# U.S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS





THE DURABILITY OF BUILDING MATERIALS

REPORT ON THE EFFECT OF ATMOSPHERIC CONTAMINANTS

ON

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NATIONAL BUREAU OF STANDARDS REPORT

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## NATIONAL BUREAU OF STANDARDS REPORT

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REPORT ON THE EFFECT OF ATMOSPHERIC CONTAMINANTS

ON

THE DURABILITY OF BUILDING MATERIALS

by

Vannie E. Gray and Harvey W. Berger

Sponsored

by

Economics Effects Research Program 2 National Air Pollution Control Administration Department of Health, Education, and Welfare 1

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#### REPORT ON THE EFFECT OF ATMOSPHERIC CONTAMINANTS

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#### THE DURABILITY OF BUILDING MATERIALS

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Vannie E. Gray and Harvey W. Berger

#### 1. ANALYTICAL PROCEDURES

In order to evaluate the effects of sulfur dioxide and ozone on paints and plastics it was necessary to set up analytical procedures to monitor and control the concentrations of these contaminants in exposure environments.

The classical technique for the analysis of SO<sub>2</sub> and O<sub>3</sub> is iodimetry. Because of its high precision and accuracy in micro-analysis and its particular applicability to iodimetric procedures, coulometry was chosen for performing chamical analyses.

Coulometry is based on Faraday's Law which states that the amount of chemical reaction that occurs in an electrochemical cell is related to the quantity of electricity passing through it. The extent of chemical reaction can be obtained, therefore, by observing the magnitude of the current and the elapsed time of the current flow; two parameters than can be measured with very high accuracy.

When coulometric titrations are performed using a constant current, the amount of chemical reaction can be calculated as follows:

## I(Amperes) X t(seconds) = Coulombs

Coulombs 96,500 Coulombs/Equivalent = Equivalents of Chemical Reaction

Equivalents X Grams Equivalent = Weight of Chemical Analyzed

The use of coulometry permits the formation of a titrant in situ. The particular advantage of this technique is the elimination of the need for standard solutions and the associated problems of storage, stability and restandardizations.

A schematic diagram of the apparatus used for the coulometric analysis of  $SO_2$  and  $O_3$  is shown in Figure I. In an acidic solution of potassium iodide the passage of electric current causes the generation of I<sub>2</sub> at the spiral platinum electrode, B.

 $2I \rightarrow I_2 + 2$  electrons

The platinum anode, A, is isolated from the test solution by a sintered glass plug to prevent chemical interference from the products of the other half-cell reaction.

Two identical platinum electrodes, C and D, are used to indicate the presence of iodine. The voltage change across these electrodes is related to the ratio of the concentrations of  $I_2$  and  $I^{-}$  as determined by the Nernst Equation. An amperometric circuit is used to measure the current response across the indicating electrodes due to changes in the iodine concentration. An electronic recorder functions as a micro-ammeter and is capable of making significant

measurements on the order of 0.1 micro-ampere.

A gas sample is bubbled directly into the test solution through a gas dispersion tube, E. The dissolution of  $SO_2$  into the aqueous potassium iodide using a flow rate of 100 ml/minute and a solution volume of 75 ml was found to be 100% efficient within experimental error. This was confirmed by the analysis of a two-stage bubbling train which showed no  $SO_2$  in the second stage. The flow rate and time were noted in order to calculate the total volume of air being sampled. Calibrated rotameters were used to measure flow rates.

The constant current source used for the coulometric titrations was capable of producing steady currents in three ranges: 43 ma; 4.3 ma and 0.43 ma. The instrument incorporates a built-in timer and reads out directly in micro-equivalents. The analyses of  $SO_2$  and  $O_3$  required the use of the lowest range and involved quantities on the order of 0.1 micro-equivalent of iodine which was generated with an accuracy of  $\pm$  0.2%.

#### 1.1 SULFUR DIOXIDE ANALYSIS

The coulometric analysis of sulfur dioxide is based on the reaction between sulfurous acid and triiodide ion. When bubbled through water or an aqueous solution sulfur dioxide dissolves and combines to form sulfurous acid.

$$H_2 0 + SO_2 \rightarrow H_2 SO_3$$

Iodine gas dissolves in an aqueous solution of potassium iodide to form the triiodide ion.

$$I_2 + KI \longrightarrow I_3 + K^+$$

The oxidation-reduction reaction between sulfurous acid and  $I_3^-$  occurs then in the same solution as follows.

$$H_2SO_3 + H_2O \rightarrow SO_4^= + 4H^+ + 2$$
 electrons  
 $I_3 \rightarrow 3I^- - 2$  electrons

For the analysis of  $SO_2 = 0.1 \text{ M}$  HCl, 0.1 M KCl solution was placed in the coulometric titration beaker and in the isolated electrode. Approximately 0.005 micro-equivalents of iodine was generated in the solution and the indicating current was recorded. After the desired gas sample containing  $SO_2$  was bubbled through the solution  $I_2$  was again generated until the indicating current returned to the previous reading. The amount of  $I_2$  required to accomplish this was equivalent to the amount of  $SO_2$  dissolved into the solution.

