

A REVIEW OF AIR POLLUTANT DAMAGE TO MATERIALS

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A REVIEW OF AIR POLLUTANT DAMAGE TO MATERIALS

PHYSICAL DAMAGE

1.0 INTRODUCTION

There is no question that the presence of air pollutants, notably sulfur oxides, particulate matter, nitrogen oxides, and ozone under the proper circumstances can exacerbate damage to non-living materials thereby producing costs to society. Material damage related to air pollution has been recognized for well over 300 years. In 1661 John Evelyn, a public spirited citizen of London, described the air pollution situation in London as follows:^{1*}

"This is the pernicious Smoake which sullyes all her Glory, superinducing a sooty Crust or Fur upon all that it lights, spoyling the moveables, tarnishing the Plate, Gildings and Furniture, and corroding the very Iron-bars and hardest Stones with these piercing and acrimonious Spirits which accompanying its Sulphure; and executing more in one year, than exposed to the pure Aer of the Country it could effect in some hundreds.

It is this horrid Smoake which obscures our Churches, and makes our Palaces look old, which fouls our Clothes, and corrupts the Waters, so as the very Rain, and refreshing Dews which fall in the several Seasons, precipitate this impure vapour, which, with its black and tenacious quality, spots and contaminates whatever is exposed to it."

His pointing out of sulfur and acid rain as causative agents appears prophetic, but "sulphure"~~is~~ used in ~~his~~ pamphlet undoubtedly had more to do with emanations from the nether regions than any special knowledge of sulfur chemistry as related to air pollution effects.

The term "Acid Rain" is a poorly understood phenomenon which has only recently drawn the attention of the scientific community in the U.S. The term

*Numbered references appear at the end of this chapter.

has been widely and indiscriminately used to describe a syndrome in which acidic gases such as sulfur and nitrogen oxides are emitted from combustion sources, transported many miles, converted to sulfates and nitrates, and deposited in or along with rain on sensitive ecosystems far removed from the supposed sources. The impact of "acid rain" on non-living materials, buildings and monuments is frequently cited as one of the serious consequences of this scenario. This assertion is made even though the greatest amount of exposed materials are located near the sources and not in the sylvan or rural settings usually associated with "acid rain" effects.

In an attempt to broaden the interpretation of what "acid rain" really is and to recognize that there is great uncertainty in the overall scenario of cause and effect, the term "acidic deposition" is coming into wider use to describe this syndrome. This broader term permits the inclusion of effects on materials such as metal corrosion or stone damage that appear to be related more to reactions between gaseous pollutants such as SO_2 and moist surfaces than damage from pre-acidified rain water.

Table 1-1, based on a review by Yocom and Upham, summarizes the types of damage that can be caused by air **pollution.**² The important points to be brought out from Table 1-1 are:

- o A variety of materials are damaged by common air pollutants.
- o Sulfur oxides figure prominently as a pollutant type which can cause damage to many materials.
- o Air pollution is only one of the environmental factors that can cause damage to materials exposed to outdoor atmospheres.

There are several fundamental problems in quantifying the extent of damage to materials from specific pollutants:

- o The types of damage associated with air pollutants tend to occur in unpolluted atmospheres and cannot be distinguished from those caused or enhanced by the presence of air pollutants. Damage can be produced by moisture, CO_2 ,

TABLE 1-1. AIR POLLUTION DAMAGE TO MATERIALS

Materials	Type of damage	Principal air pollutants	Other environmental factors
Metals	Corrosion, tarnishing	Sulfur oxides and other acid gases	Moisture, air, salt
Building stone	Surface erosion and discoloration	Sulfur oxides and other acid gases, particulate matter	Moisture, temperature fluctuations, salt, vibration, microorganisms, CO ₂
Paint	Surface erosion, discoloration	Sulfur oxides, hydrogen sulfide, ozone, particulate matter	Moisture, sunlight, microorganisms
Textiles	Reduced tensile strength, soiling	Sulfur oxides, nitrogen oxides, particulate matter	Moisture, sunlight, physical wear
Textile dyes	Fading, color change	Nitrogen oxides, ozone	Sunlight
Paper	Embrittlement	Sulfur oxides	Moisture, physical wear
Rubber	Cracking	Ozone	Sunlight, physical wear
Leather	Weakening, powdered surface	Sulfur oxides	Physical wear
Ceramics	Changed surface appearance	Acid gases, HF	Moisture

natural particulate matter, sunlight and other features of the natural environment. Thus, determining the isolated influence of a given pollutant in an ambient exposure situation is not a straightforward process.

- o Laboratory studies where individual pollutants are introduced to sensitive materials in known exposures independent of other influences tend to be operated at unrealistically high concentrations and otherwise are not representative of real life exposure situations.
- o Reduction in ambient levels of pollutants such as **SO** as the result of air pollution control efforts has significantly reduced the exposure and degree of possible damage to exposed materials. Damage identified and measured today may have been the result of much earlier exposure when concentrations were much higher.
- o Changes over recent years in the types of materials and protective coatings exposed to the atmosphere as a result of technological improvements in materials is having a fundamental effect upon the nature and extent of air pollution-induced damage to materials and associated damage costs.
- o Determination of the quantities of materials in place in relation to air pollutant exposures is a difficult task, especially when significant amounts of certain materials (e.g., fabrics, paints and paper) may be exposed to indoor environments or other locations not represented by typical ambient monitors.

The Air Quality Criteria Documents for particulate matter, sulfur oxides, nitrogen oxides and ozone contain thorough reviews of the literature on material effects related to each of the pollutant classes.^{3,4,5} This chapter will rely heavily upon those parts of these documents dealing with material effects, but will not attempt to comment on all of the primary documents referred to. Rather, those pieces of original work or reviews believed by the author to be most significant will be referred to, plus any other significant published work reported since the dates of the criteria documents.

2.0 SULFUR OXIDES

From Table 1-1 it is apparent that sulfur oxides figure prominently in many types of air pollution-induced damage to materials. Sulfur dioxide (SO_2), the principal sulfur oxide emitted to the air, originates primarily from the burning of sulfur-containing fuels and from the roasting of sulfide ores in the winning of certain non-ferrous metals. The exact mechanism by which SO_2 and other sulfur oxides damage materials are not known, but invariably moisture and oxidation to sulfates are required. There are many possible scenarios for the damage to materials by sulfur oxides, three of which are described as follows:

1. SO_2 is absorbed in moisture (condensed or from precipitation) on surfaces and is oxidized to sulfates.
2. SO_2 is oxidized to sulfates in the atmosphere and deposits on surfaces which are already wet through condensation or precipitation.
3. Rain water containing sulfates and dissolved SO_2 from the upper air or scavenged from the air falls on sensitive surfaces.

The last mentioned of these might be considered as a description of the "acid rain" syndrome alluded to earlier. The surfaces of material susceptible to air pollution damage exist in greatest abundance in urban and industrial areas close to sources of primary pollutants and not in those remote areas where "acid rain" is believed to be a problem. Furthermore, it is likely that more material damage occurs from direct contact of SO_2 and sulfates on moist surfaces than from acidic rain falling on the surfaces. As pointed out in the Introduction, the term "acidic deposition" which is supplanting the term "acid

rain" would include all of the anticipated mechanisms by which sulfur oxides contact and affect materials.

Judeikis and Stewart⁶ have shown that SO_2 deposition velocities for a variety of materials vary widely. Of these materials tested in a flow reactor, a cured cement had the highest value, 2.5 cm/sec, with asphalt exhibiting the lowest value, 0.04 cm/sec. No metals were tested in this experiment. Deposition velocities decreased as the surface became saturated with SO_2 . Humidity increased the capacity of the surface to absorb or adsorb SO_2 . The reactivity of the surface could be restored by washing or exposing the spent surface to ammonia.

2.1 FERROUS METALS

Corrosion of iron and steel in polluted atmospheres has received a great deal of attention over the years. The draft criteria document prepared by EPA³ to support air quality standards for particulate matter and sulfur oxides (PM/SO_x) contains an extensive review of the possible mechanisms for metal corrosion in the presence of sulfur oxides.

Some of the earliest work on the nature of iron corrosion in atmospheres containing sulfur oxides was that of Vernon.⁷ He showed the relative roles of SO_2 and humidity and proposed that there are critical humidities for the corrosion of metals above which SO_2 induced corrosion proceeds rapidly. He also showed that corrosion of iron proceeds from randomly distributed centers which he associated with the deposition of particulate matter. However, it may also be likely that these "centers" represent differences in the grain structure of the sample. These differences produce electrochemical cells which with a moist, conducting surface, allow current to flow and corrosion to proceed.

Many workers have advanced theories on the principal chemical reactions that describe iron and steel corrosion in the presence of SO_2 . A variety of chemical routes are possible and it is likely that several of them operate in real life atmospheric exposures. Those interested in the research on which these theories are based are directed to the references listed in the **PM/SO_x criteria document**.³ This report will not attempt to cover such background material.

According to **Nriagu**⁸, once corrosion has been initiated, the progress of the reaction is controlled largely by sulfate ions produced from the oxidation of absorbed or adsorbed SO_2 . However, the actual mechanism of SO_2 oxidation on the surface is poorly understood. The work of Johnson and co-workers in **England**⁹ appears to show that sulfur or sulfates are only a minor constituent of the corrosion products of steel. Mild steel samples were exposed to two urban areas near Manchester. One area was heavily polluted, and the other was lightly polluted. Scanning electron microscopy energy dispersive x-ray analysis and x-ray diffraction analysis of corrosion products showed them to be predominantly $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ and $\alpha\text{-FeOOH}$. Some minor amounts of sulfur were found in a few of the samples. The relative amount of corrosion produced was strongly dependent on whether or not the sample was initially wet at the beginning of the exposure.

Rust tends to protect iron and steel from further corrosion. **Nriagu**⁸ and **Sydberger**¹⁰ showed that steel samples exposed initially to low concentrations of sulfur oxides were more resistant to further corrosive attack than samples exposed continuously to high concentrations.

2.1.1 Laboratory Studies

Exposing iron and steel samples to SO_2 and humidity under controlled laboratory conditions has two principal advantages:

1. The pollutant concentrations and other influencing factors can be independently controlled in a factorial experiment and permit the quantification of each factor's impact.
2. Exposure conditions can be made more severe than in nature to accelerate the corrosion effect, thereby reducing the duration of the experiment.

