NATIONAL BUREAU OF STANDARDS REPORT

9961

~~Not for publication or for reference.~~

EVALUATION
OF THE
BRUCKSCH CONTROLLED-ATMOSPHERE WEATHERING DEVICE

Sponsored
by
Manufacturing Chemists' Association

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards[1] was established by an act of Congress March 3, 1901. Today, in addition to serving as the Nation's central measurement laboratory, the Bureau is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. To this end the Bureau conducts research and provides central national services in three broad program areas and provides central national services in a fourth. These are: (1) basic measurements and standards, (2) materials measurements and standards, (3) technological measurements and standards, and (4) transfer of technology.

The Bureau comprises the Institute for Basic Standards, the Institute for Materials Research, the Institute for Applied Technology, and the Center for Radiation Research.

THE INSTITUTE FOR BASIC STANDARDS provides the central basis within the United States of a complete and consistent system of physical measurement, coordinates that system with the measurement systems of other nations, and furnishes essential services leading to accurate and uniform physical measurements throughout the Nation's scientific community, industry, and commerce. The Institute consists of an Office of Standard Reference Data and a group of divisions organized by the following areas of science and engineering:

Applied Mathematics—Electricity—Metrology—Mechanics—Heat—Atomic Physics—Cryogenics[2]—Radio Physics[2]—Radio Engineering[2]—Astrophysics[2]—Time and Frequency.[2]

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to methods, standards of measurement, and data needed by industry, commerce, educational institutions, and government. The Institute also provides advisory and research services to other government agencies. The Institute consists of an Office of Standard Reference Materials and a group of divisions organized by the following areas of materials research:

Analytical Chemistry—Polymers—Metallurgy — Inorganic Materials — Physical Chemistry.

THE INSTITUTE FOR APPLIED TECHNOLOGY provides for the creation of appropriate opportunities for the use and application of technology within the Federal Government and within the civilian sector of American industry. The primary functions of the Institute may be broadly classified as programs relating to technological measurements and standards and techniques for the transfer of technology. The Institute consists of a Clearinghouse for Scientific and Technical Information,[3] a Center for Computer Sciences and Technology, and a group of technical divisions and offices organized by the following fields of technology:

Building Research—Electronic Instrumentation — Technical Analysis — Product Evaluation—Invention and Innovation— Weights and Measures — Engineering Standards—Vehicle Systems Research.

THE CENTER FOR RADIATION RESEARCH engages in research, measurement, and application of radiation to the solution of Bureau mission problems and the problems of other agencies and institutions. The Center for Radiation Research consists of the following divisions:

Reactor Radiation—Linac Radiation—Applied Radiation—Nuclear Radiation.

---

[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D. C. 20234.

[2] Located at Boulder, Colorado 80302.

[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		**NBS REPORT**
4216201-421.04	11 December 1968	9961

~~Not for publication or~~
~~for reference.~~

EVALUATION
OF THE
BRUCKSCH CONTROLLED-ATMOSPHERE WEATHERING DEVICE

by

Joseph E. Clark* and John L. Herndon*

Sponsored
by
Manufacturing Chemists' Association

*Research Associate of Manufacturing Chemists' Association

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

ABSTRACT

The objective of this study was to determine the correlation and acceleration of a promising new accelerated weathering device, relative to outdoor weathering of plastics.

Results from two models of the device were evaluated, using selected plastics whose outdoor performance had been measured. Samples were exposed to filtered radiation from a high-pressure mercury arc under the following conditions:

a) 13,000 ppm SO_2 in O_2, sample temperature of about 120°F;

b) 18 ppm SO_2 in O_2, sample temperature of about 50°F.

Changes were measured in color, infrared spectra, gases evolved and flexibility.

The test was found to have fairly good reproducibility, comparable to other accelerated weathering tests.

In general, similar changes were noted in both the mild and severe exposure conditions. All changes were faster and more pronounced in the severe condition. Lack of quantitative data on changes caused by the severe exposure condition prevents definitive comparison with outdoor results.

Comparison of the mild exposure condition with other accelerated tests and outdoor-weathering shows that:

a) None of the accelerated exposures are truly very fast.

b) Their success in predicting weatherability of plastics was variable. All exposures could select a few, but not all, of the less-stable plastics.

c) The Brucksch device may provide slightly faster color-change for some clear vinyls and reinforced polyester. But other clear vinyls of the same formulation were not greatly discolored, even though they "failed" outdoors.

Initial indications are that embrittlement of plastics is accompanied by higher amounts of CO_2 evolved, but further experiments are needed to conform this. CO_2 evolution varied considerably, depending on type of plastic and time of exposure. There appeared to be little or no relation between amount of CO_2 evolved and a) outdoor performance, and b) color-change in the Brucksch device.

Exploratory experiments were done with selected plastics at intermediate exposure conditions (1400 and 13,000 ppm SO_2 in O_2, about 50°F). Increasing SO_2 concentration a hundred-fold, from 18 to 1400 ppm, approximately doubles discoloration. However, a further ten-fold increase to 13,000 ppm still did not give sufficient acceleration to meet our target exposure time of 100 hours.

A polyethylene film did not show significant change at either 18 or 13,000 ppm SO_2 in O_2, even though it totally embrittled in about a year outdoors. Various exposure conditions in the device failed to deteriorate this plastic. This may be because this polyethylene has a UV absorbance peak in the wavelengths where this mercury-arc source is very deficient in energy (315-360 nm).

Operating conditions of the device are being improved, with emphasis on acceleration and correlation. The relation between SO_2 uptake or CO_2 evolution and embrittlement or discoloration is being investigated.

EVALUATION
OF THE
BRUCKSCH CONTROLLED-ATMOSPHERE WEATHERING DEVICE

EVALUATION OF THE BRUCKSCH CONTROLLED-ATMOSPHERE WEATHERING DEVICE

by

Joseph E. Clark and John L. Herndon

1. OBJECTIVE

The purpose of this report is to present an evaluation of the Brucksch Controlled-Atmosphere Weathering Device. The goal is to determine the correlation and acceleration of this accelerated weathering exposure, relative to outdoor weathering of plastics.

2. INTRODUCTION

In previous NBS Reports #9599 (Controlled-Atmosphere Tests of Plastic Films) and #9653 (Improved Device for Light-Exposure Tests of Plastic Films), Dr. William F. Brucksch described development of a new exposure device for accelerated artificial weathering. This showed promise of being a very rapid screening test for plastics proposed for outdoor use.

This report is concerned with results from the final two models evolving for the device: AIR-cooled sample holders and WATER-cooled sample holders. The latter was Dr. Brucksch's final improvement in the device.

3. EXPERIMENTAL

3.1 MATERIALS

For exposure in the WATER-cooled device, plastics were selected from the 20 materials (approved by the MCA Plastics Technical-Subcommittee) for our complementary outdoor exposure program.

In addition, selected results are reviewed herein from Dr. Brucksch's earlier experiments in the AIR-cooled device [1][1/]. Results were available for polystyrene and the same plastics as above, but in thicknesses and formulations other than those used in the outdoor program.

For a common reference point, polystyrene was also included in our later experiments in the WATER-cooled device.

Table 1 gives a complete list of the plastics discussed in this report.

[1/] Figures in brackets indicate the literature references at the end of this paper.

3.2 EXPOSURES

All data herin resulted from exposure of plastics in one of the two final models of the Bruckschdevice. Plastics were exposed for periods up to 1000 hours. The chambers containing samples were purged with oxygen for at least thirty minutes before the photo-activator (SO_2) was injected into the chamber.

The light source used in both models is a mercury-arc photochemical lamp, whose output spectrum is given in Figure 1. The lines shown are super-imposed on a continuum, typical of high-pressure mercury arcs. However, the manufacturer did not have the entire spectrum including the continuum. This figure was plotted from the only data available. This is a Hanovia 673A lamp with rating of 550 watts (145 volts, 4.4 amps input) and an arc length of 4.5 inches. It is available from Hanovia Lamp Division of Englehard Hanovia Inc., Newark, New Jersey.

Radiation reaching the samples is filtered: a) in the ultraviolet - by passage through pyrex walls, and b) in the infrared - by passage through refrigerated water.

Other common features of both models are described in previous NBS reports [1, 2]. Distinguishing features of the two models are described below.