In an acid solution the presence of air produced low results in the analysis of  $SO_2$ . Oxygen reacted with potassium iodide to form iodine which in turn reacted with  $SO_2$ . The net effect was that less  $SO_2$  was available to react with electrogenerated iodine and the coulometric analysis had a negative error. Figure II shows the effect of varying nitrogen-oxygen mixtures on the  $SO_2$  analysis.

### 1.1.1 PERMEATION TUBES

Trace concentrations of one gas within another are usually produced by dilution techniques that require elaborate equipment such as flow



control devices, manifolds, etc. Apparatus of that kind is usually unstable and requires constant attention and maintenance.

The sulfur dioxide permeation tube described by Scarengelli, Frey and Saltzman (1) is an economical, simple and extremely reliable source of low concentrations of  $SO_2$ . The tubes are prepared by condensing gaseous  $SO_2$  into varying lengths of FEP Teflon<sup>TM</sup> tubing which is sealed at both ends with glass beads. These tubes supply  $SO_2$  by diffusion of the gas through the walls of the plastic tubing. The liquid  $SO_2$  creates a vapor pressure which is constant as long as a liquid phase exists (1). The diffusion rate through the tubing is dependent on the temperature of the tube and the total amount of diffusion is proportional to the surface area or effective length of the tube.

A schematic diagram of the apparatus used for the calibration of permeation tubes is shown in Figure III. A flowmeter was used to monitor the nitrogen flow rate at 100 ml per minute. Ten feet of copper tubing was coiled and immersed in the constant temperature bath so that the nitrogen flowing over the permeation tube was first conditioned at the desired temperature. Polyethylene tubing was used to house the permeation tube inside the constant temperature bath and to make the connection between the copper coil and the dispersion tube in the coulometric titration beaker. For the most part the permeation tubes were calibrated and used at  $25\pm0.1^{\circ}$ C but some tubes were calibrated at higher temperatures to permit experimentation with higher concentrations of sulfur dioxide.

(1) Amer. Ind. Hyg. Assoc. J. <u>28</u>, 260-266 (1967) TM Trade Mark of E. I. duPont de Nemours & Co.

- 5 -

A flow rate of 100 ml per minute was used for sampling times of ten minutes so that a total volume of 1,000 ml flowed through the titration beaker. In order to obtain 2 parts per million  $SO_2$  (by volume) in that volume,  $1 \times 10^{-3}$  ml of  $SO_2$  vapor must diffuse through the permeation tube and mix with the main gas stream. At 25°C and one atmosphere pressure  $1 \times 10^{-3}$  ml is equivalent to  $2.6 \times 10^{-6}$  gram or 0.25microgram  $SO_2$  per minute. A precision of  $\pm 1\%$  in the analysis of ten minute gas samples is achieved with the analytical instrumentation used for generating iodine and indicating the end point of the  $I_2$ -SO<sub>2</sub> reaction. Six small permeation tubes of varying lengths were calibrated. Table I lists the calibration in terms of ppm  $SO_2$  in nitrogen and microequivalents  $SO_2$  per minute of diffusion per centimeter of tube length at 25°C at a flow rate of 100 ml per minute.

Large permeation tubes were prepared for exposure of samples to concentrations of SO<sub>2</sub> in the 100 ppm range. A typical calibration of such a tube at varying temperatures is shown in Figure IV. 1.1.2 MONITORING OF SO<sub>2</sub> IN EXPOSURE SYSTEM

It was necessary to monitor the concentration of  $SO_2$  in the flow systems that were designed for the exposure of paints and plastics. The apparatus, to be described later, consisted of glass tubes arranged in a train. Analysis of  $SO_2$  entering and leaving the train showed no differences in assay indicating that an insignificant amount of  $SO_2$ was being consumed.

- 6 -

#### 1.2 OZONE ANALYSIS

Ozone reacts with potassium iodide in an unbuffered neutral solution to form iodine.

$$0_3 + H_2 0 \longrightarrow 0_2 + 20H$$
 - 2 electrons  
21  $\longrightarrow I_2$  + 2 electrons

The iodine combines to form  $I_3^{-1}$  which is a stable ion and is analyzed in order to determine the extent of reaction with ozone.

The coulometric technique previously described for the analysis of  $SO_2$  was used for the analysis of ozone but in this case the recording microammeter was calibrated by generating known amounts of iodine with the constant current coulometer. This calibration in terms of micro-equivalents of iodine per micro-ampere current was then used to obtain the concentration of  $I_2$  in a test solution simply by a measurement of its current.

Air samples containing ozone, which was made with a commercial ozone generator, were bubbled directly into 2% solutions of KI. From the known flow rate, time of sampling and the total assay of ozone the concentration in parts per million was calculated.