While many of the early experiments showed clearly that corrosion rates correlate with both SO_2 and humidity, exposure consisted of SO_2 concentrations many times higher than those found in the ambient atmosphere or what are referred to as "reflux" conditions, where water and excess SO_2 were continually flushing the surface of the samples.

The most realistic set of laboratory experiments was conducted by Haynie and co-workers.¹¹ The primary advantages of this study over previous laboratory studies include the following:

- o Pollutant concentrations (SO_2 , NO_2 and O_3) were controlled at levels that encompass those found in ambient urban atmospheres.
- o Experiments were statistically designed for analysis of variance and the degree of interaction between pollutants and other environmental stresses.
- o Sunlight was simulated by a xenon arc light which approximates the spectrum of sunlight.
- o "Weathering steel" was used for the steel sample, a material used unprotected in the ambient atmosphere. Many of the previous studies used mild steel or enameling steel which would not normally be used unprotected.

Steel corrosion was determined in terms of weight loss of the steel panels. As might be expected, the results showed that there was a strong,

statistically significant relationship between steel corrosion and SO_2 concentration, together with high humidity.

2.1.2 Field Studies

A problem inherent with field studies is that iron and steel corrosion occurs even in unpolluted atmospheres, and the specific impact of SO_2 is difficult, if not impossible, to isolate completely. Therefore, the effects of SO_2 , along with moisture, can only be inferred by statistical treatment of the data.

Upham¹² exposed mild steel samples in a number of sites in and around St. Louis and Chicago. He showed that corrosion correlated well with sulfur oxide levels and increased with length of exposure. Starting in 1963, Haynie and Upham carried out a 5-year program in which three different types of steel were exposed in eight major metropolitan areas in the United States.¹³ Multiple regression analyses showed significant correlations between average SO_2 concentrations and all three types of steel.

Starting in 1964, Haynie and Upham¹⁴ exposed enameling steel samples for 1 and 2 years at 57 stations of the National Air Sampling Network. Pollutants of interest were SO_2 , total suspended particulate matter, and the sulfate and nitrate content of the particulate matter. Multiple linear regression and non-linear curve fitting techniques were used to analyze the relationship between corrosion behavior of steel and pollutant concentrations. A best fit empirical function was developed relating sulfate in particulate matter and humidity to corrosion. However, the authors stated that SO_2 rather than sulfate was the causative agent in producing corrosion and the relationship was transformed into one based on SO_2 from a linear regression between sulfate and SO_2 . The corrosion or damage function is:

$$\text{cor} = 325 \sqrt{t} e^{[0.00275\text{SO}_2 - (163.2/\text{RH})]}$$

where

cor = depth of corrosion, μm

t = time, years

SO_2 = SO_2 concentration, $\mu\text{g}/\text{m}^3$

RH = average relative humidity, percent

Figures 2-1 and 2-2 show plots of pseudo corrosion rate (cor/\sqrt{t}) versus relative humidity and SO_2 concentrations, respectively. Comparison of these two graphs shows that the sensitivity of corrosion to humidity is far greater than that for SO_2 , especially at levels of SO_2 normally experienced in urban areas.

For example, referring to Figure 2-1, if one were comparing relative corrosion at 55 percent relative humidity in two areas with average levels of 80 and 160 $\mu\text{g}/\text{m}^3$, a very significant difference in relative air pollutant levels, the difference in relative corrosion would be only 3 percent. On the other hand, from Figure 2-2, if one were comparing relative corrosion at a constant SO_2 level of 100 $\mu\text{g}/\text{m}^3$ between two areas with a moderate difference in average relative humidity (55 and 65 percent), the difference in relative corrosion rate would be 14 percent.

Other damage functions relating steel corrosion to SO_2 and humidity (or time of wetness) have been developed by Chandler and Kilcullen,¹⁵ and Guttman and Sereda.¹⁶

A more recent study of material damage in the St. Louis area in 1974-75 by Mansfeld¹⁷ included the use of special atmospheric corrosion monitors which measure the length of time that a corrosion panel is wet enough for electrochemical corrosion to take place. His sample exposure array included weathering steel, galvanized steel, house paint and marble. Concentrations of SO_2 measured

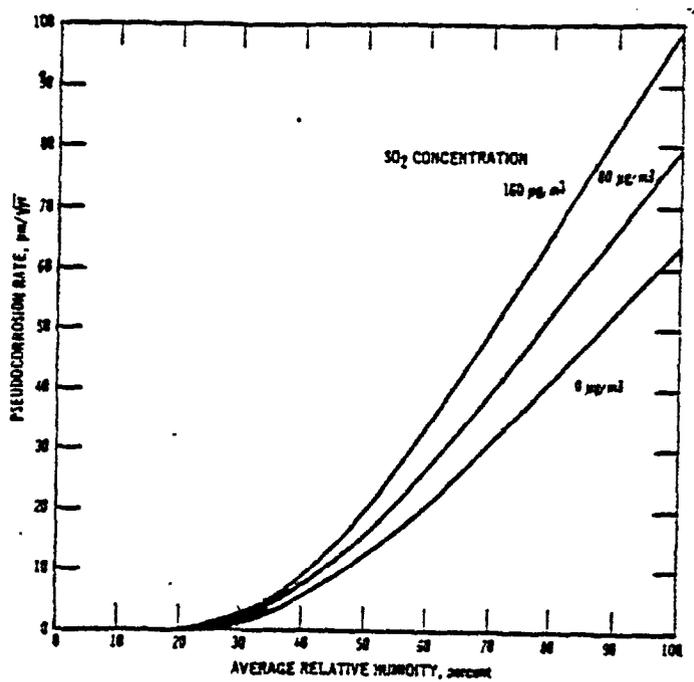


FIGURE 2-1. Steel corrosion behavior as a function of average relative humidity at three average concentration levels of sulfur dioxide. (Ref. 14).

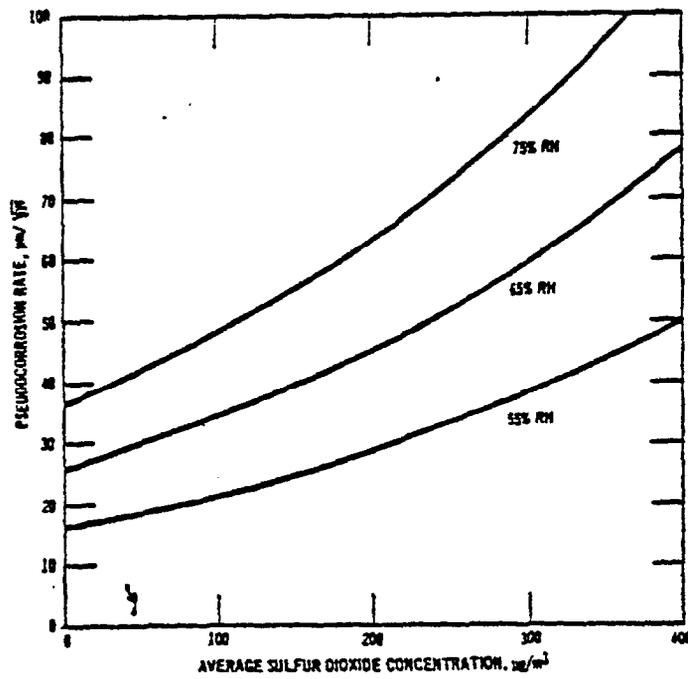


FIGURE 2-2. Steel corrosion behavior as a function of average sulfur dioxide concentration and average relative humidity. (Ref. 14).

in this study were an order of magnitude lower than those measured by Upham's 1957 study.¹² The low concentrations of SO_2 may be one of the reasons Mansfeld was not able to show any significant correlation between corrosivity and pollutant levels.

2.1.3 Areas of Needed Research

While much effort has been expended in defining the mechanisms of attack of SO_2 and moisture on iron and steel, one cannot help but wonder how important this problem is in view of the following factors:

- o Except for weathering steel there is a question of how much unprotected steel is actually in service.
- o Levels of SO in the United States and other parts of the world have been reduced significantly through control efforts, and may exert only an insignificant effect on iron and steel corrosion.

Before more research is carried out on the mechanisms of damage, studies directed at the above two questions should be initiated.

Gerhard and Haynie¹⁸ have given some limited consideration to a possible role of air pollutants (notably SO_2) in catastrophic failure of metals -largely in relation to stress corrosion. This is an extremely complex area and one susceptible to misinterpretation because of the potential for significant accidents which endanger human lives. An independent assessment should be made of this entire area coupled with laboratory research to assess its importance, especially in an era of decreasing (or stabilizing) air pollutant levels.

2.2 NONFERROUS METALS

The corrosion rates of commercially important nonferrous metals in polluted atmospheres, although generally less than those for steel, cover a wide range. The relative corrodibility of some of these nonferrous metals can be compared in Table 1-2. This summary of 20 years of investigation by the ASTM Committee

TABLE 1-2. WEIGHT LOSS OF METAL PANELS^a AFTER 20 YEARS EXPOSURE IN VARIOUS ATMOSPHERES (ABOUT 1930 - 1954)^b

City	Exposure classification	Average loss in weight, %					
		Commercial copper (99.9% + Cu)	Commercial aluminum (99% + Al)	Brass (85% Cu, 15% Zn)	Nickel (99% + Ni)	Commercial lead (99.92% Pb, 0.06% Cu)	Commercial zinc (99% Zn, 0.85% Pb)
Altoona, Pennsylvania	Industrial	6.1	---	8.5	25.2	1.8	30.7
New York, New York	Industrial	6.4	3.4	8.7	16.6	---	25.1
La Jolla, California	Seacoast	5.4	2.6	1.3	0.6	2.1	6.9
Key West, Florida	Seacoast	2.4	---	2.5	0.5	---	2.9
State College, Pennsylvania	Rural	1.9	0.4	2.0	1.0	1.4	5.0
Phoenix, Arizona	Rural	0.6	0.3	0.5	0.2	0.4	0.8

^aPanels - 9 x 12 x 0.035 in (22.86 x 30.48 x 0.089 cm).

^bRef 19.

on Atmospheric Corrosion compares corrosion rates for different metal formulations and under different exposure conditions.¹⁹

Assuming that Altoona, PA and New York, NY represented locations with high SO_2 and particulate matter concentrations in the period 1930-54, it is clear that nickel and zinc are the most susceptible of the six metals studied. Of these two, zinc is by far the more important because of its extensive use in galvanizing to protect steel in the ambient atmosphere.