3.2.1 AIR-Cooled Sample Holders

This earlier model of the device was used by Dr. Brucksch to obtain the results reviewed herein, with 13,000 parts per million (ppm) SO_2 in O_2. Sample chambers were cylindrical. With 88°F cooling water in the condenser surrounding the arc, Dr. Brucksch found the following film temperatures:

Clear polystyrene = 113°F
White PVC = 119°
Black PVC = 168°

3.2.2 WATER-Cooled Sample Holders

This later model of the device was used by the present authors to obtain the results presented herein, with 18 ppm SO_2 in O_2. Sample chambers were of flat form. With 40°F cooling water in the bath around the lamp and sample chambers, Dr. Brucksch found the following film temperatures:

Clear polystyrene = 50°F
White PVC = 45°
Black PVC = 48°

Conditions in both models of the device are summarized in Table 2.

3.3 PROPERTIES MEASURED

In architectural applications, color can be singled out as the property of most importance to the majority of observers. This assumes, of course, retention of at least minimal physical properties. Infrared (IR) spectrophotometric analysis is a common and relatively simple means of measuring the onset of oxidation and other chemical changes. Gas chromatographic (GC) analysis has been found to yield unique evidence for the evolution of volatiles from photo-oxidizing materials. Thus, color, IR and GC measurements were selected to measure deterioration of the exposed plastics, and flexibility was estimated by hand.

3.3.1 Color

Color of the original and exposed samples was measured with a Meeco "absolute" tristimulus colorimeter, Colormaster Model V (Manufacturers Engineering & Equipment Corp., Warrington, Pa.). This instrument measures green (G), red (R) and blue (B) coordinates at 45-degree illumination and 0-degree observation angle. Calculation of E, Adams total color difference, was done by use of Reilly's modification of Glasser's cube-root formula, which is believed to be the best improvement of Adams chromatic-value formula [3].

Calculations were done on the NBS Univac 1108 computer, using our "OMNITAB" english-language program for the equations:

$$L = 25.29\ G^{1/3} - 18.38$$
$$a = 106.0\ (R'^{1/3} - G^{1/3})$$
$$b = 42.34\ (G^{1/3} - B^{1/3})$$
$$(R' = 0.8R + 0.2B)$$

$$E = [(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2]^{1/2}$$

3.3.2 Gas Chromatographic Analysis

Analysis of the gaseous atmospheres in the closed sample chambers was performed at 100, 500 and 1000 hour intervals. Early stages of oxidation are detected by this technique, by measurement of CO_2 and H_2O evolved.

Gas samples (200 micro-liters) were taken from the sample chambers with a gas-tight syringe (Hamilton Co., Whittier, California) and injected into an Anakro Model 1A gas chromatograph (Nester & Faust, Newark, Delaware). Results were recorded on a Sargent Model SR potentiometric recorder (E. H. Sargent and Co., Chicago, Illinois). Temperature of injection port and column was 75°F, and detector temperature was 85°F. A thermal conductivity detector was used with a 6 ft. x 4 mm ID glass column of 80/100 mesh Porapak Q.

Retention times on the column were used for qualitative identification of the CO_2 and H_2O. Peak heights were used to measure their concentrations.

3.3.2.1 Calibration of Peak-height vs Concentration

Figure 2 shows the linear relation between G.C. peak-height and concentration of CO_2, H_2O and SO_2. These calibrations were used to calculate microliters of gas evolved during photodegradation, from the recorded chromatograph response. Calibration factors were calculated from the slopes of linear portions of the curves. Gas concentrations measured in these experiments were in the range of the calibrations.

The calibration for SO_2 is included for future reference, as well as for application to the relative data in earlier NBS reports [1, 4]. Calibration was accomplished by a permeation tube that emits 0.686 milligrams of SO_2 per hour at 35°C [5]. The permeation tube consists of a 0.30 cm I.D., 12.65 cm length of FEP Teflon tubing, with two glass beads used to seal each end of the tubing. After the tube has been filled with SO_2 it is placed in a closed system with a rubber septum at one end. Quantities of SO_2 that have permeated the tubing may be quantitatively analyzed in the gas chromatograph.

To calibrate CO_2, a controlled atmosphere chamber of known volume was flushed with helium for 30 minutes. The chamber was closed and a septum placed over one end. A known quantity of CO_2 was then injected into the chamber using a gas-tight syringe. Samples from the chamber were injected into the gas chromatograph for analysis; this was done using numerous concentrations of CO_2.

Water was calibrated with samples from various atmospheres of known relative humidity and temperature, and analyzing them in the Gas Chromatograph.

3.3.3 Infrared Spectrophotometric Analysis

IR transmission spectrophotometric measurements were made on the thin plastics in an attempt to detect changes in chemical structure. Thick or pigmented samples could not be measured by this method, because insufficient radiation was transmitted through these specimens.

The most frequently observed changes were:

a) near 3.0 microns (often characteristic of -OH and -NH bonds)
b) near 5.8 microns (often characteristic of carbonyl-type bonds)
c) in 7-12 micron range (carboxyl, sulphur-groups, vinyls and others).

Sulphur groups (RSO_2, R-SO-R, $-SO_3H$) show characteristic peaks in the 7-10μ range. Sulfate ($SO_4^=$) absorbs in the 8-9μ region.

3.3.4 Qualitative Flexibility Estimate

Specimens were bent by hand to determine if physical deterioration had occurred. Embrittlement was obvious by the degree of bending which the sample could accommodate without breaking.

4. RESULTS

Tables 3 to 9 summarize observations on plastics exposed in both models of the device.

4.1 SEVERE EXPOSURE CONDITION

Table 3 gives qualitative observations of Dr. Brucksch [1] at 13,000 ppm SO_2 in O_2 with AIR-cooled sample chambers. At this higher concentration of SO_2 and estimated sample temperature near 115-120°F, five types of clear films showed changes within 3 days (to 67 hours).

Significant discoloration of most samples was observed; but only unstabilized formulations of polystyrene and PETP films embrittled. (Stabilized PETP-5 discolored, but did not embrittle.) Moderate IR spectral changes indicated chemical changes for all materials measured.

4.2 MILD EXPOSURE CONDITION

Tables 4 to 9 show color-difference, G.C., I.R. and flexibility observations at 18 ppm SO_2 in O_2 with H_2O-cooled sample chambers. At this lower concentration of SO_2 and cool samples at 45-50°F, changes were measured for up to 6 weeks (1000 hours). Nine types of clear or white and thin to thick plastics were exposed.

At 4 days (100 hours) barely visible discoloration of most samples was noted, but RP-60 and clear PVC-B60 did discolor significantly. Only unstabilized polystyrene film became slightly brittle. Slight or negligible IR-spectral changes were observed.

By 3 weeks (500 hours) more discoloration was generally observed, and RP-60 and clear PVC-B60 discolored to an objectionable degree. Unstabilized polystyrene film totally embrittled and failed. Moderate IR-spectral changes were seen for some plastics.

By 6 weeks (1000 hours) discoloration was not greatly different from results in half that time. Clear PVC-C4 film began to embrittle slightly. IR-spectral changes became more pronounced.

4.2.1 Gases Evolved

All 18 ppm SO_2 was taken up by the plastics in the mild exposure condition by 500 hours. That is, gas chromatography did not show any SO_2 peak at that time. Therefore, SO_2 uptake could not be used as an index of rate of photooxidation in these experiments. For experiments planned at higher SO_2 concentrations, its uptake will be measured. Gray's results on PVC [4] indicated that SO_2 uptake may be more promising than CO_2 evolution, for measuring photodegradation of PVC.

As noted in the following section on reproducibility, there was no highly significant difference in amount of H_2O evolved from any of the plastics.

CO_2 evolution varied considerably, depending on the type of plastic and time of exposure. Dr. Brucksch has already shown [1] that CO_2 is generated more rapidly at higher concentrations of SO_2.

At 100 hours in 18 ppm SO_2, we found that CO_2 evolved ranged from about 0.01 to 0.5 microliter. At 500 hours, the range was from about 0.10 to 4 microliters... a ten-fold increase in range. The latter value was the most CO_2 evolved for any time at 18 ppm SO_2; it corresponded to totally embrittled polystyrene. [G.C. measurements were not done on PVC-C4 at 1000 hours, the only other specimen to embrittle.] Thus, initial indications are that embrittlement is accompanied by higher amounts of CO_2 evolution. More experiments are necessary to confirm this.