#### 1.2.1 MONITORING OF OZONE CONCENTRATION

Ozone was monitored in the exposure apparatus, to be described later, by aspirating air samples from the apparatus and bubbling them through potassium iodide solutions which were then analyzed for iodine. Sampling times of 20 minutes and a sampling rate of 2,000

- 7 -

ml per minute were used for ozone concentrations on the order of 0.5 ppm. For a total flow of 40,000 ml, 0.5 ppm is equivalent to 0.02 ml ozone or 39 micrograms at 25°C and one atmosphere pressure. Coulometric indicator current changes of 1.5-2 microamperes were measured with a precision of  $\pm 1\%$ . A voltage control on the ozone generator permitted control of the amount of ozone produced by the instrument. 2. MATERIAL EVALUATION

#### 2.1 PLASTICS

Two poly(vinyl chloride) plastics of "rigid" type were used in this study. The components and proportions of each are:

|                           | <u>Parts by Weight</u> |       |  |
|---------------------------|------------------------|-------|--|
| <u>Material</u>           | PVC-A                  | PVC-B |  |
| Ge 103EP                  | 100.0                  | 100.0 |  |
| Ti Pure R-101             | 10.0                   | -     |  |
| Ethylene Bis-stearamide   | 1.0                    | 1.0   |  |
| Acryloid K-120            | 15.0                   | 15.0  |  |
| Argus Mark-235 (BaCd)     | 3.0                    | 3.0   |  |
| Argus Mark C (Phosphite)  | 1.0                    | 1.0   |  |
| Argus Drapex 4.4 (Epoxy)  | 2.0                    | 2.0   |  |
| Admex 746 (Epoxy)         | 3.0                    | 3.0   |  |
| Cyasorb UV-9              | -                      | 0.5   |  |
| Plaskon 103 (Chlorinated) | -                      | 10.0  |  |

The above are two commercial formulations of the type normally used for outside applications. The pigmented material (PVC-A) does not contain ultraviolet stabilizers and the clear material does.

#### 2.1.1 SAMPLE PREPARATION AND PHYSICAL TESTING

Rectangular samples (2 cm x 12 cm) were cut from sheets of poly(vinyl chloride) that were either 0.100 mm or 0.250 mm thick. After exposure these specimens were cut into a "dogbone" shape whose flat section was 1.0 cm wide and 4.5 cm long. The thickness of this reduced section was measured to the nearest 0.001 mm with a dial thickness gage.

The specimens (12 cm - overall length) were mounted in a testing machine equipped with serrated grips set at a gage length of 6.35 cm. They were subjected to tensile tests at a crosshead speed of 0.2 cm/min between grips. The chart speed was maintained at 5.0 cm/min. The tensile test was continued until the load-elongation curve passed through a maximum load. This maximum was used to calculate tensile strength and per cent elongation. Duplicate specimens were used in all exposure tests. Duplicate control specimens were also used in the physical tests.

#### 2.2 PAINTS

Three different coatings were obtained for the evaluation of the effects of sulfur dioxide and ozone on the physical properties of paints. The choice of paints was based on the large quantities of these materials used by the Federal Establishment.

- 9 -



A polyvinyl acetate latex paint, an acrylic latex paint and a linseed oil base paint were purchased from the Government Services Administration under Federal Specifications TT-P-55b, TT-P-0019b and TT-P-102a respectively. The three white paints were shipped in gallon cans and were transferred to quart and pint size glass jars when received.

#### 2.2.1 SAMPLE PREPARATION

Three requirements had to be met in the experimental technique for the preparation of paint film samples to be used for physical testing. First, the measurement of the tensile strength and elasticity of paint films demands, of course, that the paint film be free and unsupported. Second, the techniques devised for the exposure of paint samples to air contaminants in various apparatus required that the paint films have a firm and strong backing. Third, the method used for stripping the film from its substrate must necessarily be such that no prestressing of the film occurs.

Paint films made for this work were prepared by following a modification of the technique described in ASTM Method D 2370-65T. An 0.010 inch doctor blade was used to draw the paint down on a sheet of tin foil mounted on a glass plate.

The most critical factor in making precise measurements of the physical properties of paints is the presence or absence of defects in the paint film. Fine dust particles on the glass plate will press through the tin foil and cause thin spots on the final paint film.

To minimize this the glass plate was washed with isopropyl alcohol and a vigorous stream of air was played over the plate to prevent dust from settling on it prior to the placement of the tin foil. The alcohol was also used to make contact between the foil and the plate for squeegee purposes. An advantage to the use of this alcohol is its rapid evaporation when the foil is removed from the glass plate after the paint has cured.

Since thick tin foil is not manufactured as uniformly as thinner foil and the thinner material is pressed on glass plate more easily to form a better surface, it was planned to use 0.0015 inch tin foil for the preparation of the paint films. It was found, however, that this thickness was not sufficient to support films mounted vertically in exposure tubes. The acrylic latex exposed in a Weatherometer on the 0.0015 inch foil twisted and curled. It was necessary, therefore, to resort to 0.005 inch foil which could resist the forces of the paint itself and could also submit to somewhat rougher handling.