Figure 2-3 from the work of Sydberger and Vannenberg²⁰ shows adsorption of SO_2 with time at 90 percent relative humidity for iron and three nonferrous metals. The characteristics of these curves appear to correlate with the relative susceptibility of the metals to SO_2 attack.

2.2.1 Aluminum

Aluminum is considered to be quite resistant to SO_2 -induced corrosion because of the highly inert oxide layer formed on the surface. However, the presence of high concentrations of particulate matter can produce a mottled or pitted surface in the presence of SO_2 . In view of efforts to control emissions of SO_2 and particulate matter in the United States--especially larger particles or agglomerates that could act as centers for corrosion initiation, SO_2 -induced surface corrosion of aluminum does not appear to be a significant problem.

Possible stress corrosion of aluminum in the presence of SO_2 is potentially a more serious problem than surface corrosion. Haynie and co-workers¹¹ found, as part of their extensive chamber studies, that stress aluminum samples exposed to 79 and 1310 $\mu\text{g}/\text{m}^3$ of SO_2 lost approximately 8.6 and 27.6 percent of their bending strength, respectively.

2.2.2 Copper

Copper and copper alloys in most atmospheres develop thin, stable surface films, which inhibit further corrosion. Initial atmospheric corrosion is a

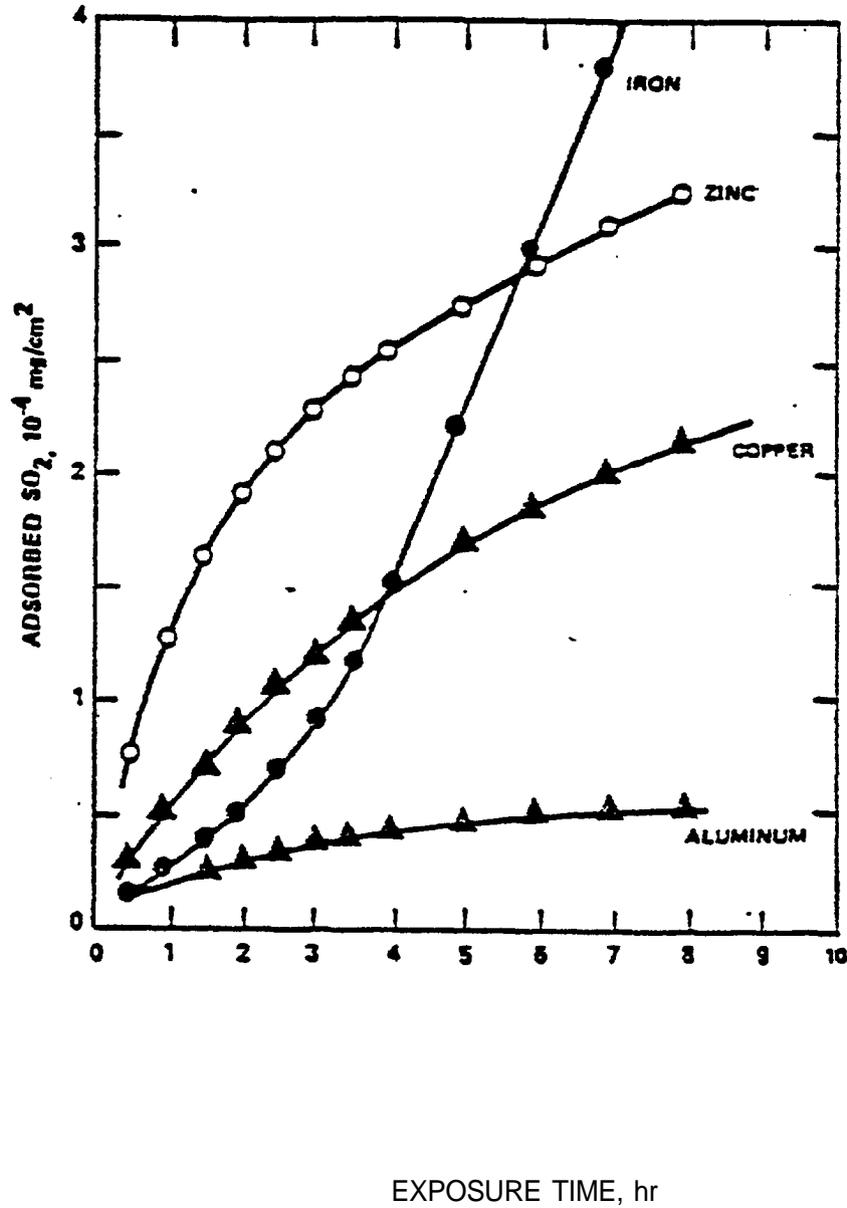


FIGURE 2-3. Adsorption of sulfur dioxide on polished metal surfaces is shown at 90 percent relative humidity.

Source: Adapted from Sydberger and Vannenberg²⁰.

brown tarnish of mostly copper oxides and sulfides which can thicken to a black film. Then in a few years, the familiar green patina forms. Analysis of this film indicates it to be either basic copper sulfate or, in marine atmospheres, basic copper chloride, both of which are extremely resistant to further atmospheric attack.

2.2.3 Zinc

The primary use of zinc other than as an alloying metal with copper to produce brass, is in galvanizing steel to make it resistant to corrosion in the atmosphere. Zinc is anodic with respect to steel such that when zinc and steel are in contact with an electrolyte, the current flow protects the steel from corrosion at the expense of some oxidation of zinc.

Because of its economic importance, the behavior of zinc in polluted atmospheres has been studied intensively by a number of workers. **Guttman²¹** carried long-term measurements of atmospheric corrosion of zinc in the Birchbank, near Trail, B.C., in Canada, starting in 1958. He developed an empirical damage function for zinc corrosion in relation to SO_2 concentrations and "time-of-wetness". Time of wetness was measured by means of a dew detector. SO_2 was measured by lead peroxide sulfation candles and conductimetric SO_2 measurements. His empirical damage function is:

$$y = 0.005461(A)^{0.8152} \times (B + 0.02889)$$

where

y = corrosion loss, mg for a 3 x 5 in. panel

A = time of wetness, hr

B = atmospheric SO_2 content during the periods the panels were wet.

One can question the validity of the SO_2 data based on the unreliability of the methods used.

Haynie and Upham²² carried out an extensive zinc corrosion study in eight cities where zinc panels were exposed while concurrently collecting data on SO_2 , temperature and humidity. They developed the following empirical damage function relating zinc corrosion to SO_2 levels and relative humidity.

$$y = 0.001028 (\text{RH} - 48.8) \text{SO}_2$$

where

y = corrosion rate, $\mu\text{m}/\text{yr}$

RH = average annual relative humidity

SO_2 = average SO_2 concentration, $\mu\text{g}/\text{m}^3$

The damage coefficients for these two functions plus functions developed from four other studies were compiled by EPA.³ These coefficients are compared in Table 1-3. Note that the SO_2 coefficients vary over a factor of over four and that the chamber study (Haynie et al., 1976¹¹) has by far the lowest SO_2 coefficient. The chamber study isolated the specific influence of SO_2 and the studies carried out in the ambient atmosphere include the joint effect of SO_2 and particulate matter containing sulfates, chlorides, nitrates and other anions; thus the difference in SO_2 coefficient (and its direction) between the chamber study and those for outdoor exposures appears reasonable. If the two studies using lead peroxide candles (Guttman and Sereda¹⁶ and Guttman²¹) are not considered, one could infer that earlier atmospheric exposures (Haynie and Upham²² and Cavendar et al.²³) represent a situation where the SO_2 coefficient greatly overpredicts the effect because of high concentrations of particulate matter and a variety of anions that also affect zinc corrosion. The recent study by Mansfeld¹⁷ was carried out in St. Louis after pollutant levels were greatly reduced from those found during the exposure of the 1960's, and may represent a situation more closely simulating that of the chamber studies which were carried out in the absence of particulate matter.

TABLE 1-3. EXPERIMENTAL REGRESSION COEFFICIENTS WITH ESTIMATED STANDARD DEVIATIONS FOR SMALL ZINC AND GALVANIZED STEEL SPECIMENS OBTAINED FROM SIX EXPOSURE SITES*

Study	Time-of-wetness coefficient, $\mu\text{m}/\text{yr}$	SO_2 coefficient, $(\mu\text{m}/\text{yr})/(\mu\text{g}/\text{m}^3)$	Number of data sets
CAMP (Haynie and Upham, 1970)	1.15 ± 0.60	0.081 ± 0.005	37
ISP (Cavender et al., 1971)	1.05 ± 0.96	0.073 ± 0.007	173
Guttman, 1968 ²¹	1.79	0.024	>400
Guttman and Sereda, 1968	2.47 ± 0.86	0.027 ± 0.008	136
Chamber study Haynie et al., 1976)	1.53 ± 0.39	0.018 ± 0.002	96
St. Louis (Mansfeld, 1980)	2.36 ± 0.13	0.022 ± 0.004	153

*From Ref. 3

2.2.4 Areas of Needed Research

As noted above, a considerable amount of research has already been carried out on the atmospheric corrosion of zinc. Other nonferrous metals are not as important as zinc because of lesser amounts being exposed to the outdoor atmosphere, their greater resistance to SO_2 and declining SO_2 concentrations in most urban areas in the United States. However, two areas where further work is needed are:

1. Substantiation of the SO_2 damage coefficient based on present day levels of SO_2 and particulate matter in a number of cities. Development of damage coefficients for particulate matter.
2. Further study of stress corrosion of aluminum and aluminum alloys in relation to ambient SO_2 exposures.

2.3 PAINT

Paint consists of pigment and vehicle. Pigments, such as titanium dioxide and zinc oxide, provide color, hiding power, and durability. The vehicle provides the film-forming properties of the paint and contains resin binders, solvents and additives. Together the pigment and vehicle protect the underlying surface and enhance the attractiveness or neatness of the exposed surface. Air pollution may limit both of these functions by damaging the protective coating and exposing the underlying surface to attack. The most important potential effects of SO_2 on paints are interference with the drying process and acceleration of the normal erosion process.