At any given time (e.g., 500 hours) there appears to be little relation between CO2 evolved and color-difference.

4.2.2 Reproducibility

Precision of the test is fairly good, as shown by repeat exposures and property-measurements. Color (Table 4) and evolved gases (Table 6) were measured in numerous identical repeat experiments with 5 plastics.

Color change was usually repeated within about 1.5 Adams units of total color difference. The greatest observed standard deviation was 0.90; so the worst case would be expected to include 95% of repeat exposures within 1.8 units of color difference (two standard deviations). This compares well with experience with other accelerated weathering tests.

Evolution of CO_2 and H_2O was measured by gas chromatography. Coefficient-of-variation (standard deviation divided by the average) was used to measure reproducibility of these results. This was used because of the highly significant differences between averages for CO_2 evolution.

Overall coefficient-of-variation for CO_2 evolution was about 11%, indicating fair reproducibility.

For H_2O evolution, the overall coefficient-of-variation was about 18%. This low precision shows that there was no highly significant difference among values for H_2O evolved from the plastics.

Since the G.C. peak for water was non-symmetrical, this may mean that the peak-height method used was not a good measurement of H_2O concentration. A better method would be to measure area under the H_2O-curve. Furthermore, other chromatograph operating conditions might improve this measurement.

4.3 COMPARISON OF BOTH CONDITIONS

The only quantitative data available for both 18 and 13,000 ppm SO_2 exposures are from IR-spectra. Color and flexibility may be qualitatively compared. Seven identical materials were run in both conditions: PE-1, PVF-1, PETP-5, PVC-B4, -B10, -C10 and PS-1.

In general, similar changes in IR-spectra were noted in both conditions. But all changes were more pronounced and faster at 13,000 ppm SO_2.

For example, polystyrene (PS-1) formed carbonyl-type bonds (5.8μ) and sulphur-groups (7-10μ) in both conditions. It showed hydroxyl-bonds (3μ) only at 13,000 ppm SO_2. It embrittled totally in both conditions.

Clear vinyls (PVC-B4, -B10 and -C10) showed slight formation of hydroxyl-bonds (3μ) in both exposure conditions. Discoloration of PVC-C10 occurred in both conditions, but the PVC-B's discolored greatly only at 13,000 ppm SO_2.

(White vinyls were run only in the mild condition.)

PVF-1 showed slight carbonyl formation (5.8μ) in both exposures. Decrease of the small 6.5μ peak was probably due to depletion of an additive. It discolored considerably at 13,000 ppm SO_2, but hardly at all at 18 ppm SO_2.

Polyethylene terephthalate (PETP-5) hydrolyzed slightly (3μ) at 13,000 ppm SO_2, but not at all at 18 ppm SO_2. In these milder conditions, the only noticeable change was appearance of a small unidentified peak at about 15μ.

Polyethylene film (PE-1) did not show any significant change in either exposure condition. [Note: Outdoors, this film totally embrittled in about 1 year!] In fact, PE-1 did not discolor, embrittle or form carbonyl even after 1000 hours exposure to 18 ppm SO_2. This might be due to the scarcity of lamp radiation between 315-360 nm in the ultraviolet (See Figure 1).

4.4 COMPARISON WITH OUTDOOR WEATHERING RESULTS

We have previously reported results on discoloration of many of these plastics outdoors [6]. A report on physical property changes is in preparation [7].

Color change was classified as:

CLASS	Adams (E) Color Difference
A	0-5
B	5-10
C	10-15
D	15-20
E	20-25
F	Greater than 25

Table 10 compares the color-class of plastics outdoors (Arizona, Florida, Washington, D. C.) at 2 years with the same plastics in the mild exposure condition (18 ppm SO_2 in O_2, 45-50°F sample temperature). In both cases, ranking is based on the highest color-difference (E) value attained at any time.

The mild exposure condition greatly discolors only two of the plastics: PVC-B60 is CLASS "C" and RP-60 is CLASS "D". Outdoors, these two plastics were CLASS "E" and "D", respectively. Thus, two plastics which discolored badly outdoors also discolored badly in this laboratory exposure. Color-CLASS "D" was accurately predicted for RP-60, but the prediction for PVC-B60 was two classes better than actual performance.

Three failures by discoloration outdoors (PVC-B4, -B10, and -C10) remained color-CLASS "A" in this laboratory exposure.

Two failures by embrittlement outdoors (PE-1, clear PVC-B4) did not embrittle noticeably in this laboratory exposure.

One failure by embrittlement outdoors (PVC-C4) did embrittle slightly by 1000 hours in the mild exposure condition.

The lack of quantitative data on the severe exposure condition prevents definitive comparison with outdoor results and makes comparison inconclusive.

4.5 COMPARISON WITH OTHER ACCELERATED EXPOSURES

Table 16 summarizes discoloration results outdoors and in various accelerated exposures, including the Brucksch device. The plastics are listed in order of increasing color-difference from their original specimen. Ranking within any given CLASS is also in order of increasing discoloration.

It can readily be seen that none of the accelerated exposures are truly very fast. As expected, different exposure conditions caused rapid discoloration of different plastics. The Brucksch device may provide slightly faster color-change for some clear vinyls (PVC-B60 and -C60) as well as reinforced polyester (RP-60). However, other clear vinyls of the same formulation (PVC-B4, -B10 and -C10) were not greatly discolored, even though they "failed" outdoors.

The other exposures achieved similar variable success. All these accelerated exposures appeared capable of picking out at least a few of the less-stable plastics.

If 1 year outdoors is approximately equated to 3 weeks (500 hours) in these devices, an acceleration factor of about 20 is achieved. This means that a material of 20 years life might require 1 year of "accelerated" testing; and only moderate confidence could be placed in the prediction. Obviously, better means of prediction are still needed.

5. CONCLUSIONS

Overall precision of the test is fairly good.

In general, similar changes in IR-spectra were noted in both the mild and severe exposure conditions. All changes were faster and more pronounced in the severe condition.

At higher SO_2 concentration in O_2 and higher temperature, (13,000 ppm SO_2, 115-120°F) five types of clear plastic films showed changes within 3 days. Significant discoloration of most samples was observed; but only unstabilized formulations of polystyrene and polyethylene terephthalate films embrittled. Stabilized polyethylene terephthalate discolored, but did not embrittle. Moderate IR-spectral changes indicated chemical changes for all materials measured.

At lower SO_2 concentration in O_2 and lower temperature (18 ppm SO_2, 45-50°F), clear and white-pigmented plastics deteriorated more slowly. At 4 days, barely visible discoloration of most samples was noted, and two plastics which discolored significantly outdoors (RP-60, PVC-B60) discolored considerably. Only unstabilized polystyrene film became slightly brittle. Very slight change was noted in IR spectra.

Continuing exposure to 500 and 1000 hours in the mild condition caused the above changes to become more pronounced. At 1000 hours, clear PVC-B4 film (which embrittled outdoors) began to embrittle slightly.

Initial indications are that embrittlement is accompanied by higher amounts of CO_2 evolved, but further experiments are needed to confirm this.

All 18 ppm SO_2 was taken up by the plastics, so its rate of uptake could not be used as an index of photo-oxidation. There was no highly significant difference in amount of H_2O evolved from any of the plastics. CO_2 evolution varied considerably, depending on type of plastic and time of exposure. There appears to be little or no relation between amount of CO_2 evolved and a) outdoor performance, and b) color-change in the device.

Comparison with outdoor-weathering results indicated that two plastics which discolored greatly outdoors were also greatly discolored in the mild exposure condition. Three clear vinyls failed by discoloration outdoors (PVC-B4, -B10, -C10) but remained color-CLASS "A" in this laboratory exposure.

Two failures by embrittlement outdoors (PE-1, clear PVC-B4) did not embrittle noticeably at 18 ppm SO_2.

One failure by embrittlement outdoors (PVC-C4) did embrittle slightly by 1000 hours in this mild exposure condition.

Lack of quantitative data on the severe exposure condition prevents definitive comparison with outdoor results.

Initial experiments have been done with selected plastics at intermediate exposure conditions (1400 and 13,000 ppm SO_2, 45-50°F.). Results are given in Appendix I. These data indicate that discoloration at 500 hours is approximately doubled by the 100-fold increase in SO_2 concentration to 1400 ppm. However, a further ten-fold SO_2 increase to 13,000 ppm still did not give sufficient acceleration to meet our target exposure time of 100 hours.