Early experience with the tensile testing of paint films indicated that rectangularly cut samples were failing prematurely because of breaking at the edges of the testing machine's gripping surfaces. Several dog-bone shaped samples were evaluated and the design of the final choice is shown in Figure V. The dimensions of the sample were dictated by restrictions set by the sizes of exposure tubes and other apparatus used in the program.

- 11 -

After the appropriate curing time the tin foil and dried paint film were removed from the glass plate and placed on a large pad of writing paper. A template of the dimensions shown in Figure V was placed on the paint surface and the sample was cut by slicing through the paint and tin foil and into the paper with a surgical type scalpel.

After exposure to SO<sub>2</sub> and O<sub>3</sub> or other treatment the samples were placed, paint surface upward, on a pool of mercury where the tin foil was permitted to amalgamate. Thin foils were amalgamated completely but this was not the case with the 0.005 inch material. After approximately one half hour mercury crept between the foil and the undersurface of the paint film so that it was possible to lift the film free of the foil without prestressing.

#### 2.2.2 PHYSICAL TESTING

A Universal testing machine was used to measure the tensile strength and elasticity of paints. The instrument was equipped with a low capacity load cell capable of measuring loads as low as 0.6 kg for full recorder response. The gage length, or distance between the sample gripping laws was set reproducibly at 9.3 cm. Figure VI shows a view of the paint film mounted in the testing machine. The grips were constructed with hard rubber faces and the free paint films were taped directly to them to prevent slipping and to aid in the alignment of the paint film in the grips.

- 12 -

The parameters with which we were concerned in this program were the maximum load in kilograms, and the total elongation, in centimeters, up to the breaking point after straining at a constant rate. Both of these properties are affected by the rate of loading of the specimen. Figures VII and VIII show the effect of the rate of elongation on the maximum tensile load and the total elongation respectively. The overall effect of increasing the rate of loading is that the material appears to become more brittle. The choice of an appropriate testing speed depends on instrumental capabilities and also on the time required to strain the film to its breaking point. Figure IX shows the effect of loading rate on the actual time to break or total elapsed testing time for the sample. The curves follow the hyperbolic function 1/T vs. T. For the acrylic latex a loading rate of 10 cm/minute required a testing time of one second. For the PVA latex the same rate required almost 2 minutes to cause film rupture. The choice of loading rates was, of necessity, arbitrary and it was decided to make it on the basis of comparable times to break. The rates of elongation for the three paints were based on 30 seconds to break for freshly cured samples and are listed in Table II.

The major factor in determining the precision of the physical testing was, as previously mentioned, the presence of defects in the film. Defects lower the maximum load that a film can sustain and also cause premature rupturing. The initial response of the film to loading

- 13 -

is less sensitive to defects than is the ultimate film performance. The measurement of a modulus of elasticity is a mathematical means of taking advantage of this feature as well as a way of minimizing other variations. Figure X shows a typical stress-time curve for a PVA latex and the measurements that are obtained graphically.

#### 3. SULFUR DIOXIDE STUDIES

The first phase of the air pollution program was the exposure of paints to sulfur dioxide. During this initial period the techniques were developed and the apparatus was designed and built for this and subsequent work on the project.

Three basic experiments were devised for the evaluation of the effects of  $SO_2$  on paints and plastics. The first was the exposure to 2 ppm  $SO_2$  in air in the absence of radiant energy. The second was a similar exposure to 100 ppm  $SO_2$  in air and the third was an exposure to 2 ppm  $SO_2$  in air in a Xenon arc Weatherometer.

For the dark exposures a system of glass tubes was used to treat one half of the samples to contaminated air while the other half was used as controls under the same temperature and humidity conditions. The apparatus, previously described for the calibration of permeation tubes, was used to provide the required amount of SO<sub>2</sub>. Either compressed air was passed over the permeation tube and through the system or vacuum was set up at the exiting end of the system so that preconditioned air would be brought through the apparatus.

- 14 -

The size of the tubes used for the dark experiments permitted the exposure of a large number of samples. The use of the Weatherometer, however, presented some problems. Each sample must directly face the centrally located source of radiant energy. The number of samples and controls that could be exposed at one time was, therefore, seriously limited. In addition, a new apparatus had to be constructed to permit a flow system to operate within the confines of the accelerated weathering device. Figure XI shows the exposure tubes arranged in the Weatherometer.

Laboratory compressed air was filtered, split into various streams, and directed to either the SO<sub>2</sub> contaminating function or the control function. By regulating the rates of air flow at various points and the use of water towers, the air passing through the tubes in the Weatherometer was controlled at 100°C and 35% R.H.

#### 4. OZONE STUDIES

The restrictions on the number of samples that could be exposed in the Xenon Arc Weatherometer prompted the decision to use an entire weathering instrument as an ozone chamber.