Holbrow²⁴ has reported a number of experiments to determine effects of sulfur dioxide on newly applied paints. Drying time for various oil-base paints exposed to 2620 to 5240 $\mu\text{g}/\text{m}^3$ (1-2 ppm) of sulfur dioxide was increased

50-100 percent. Films thus dried had either softer finish or, in some cases, a more brittle finish, and as a result of either change the paints were likely to provide less than optimum durability. Discoloration of Brunswick green paints were noted if the fresh paints were exposed to sulfur dioxide, warmth, and moisture. Under these conditions, the lead chromate in the pigment was bleached and became blue. It should be pointed out, however, that these experiments were carried out at SO_2 concentrations an order of magnitude or more above those usually experienced in urban atmospheres. Thus far no experiments have been carried out on the effect of SO_2 on drying time of water-based latex paints.

Campbell and co-workers²⁵ carried out an extensive study of paint erosion for a variety of paint types and exposure conditions (including SO_2 and O_3). Both chamber and field experiments were conducted. The researchers evaluated four important types of paint: (1) house paints (acrylic latex and oil-based); (2) a urea-alkyd coil coating; (3) a nitrocellulose-acrylic automotive refinishing paint; and (4) an alkyd industrial maintenance coating. In the chamber studies, paints were exposed to five separate controlled environmental conditions; (1) clean air; (2) sulfur dioxide at $262 \mu\text{g}/\text{m}^3$ (0.1 ppm); (3) sulfur dioxide at $2620 \mu\text{g}/\text{m}^3$ (1.0 ppm); (4) ozone at $196 \mu\text{g}/\text{m}^3$ (0.1 ppm); and (5) ozone at $1960 \mu\text{g}/\text{m}^3$ (1.0 ppm). The exposure chamber operated on a 2-hour light-dew cycle consisting of 1 hour of xenon light at 70 percent relative humidity and a black panel temperature of 66°C , followed by 1 hour of darkness at 100 percent relative humidity and 49°C during which period moisture condensed on the coated panels. To assess the influence of simulated sunlight, one group of panels was exposed to the light cycle while a like group of panels were exposed shaded from light during the entire exposure period. Erosion measurements

were made after exposure periods of 400, 700, and 1000 hours; erosion rates were then calculated.

Generally, exposures to 2620 $\mu\text{g}/\text{m}^3$ (1 ppm) sulfur dioxide or 1960 $\mu\text{g}/\text{m}^3$ (1 ppm) ozone produced statistically significant erosion rate increases compared to clean air (zero pollution) conditions. Erosion rate increases, however, varied considerably among paint types. Oil-based house paint, experienced the largest erosion rate increases, latex and coil coatings moderate increases, and the industrial maintenance coating and automotive refinish the smallest increases. Exposures to sulfur dioxide produced higher erosion rates than ozone for three of the paints; however, of more importance was that sulfur dioxide produced much larger erosion rate increases than ozone. Unshaded panels eroded more than shaded panels. Table 1-4 presents erosion rate data for the unshaded exposures. Exposures to 0.1 ppm pollutants did not produce significant erosion rate increases over clean air exposures.

Field exposures were conducted at four locations with different environments: (1) rural--clean air, (2) suburban, (3) urban--sulfur dioxide-dominant (annual mean level 60 $\mu\text{g}/\text{m}^3$), (4) and urban--oxidant-dominant (annual mean ozone level 40 $\mu\text{g}/\text{m}^3$). Panels were exposed facing both north and south, and were evaluated after 3, 7, and 14 months exposure. Table 1-5 shows the erosion rate results for the various coatings exposed facing south. In most cases, southern exposures produced somewhat larger erosion rates; this agrees with the unshaded versus shaded results of the laboratory study. Oil-based house paint again experienced by far the largest erosion rate increases, followed in order by the coil coating, latex house paint, industrial maintenance paint, and automotive refinish. Generally, the oxidant-dominant environment was more damaging than the sulfur dioxide dominant environment. It is noteworthy that the oil-based house paint and coil coating experienced the largest erosion

TABLE 1-4. PAINT EROSION RATES AND T-TEST PROBABILITY DATA FOR CONTROLLED ENVIRONMENTAL LABORATORY EXPOSURES*

Mean erosion rate (mil loss x 10 ⁻⁵ /hour with 95% confidence limits) for unshaded panels and probability that differences exist			
Type of paint	Clean air control	SO ₂ (1.0 ppm)	O ₃ (1.0 ppm)
House paint oil	20.1 ± 7.2	141.0 ± 19.0 99%	44.7 ± 10.5 99%
latex	3.5 ± 1.5	11.1 ± 1.0 99%	8.5 ± 5.9 93%
Coil coating	11.9 ± 2.3	34.1 ± 4.7 99%	14.9 ± 2.5 94%
Automotive refinish	1.8 ± 0.8	3.1 ± 2.6 75%	5.1 ± 1.3 99%
Industrial maintenance	18.6 ± 5.1	22.4 ± 7.0 66%	28.1 ± 14.0 85%

*Ref. 25

rate increases in both the field and laboratory sulfur dioxide exposures. These coatings were the only ones that contained a calcium carbonate extender-- a substance that is sensitive to attack by acids.

Spence et al.²⁶ summarized the result of paint exposure to several gaseous pollutants from the full scale chamber studies reported by Haynie et al. and discussed earlier in relation to metal exposures. Four classes of painted surfaces were evaluated: oil base house paint, vinyl-acrylic latex house paint, vinyl coil coating, and acrylic coil coating. Significant questions can be raised as to how well the dew/light and temperature cycle and constant levels of SO_2 represent real life ambient exposure; however, they found a strong correlation between paint erosion for the oil base house paint and SO_2 and humidity. The vinyl and acrylic coil coating were unaffected, but blistering was noted on the latex house paint. It was not certain if the blistering was the result primarily of SO_2 or moisture.

TABLE 1-5. PAINT EROSION RATES AND T-TEST PROBABILITY DATA FOR FIELD EXPOSURES*

Type of paint	Mean erosion rate (mil loss x 10^{-5} /month with 95% confidence limits) for panels facing south and % probability that differences exist			
	Rural (clean air)	Suburban	Urban (SO dominant)	Urban (oxidant dominant)
House paint oil	4.3 ± 7.5	14.8 ± 2.6 99.3%	14.2 ± 4.9 98.1%	21.0 ± 6.2 99.2%
latex	1.8 ± 0.5	3.0 ± 0.7 99.2%	3.8 ± 0.3 97.8%	6.5 ± 5.6 94.3%
Coil coating	2.1 ± 0.8	10.0 ± 1.9 99.9%	9.5 ± 0.8 99.9%	8.8 ± 1.7 99.9%
Automotive refinish	0.9 ± 1.1	2.3 ± 0.7 97.6%	1.6 ± 0.4 86.2%	1.7 ± 0.4 91.6%
Industrial maintenance	3.6 ± 1.6	8.2 ± 4.2 97.3%	6.6 ± 3.9 91.2%	7.8 ± 2.4 99.7%

*Ref. 25

A multiple linear regression relationship was developed for the joint influence of SO_2 and relative humidity on the oil-base house paint:

$$E = 14.3 + 0.0151 SO_2 + 0.388 RH$$

where

$$\begin{aligned} E &= \text{erosion rate of } \mu\text{m/year} \\ SO_2 &= \text{concentration of } SO_2 \text{ in } \mu\text{g/m}^3, \text{ and} \\ RH &= \text{relative humidity in percent} \end{aligned}$$

This relationship indicates that paint erosion is significantly more sensitive to changes in humidity than SO_2 . If we take the same hypothetical values used in testing the steel corrosion function discussed earlier (80 and 160 $\mu\text{g/m}^3$ of SO_2 at 55 percent RH, and 55 and 65 percent RH at 100 $\mu\text{g/m}^3$ SO_2), we find that the large change in SO_2 will produce a 3 percent change in erosion and the moderate change in RH will produce a 10 percent change in erosion.

The present understanding of damage to paint from air pollution is based primarily upon two sets of chamber studies and one set of field exposures. Since the field studies were carried out in the early 1970s, there is a need for further laboratory and field studies to determine the importance of paint damage from present day levels of sulfur oxides. Furthermore, these studies should include present day formulations (especially water-based paints) that may have a different response to air pollutants than those used earlier.

2.4 TEXTILES

Sulfur oxides are capable of weakening natural and some synthetic fibers. Cotton and its relative, viscose rayon, are cellulose fibers and can be weakened by SO_2 by breakage of the cellulose chain at the glucoside linkage. Polyamides such as Nylons 6 and 66 can be weakened by SO_2 and acid sulfate aerosols, especially when such fibers are small in diameter and under tension. Polyester, acrylic, and polypropylene fibers are resistant to SO_2 damage, but certain of these fibers may be susceptible to damage from acidic particles containing sulfates.

Byrsson and co-workers²⁷ exposed cotton fabrics to the outdoor atmosphere for 1 year at several sites in St. Louis, Missouri, and Chicago, Illinois. Individual samples were removed from the exposure rack each month. Sulfur oxide concentrations were estimated by means of lead peroxide sulfation plates. Figure 2-4 shows the effect of exposure time on the relative breaking strength of cotton duck at two levels of average sulfation rate.

Zeronian²⁸ carried out laboratory exposures in which he exposed cotton and rayon fabrics for 7 days to clean air with and without $250 \mu\text{g}/\text{m}^3$ (0.1 ppm) sulfur dioxide. Both controlled environments included continuous exposure to artificial light (xenon arc) and a water spray turned on for 18 minutes every two hours. Loss in strength for all fabrics exposed to clean air averaged 13 percent, while the fabrics exposed to air containing sulfur dioxide averaged 21 percent. Zeronian et al.²⁹ also exposed fabrics made from manmade fibers--nylon, polyester, and modacrylic--to controlled environmental conditions similar to the cotton exposures, except that the sulfur dioxide level was $486 \mu\text{g}/\text{m}^3$ (0.2 ppm). He found that only the nylon fabrics were affected, losing 80 percent of their strength when exposed to sulfur dioxide and only 40 percent when exposed in clean air.

While it has been clearly demonstrated that SO_2 can damage some textiles, there are some fundamental questions on the current relative importance of this potential problem in relation to other air pollution material effects problems:

1. How much susceptible material is still in use in outdoor exposures? To what extent have coated fabrics and more resistant synthetic fabrics supplanted cotton duck?