Polyethylene film (PE-1) did not show any significant change in either exposure condition, even though it totally embrittled in about a year outdoors. Further experiments have been done with this plastic under various exposure conditions (see Appendix II). In 100 hours, its slight discoloration (about 2 units) was not increased by presence or higher concentrations of O_2 or SO_2. Increasing oxygen concentration increased CO_2 evolution; but 10,000-fold increase in SO_2 concentration increased CO_2 evolution by only about 50%. It did not embrittle under any of the accelerated conditions used in the Brucksch device.

This polyethylene has a UV absorbance peak in the wavelengths where this mercury-arc source is very deficient in energy (315-360 nm).

6. RECOMMENDATIONS

Operating conditions of the device should be improved, with emphasis on acceleration and correlation.

More accelerated deterioration may be achieved by increasing temperature and SO_2 concentration.

An efficient way to improve both acceleration and correlation would be to replace the mercury-arc source with a xenon-arc. This is recommended.

The relation between CO_2 evolution and embrittlement or discoloration should be investigated, to determine usefulness of this early detection technique. Absorption of SO_2 should be studied for the same purpose.

7. ACKNOWLEDGMENTS

The technical assistance of H. W. Berger and V. E. Gray of the NBS staff is gratefully acknowledged.

8. REFERENCES

[1] "Controlled-Atmosphere Tests of Plastic Films", W. F. Brucksch, Jr., NBS Report #9599, August 1967.

[2] "Improved Device for Light-Exposure Tests of Plastic Films", W. F. Brucksch, Jr., NBS Report #9653, November 1967.

[3] "Significance of Recent CIE Recommendations for Color Measurement", F. W. Billmeyer, Jr., Color Engineering, 6, No. 1, 36, Jan-Feb 1968.

[4] "Use of SO_2 to Study Photodegradation Rates of PVC Plastics", V. E. Gray, NBS Report #9648, November 1967.

[5] "Evaluation of Teflon Permeation Tubes for Use with SO_2", F. P. Scaringelli, S. A. Frey and B. E. Saltzman, American Industrial Hygiene Assn. Journal, 28, 260, May-June 1967.

[6] "Outdoor Performance of Plastics: I. Introduction and Color-Change", J. E. Clark, N. E. Green and P. Giesecke, NBS Report #9912, September 1968.

[7] "Outdoor Performance of Plastics: II. Physical Properties", J. E. Clark, G. E. Fulmer and R. Neuman, NBS Report, in press.

LIST OF TABLES

TABLE

APPENDIX I

APPENDIX II

TABLE 1

PLASTICS USED IN THIS STUDY

BASE POLYMER	PLASTIC	DESIGNATION	DESCRIPTION
Polyethylene	Translucent - 1 mil	PE-1	Commercial/Not stabilized for outdoors.
	- 5 mil		Commercial/Outdoor grade.
	- 10 mil		Commercial/Not stabilized for outdoors.
	- 60 mil	PE-60	ditto
Poly (methyl methacrylate)	Clear - 60 mil	PMMA-60	Commercial/Outdoor grade
Poly (vinyl fluoride)	Clear - 1 mil	PVF-1	Commercial/Outdoor grade/No UV absorber
	- 4 mil		Experimental.
Poly (ethylene terephthalate)	Clear - 1 mil		Commercial/Not stabilized for outdoors.
	- 5 mil	PETP-5	Commercial/Outdoor grade
	- 10 mil		Commercial/Not stabilized for outdoors.
Polyester/$_{\text{x-linked}}$	Clear - 60 mil	RP-60	Commercial/Outdoor grade/Styrene-modified
Poly (vinyl chloride)	Clear - 4 mil	PVC-B4	Experimental/Barium-cadmium stabilizer
	- 10 mil	-B10	ditto
	- 60 mil	-B60	ditto
	Clear - 4 mil	PVC-C4	Experimental/Tin stabilizer
	- 10 mil	-C10	ditto
	- 60 mil	-C60	ditto
	White - 4 mil	PVC-A4	Experimental/Barium-cadmium stabilizer/TiO_2 pigment
	- 10 mil	-A10	ditto
	- 60 mil	-A60	ditto
	White - 4 mil	PVC-D4	Experimental/Tin stabilizer/TiO_2 pigment
	- 10 mil	-D10	ditto
	- 60 mil	-D60	ditto
Polystyrene	Clear - 1 Mil	PS-1	Commercial/Not stabilized for outdoors

TABLE 2

EXPOSURE CONDITIONS USED

Sample-Chamber Cooling	Est. Sample Temperature	ppm of SO_2*	Condition
AIR	115-120°F	13,000	"SEVERE"
WATER	45-50°F	18	"MILD"

*Note: About 2 ppm SO_2 is the highest outdoor concentration ever measured by Public Health Service.

TABLE 3

EFFECTS ON PLASTICS EXPOSED IN 13,000 PPM SO_2 IN O_2*

(Estimated Temperature of 115-120°F)

Plastic	Exposure Time	Change in Color	Change in Flexibility	Change in IR-Spectrum (μ)
PE-1	42.6 Hours	Slight	None	5.8 (slight)
-5	66.6 Hours	Lt. Brown	None	3.0, 5.8, 7.-12.
-10	42.6 Hours	Lt. Tan	None	3.0, 5.8, 7.-12.
	66.6 Hours	Lt. Brown	None	3.0, 5.8, 7.-11.
PVF-1	42.6 Hours	Dk. Amber	None	5.8
-4	45.0 Hours	Tan	None	2.9, 5.8
	66.6 Hours	Lt. Brown	None	--
PETP-1	42.6 Hours	None	Brittle	2.7-3.7
-5	45.0 Hours	Amber	None	2.7-3.7 (slight)
	66.6 Hours	Yellow-Green	None	--
-10	45.0 Hours	Lt. Amber	Crease White	--
	66.6 Hours	Slight	Brittle	--
PVC-B4	42.6 Hours	Amber	None	"Slight"
-B10	45.0 Hours	Lt. Amber	None	3.0 (slight)
	66.6 Hours	Pale Buff Green	None	--
PVC-C10	45.0 Hours	Amber	None	2.8-3.3
	66.6 Hours	Pale Buff Green	None	--
PS-1	45.0 Hours	Dk. Brown	Brittle	3.0, 5.8, 7.-10.

---

* Results abstracted and quoted from Reference 1.

TABLE 4

COLOR DIFFERENCE

(18 ppm SO_2, 45-50°F)

Plastic	HOURS OF EXPOSURE 100	500	1000
PE-1	0.3	2.5	1.9
-60	2.1	1.8	1.9
PMMA-60	0.6	0.9	1.4
PVF-1	1.6	0.2	1.9
PETP-5	1.3	(2.4)	2.2
RP-60	5.2	17.8	23.8
PVC-B4	0.3	0.9	2.1
-B10	1.0	1.4	0.5
-B60	10.2	14.9	--
PVC-C4	1.4	1.5	0.6
-C10	1.0	(2.1)	(4.6)
PVC-A4	0.8	(1.0)	(1.0)
-A10	.9	1.3	--
PVC-D4	1.3	1.7	4.5
-D10	1.3	(2.8)	5.2
-D60	3.8	4.0	--
PS-1	1.0	(+)	--
Average	2.0	3.6	4.0

( ) Numbers in parentheses are averages of several runs (see Table 4).

\+ Totally embrittled.