Compressed oxygen was passed, at a controlled slow rate, through the ozone generator and into the interior cavity of a Carbon-Arc Weatherometer. The ozone concentration was monitored by aspirating air samples from inside the Weatherometer into a solution of potassium iodide for the analysis of I<sub>2</sub> as previously described. Figure XII is

![](_page_33_Picture_0.jpeg)

a schematic diagram of the apparatus. The paint and plastic samples were mounted directly on a revolving drum inside the Weatherometer. Temperature and humidity were controlled by the instrument at 90°C dry bulb and 86°C wet bulb conditions (85% R.H.). The only disadvantage to this procedure is that control samples could not be exposed simultaneously.

Thus far, paints have been exposed to approximately 0.5 ppm  $0_3$ in air in the carbon arc weatherometer for 750 hours. The experiment will continue for an additional 500 hours followed by 1000 hours of exposure of the same materials, in the absence of  $0_3$ , for the purpose of obtaining control data.

#### 5. PHYSICAL TESTING RESULTS

#### 5.1 PLASTICS

The tensile properties of poly(vinyl chloride) materials were tested as described in section 2.1.1. Tables III and IV show the results from the dark exposure of vinyl materials to sulfur dioxide atmosphere at 2 and 100 ppm levels. Tables III and IV also give the reproducibility of the tensile strengths of the physical tests. The thin PVC-A material (0.100 mm thickness) gave poorer reproducibility than did the thicker PVC-A and the two PVC-B thicknesses.

The data in Table III show that exposure to 2.0 ppm  $SO_2$  in air (50% R.H.) has no appreciable effect on the tensile strength and elongation of vinyl plastics. From this three week study it was apparent

- 16 -

![](_page_35_Picture_0.jpeg)
that greater concentrations of  $SO_2$  were needed. At most, periods of only a few months' exposure would be required for testing. From earlier work it had been found that 4.4%  $SO_2$  in air produced significant physical property changes after only one day exposure. Therefore, it was decided that tests be conducted at a 100 ppm level of  $SO_2$  in air. It was hoped that this level of  $SO_2$  would produce meaningful results in reasonable periods of time.

The results for 100 ppm  $SO_2$  tests are shown in Tables IV and V. The tensile strength of the PVC materials after 42 days' exposure has not changed significantly. The elongation also does not appear to have changed except for the thin PVC-A. The 0.100 mm material showed a change in per cent elongation but did not show a corresponding change in tensile strength. This elongation change is probably real, as it was found in the studies at higher concentrations (4.4%  $SO_2$ ) that pigmented PVC-A adsorbed more  $SO_2$  at a faster rate than did clear PVC-B. Therefore, earlier changes should be induced by this increased adsorption into the thin white material.

From these studies it appears that a 2 to 6 month exposure to 100 ppm of SO<sub>2</sub> is needed to cause significant changes in the tensile properties of PVC plastics. It was found in the earlier work that barium-cadmium heat stabilizers are sensitive to high concentrations of sulfur dioxide. Other heat stabilizers (lead or tin compounds) may not be as sensitive.

#### 5.2 PAINTS

## \_.1 EFFECTS OF SO2

After a one month exposure of the PVA and acrylic latex paints to 2 ppm  $SO_2$  in the absence of light, the physical testing showed no significant differences in the maximum tensile strengths and elongations between the test specimens and controls. On the basis of these results, it was decided to abandon exposures to low concentrations of  $SO_2$  in dark experiments, and to use 100 ppm  $SO_2$  to accelerate changes. Tables VI and VII show the results obtained for the exposures of PVA and acrylic latex paints to 100 ppm  $SO_2$  in air at approximately 25°C and 50% R.H. in the dark.

The test results for the 17 and 25 day exposures showed a lower tensile strength for both the PVA and acrylic specimens that had been exposed to sulfur dioxide. The 38 day tests, however, showed no significant difference in the tensile strength between the controls and the samples exposed to sulfur dioxide. It appears that sulfur dioxide (at the 100 ppm level) does interfere with the early stages of dark aging of PVA and acrylic paints.

The data indicates that after more than one month for the PVA latex and almost two months for the acrylic, the exposure to 100 ppm  $SO_2$  does not have a meaningful effect on the tensile strength or elasticity on those materials.

The results for the exposures of the three test paints to 2 ppm  $SO_2$  in air in the Xenon arc weatherometer are listed in Tables VIII,

IX and X. In the case of the PVA latex, the decreasing difference in the maximum load and the increasing difference of the elongation indicates that the  $SO_2$  had a retarding effect on the embrittlement of the paint by exposure to the Xenon arc.

The data in Table VI for the tensile strengths after 25 and 38 days of dark aging are found to be almost identical with those in Table V for 19 and 42 hours of light exposure. Thus, it appears that one hour of light aging is equivalent to about 25 hours of dark aging. The elongation results for 157 hour exposure to sulfur dioxide (see Table VIII) were obviously in error - possibly because of film defects.

