highly industrial areas led to longer service life. He indicated that the longer life was probably caused by decreased UV radiation of the paint film and the neutralizing of acid by alkaline deposits.

Karyakina and Viktorova[98] developed a method for evaluating the susceptibility of paint to dirt pick-up: The difference in luminosity before and after exposure yielded a value for dirt retention. Raaschou-Nielsen et al.[99] reported that dirt retention by painted surfaces can be a serious problem in industrial areas and they investigated the factors affecting dirt retention. They found that dirt retention increased with increased tack and decreased T_g. They also developed an accelerated test method.

Combined Effects

The only quantitative cause and effect information is based on the research by Spence and coworkers and is contained in a review by Haynie.[100] The incremental effects include only increased erosion of the paint caused by the dissolution of $CaCO_3$ or silicate-containing extender pigments. Haynie attempted to establish the decrease in durability of paint exposed to SO_2 as related to the increase in painting frequency necessitated by increased erosion. He developed an equation on the basis of the erosion data obtained from painted specimens exposed to SO_2 and moisture. The model predicts the increase in erosion over the estimated typical erosion at a pH of 5.2 and an SO_2 concentration of 0 (representative of a clean environment).

Haynie's model takes into consideration SO_2 concentration and rain acidity. but it applies only to erosion of the paint coating and does not consider some of the more serious modes of paint degradation such as cracking and loss of adhesion. "Just based on the variability of the available data. the magnitude of the error in any economic cost estimate will be the same as the estimate. This means the cost could be zero or twice as much as the estimate. Assumptions in economic analysis increase this error."[100] With the present state of knowledge. many research gaps exist.

CONCLUSIONS

The study of acidic deposition effects on the service life of painted wood is complicated by several factors. These include:

- a wide range of types of substrates and finishes:
- variability of these materials:
- variability in weathering conditions from year to year and place to place: and
- inconsistencies in the results between outdoor weathering and "accelerated" weathering.

Synergism and other interactions among these factors further complicate these studies. A comprehensive model that encompasses all the modes of degradation of painted wood and includes the incremental effects of acidic deposition on these modes cannot be determined at this time. In general. it has not yet been possible to quantify the effects of acidic deposition for isolated modes of degradation because these effects are often obscured by the variability of painted wood. Some effects have been identified.

Effects of Acidic Deposition

The reaction of acid with the alkaline components of paint is the only well documented degradation mechanism that could affect a large amount of paint in service. It would be prudent to avoid using these components in formulating paints for use in areas of high pollution and/or acidic deposition. On the basis of the run-off data from Steubenville, Ohio. the dissolution of $CaCO_3$ is less than expected because of the neutralizing effect of alkaline dry deposition. The values from clean sites might better represent the actual risk over wide geographic areas.

Sulfur dioxide has the potential to affect the durability of coatings on wood. although causes and effects have not been determined for any of the paint components at risk. In addition, SO_2 can have little effect over large geographic areas because it is converted to sulfuric acid. Only the alkaline components have been proven to be at risk to low acid concentrations typical of those found in acidic deposition. and even those effects are complicated by a combination of factors.

In the absence of obvious catastrophic failure. the service life or durability of finished wood is usually determined by compiling several performance criteria such as gloss, cracking. peeling. etc.. to obtain an overall evaluation. In addressing the question of the effect of acidic deposition on painted wood. even more factors come into play. Compilation of the various results reviewed here into an overall performance criteria should also include the other major factors that contribute to paint system degradation.

Despite all the research into the degradation of finishes. cause and effect relationships are still not possible. To expect a single model to explain all wood finishes or even all paints is unrealistic. A more reasonable approach is to consider a type of finish—and substrate. if applicable—and attempt to quantify the most common degradation mechanism for this finish. For example. in the research on erosion of $CaCO_3$ -containing paints, researchers were well on their way to quantitatively defining a cause and effect relationship for this pigment in two types of finish.

It is possible to evaluate several degradation mechanisms and to discuss the influences of acids and other pollutants on these mechanisms. It is even possible to obtain reasonable cause and effect relationships for some of these degradation mechanisms. It is not possible to combine these into a model that quantifies the effect. The investigations of effects at the paint/wood interface are not conclusive. It has been shown that SO_2 diffuses through paint and reacts with the wood under the paint, but loss of paint adhesion has not been measured. It should be noted. however. that the standard deviation of the adhesive strength of both exposed and unexposed paint coatings on wood is quite high and any loss of adhesion caused by the acidic environment would not be obvious.

Research Potentials

The isolated effects of acidic deposition on painted wood cannot be evaluated until the mechanisms of paint degradation under non-acidic conditions are known. Rigorous scientific and technical bases have not been established for evaluating paint degradation under normal exposure. Paint evaluation has focused primarily on quick assessment of formulations using accelerated test methods or empirical evaluation of specimens during and after field exposure. There has been no long-term research commitment to the study of materials properties of paint and its components, particularly when combined with a substrate.

A number of publications have dealt with new instrumental techniques for determining paint characteristics. and. although these characteristics have been used in a few cases to monitor changes in paint coatings as they weather. this information has not established clear mechanisms of failure or correlated laboratory data with service life of paint coatings in the field. In general. research on the modes of paint failure has not addressed fundamental material considerations or assessed chemical changes and interactions among the weathering factors and paint components. No equation is available for combining the various degradation factors into an overall model that quantifies degradation for panels exposed to normal weathering conditions. In addressing acidic deposition research. scientists have had to address both problems: the basic research on weathering of paints and the incremental effects of acid deposition.