TABLE 5

REPRODUCIBILITY OF EXPOSURE: COLOR

(18 ppm SO_2, 45-50°F)

	Time	E	Average	Standard Deviation
PETP-5	500 Hrs.	1.5 2.7 2.5 2.8 2.6	2.4	0.73
PVC-C10	500 Hrs.	2.5 1.8 2.0 2.2	2.1	0.75
PVC-C10	1000 Hrs.	3.0 6.3	4.6	0.33
PVC-A4	500 Hrs.	1.0 1.1 1.0	1.0	0.25
PVC-A4	1000 Hrs.	1.1 0.9	1.0	0.25
PVC-D10	500 Hrs.	4.8 1.7 1.9	2.8	0.90
PS-1	500 Hrs.	Embrittled Embrittled Embrittled	Embrittled	--

TABLE 6

GASES EVOLVED (micro-liters)

(18 ppm SO_2, 45-50°F)

	Time of Exposures (Hours)					
	100		500		1000	
PLASTIC	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O
PE-1	0.03	2.9	0.08	2.2	--	--
-60	0.03	2.5	0.66	2.9	0.27	4.6
PMMA-60	0.03	3.1	0.12	1.6	0.29	4.2
PVF-1	0.15	2.9	0.35	2.9	--	--
PETP-5	0.30	6.2	(1.05)	(3.0)	2.16	3.7
RP-60	0.10	3.3	0.88	1.9	2.60	4.2
PVC-B4	0.07	2.0	0.17	2.0	--	--
-B10	0.12	1.8	0.17	2.2	1.70	3.3
-B60	0.06	2.5	0.28	3.1	--	--
PVC-C4	0.10	2.0	0.19	2.2	--	--
-C10	0.12	2.9	(0.31)	2.9	(0.97)	(3.8)
PVC-A4	0.14	2.2	(0.27)	(3.2)	0.44	2.9
-A10	0.07	2.0	0.15	2.9	--	--
PVC-D4	0.15	2.5	(0.29)	(5.1)	1.13	2.9
-D10	0.10	2.9	(0.52)	(3.3)	1.09	3.3
-D60	0.09	2.9	0.55	4.1	--	--
PS-1	0.45	2.0	(3.45)	(2.6)	--	--
Average	0.12	2.7	0.56	2.8	1.2	3.7

( ) Numbers in parentheses are averages of several runs (See Table 7)

TABLE 7

REPRODUCIBILITY OF EXPOSURE: GAS EVOLVED (μl)

(18 ppm SO_2, 45-50°F)

				Average		Coefficient of Variation	
PLASTIC	TIME (Hrs)	CO_2	H_2O	CO_2	H_2O	CO_2	H_2O
PETP-5	500	1.24	4.1	1.05	3.0	31.9%	28.4%
		1.13	3.5				
		1.09	2.9				
		1.09	2.9				
		0.71	1.8				
PVC-C10	500	0.34	2.9	0.31	2.9	11.6%	0. %
		0.29	2.9				
	1000	0.97	4.1	0.97	3.8	0. %	11.1%
		0.97	3.5				
PVC-A4	500	0.26	2.0	0.27	3.2	8.1%	39.1%
		0.27	3.5				
		0.30	4.1				
PVC-D4	500	0.30	5.2	0.29	5.1	4.8%	2.7%
		0.28	5.0				
PVC-D10	500	0.48	2.9	0.52	3.3	12.7%	13.5%
		0.62	3.9				
		0.51	3.5				
		0.48	3.1				
PS-1	500	3.12	2.5	3.45	2.7	9.0%	28.0%
		4.28	3.7				
		3.79	2.5				
		2.63	2.0				
OVERALL						11.2%	17.5%

TABLE 8

IR-SPECTRAL CHANGE (microns)

(18 ppm SO_2, 45-50°F)

PLASTIC	HOURS OF EXPOSURE 100	 500	 1000
PE-1	None	None	None
PVF-1	6.5 (decrease)	5.8, 6.5 (decrease)	5.8, 6.5 (decrease)
PETP-5	None	14.5-15.6	14.5-15.6
PVC-B4	None	None	None
-B10	None	None	None
-C4	None	None	2.8-3.0
-C10	None	3.0 (slight)	2.8-3.3
-A4	None	None	None
-A10	None	6.0-6.7	--
-D4	None	None	None
-D10	None	None	None
PS-1	5.6-6.2, 7.8-9.4	+	--

+ Totally embrittled.

TABLE 9

FLEXIBILITY CHANGE

(18 ppm SO_2, 45-50°F)

	HOURS OF EXPOSURE		
	100	500	1000
PE-1	None	None	None
-60	None	None	None
PMMA-60	None	None	None
PVF-1	None	None	None
PETP-5	None	None	None
RP-60	None	None	Slightly Brittle
PVC-B4	None	None	None
-B10	None	None	None
-B60	None	None	--
-C4	None	None	Slightly Brittle
-C10	None	None	None
-A4	None	None	None
-A10	None	None	--
-D4	None	None	None
-D10	None	None	None
-D60	None	None	--
PS-1	Slightly Brittle	Totally Brittle	--

TABLE 10

COLOR-CLASS OF PLASTICS

CLASS	OUTDOORS/2 YEARS	18 ppm SO_2, 45-50°F/500 hours
Ⓐ	PE-1 [1] PMMA-60 PVF-1	PE-1 [3] PE-60 PMMA-60 PVF-1 PETP-5 PVC-B4 [3] -B10 -C4 [4] -C10 -A4 -A10 -D4 -D10 -D60
Ⓑ	PE-60 PETP-5 PVC-C4 [2] -A4 -A10 -D4 -D10 -D60	-
Ⓒ	-	PVC-B60
Ⓓ	RP-60	RP-60
Ⓔ	PVC-B60	-
Ⓕ	PVC-B4 [2] -B10 -C10	-

[1] Film embrittled completely at all sites in 1/2 to 1-1/2 years.

[2] Film embrittled in Arizona in 1 to 2 years.

[3] No embrittlement.

[4] Slight embrittlement by 1000 hours.

TABLE 11

COLOR-CLASSIFICATION BY WEATHERING-TESTS

(500 hours)