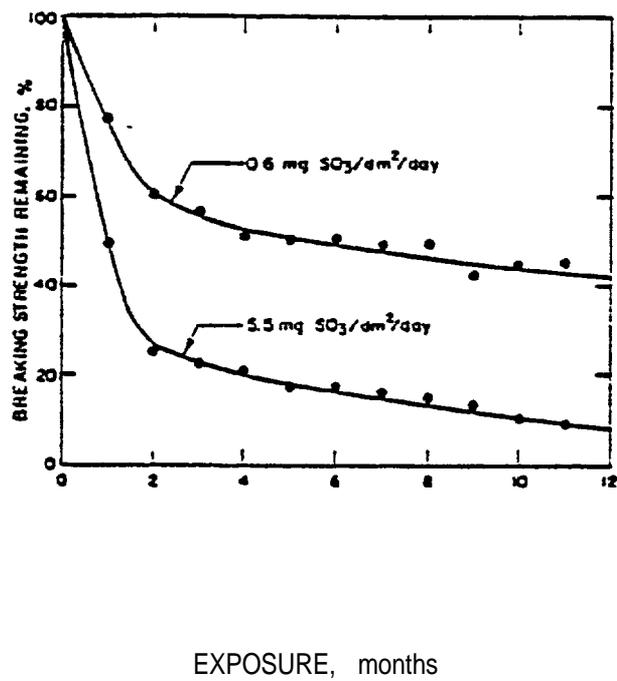


Figure 2-4. Effects of sulfation and time on tensile strength of cotton duck (Ref 27)

2. Textiles spend most of their useful life indoors where SO_2 concentrations are generally less than half of those outdoors.
3. Outdoor levels of SO_2 in urban areas have been reduced drastically from those levels that existed in the early 1960s in cities like St. Louis and Chicago where several material damage studies have been carried out.
4. Products made of textiles (clothing, draperies, etc.) tend to be replaced long before air pollution has a significant effect on useful life.

These questions must be addressed before further research is carried out on the effect of air pollutants on textiles.

2.5 BUILDING MATERIALS AND WORKS OF ART

Sulfur oxides are involved in the deterioration of several types of building materials. The importance of this damage is partly a problem of loss in structural integrity, but more important is the destruction and disfigurement of buildings, monuments and other structures and articles of great historical and artistic value. Such damage transcends the mundane consideration of replacement value of articles and surfaces used in our everyday lives. The damage to priceless buildings and works of art is not nearly the problem in the United States that it is in Europe and parts of Asia because there are few buildings over 200 to 300 years old here. Americans have a tendency to demolish buildings that are thought to have outlived their usefulness. However, more and more old buildings are now being preserved as a result of high construction costs and an increased interest in our architectural and historical heritage. This trend will place increased importance on the effects of air pollution on older material surfaces.

Air pollution damage to the buildings and monuments on the Acropolis is one of the most serious and widely publicized air pollution damage situations in the world and has been the subject of several international conferences.^{30,31}

Yocom³² has summarized the air pollution related damage to buildings on the Acropolis in terms of four problems:

1. Sooty encrustation of gypsum in protected areas from the reaction between marble and sulfur oxides.
2. Loss of surface detail in areas exposed to the weather from the dissolution of gypsum.
3. Cracking of joints repaired earlier by means of iron pins which have corroded and expanded.
This corrosion is thought to have accelerated as a result of sulfur oxides.
4. Threatened collapse of the Porch of the Caryatids on the Erechthion because the steel member installed about 1900 to support the roof is badly corroded.

Similar cases have been reported elsewhere. The Coliseum and Arch of Titus in Rome, Italy, and the San Marco Basilica in Venice, Italy, all show accelerated decay attributable to air pollution. The situation in Florence, Italy, is described as disastrous. In France, conservation specialists have removed statues from the exterior of cathedrals and replaced them with copies. A team of experts has been fighting decay and corrosion destroying the massive, twin-spired Cologne Cathedral, the most magnificent church building of the German high gothic era of around 1200 A.D.. Polluted atmospheres are threatening centuries-old shrines, temples, and buildings in highly industrial areas of Japan. Cleopatra's Needle, the large stone obelisk moved from Alexandria, Egypt, to London, England, has suffered more deterioration in the atmosphere

of London in 85 years than in the earlier 3000 or more years of its history. Another ancient Egyptian obelisk standing in Central Park in New York City, New York, shows similar decay.

The protection and repair of the old buildings and cathedrals of England has been thoroughly discussed by several authors.^{33,34} Aside from air pollution, severe damage is caused by vibrations from vehicular traffic which accelerate damage from pollutants and weathering from natural causes; for example, freezing and thawing.

In Germany, Luckat³⁵ has investigated the damage to various types of limestones and has tested several systems for protection of exposed stone. He found a silicic acid ester together with a water repellent to be more effective than several other systems tested. Riederer,³⁶ on the other hand, plays down the stone damaging mechanism involving conversion of SO_2 to sulfates followed by conversion of surface stone to gypsum. He claims that surface encrustations consist of mud and soot imbedded in gypsum, but that gypsum formation does not involve the underlying carbonate stone. His reason for making this claim is that when the encrustation is removed, there is no apparent loss of surface detail.

Longinelli and Bartelloni^{36a} have carried out research on damage to building stone in Venice, Italy. In their work they used isotopic analysis of O, S, and C in rainwater and stone to show that damage to buildings, which has been most severe since 1900, to be caused primarily by sulfur-bearing air pollutants. In spite of the proximity of Venice to the sea, sea water spray and aerosols play only a minor role in this deterioration.

Recently it has been found that sulfur consuming bacteria may be directly or indirectly responsible for a significant amount of stone damage. Hansen,³⁷

in summarizing the work of Curri in Italy, points out that the microbe, thiobacillus thioparus, one of several sulfur converting organisms, converts atmospheric SO_2 to sulfuric acid which it uses as a digestive fluid to attack carbonate stone. The CO_2 gas produced is the food of the organism. One method proposed to stop this type of attack is to treat the surface with an antibiotic or bactericide.

Glass or ceramic surfaces are thought to be impervious to damage from all air pollutants except perhaps fluorides. However, it has been found that certain types of medieval glass used in stained glass windows were made with potash derived from woodashes because the medicinal artisans were isolated from the sources of soda ash.³⁸ The potassium salts in such glass are more soluble than sodium salts, and the glass surface simply leaches away.

Because of the importance of air pollution damage to priceless and irreplaceable buildings, monuments and works of art, there is an urgent need for a well-conceived, integrated research effort covering a broad front to attack this problem. The elements include but are not limited to:

- o Identification of damage mechanism and the specific pollutants and other environmental effects responsible for damage.
- o Strategies for air quality control.
- o Methods of protection and/or isolation to retard damage.
- o Methods of restoration.

2.6 OTHER EFFECTS OF SULFUR OXIDES

Sulfur oxides are capable of damaging a number of other materials or material systems. However, the importance of these effects is much less than those discussed above.

2.6.1 Leather

Sulfur oxides cause leather to lose much of its strength and ultimately to disintegrate. As early as 1843, Faraday came to the conclusion that the

rotting of leather upholstery on chairs in a London club was the direct result of sulfur compounds in the air^2 . The storage of leather bound books in libraries can pose a serious problem. The bindings of books stored in the open in rooms with polluted air were found to deteriorate much more rapidly than those stored in confined spaces or inside glass cases. Chemical decay of bookbindings can be observed initially by the cracking that takes place on the top inside hinges of the book. The cracks gradually spread apart, and as further material is exposed, the leather loses its resiliency and disintegrates to a reddish brown powder. After some time, the entire back may become detached.

2.6.2 Paper

Paper made prior to about 1750 is not seriously damaged by sulfur dioxide. This date is about the point in history when chemical methods for papermaking were introduced. Apparently, the small amounts of metallic impurities in "modern" paper accelerate the conversion, in the presence of moisture, of absorbed sulfur dioxide to sulfuric acid. In any event, paper is essentially cellulose and can be hydrolyzed by acids. The ultimate effect on paper is to make it more brittle.

The problem of paper embrittlement is most serious in libraries, many of which have incorporated air purification systems (scrubbers and dry adsorbers) to reduce SO_2 concentrations in the interior environment.

2.6.3 Electrical Contacts

Gaseous and particulate pollutants have been a source of trouble to the electronics industry. Low power electrical contacts such as those used in computers and sophisticated instrumentation are especially susceptible. Copper and silver contacts are susceptible to sulfur containing gases (SO_2 and H_2S) through the production of sulfides and/or oxides on the contact surface, thus producing an increase in electrical resistance.

This problem has been reduced in severity through plating the contact surface with precious metals, providing air purification systems for the atmosphere surrounding the electronic equipment, and through the reduction of ambient air pollution levels.

3.0 PARTICULATE MATTER

The primary effect of particulate matter on materials is the soiling of surfaces. However, like sulfur oxides, particulate matter, under the proper conditions, can enhance surface damage particularly in serving as centers for condensation of moisture and adsorption of gaseous pollutants. While soiling itself does not necessarily create direct damage, removal of the particulate matter by cleaning can increase wear and shorten the life of the article being cleaned.

If it is difficult to isolate sulfur oxide damage from the environmental effects, it is far more difficult to isolate the specific influence of particulate matter. There are several reasons for this:

- o High levels of sulfur oxides and particulate matter tend to coexist.
- o Particles offer surfaces for the adsorption of gaseous pollutants. Thus damage appearing to be related to a particle may be the result of adsorbed gaseous pollutants.
- o SO_2 converts to sulfates in the atmosphere and on surfaces. Such sulfates are in particulate form, but are more related to atmospheric mission of SO_2 than particulate matter.

3.1 CORROSION OF METALS

Some of the experiments of Vernon⁷ showed that moist air polluted with SO_2 and particles of charcoal produced corrosion much more rapidly than air containing SO_2 and moisture alone. He reasoned that the effect of the particles was primarily physical in that they increased the concentration of SO_2 by adsorption and created "hot spots" of SO_2 concentration. Sanyal and Singhanian³⁹

writing in 1956 stated that particulate matter had a "profound" effect on corrosion rates. They believed that the influence of particulate matter on corrosion was related to its electrolytic, hygroscopic and/or acidic properties, and its ability to absorb corrosive pollutant gases.

While these laboratory studies appear to show a strong influence of particulate matter with corrosion, field studies have not confirmed this effect. However, as pointed out in Section 22.3, the differences in SO_2 damage functions for zinc and galvanized steel based on air quality/corrosion data between the early 1960's and mid 1970's may reflect in part differences in particulate matter levels between the two periods.

3.2 BUILDING MATERIALS

The primary effect of particulate matter on building materials is soiling. Thus the ultimate impact is aesthetic rather than a loss in physical strength or integrity. Dark particulate matter largely from combustion sources has blackened buildings in many urban areas of the world. Rainwater tends to remove such deposits in areas exposed to the weather giving buildings a streaked or mottled appearance depending upon the surface characteristics of the building.