The acrylic latex was affected by SO<sub>2</sub> to a lesser degree than were the PVA films. For the acrylic there was virtually no effect due to SO<sub>2</sub> on the tensile strength after prolonged exposure, but there was a change in the elongations after 200 hours. Comparison of the data for control specimens also showed that acrylic films are not as sensitive to light aging as were PVA films. Acrylic films required 256 hours of light exposure to equal the aging of 17 days in the dark (see Tables VII and IX).

Table X presents the data for linseed oil paint exposed to sulfur dioxide and light. With this material sulfur dioxide appears to accelerate the aging and hastens the embrittlement of the films. The tensile strength is the more significant parameter for this material.

- 19 -

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#### 5.2.2 EFFECTS OF OZONE

The exposure of the three paints to 0.5 ppm  $0_3$  in a carbon arc weatherometer is now in progress. A total of 1,000 hours exposure is planned for both test samples and controls. The total time required to complete this experiment is estimated at four months. Almost 1/3 of that time has elapsed and data has been obtained for the three paints for up to 750 hours exposure. The preliminary data is listed in Table XI.

#### 6. ACKNOWLEDGMENTS

We gratefully acknowledge the help of Dr. P. G. Campbell in the studies of paint; and L. F. Skoda in the development and carrying-out of the physical testing method used for paints and plastics.

## TABLE I

## PERMEATION TUBE CALIBRATION

| Tube Length, cm | ppm SO <sub>2</sub> | microeq.min      | - |
|-----------------|---------------------|------------------|---|
| 2.25            | 2.22                | .00804           |   |
| 2.35            | 2.30                | .00800           |   |
| 3.60            | 3.57                | .00809           |   |
| 3.60            | 3.48                | .00788           |   |
| 5.20            | 5.06                | .00794           |   |
| 5.30            | 5.22                | .00804           |   |
|                 |                     |                  |   |
|                 |                     | Avg00800 ± .0000 | 0 |

## TABLE II

#### RATES OF ELONGATION

| Material            | <u>Rate (cm/minute)</u> |
|---------------------|-------------------------|
| PVA Latex Paint     | 20                      |
| Acrylic Latex Paint | 1                       |
| Linseed Oil Paint   | 1                       |

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#### TABLE III

| Exposure<br>(Days) | *Tensile St<br><u>PVC-A</u> | rength (Kg/cm <sup>2</sup> )<br><u>PVC-B</u> | <u>*Elongat</u><br><u>PVC-A</u> | <u>ion (%)</u><br><u>PVC-B</u> |
|--------------------|-----------------------------|--|---------------------------------|--------------------------------|
| 0**                | 478±13                      | 456±10                                       | 2.19                            | 2.18                           |
| 5                  | 465                         | 464  | 2.18                            | 2.34                           |
| 14                 | 475                         | 462  | 2.20                            | 2.22                           |
| 20                 | 483                         | 459  | 2.16                            | 2.24                           |

THE TENSILE PROPERTIES OF PIGMENTED AND UNPIGMENTED POLY(VINYL CHLORIDE) EXPOSED TO 2 PPM SO<sub>2</sub> (50% R.H., DARK EXPOSURE)

\* All data except <u>0</u> days exposure is average of duplicates.
\*\* Data is average for six specimens.

#### TABLE IV

#### THE TENSILE STRENGTH OF PIGMENTED AND UNPIGMENTED POLY(VINYL CHLORIDE) EXPOSED TO 100 PPM SO (50% R.H. DARK EXPOSURE) 2

| Fyposure | *M                | *Maximum Tensile Strength (Kg/cm <sup>2</sup> ) |                          |                        |  |  |  |  |  |
|----------|-------------------|---|--------------------------|------------------------|--|--|--|--|--|
| (Days)   | White<br>0.250 mm | 0,100 mm  | <u>Clear</u><br>0.250 mm | <u>PVC</u><br>0.100 mm |  |  |  |  |  |
| 0**      | 471±10            | 484±17  | 452±11                   | 438±10                 |  |  |  |  |  |
| 8        | 461               |   | 454                      |                        |  |  |  |  |  |
| 13       |                   | 444   |                          | 429                    |  |  |  |  |  |
| 17       | 485               |   | 452                      |                        |  |  |  |  |  |
| 24       |                   | 469   |                          | 444                    |  |  |  |  |  |
| 38       | 459               |   | 440                      |                        |  |  |  |  |  |
| 42       |                   | 477   |                          | 439                    |  |  |  |  |  |

\* All data except <u>0</u> days exposure shows average of duplicates. \*\* Data is average for six specimens  $(\bar{x} \pm \mathbf{0})$ .