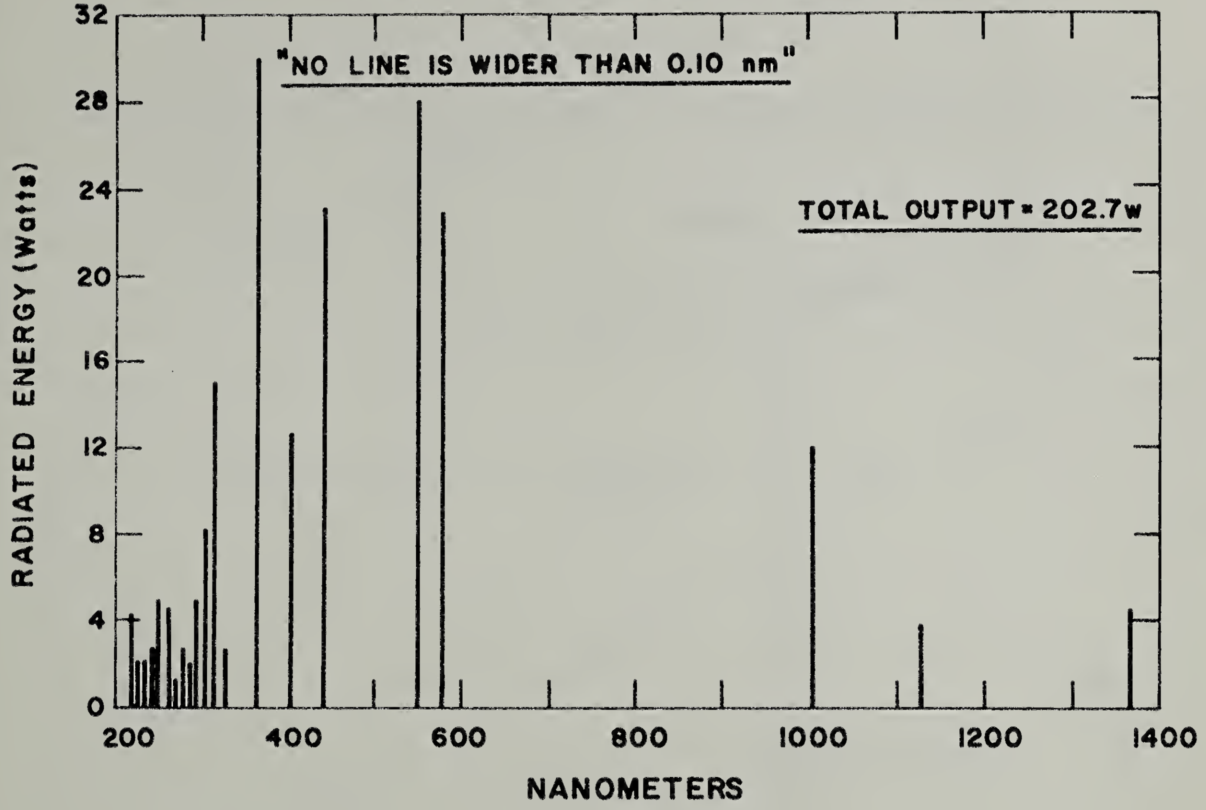
COLOR-	OUTDOORS		BRUCKSCH DEVICE		FS/BL	ENCLOSED CARBON		SUNSHINE CARBON		ATLAS XENON		X E N O T E S T 450					
CLASS	(2 YR)	(1 YR)	18 ppm SO_2 50°F	1400 ppm SO_2 50°F		DRY	WET	DRY	WET	DRY	WET	30% RH Light DRY	30% RH Light WET	30% RH Lt/Dark DRY	30% RH Lt/Dark WET	90% RH Lt/Dark DRY	90% RH Lt/Dark WET
Ⓐ	PVC-A60 PVF-1 PMMA-60 PE-1	PVC-A60 -A10 -A4 PVF-1 PMMA-60 PVC-B4 -C10 -C4 -B10 -D60 -M60 PE-1	PVF-1 PVC-B4 PMMA-60 PVC-A4 -A10 -B10 -C4 -D4 PE-60 PVC-C10 PETP-5 PE-1 PVC-D10 PVC-D60	PVC-C10 -A4 PETP-5 PVC-D10	PVC-A60 PMMA-60 PVC-A10 -A4 -B4 -D4 -D10 -C10 -B10 PVF-1 PE-60 PETP-5 PVC-M60 -D60 PE-1	PVC-A10 PMMA-60 PVC-A4 PVF-1 PETP-5 RP-60	PMMA-60 PVC-A4 PETP-5 PVF-1 RP-60 PVC-A10		PVC-A60 PMMA-60 PVC-B4 -A4 -A10 PETP-5 PVC-B10 PVF-1 PVC-D60 -D10 -D4 PE-1 PVC-N60	PVC-A4 -A10 PMMA-60 PETP-5 PE-60 RP-60 PVC-M60 PVF-1	PMMA-60 RP-60 PVC-A60 PVF-1 PETP-5 PVC-A4 -A10 PE-1	PMMA-60 PVC-A60 -B4 -D10 -B60 -D60 PE-60 PVC-M60 PVF-1 RP-60 PVC-C10 -A4 -A10 PE-1	PETP-5 RP-60 PVF-1 PMMA-60 PVC-A4 -M60 -A10 -C10 -D60 -A60 -B60 -D4 -B4 -D10	PVC-A10 -A4 PVF-1 PE-60 PVC-B4 -D10 PMMA-60 PVC-A60 PETP-5 PVC-D60 -M60 RP-60 PVC-D4 PE-1 PVC-C10 -C4 -B60	PVF-1 PVC-B4 -C4 -A10 -D60 -M60 PMMA-60 PETP-5 PVC-A60 -N60 PE-1 PVC-B60 -C10 RP-60	PVC-C4 -C10 -D10 PETP-5 PVF-1 PVC-B4 -A4 -A10 -D60 PE-60 PMMA-60 PVC-M60 -D4 -A60 PE-1 PVC-B60	PVC-C10 -C4 PETP-5 PVC-A60 PVF-1 PVC-B4 -D60 -A10 -A4 -M60 -D4 -D10 PMMA-60 PE-1 PE-60
Ⓑ	PVC-A4 -A10 -D60 -M60 -C4 PETP-5 PVC-D4 -D10 PE-60	PE-60 PETP-5 PVC-D4 -B60 -D10 -N60	-	-	PVC-B60 RP-60	PVC-N60 -M60	PVC-M60 -N60 PE-60		RP-60 PVC-M60	PVC-N60	PVC-M60	PVC-C4 -D4	PVC-C4 PE-60 -1	-	PE-60	PVC-N60	PVC-B60
Ⓒ	-	PVC-C60 RP-60	PVC-B60	-	PVC-N60	PE-60	-		PE-60	-	PVC-N60	PVC-N60 PETP-5 PVC-B10	PVC-N60	PVC-B10	PVC-B10 -D4	PVC-B10	PVC-B10 -N60
Ⓓ	RP-60 PVC-C60	-	RP-60	-	-	-	-		-	-	-	-	-	-	PVC-D10	RP-60	RP-60
Ⓔ	PVC-B60	-	-	-	-	-	-		-	-	PE-60	-	-	-	-	-	-
Ⓕ	PVC-B4 -N60 -B10 -C10	-	-	-	-	-	-		-	-	-	-	-	-	-	-	-