It is often claimed that particulate matter deposits on stone surfaces carry acids and soluble salts to the surface thereby causing chemical damage: On the other hand, Riederer³⁶ believes that air pollutants including particulate matter have little effect on building stone. He believes that the sooty encrustations of gypsum and organic material do not involve chemically, the underlying stone.

It is clear that the possible direct and indirect damage to building materials by particulate air pollution is not well understood, and further research is needed.

3.3 PAINTS

As in the case of building materials, the primary effect of particulate matter on paint is soiling. Soluble salts such as iron sulfate contained in deposited particles can also produce staining.

Chemically active large particles such as acid smut from oil-fired boilers, mortar dust near building demolition sites or iron particles from grinding operations can severely damage automotive paint. The effects range from discoloration of the paint film to ultimate penetration of the paint film and corrosion of the underlying metal in the vicinity of individual particles. Large particles becoming imbedded in a freshly painted surface can act as wicks to transfer moisture and corrosive pollutants such as SO_2 to the underlying material surface.

3.4 FABRICS

Large particles imbedded in fabrics are capable of causing physical damage to fabrics that receive considerable flexing. Soiling from particulate matter does not normally cause direct damage to fabrics, but increased cleaning frequency reduces the service life of articles made of fabric. However, the stresses of the natural environment, sunlight and water vapor, and gaseous pollutants such as NO_2 , ozone and SO_2 are much more important than those related to particulate matter. Furthermore, articles made of fabric (clothes, curtains, rugs, upholstered furniture, bedding, etc.) tend to spend most of their lives indoors where levels of particulate matter and other pollutants tend to be lower than those out of doors. Therefore, the extent of physical damage to fabrics from outdoor levels of particulate matter are especially difficult to assess. Furthermore, new, more resistant fabrics and fabric treatment or coating processes have tended to minimize the deleterious effects of particulate matter on fabrics.

4.0 NITROGEN OXIDES

It has been demonstrated that nitrogen oxides (principally NO_2) are capable of damaging several types of materials. The most significant effect is on certain types of fabric dyes. NO_2 is also involved in the weakening of some fabrics, causing deterioration of certain types of plastic materials, and in the corrosion of metals.

The ability of NO_2 to be converted into nitrates in the atmosphere is part of the "acidic deposition" or "acid rain" problem. While elevated levels of nitrates are often found in acidic rain water, the relative importance of anthropogenic nitrogen oxides in any material damage caused by acidic rain (e.g., metal corrosion, or stone damage) is not known. It is the author's opinion that any such indirect effect of nitrogen oxides is small in comparison with effects related to sulfur oxides.

To put the role of nitrogen oxides in damaging fabrics and fabric dyes in perspective, these materials usually spend most of their useful lives in the indoor environment where levels of NO_2 are quite different than those outdoors. In homes or other structures with no sources of NO_2 (e.g., gas fired cooking stoves) indoor levels are invariably less than those outdoors. However, Yocom and coworkers⁴⁰ showed that concentrations of NO_2 inside homes with gas cooking stoves can be several times outdoor concentrations. However, the concentration gradient from the kitchen near the sources to other parts of the house is extremely steep because of the short half life of NO_2 in homes. In warehouses where fabric and clothing are stored, indoor levels of NO_2 would be elevated where unvented heaters and combustion powered fork-lift trucks are used.

Another aspect of defining the real life exposure of fabric, and especially clothing, to oxides of nitrogen relates to use of chamber studies to establish

the exposure/effect relationship. Chamber studies show the relationship between material effects to exposures without the complicating influence of other pollutants and wide variations in other environmental factors such as temperature and humidity. Chamber exposures are generally carried out as dynamic systems where concentrations are maintained by adding known amounts of the pollutant gas to a moving air stream which is maintained at predetermined temperature and humidity conditions with or without the exposure to simulated sunlight. A serious question arises as to the meaning of chamber study data when applied to real life exposures, particularly indoor exposures where these materials spend most of their lives. Indoor exposures tend to be quite static (that is, where there is little or no replenishment of the NO_2). An example of a static exposure would be a closet where fabrics in the form of clothing are stored for long periods of time. If one further considers closet storage where there is a large surface area for adsorption or absorption of NO_2 , one would expect the concentrations to which clothing is exposed to be a very small fraction of the concentrations existing in the house as a whole. Furthermore, assuming no sources of NO_2 inside the house, the general indoor concentration would be expected to be a small fraction of that outdoors. Thus, in this scenario the outdoor concentration bears little resemblance to the concentration regime to which the materials are being exposed, and chamber studies designed to determine the effects of a pollutant or material in which the presumed outdoor concentrations are being depicted tend to be misleading.

4.1 DYED FABRICS

The fading of textile dyes by air pollutants, primarily nitrogen dioxide and ozone, has been a particularly vexing problem for the textile industry during much of the twentieth century. The problem first surfaced just prior to World War I, when a German dye manufacturer investigated some unusual cases

of fading of stored woolen goods.⁴¹ The cause was traced to nitrogen oxides in the air produced by open electric-arc lamps and incandescent gas mantles. All the susceptible dyes contained free or substituted amino groups.

In subsequent years, increased replacement of older forms of lighting with electric filament lamps led to a general decline of the wool-fading problem. In the mid-1920's, however, a newly developed manmade fiber, cellulose acetate rayon, was introduced. Since traditional dyes were of little use on this fiber, chemists developed an entirely new line of dyestuffs called disperse dyes. Many are derived from anthraquinone and therefore contain amino groups. Shortly thereafter, a puzzling type of fading began to show up on blue, green, and violet shades of dyed acetate goods. This mysterious fading was called "gas fading" because it was frequently observed in rooms heated by gas heaters.

During the 1930's, acetate fading became a serious problem. Dye and fiber chemists, apparently unaware of the earlier German work, devoted considerable efforts toward a solution. These efforts culminated in 1937 when Rowe and Chamberlain⁴² systematically investigated the fundamental chemistry of dye degradation and independently reached the same conclusions as the earlier German team. Since then, much research has been carried out in an effort to understand gas fading and to develop ways of preventing it. Upham and Salvin⁴³ have summarized much of the information on this subject up to 1975.

The ability of a fiber to absorb NO_2 plays an important role in dye fading mechanism. For example, Salvin⁴⁴ showed that cellulose acetate is an excellent absorber of NO_2 . Polyester and polyacrylic fibers have low absorption rates for NO_2 . Nylon, cotton, viscose rayon and wool have intermediate rates.

Table 4-1 based on a compilation prepared by U.S. Environmental Protection Agency in the Draft Air Quality Criteria Document for Nitrogen Oxides⁵ shows the results of both chamber and field tests of dye fading on cellulose acetate and celluloses (cotton and rayon).

TABLE 4-1. FADING OF DYES ON CELLULOSE ACETATE AND CELLULOSICS
(COTTON AND RAYON) BY NITROGEN DIOXIDE
(From Reference 5)

Dyed Fibers	Exposure	Pollutant	Concentration of Pollutant		Time	Effect	Reference
			$\mu\text{g}/\text{m}^3$	ppm			
Acetate	Gas heated rooms	NO_2	3,760	2.0	N/A	Fading	Rowe and Chamberlain, 1937 ⁴²
Acetate	Chamber	NO_2	3,760	2.0	16 hr	Fading	Seibert, 1940 ⁴⁵
Acetate	Pittsburgh-urban, Ames-rural	NO_2 - O_3		N/A	6 mo	Fading	Salvin and Walker, 1955 ⁴⁶
Acetate	Chamber	NO_2	3,760	2.0	16 hr	Fading	Salvin, et al., 1952 ⁴⁴
Cotton-Rayon	Clothes dryer	NO_2	1,128 - 3,760	0.6 - 2.0	1 hr cycle	Fading	McLendon and Richardson, 1965 ⁴⁷
Acetate-Cotton, Rayon	Los Angeles	NO_2 + O_3 + SO_2	489 + 312 + 131	0.26 + 0.21 + 0.05	30 to 120 days	Fading	Salvin, 1964 ⁴⁸
	Chicago	NO_2 + O_3 + SO_2	414 + 10 + 655	0.22 + 0.005 + 0.25			
Cotton-Rayon	Chamber	SO_2 - NO_2	3,760	2.0	16 hr	Fading	Salvin, 1969 ⁴⁹
Cotton-Rayon	Chamber	SO_2 - NO_2 and O_3		N/A	54 hr	Fading	Ajax et al., 1967 ⁵⁰

TABLE 4-1 (Continued).

Dyed Fibers	Exposure	Pollutant	Concentration of Pollutant		Time	Effect	Reference
			$\mu\text{g}/\text{m}^3$	ppm			
Range of Fibers	Field-Urban, Rural	$\text{SO}_2\text{-NO}_2\text{+O}_3$	N/A		24 mo	Fading	Belion, 1972 ⁵¹
Range of Fibers	Chamber	NO_2	94-940	0.05-0.5	12 wk	Fading	Belion, 1973 ⁵²
Range of Fibers	Chamber	NO_2 + Xenon arc radiation	940	0.5	10 to 80 hr	Fading	Hemphill et al., 1976 ⁵³
Acetate-Cotton, Rayon	Chamber	NO_2	94-940	0.05-0.5	N/A	Fading	Upham et al., 1976 ⁵⁴
Acetate-Cotton, Rayon	Survey	$\text{NO}_2, \text{SO}_2, \text{H}_2\text{S}$	Service Complaints		N/A	Fading	Upham and Salvin, 1975 ⁵⁵

The American Association of Textile Chemist and Colorists (AATCC)⁴⁸ exposed a wide range of fibers and dyes to the atmosphere of four U.S. cities representing different air quality and meteorological regimes. Exposures were made in cabinets to isolate the samples from sunlight. Air quality was monitored for SO_2 , NO_x , and O_3 . Fading was demonstrated on a range of fabrics including cotton and rayons, and several types of dyes (vat, sulfur and fiber-reactive) applicable to cellulose exhibited color change. However, the results were not able to show the degree of responsibility for each of the pollutants in the effects noted.

In an expansion of the AATCC field program Beloin⁵¹ exposed 67 dye-fabric combinations, using 56 dyes, at 11 urban and rural sites in the United States. As in the case of the AATCC works, the fabric samples were exposed in covered, louvered cabinets to exclude light, and ambient levels of SO_2 , NO_x and O_3 were monitored. Urban sites produced more fading than rural sites. Fading also increased with both temperature and humidity. The data were not able to show the effect of specific pollutants, but statistical analysis identified NO_2 concentrations as a significant variable.