| Fynosure |                   | *Elongation (Per Cent) |                          |                        |  |  |  |  |
|----------|-------------------|------------------------|--------------------------|------------------------|--|--|--|--|
| (Days)   | White<br>0.250 mm | <u>PVC</u><br>0.100 mm | <u>Clear</u><br>0.250 mm | <u>PVC</u><br>0.100 mm |  |  |  |  |
| 0**      | 2.22              | 2.12                   | 2.30                     | 2.23                   |  |  |  |  |
| 8        | 2.27              |                        | 2.22                     |                        |  |  |  |  |
| 13       |                   | 2.05                   |                          | 2.17                   |  |  |  |  |
| 17       | 2.17              |                        | 2.27                     |                        |  |  |  |  |
| 24       |                   | 1.88                   |                          | 2.13                   |  |  |  |  |
| 38       | 2.19              |                        | 2.27                     |                        |  |  |  |  |
| 42       |                   | 1.89                   |                          | 2 30                   |  |  |  |  |

## THE ELONGATION OF PIGMENTED AND UNPIGMENTED POLY(VINYL CHLORIDE) EXPOSED TO 100 PPM SO<sub>2</sub> (50% R.H., DARK EXPOSURE)

\* Data is average for duplicate specimens (except for <u>0</u> days exposure)
\*\* Data is average for <u>6</u> specimens

#### TABLE V



TABLE VI

## EFFECT OF 100 PPM SO<sub>2</sub> IN AIR ON PVA LATEX PAINT AT 50% R.H. IN ABSENCE OF RADIANT ENERGY

| Days     | М              | aximum      | Load, kg   |                | Total Elongation, cm |             |                   |                |
|----------|----------------|-------------|------------|----------------|----------------------|-------------|-------------------|----------------|
| Exposure | <u>Control</u> | <u>so</u> 2 | Difference | <u>%Diff</u> . | <u>Control</u>       | <u>so</u> 2 | <u>Difference</u> | <u>%Diff</u> . |
| 17       | 0.22           | 0.19        | -0.03      | -14            | 24.4                 | 26.3        | +1.9              | +8             |
| 25       | 0.31           | 0.28        | -0.03      | -10            | 11.8                 | 13.7        | +1.9              | +14            |
| 38       | 0.28           | 0.30        | +0.02      | +7             | 14.2                 | 10.8        | -3.4              | <b>-</b> 32    |

#### TABLE VII

# EFFECT OF 100 PPM SO<sub>2</sub> IN AIR ON ACRYLIC LATEX PAINT AT 50% R.H. IN ABSENCE OF RADIANT ENERGY

| Days     | М              | aximum      | Load, kg   |                | То             | tal El      | ongation, cm |               |
|----------|----------------|-------------|------------|----------------|----------------|-------------|--------------|---------------|
| Exposure | <u>Control</u> | <u>so</u> 2 | Difference | <u>%Diff</u> . | <u>Control</u> | <u>so</u> 2 | Difference   | <u>%Diff.</u> |
| 17       | 0.58           | 0.42        | -0.16      | -28            | 1.5            | 0.9         | +0.4         | +80           |
| 25       | 0.71           | 0.41        | -0.30      | -43            | 0.4            | 0.2         | -0.2         | -50           |
| 53       | 0.58           | 0.63        | +0.05      | +9             | 0.6            | 0.5         | -0.1         | -17           |



### TABLE VIII

## EFFECT OF 2 PPM SO, IN AIR ON PVA LATEX PAINT AT 35% R.H. IN<sup>2</sup>XENON ARC WEATHEROMETER

| Hours    |                | Maximum Load, kg |            |                 | Total Elongation, cm |             |            |                 |
|----------|----------------|------------------|------------|-----------------|----------------------|-------------|------------|-----------------|
| Exposure | <u>Control</u> | <u>so</u> 2      | Difference | <u>% Diff</u> . | <u>Control</u>       | <u>so</u> 2 | Difference | <u>% Diff</u> . |
| 19       | 0.27           | 0.29             | + 0.02     | + 7             | 15.1                 | 13.3        | - 1.8      | -12             |
| 43       | 0.30           | 0.32             | + 0.02     | + 7             | 12.9                 | 11.8        | - 1.1      | - 9             |
| 93       | 0.34           | 0.36             | + 0.02     | + 6             | 9.3                  | 9.7         | + 0.4      | + 4             |
| 157      | 0.33           | 0.33             |            | 0               | 9.0                  | 4.2         | - 4.8      | <b>-</b> 54     |
| 202      | 0.38           | 0.37             | - 0.01     | - 3             | 6.2                  | 8.7         | + 2.2      | +36             |
| 252      | 0.41           | 0.39             | - 0.02     | - 5             | 4.9                  | 8.2         | + 3.3      | +68             |
| 510      | 0.67           | 0.54             | - 0.13     | -19             | 1.0                  | 2.3         | + 1.3      | +130            |