LIST OF FIGURES

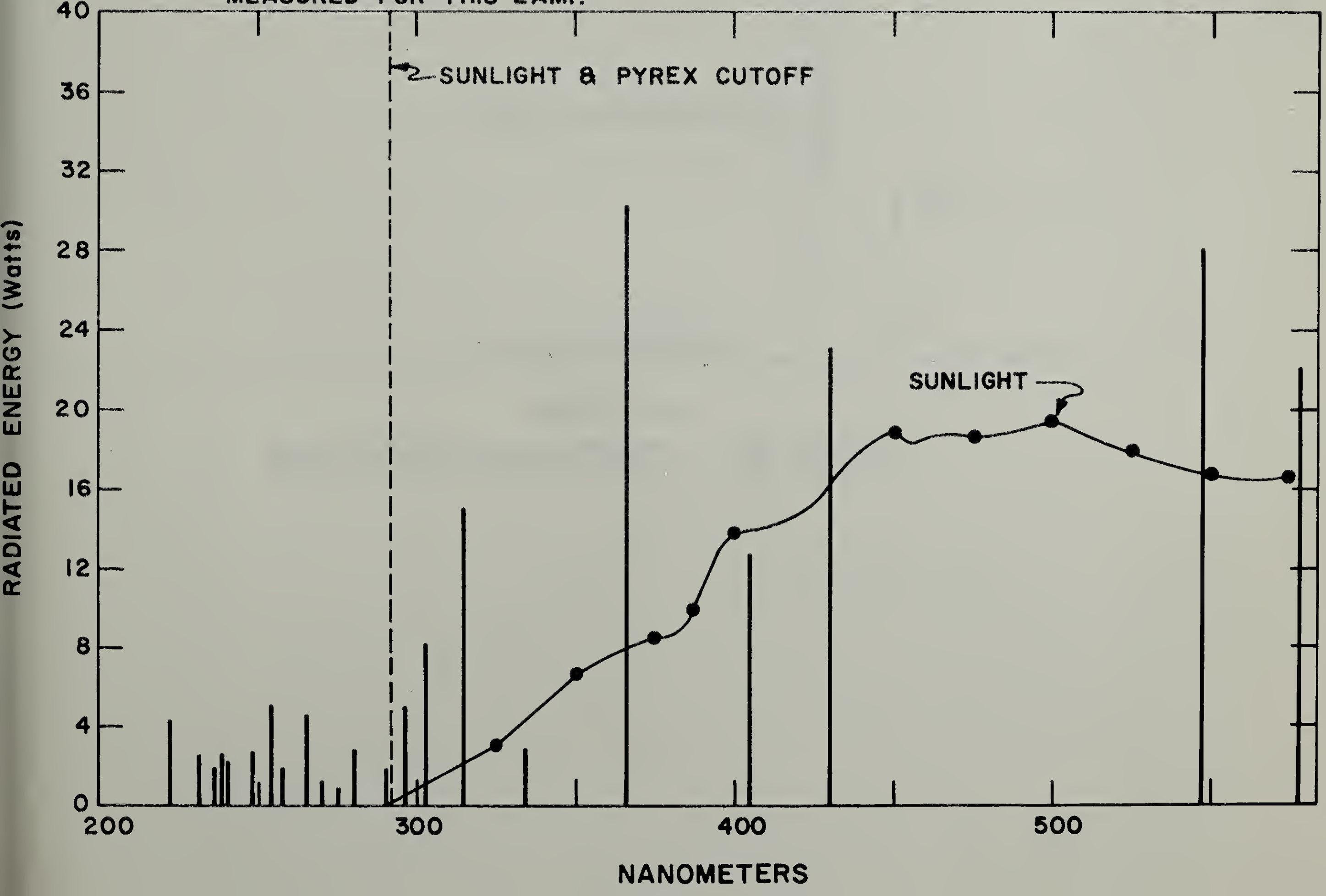
FIGURE

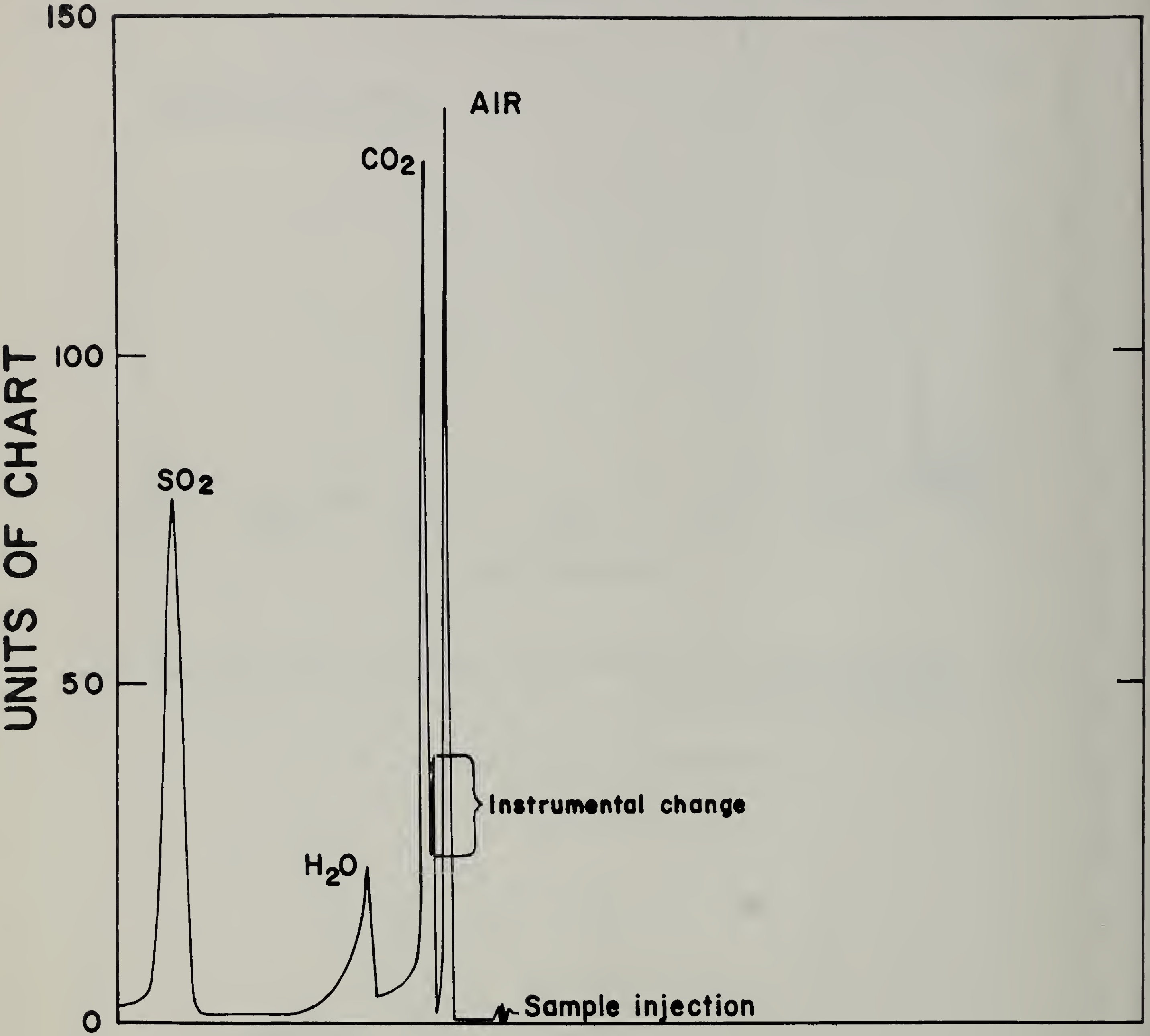
HANOVIA 673 A

HIGH PRESSURE QUARTZ Hg-vapor lamp (550w)

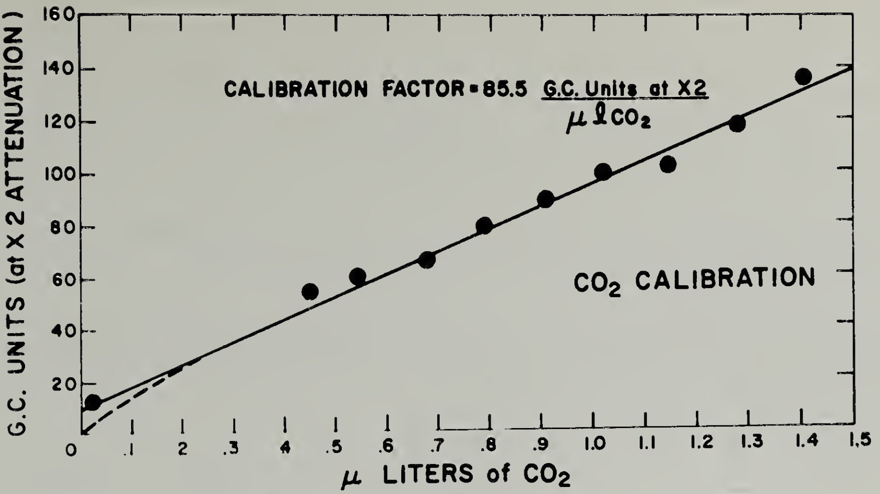


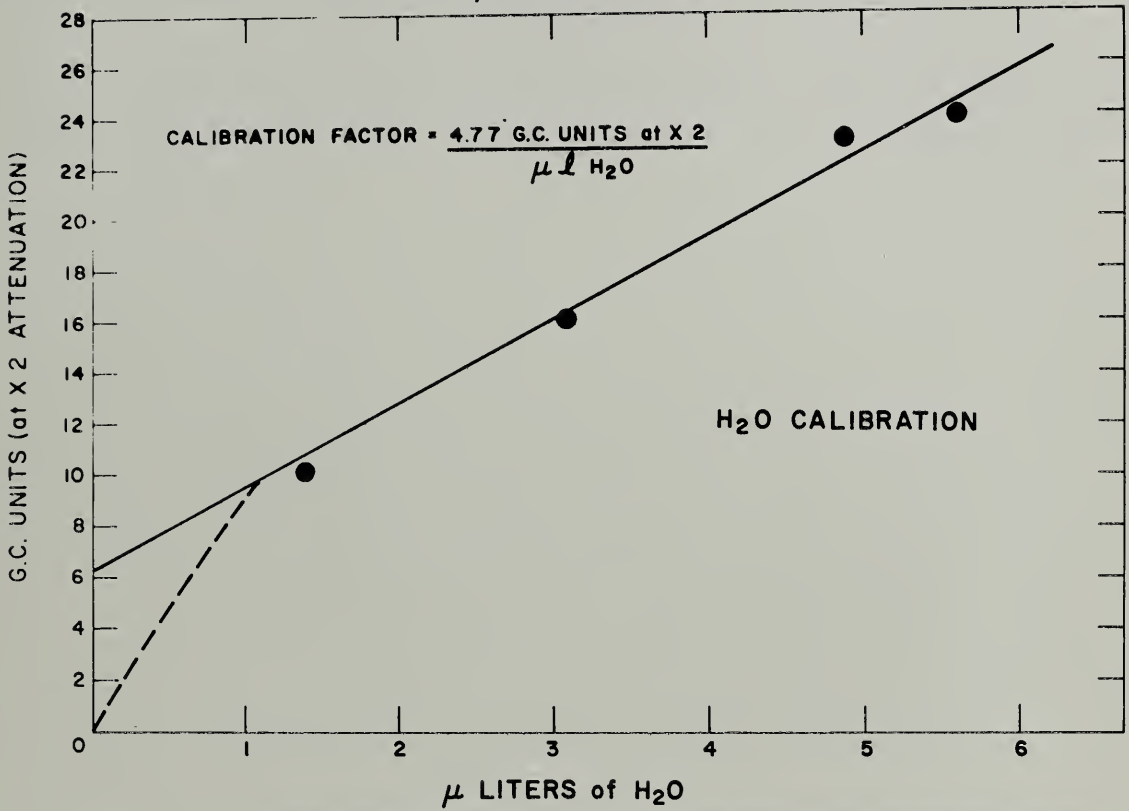
NOTE: THESE LINE ARE SUPER-IMPOSED ON A CONTINUUM, WHICH HAS NOT BEEN MEASURED FOR THIS LAMP.