Beloin⁵² also carried out a laboratory study in which 20 dyed fabrics were exposed to individual pollutants (SO_2 , NO , NO_2 and O_3) at two levels of concentration, relative humidity and temperature. Severe fading occurred at high humidity and temperature (90 percent RH and 32°C) and high NO_2 level (940 $\mu\text{g}/\text{m}^3$) in eight of nine samples of cotton or viscose. Significant fading also occurred at high humidity and moderate NO_2 level (94 $\mu\text{g}/\text{m}^3$).

The above laboratory results were confirmed in chamber tests conducted by Upham and coworkers⁵⁴.

Dyed nylon fabrics are also susceptible to fading in polluted atmospheres but are not as sensitive in this respect as cotton, rayon, and cellulose

acetate. Dyed polyester fabrics are more resistant to NO_2 damage than nylon. Table 4-2 is a summary by U.S. Environmental Protection Agency⁵ of the work of several researchers on field and laboratory exposures of dyed nylon and polyester fabrics to NO_2 . Field exposure of a range of dyes on nylon to urban atmospheres containing NO_2 , SO_2 and O_3 produced significant dye fading. Dyed polyester fabrics were unaffected.

The fading of permanent press and double-knit polyester in chamber tests (see Table 4-2 and References 55 and 56) does not occur in the fiber matrix. Dye which migrates into the surface resins and surfactants applied to these fabrics during manufacture is affected by NO_2 .

In addition to dye fading, a number of workers have shown that NO_2 can be responsible for yellowing of white fabrics. Such yellowing is often exacerbated by fabric whiteners, softeners, and static compounds and other surface treatment materials. The results of this work has been summarized by U.S. Environmental Protection Agency⁵.

4.2 LOSS OF FIBER STRENGTH

Nitrogen oxides (especially NO_2) like sulfur oxides are capable of weakening cellulose and nylon fibers by acid hydrolysis. However, the question must be asked as to how important this effect is in view of the predominant use of fabrics indoors and the trend of using more resistant fabrics in the outdoor environment.

Field and laboratory studies of the effects of nitrogen oxides on fiber strength are somewhat inconclusive. One chamber study by Morris⁵⁷ exposed cotton samples in two chambers to sunlight, but the air for one chamber was filtered through activated carbon which presumably removed NO_2 , O_3 , SO_2 and other pollutants. Since the study was carried out in Berkeley, California, it was reasoned that little SO_2 was present and the principal gaseous pollutant

TABLE 4-2. EFFECT OF NITROGEN DIOXIDE ON FADING OF DYES ON NYLON AND POLYESTER
(From Reference 5)

Dyed Fibers	Exposure	Pollutant	Concentration of Pollutant		Time	Effect	Reference
			$\mu\text{g}/\text{m}^3$	ppm			
Nylon	Chicago Los Angeles	$\text{NO}_2, \text{SO}_2, \text{O}_3$	188	0.1	30 to 120 days	Fading	Salvin, 1964 ⁴⁸
			282	0.15	30 to 120 days		
Polyester	Chicago Los Angeles	$\text{NO}_2, \text{SO}_2, \text{O}_3$	376	0.2	30 to 120 days	Unchanged	Ibid.
			282	0.15	30 to 120 days		
Nylon	Urban Sites	$\text{NO}_2, \text{SO}_2, \text{O}_3$	376	0.2	3 to 24 months	Fading	Belion, 1972 ⁵¹
Polyester	Urban Sites	$\text{NO}_2, \text{SO}_2, \text{O}_3$	376	0.2	3 to 24 months	Unchanged	Ibid.
Nylon	Chamber High Humidity	NO_2	188 to 1,880	0.1 to 1	12 weeks	Fading	Belion, 1973 ⁵²
Polyester	Chamber High Humidity	NO_2	188 to 1,880	0.1 to 1	12 weeks	Unchanges	Ibid.
Nylon	Chamber High Humidity	NO_2	376	0.2	48 hours	Fading	Imperial Chemi- cal Industires ⁵⁵
Nylon	Chamber High Humidity Xenon Arc	NO_2	940	0.5	30 to 120 hrs	More fading than without NO_2	Hemphill, 1976 ²³
Polyester Permanent Press	Chamber	NO_2	940	0.5	16 hours	Fading	Salvin, 1966 ⁵⁵
Polyester Textured Double Knit	Chamber	NO_2	940	0.5	16 hours	Fading	Urbanik, 1974 ⁵⁶

in the ambient atmosphere was NO_2 . Loss of fiber strength was greatest in the presence of unfiltered air and was attributed to the presence of NO_2 .

The work of Zeronian²⁹ was also inconclusive. He exposed various fibers to xenon arc radiation and air containing $376 \mu\text{g}/\text{m}^3$ of NO_2 at several combinations of temperature and relative humidity. While considerable loss in strength occurred, the differential effect of NO_2 and radiation could not be isolated.

4.3 EFFECTS ON PLASTICS AND ELASTOMERS

The increased use of synthetic organic materials such as polyolefins, polyvinyl chloride, polyacrylonitrile, and polyamides in a variety of consumer and other manufactured products and the maintenance of their strength places some importance on the effects of air pollutants on these materials. Plastic and elastomeric materials are formulated to maximize aging properties. The "weathering" or aging of these materials is dominated by the effect of sunlight the importance of which is intensified by the increased use of plastics in automobiles.

Polymers representing the structures in plastics, as well as textiles, were exposed by Jellinek et al.⁵⁸ to the action of SO_2 , NO_2 , and ozone. The polymers tested included polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyacrylonitrile, butyl rubber and nylon. All polymers suffered deterioration in strength. Butyl rubber was more susceptible to SO_2 and NO_2 than other polymers. However, the effect of O_3 on the rubber was more pronounced than that of the SO_2 or the NO_2 .

Jellinek⁵⁹ examined the reaction of linear polymers, including nylon and polypropylene, to NO_2 at concentrations of 1,880 to 9,400 $\mu\text{g}/\text{m}^3$. Nylon 66 suffered chain scission. (Chain scission produces polymers having lower molecular weights and lower strength.) Polypropylene tended to crosslink. Chain scission of polymers caused by small concentrations of SO_2 and NO_2 took place in the presence of air and UV radiation.

The action of NO_2 and O_3 on polyurethane also was investigated by Jellinek.⁶⁰ The tensile strength of linear polyurethane was reduced by NO_2 alone and also by NO_2 plus O_3 . Chain scission resulting in lower molecular weights and formation of nitro- and nitroso-groups along the polymer backbone occurred upon exposure to NO_2 .

4.4 CORROSION OF METALS

Nitrogen oxides, as potentially acid pollutants, are implicated in several types of corrosion: pitting, selective leaching, and stress corrosion. However, their role in outdoor corrosion of metals is much less important than that of sulfur oxides. U.S. Environmental Protection Agency' has summarized the principal research results on the effects of nitrogen oxides and nitrates on metals. Table 4-3 summarizes this work in qualitative terms.

Probably the most significant form of nitrogen oxides damage to metals is stress corrosion of non-ferrous springs where nitrate containing deposits appear to be implicated. Hermance and his associates^{61,62,63} at Dell Telephone Laboratories have carried out a considerable research effort to better understand this problem which has caused failures in, telephone switching equipment at various places in the U.S. An important finding of this work was that nitrate salts are more hygroscopic than chlorides on sulfate salts. Thus nitrate deposits may lower threshold humidity requirements for the production of electrolytic corrosion effects.

As was discussed in Section 2.1.3 Gerhard and Haynie¹⁸ pointed out the possible implication of acidic air pollution in the catastrophic failure of metals. The reference to this work in Table 4-3 is perhaps some what inappropriate since they clearly emphasized sulfur oxides rather than nitrogen oxides.

TABLE 4-3. CORROSION OF METALS BY NITROGEN DIOXIDE
(From Reference 5)

Metal	Exposure	Pollutant	Effect	Reference
Nickel Brass	Los Angeles	Nitrates	Strength loss	Hermance et al. 1971 ⁶¹
Nickel Brass	Los Angeles	Nitrates	Strength loss	McKinney and Hermance, 1967 ⁶²
Nickel	Los Angeles New York	Nitrates	Corrosion	Hermance, 1966 ⁶³
Tungsten	Chamber	NO ₂	Change oxide	Lazareva, 1973 ⁶⁴
Electric contacts	Field	NO ₂ -SO ₂ -H ₂ S	Corrosion film	Chiaranzelli and Joba, 1966 ⁶⁵
Metal Parts	Field	NO ₂ -SO ₂ -O ₃	Failure	Gerhard and Haynie, 1974 ¹⁸

5.0 OZONE

Ozone is an extremely reactive gas with the ability to react with many organic materials, both natural and manmade. Materials especially susceptible to ozone attack are elastomers (rubber), textile fibers and dyes, and some types of paints. While there are other strong oxidizing materials in polluted atmospheres, ozone is the most abundant of such active oxidants. Depending upon the structure of susceptible organic polymers, the effect of ozone is through chain-scissioning or cross-linking, or both. The first of these effects produces a reduction in molecular weight and decrease in tensile strength, while the second tends to increase the rigidity of some polymers making them more brittle and less resilient.

5.1 ELASTOMERS

The aging of cracking of natural rubber has long been associated with exposure to the atmosphere and was originally thought to be the result of sunlight. Williams⁶⁰ and, later, Van Rossem and coworkers⁶⁷ showed that ozone rather than sunlight was the cause of rubber cracking from atmospheric exposure. In the 1940's and 50's it was recognized by Norton,⁶⁸ Newton,⁶⁹ and Crabtree and coworkers^{70,71} that in addition to ozone, other reactive species in atmospheres polluted with photochemical smog could produce rubber cracking. In work performed in the early days of the Los Angeles smog problem, Bradley and Haagen-Smit⁷² developed a method for measuring atmospheric ozone concentrations using stressed rubber samples and measuring crack depth at the end of specified exposure periods. For several years, this method was considered to be the most reliable and specific method for atmospheric ozone measurement.

The cracking of natural rubber is initiated by ozone attack at the double bond. Therefore synthetic elastomers such as, styrene-butadiene, polybutadiene,

and polyisoprene are also susceptible to ozone damage. Elastomeres with saturated chemical structures or which contain halogen atoms tend to be ozone resistant.