#### TABLE IX

## EFFECT OF 2 PPM SO<sub>2</sub> IN AIR ON ACRYLIC LATEX PAINT AT 35% R.H. IN XENON ARC WEATHEROMETER

| Hours Ma: |                |             | Maximum Load, kg |                 |         | Total Elongation, cm |            |                 |  |
|-----------|----------------|-------------|------------------|-----------------|---------|----------------------|------------|-----------------|--|
| Exposure  | <u>Control</u> | <u>so</u> 2 | Difference       | <u>% Diff</u> . | Control | <u>so</u> 2          | Difference | <u>% Diff</u> . |  |
| 19        | 0.33           | 0.37        | + 0.04           | +12             | 2.0     | 1.7                  | - 0.3      | <b>-</b> 15     |  |
| 45        | 0.42           | 0.45        | + 0.03           | + 7             | 1.6     | 1.7                  | - 0.2      | - 13            |  |
| 66        | 0.49           | 0.47        | - 0.02           | - 4             | 1.0     | 0.9                  | - 0.1      | - 10            |  |
| 88        | 0.47           | 0.48        | + 0.01           | + 2             | 0.8     | 0.8                  | - 0.2      | <b>-</b> 25     |  |
| 199       | 0.55           | 0.61        | + 0.06           | +11             | 0.3     | 0.4                  | + 0.1      | + 34            |  |
| 210       | 0.54           | 0.59        | + 0.05           | + 9             | 0.4     | 0.8                  | + 0.4      | +100            |  |
| 256       | 0.60           | 0.65        | + 0.05           | + 8             | 0.2     | 0.2                  |            | 0               |  |
| 510       | 0.70           | 0.68        | + 0.02           | + 3             | 0.2     | 0.4                  | + 0.2      | +100            |  |

#### TABLE X

## EFFECT OF 2 PPM SO<sub>2</sub> IN AIR ON LINSEED OIL PAINT AT 35% R.H. IN XENON ARC WEATHEROMETER

| Hours    |                | Maxim       | um Load, kg |         | То             | tal El      | ongation, cm |                 |
|----------|----------------|-------------|-------------|---------|----------------|-------------|--------------|-----------------|
| Exposure | <u>Control</u> | <u>S0</u> 2 | Difference  | % Diff. | <u>Control</u> | <u>S0</u> 2 | Difference   | <u>% Diff</u> . |
| 42       | 0.31           | 0.31        |             | 0       | 1.7            | 1.6         | - 0.1        | - 6             |
| 96       | 0.47           | 0.49        | + 0.02      | + 4     | 1.3            | 1.2         | - 0.1        | - 8             |
| 162      | 0.70           | 0.77        | + 0.07      | + 10    | 0.9            | 0.8         | - 0.1        | - 11            |
| 192      | 0.70           | 0.74        | + 0.04      | + 6     | 0.9            | 0.8         | - 0.1        | - 11            |
| 510      | 1.38           | 1.93        | + 0.55      | + 40    | 0.2            | 0.2         | 0            | 0               |

## TABLE XI

## EFFECT OF 0.5 PPM $O_3$ on paints in Carbon arc weatherometer

|           |                            | 258 Hours | 490 Hours | 771 Hours |
|-----------|----------------------------|-----------|-----------|-----------|
| Polyvinyl | Maximum Load, kg           | 0.43      | 0.52      | 0.83      |
| Acetate   | Total Elongation, cm       | 5.5       | 3.5       | 0.7       |
| Latex     | Half Secant Modulus, kg/cm | 1.1       | 4.0       | 6.0       |
| Acrylic   | Maximum Load, kg           | 0.67      | 0.74      | 0.81      |
| Latex     | Total Elongation, cm       | 0.5       | 0.3       | 0.2       |
|           | Half Secant Modulus, kg/cm | 9.7       | 13.1      | 18.0      |
| Linseed   | Maximum Lo <b>a</b> d, kg  | 1.13      | 1.69      | 1.65      |
| 0i1       | Total Elongation, cm       | 0.4       | 0.3       | 0.2       |
|           | Half Secant Modulus, kg/cm | 5.1       | 9.0       | 13.7      |







A. ISOLATED P1 GENERATING ELECTROD B. SPIRAL P1 GENERATING ELECTRODE C.B.D. IDENTICAL P1 FOIL INDICATING ELECTRODES

COULOMETRIC CELL WITH

ELECTRODES, GAS DISPERSION TUBE FOR INTRODUCING GAS SAMPLE AND

MAGNETIC STIRRING BAR.

FIG. I









SCHEMATIC DIAGRAM OF APPARATUS USED FOR CALIBRATION OF PERMEATION TUBES





## FIGURE IV

CALIBRATION CURVE FOR LARGE PERMEATION TUBE





## FIGURE V










## FIGURE VII





## FIGURE VIII









CW/WIN RATE

FIGURE IX



GRAPHICAL INTERPRETATION OF STRESS TIME-CURVE



t<sub>2</sub>= Time to Break

Total Elongation= t2 X Rate of Loading (cm/min)

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Figure XI





FIGURE XII

SCHEMATIC DIAGRAM OF OZONE EXPOSURE APPARATUS









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