To close this research gap, this researcher recommends two research tracks: (1) one that investigates changes in the paint film (both surface and bulk) independent of substrate. and (2) one that investigates the paint/substrate interface (including both substrate and film properties). The first approach focuses on the effects at the paint surface that are primarily driven by the photo-oxidation of the paint film components and includes the study of bulk properties of the film. The second takes into consideration the bulk properties of the substrate, the original surface of the substrate. and the nature of the interface formed by the coating and substrate. This binary approach would measure the effects of chemicals that diffuse through the film, and describe the materials properties of both the coating and substrate.

This approach demands a determination of fundamental materials properties, both chemical and physical. of painted wood as it weathers under various conditions. both in the laboratory and in the field. Research of this nature requires a long-term commitment. A study of the effects of acidic deposition on painted wood should begin with basic studies of the polymers most commonly used in paint including new ones now being developed. The research should include laboratory and field exposures with controlled exposures to various environmental factors including. but not limited to, acid. Cause and effect determinations demand experimental designs that include ranges of concentrations of various acids and their precursors and combinations of these pollutants. Long-term exposure to concentrations typical of those found in the environment is essential. The minimum concentrations should be typical of those found in suburban areas in northeastern United States and the maximum should be typical of those found in major industrial areas. The exposure periods should be several years. The critical factor in these experiments will be determining the changes in materials properties. particularly the subtle chemical changes in films of the pure polymers. coatings of these polymers on wood. and the wood/polymer interface. These determinations can be made using currently available techniques that include analysis of run-off from specimens and nondestructive and destructive chemical analysis and mechanical testing.

As the research with the polymer progresses. finishes should be formulated using these polymers and a similar range of experiments conducted using these finishes. The finishes should include several common pigments including acid-sensitive extenders such as $CaCO_3$, but this should be a minor part of the program. It might be necessary to evaluate chemical changes in pigments and other minor components as well as in the polymer. Exposure regimes (both laboratory and field) for the paints should parallel those developed using the polymers. The research must include measurement of subtle changes in materials properties of all components of the paint system.

In a particular failure mode. it is necessary to identify the rate-determining step and to define any synergism in the degradation processes. In addition. the chemical changes associated with embrittlement, chain scission. loss of adhesion. and surface degradation should be defined. By understanding the chemical changes under various experimental conditions. both in the laboratory and in the field. that effect the various modes of failure. it may be possible to delineate the factors that catalyze acidic deposition. Such an understanding gives the background information necessary for determining the mechanisms of acidic attack of painted wood and the effect of acid on the rate-determining step in that failure mode.

Understanding of materials properties obtained through rigorous laboratory experiments will provide insight into the subtle changes that occur in field exposure. The evaluation of field exposure data must include the materials property link between specimens exposed in the field and those exposed under laboratory conditions. In outdoor testing, it should be the chemical changes and changes in mechanical properties of all components that define the finish performance. Visual evaluation is not likely to differentiate acid-induced degradation from normal degradation on painted wood. The isolation of degradation products unique to a particular degradation mechanism could well lead to new methods for accelerated evaluation procedures.

A research effort of this magnitude would require the formation of a research team comprising experts from many disciplines and would require substantial financial commitment. Are the benefits worth the price'? On the basis of acidic deposition effects to painted wood. probably not. On the basis of understanding the mechanisms of paint degradation. the elucidation of links between accelerated weathering data and field data. the design of better paints. and determining the effects of pollution on paint performance. the answer is clearly "Yes."

The commitment to such a research program may be forced by events at hand. The most serious concern throughout the paint industry in the United States is compliance with volatile organic compound (VOC) legislation. Many of the traditional finishes used on wood will no longer be acceptable because of this legislation (including oil-based semi-transparent stains, oil- and alkyd-based primers and topcoats. solventborne water repellents and solventborne water-repellent preservatives). Environmental concerns will probably not require that latex formulations be changed. but these finishes may not give the properties that many consumers prefer. As traditional finishes are removed from the marketplace. their replacements might require a new generation of finishes. The durability of these should be determined and acidic environments should be a part of the experimental protocol. Previous studies on assessing acid degradation of finishes (particularly those on oil- and alkyd-based formulations) will probably not apply to these new finishes.

The introduction of these new low VOC finishes might also be complicated by changes within the wood industry. The change away from traditional species such as redwood and western redcedar will probably continue. More hardwoods will probably be used—not only domestic but also tropical species. The trend toward faster-grown, smaller-diameter trees will probably continue. Wood from these different species and smaller trees will not have the same properties as wood from traditional slower-grown species. New composite materials will be developed and will include new adhesives. These composites will be all wood-bases or Combinations of wood and nonwood materials. Compatibility of these new substrates with new finishes will be a major challenge regardless of the effects of acidic deposition.

More research is needed to formulate comprehensive and fundamental understanding of the performance of painted wood under normal exposure conditions. When these data have been generated, cause and effect patterns and failure mechanisms can be defined. Then, the relative effects of acidic exposure to finished wood can be assessed and evaluated as part of the greater picture of materials degradation in the United States.

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