Mueller and Stickney⁷³ reviewed the physical and economic effects of air pollution on elastomers and discussed the development on rubber additives to combat ozone attack. These are generally aromatic amines and phenols. Such materials are widely used in rubber formulations to be used in tires, conveyor belts, automotive parts, and cable insulation. It has been reported by the U.S. Environmental Protection Agency that tire manufacturers have increased the amount of antiozonants added to tires earmarked for the Los Angeles area.⁵

Considerable research has been conducted to develop dose-response relationships between exposures of rubber to ozone, but it is not particularly pertinent to this discussion because most of the work has been done at elevated ozone levels with susceptible rubber formulations (without antiozonants). One exception is the work of Edwards and Storey,⁷⁴ who determined the effects of ozone at approximately $490 \mu\text{g}/\text{m}^3$ on two styrene-butadiene rubber formulation at several levels of antiozonant. In the course of this work a damage function was developed relating the dose to produce visible cracks with the level of antiozonant in the rubber. In the chamber studies of Haynie et al.¹¹ referred to earlier, rubber samples of the type used in the white side walls of top quality steel-belted tires were exposed to ozone at 160 and $1000 \mu\text{g}/\text{m}^3$ and two levels strain (10 and 20%) for 1000 hours. Table 5-1 from this work shows clearly that ozone concentrations and to some degree strain influence cracking rate.

5.2 FABRICS

In Section 4.0 it will be shown that nitrogen oxides can cause fading of fabrics and weakening of textile fibers. Ozone can produce similar effects.

TABLE 5-1. CRACKING RATES OF WHITE SIDE WALL TIRE SPECIMENS

Ozone Concentration $\mu\text{g}/\text{m}$ (ppm)	Strain %	Mean Cracking Rate \pm S.D. ^a $\mu\text{m}/\text{yr}$
160 (0.08)	10	10.36% \pm 7.76
	20	11.70% \pm 7.22
1000 (0.5)	10	19.80% \pm 9.64
	20	24.09% \pm 6.24

^aS.D. = Estimated standard deviation of the mean.

(From reference 11).

However, the same points about indoor exposure brought up in the section on nitrogen oxides are also applicable here. In addition, there are few sources of ozone indoors, and since ozone reacts rapidly with indoor surfaces, indoor concentrations are usually a very small fraction of those outdoors.

While the effects of nitrogen oxides on fabric dyes were first noted before World War I, it was not until 1955 that Salvin and Walker⁴⁶ showed similar effects from atmospheric ozone on specially developed blue disperse dyes designed to resist the effects of NO_2 . However, ozone fading of dyes was manifested in a bleached or washed-out appearance rather than the reddening which is characteristic of the effects of NO_2 on the most sensitive dyes. These workers coined the term "O-fading" to describe this newly discovered phenomenon.

Salvin⁷⁵ noted another type of fading on polyester-cotton/permanent press fabrics stored in warehouses in California, Texas and Tennessee in the United States. The combination of fibers and dyes were thought to be resistant to the effects of air pollution. After careful investigation it was found that the fading had occurred in dye which had migrated into the permanent press materials and not in the fiber itself. Salvin in this same work also showed that humidity is an important factor in ozone fading of textile fibers.

Beloin^{51,52} carried out both field and laboratory exposures of several fabric-dye combinations. As was pointed out earlier, the field studies at several U.S. urban areas were not able to distinguish the relative effect of NO_2 , O_3 or SO_2 , but the controlled environment laboratory studies at 100 and 1000 $\mu\text{g}/\text{m}^3$ ozone showed fading. The higher concentration produced the greater fading. This study also confirmed that humidity and to a lesser extent temperature are factors in ozone fading of dyes. The chamber studies of Haynie

et al.¹¹ which included exposure of drapery materials also confirmed these results.

Cellulose fibers are susceptible to oxidation. Therefore one would expect that cotton and other cellulose-based fibers would be vulnerable to ozone attack. Bogarty et al.⁷⁶ exposed samples of cotton duck and print cloth to air containing ozone in the range between 40 and 120 $\mu\text{g}/\text{m}^3$ in the absence of light. Samples were exposed both wet and dry. Damage was measured in terms of fluidity (reciprocal of viscosity) of dissolved samples of the cloth. An increase in fluidity indicates depolymerization from chemical attack (e.g., O_3 , SO_2 or NO_2). Biological attack, while affecting fiber strength, does not change the average size of the fiber molecules.

After 50 days exposure, the cloth samples exposed to both ozone and high moisture levels showed increased fluidity. In addition, these samples exhibited a 20 percent reduction in breaking strength. The samples exposed dry to ozone showed no significant change. These workers believed that ozone's relatively high solubility in water promotes the action of ozone on cotton. But in spite of these results, they believed that ambient concentrations of ozone are a minor influence when compared with the effects of sunlight, heat, alternate wetting and drying, and biological attack. The work of Morris⁵⁷ conducted at concentrations ten times higher than those of Bogarty but at ambient humidity levels showed no appreciable change in fluidity or breaking strengths.

Kerr et al.⁷⁷ studied the joint effect of ozone and simulated washing-drying cycles on dyed print cloth over a 60-day exposure period. Ozone concentrations averaged 1500 $\mu\text{g}/\text{m}^3$. Breaking strength decreased 18 percent for samples exposed to both ozone and the wash/dry cycles compared to 9 percent for samples exposed only to the wash/dry cycles.

The work of Zeronian et al.²⁹ showed that ozone at 400 $\mu\text{g}/\text{m}^3$ over a 7-day exposure period had no effect on modacrylic (Dynel) and polyester (Dacron) fibers and a slight effect on acrylic (Orlon) and Nylon 66.

5.3 PAINTS

The primary deleterious effect of ozone on paint is accelerated erosion of the paint film. Weight loss converted to thickness loss over a specified exposure period is the usual method of measuring this effect on test panels, thereby permitting a prediction of the life of the film through extrapolation of the exposure data.

There are two research efforts that represent the bulk of knowledge on the effects of ozone on paints. These studies were mentioned in Section 2.3. Campbell et al.²⁵ at the Sherwin-Williams Paint Company carried out both laboratory and field studies on five different types of paints: oil and latex house paints, urea-alkyd coil coating, nitro cellulose/acrylic automotive paint, and alkyd industrial maintenance coating. Spence et al.²⁶ at U.S. Environmental Protection Agency conducted laboratory chamber studies on four classes of painted surfaces: oil base house paint, vinyl-acrylic latex house paint, vinyl coil coating, and acrylic coil coating.

In the laboratory work of Campbell et al.,²⁵ exposures both shaded and unshaded at 2000 $\mu\text{g}/\text{m}^3$ produced measurable erosion effects with oil-based house paint showing the greatest erosion rate; the industrial maintenance coating showed a moderate erosion rate; and the latex, coil and automotive coatings showed the least effect. The unshaded samples, as one would expect, showed the greatest erosion rates. Exposures at 200 $\mu\text{g}/\text{m}^3$ did not produce statistically significant erosion rates. In this same work, field exposures at several United States locations did not produce as clear cut results as the laboratory tests; however, the higher erosion rates of paints exposed in

Los Angeles as compared with other locations were ascribed to higher ozone levels as compared with other locations.

The Spence et al.²⁶ study was designed to show the separate and joint influence of several gaseous pollutants (SO_2 , O_3 and NO_2) and other environmental factors. Statistically significant effects of ozone were measured for the vinyl and acrylic coil coating. The oil-based house paint contained a calcium carbonate filler which was strongly effected by moisture and SO_2 . This effect marked any possible effect by ozone on this paint.

A damage function for acrylic coil coating at 90% relative humidity was developed as follows:

Erosion rate = $0.159 + 0.000714 \text{ O}_3$ where erosion rate is in $\mu\text{m}/\text{yr}$ and O_3 is in $\mu\text{g}/\text{m}^3$.

While the effect of ozone on this type of coating is statistically significant, it is somewhat academic because at an average O_3 level of $100 \mu\text{g}/\text{m}^3$ this function predicts that a 20 μm -thick film would last over 80 years.

6.0 OTHER POLLUTANT EFFECTS

The foregoing sections have described the effects of those criteria pollutants which are capable of producing effects on materials. Volatile organic materials and carbon monoxide are believed to have no significant effects on materials. However, several other gaseous pollutants that have from time to time been emitted from industrial and natural sources should be briefly noted.

6.1 HYDROGEN SULFIDE

Hydrogen sulfide can be emitted from a number of anthropogenic sources: polluted salt water, coke making, oil refineries, pulp and paper manufacture, chemical manufacture and other sources. Natural sources include decomposing vegetable and animal matter, volcanoes and geothermal operations.

Yocom and Upham² have summarized some of the effects on materials which include tarnishing of non-ferrous metals, discoloration of lead-based paint, and damage to electrical contacts. While such problems have been noted in the past in many urban areas, control of H_2S sources and changes in exposed materials (e.g., use of titanium oxide rather than lead oxide in paints) have significantly reduced their severity in recent years.

6.2 FLUORIDES

Hydrogen fluorides and other fluorine-containing materials are emitted from a number of industrial processes including glass or frit manufacture, fertilizer production, and aluminum manufacture. Under extremely high concentration levels, HF and SiF_4 can etch glass and other high silica materials. Some experiments have been conducted that demonstrate this effect.⁷⁸ One would also expect other types of material damage, especially metal corrosion, at these high levels. However, efforts to control fluoride emissions because of the extreme sensitivity of vegetation to fluorides have essentially eliminated any problem of material damage from ambient concentrations.

6.3 AMMONIA

Ammonia occurs in the atmosphere from natural sources, especially anaerobic decomposition of proteinaceous material and from a number of industrial processes, e.g., by-product coke manufacture and a variety of chemical processes. However, its extreme solubility in water and ability to react with acidic components of the atmosphere assure that it normally exists in low atmospheric concentrations except near strong sources.

At high concentrations it is able to corrode a number of non-ferrous metals such as copper, tin, zinc and their alloys. Ferrous alloys are generally resistant, but stress corrosion can be produced in carbon steels.

Ammonia, again at high concentrations, can soften wood through interaction with cellulose fibers and can soften natural rubber. Some plastics also can be adversely affected by ammonia, notably epoxy fiberglass, nylons and polyvinyl chloride under certain conditions of temperature and concentration.

In general, ammonia is not a significant air pollutant with respect to material damage.

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