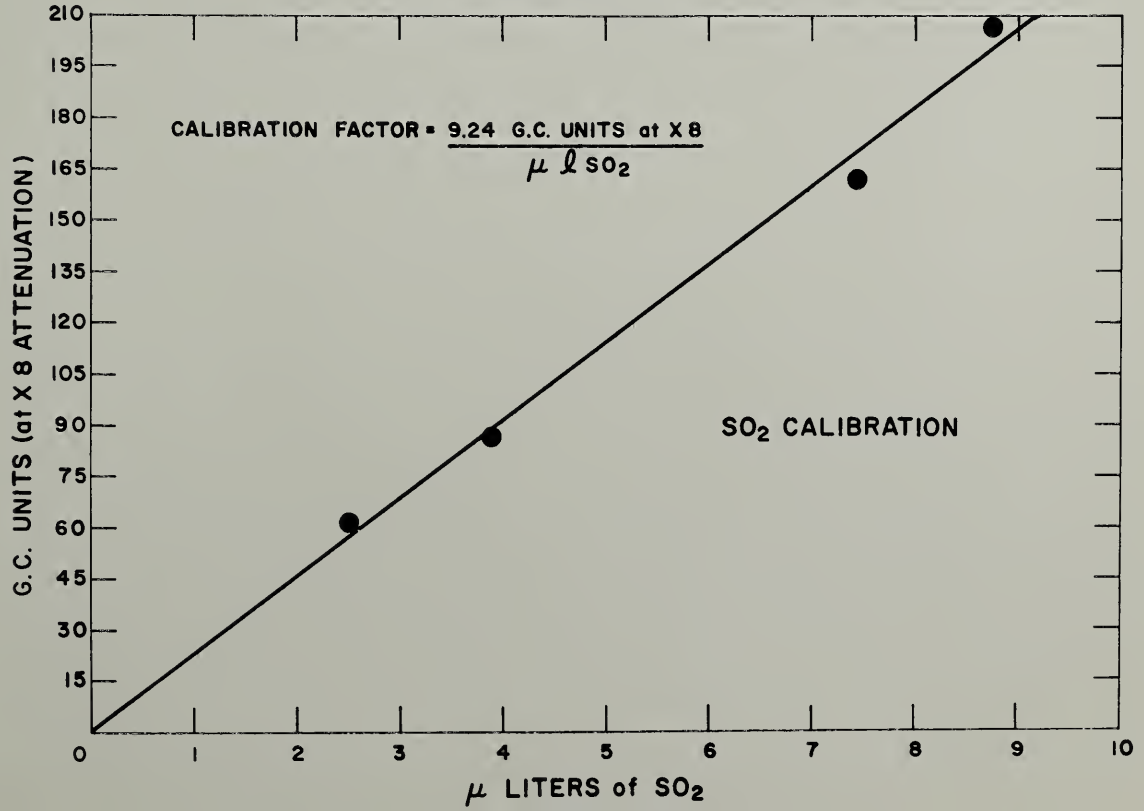




TYPICAL CHROMATOGRAM


CALIBRATION FACTOR = 85.5 G.C. Units at X2 / μℓ CO₂
CO₂ CALIBRATION
G.C. UNITS (at X 2 ATTENUATION)
μ LITERS of CO₂
0
20
40
60
80
100
120
140
160
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
1.4
1.5


CALIBRATION FACTOR = 4.77 G.C. UNITS at X 2 / μℓ H₂O
H₂O CALIBRATION
G.C. UNITS (at X 2 ATTENUATION)
μ LITERS of H₂O
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
1
2
3
4
5
6


CALIBRATION FACTOR = 9.24 G.C. UNITS at X 8 / μℓ SO₂
SO₂ CALIBRATION
G.C. UNITS (at X 8 ATTENUATION)
μ LITERS of SO₂
0
15
30
45
60
75
90
105
120
135
150
165
180
195
210
1
2
3
4
5
6
7
8
9
10

APPENDIX I

EXPLORATORY EXPERIMENTS AT HIGHER SO_2 CONCENTRATIONS

In the H_2O-cooled device (45-50°F), a few exposures have been done to determine how much acceleration is achieved by increasing SO_2 concentration.

Concentrations of 1400 and 13,000 ppm SO_2 were selected. Tables 12 to 15, following, summarize these preliminary results.

It is apparent that even the high concentration of 13,000 ppm SO_2 did not give great enough acceleration to meet our target exposure time of 100 hours. Even higher gas and moisture concentrations, as well as higher temperatures, may be required.

TABLE 12

COLOR-DIFFERENCE

(1400 and 13,000 ppm SO_2/45-50°F)

1400 ppm SO_2

Plastic	500 Hours	1000 Hours
PETP-5	3.4	---
PVC-C10	1.0	6.8
-A4	3.8	5.1
-D10	5.8	6.8

13,000 ppm SO_2

Plastic	100 Hours
PE-1	1.9
PVF-1	1.6
RP-60	3.0
PVC-B4	1.0
-B60	1.0
-D10	1.5
PS-1	0.9

TABLE 13

GASES EVOLVED (µl)

(1400 and 13,000 ppm SO_2/45-50°F)

1400 ppm SO_2

Plastic	500 Hours		1000 Hours	
	CO_2	H_2O	CO_2	H_2O
PETP-5	5.05	4.5	----	---
PVC-C10	1.06	3.5	3.13	6.9
-A4	1.98	3.7	7.56	3.1
-D10	2.61	3.1	5.42	3.1

13,000 ppm SO_2

Plastic	100 Hours	
	CO_2	H_2O
PE-1	0.05	2.7
PVF-1	0.12	10.2
RP-60	0.11	9.8
PVC-B4	0.08	1.9
-B60	0.06	9.8
-D10	0.08	7.3
PS-1	0.23	3.1

TABLE 14

IR-SPECTRAL CHANGE (microns)

(1400 and 13,000 ppm SO_2/45-50°F)

1400 ppm SO_2

Plastic	500 Hours	1000 Hours
PETP-5	15.0-15.7	----
PVC-C10	2.9-3.3	2.8-3.3
-A4	6.4 (broadening)	12-14 (brodening)
-D10	None	None

13,000 ppm SO_2

Plastic	100 Hours
PE-1	None
PVF-1	6.1, 9-12
RP-60	None
PVC-B4	None
-B60	None
-D10	None
PS-1	5.65 (slight)

TABLE 15

FLEXIBILITY CHANGE

(1400 and 13,000 ppm SO_2/45-50°F)

1400 ppm SO_2

Plastic	500 Hours	1000 Hours
PETP-5	None	----
PVC-C10	None	None
-A4	None	None
-D10	None	None

13,000 ppm SO_2

Plastic	100 Hours
PE-1	None
PVF-1	None
RP-60	None
PVC-B4	None
-B60	None
-D10	None
PS-1	Slightly brittle

APPENDIX II

UNSTABILIZED POLYETHYLENE FILM (PE-1) EXPOSURE

In the H_2O-cooled device (45-50°F), exposures were conducted on a polyethylene film which embrittled outdoors in about a year.

Table 16 summarizes the results of exposure for 100 hours to increasingly severe conditions.

Slight discoloration of about 2 units was not increased by presence or higher concentrations of O_2 or SO_2. Presence of O_2 tripled CO_2 evolution; but 10,000-fold increase in SO_2 concentration increased CO_2 evolution by only about 50%. No changes were observed in IR-spectra or flexibility.

It is noteworthy that at these SO_2 concentrations up to 13,000 ppm, all SO_2 was taken up within 100 hours.

Also, this polyethylene has a UV absorbance peak in the wavelengths where the mercury-arc source is very deficient in energy (315-360 nm).

TABLE 16

UNSTABILIZED POLYETHYLENE FILM (PE-1) EXPOSURE

(45-50°F/100 Hours)

Condition	Color-Difference (E)	Gas Evolved		IR-Spectral Change (microns)	Flexibility Change
		CO_2	H_2O		
100% Helium	2.2	0.012 µl	2.7 µl	None	None
100% Oxygen	2.2	0.035	2.9	None	None
18 ppm SO_2/O_2	2.1	0.047	2.9	None	None
1400 ppm SO_2/O_2	1.9	0.047	2.9	None	None
13,000 ppm SO_2/O_2	2.5	0.058	2.9	None	None


DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS