~~NOT FOR PUBLICATION OR FOR REFERENCE~~

NATIONAL BUREAU OF STANDARDS REPORT

10504

FINAL PROJECT REPORT ON THE EFFECTS OF ATMOSPHERIC CONTAMINANTS ON THE DURABILITY OF BUILDING MATERIALS

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 four broad program areas. 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, the Center for Radiation Research, the Center for Computer Sciences and Technology, and the Office for Information Programs.

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 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 Measurement Services and the following technical divisions:

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

THE INSTITUTE FOR MATERIALS RESEARCH conducts materials research leading to improved methods of measurement standards, and data on the properties of well-characterized materials needed by industry, commerce, educational institutions, and Government; develops, produces, and distributes standard reference materials; relates the physical and chemical properties of materials to their behavior and their interaction with their environments; and provides advisory and research services to other Government agencies. The Institute consists of an Office of Standard Reference Materials and the following divisions:

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

THE INSTITUTE FOR APPLIED TECHNOLOGY provides technical services to promote the use of available technology and to facilitate technological innovation in industry and Government; cooperates with public and private organizations in the development of technological standards, and test methodologies; and provides advisory and research services for Federal, state, and local government agencies. The Institute consists of the following technical divisions and offices:

> Engineering Standards—Weights and Measures — Invention and Innovation — Vehicle Systems Research—Product Evaluation—Building Research—Instrument Shops—Measurement Engineering—Electronic Technology—Technical Analysis.

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 consists of the following divisions:

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

THE CENTER FOR COMPUTER SCIENCES AND TECHNOLOGY conducts research and provides technical services designed to aid Government agencies in the selection, acquisition, and effective use of automatic data processing equipment; and serves as the principal focus for the development of Federal standards for automatic data processing equipment, techniques, and computer languages. The Center consists of the following offices and divisions:

> Information Processing Standards—Computer Information — Computer Services — Systems Development—Information Processing Technology.

THE OFFICE FOR INFORMATION PROGRAMS promotes optimum dissemination and accessibility of scientific information generated within NBS and other agencies of the Federal government; promotes the development of the National Standard Reference Data System and a system of information analysis centers dealing with the broader aspects of the National Measurement System, and provides appropriate services to ensure that the NBS staff has optimum accessibility to the scientific information of the world. The Office consists of the following organizational units:

> Office of Standard Reference Data—Clearinghouse for Federal Scientific and Technical Information[3]—Office of Technical Information and Publications—Library—Office of Public Information—Office of International Relations.

---

[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
4216207

DEC 24 1970

NBS REPORT
10504

FINAL PROJECT REPORT ON THE EFFECTS OF ATMOSPHERIC CONTAMINANTS
ON
THE DURABILITY OF BUILDING MATERIALS

by

Harvey W. Berger
Max Tryon
Elizabeth J. Clark
Leopold F. Skoda

Materials Durability and Analysis Section
Building Research Division
Institute for Applied Technology
National Bureau of Standards

Sponsored By

The National Air Pollution Control Administration
and
National Bureau of Standards

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

ACKNOWLEDGEMENT

The authors thank their colleagues - A. J. Turner for his aid in measuring color changes and scratch resistance; W. J. Rossiter for his analyses of the components of the NAPCA Effects Package and W. D. Hayes, Jr. for his measurements of ultraviolet radiation levels.

CONTENTS

I. Introduction

A. Scope

Previous studies have been made on the effects of high concentrations of sulfur dioxide and/or ozone on building materials. The results of such efforts are academically significant but have only a theoretical relationship to the real-life performance of building materials in in-use situations.

The exposure of materials to low level concentrations of air pollutants in an accelerated weathering environment or at a contaminated outdoor weathering site is a realistic and pragmatic approach to materials evaluation. This approach does, however, present some difficult analytical problems. The changes, if any, in the properties of materials due to their exposure to air pollutants will, in all likelihood, be superimposed on the changes caused by the major weathering factors in the test environment. The identification of small changes occurring on a larger background requires, therefore, measurement and analytical techniques that are particularly sensitive to the changes with which one is concerned.

The design of this project could have been one in which the number of variables was restricted to the minimum that could be studied with a maximum of thoroughness. Rather than that approach, however, we have decided to investigate a broad spectrum of materials, substrates and test methods in an attempt to identify those areas of research and measurement that have the greatest potential for successfully evaluating the effects of air pollutants. The result of this approach is data of varying quality, weaknesses and failure of test design and some unpredicted successes, new insights, and a much more valid and educated approach to further research in the area of materials durability.

B. Project History

The study of the effects of air pollutants on the durability of organic coatings was initiated in September, 1967. NBS Report 9927 which was submitted on September 26, 1968 contained the results of the study up to that date.

In spite of the discontinuation of funding for this Project by NAPCA, certain areas of investigation were carried on beyond June 30 and are continuing at present. Outdoor exposures and monitoring of air contaminants are being maintained in order to determine if there are long-term pollution effects which can be correlated with accelerated exposures.

NBS Report 9927, described in detail the procedures used for the coulometric analyses of sulfur dioxide and ozone and, the preparation and testing of plastic and paint samples.

Pigmented PVC plastic sheet and non-pigmented PVC sheet containing UV stabilizers were cut into dogbone-shaped specimens and subjected to tensile testing after exposure to a variety of laboratory controlled conditions. Polyvinyl acetate latex, acrylic latex and linseed oil paints were drawn down and cured on tin foil and then cut into dogbone-shaped samples. After exposure, the tin foil was amalgamated to provide free paint films for tensile testing.

The exposures of the paints and plastics to 2ppm SO_2 and 100ppm SO_2 in the absence of radiant energy did not lead to significant changes in tensile properties. The exposure to 2ppm SO_2 in the Xenon arc Weatherometer indicated that SO_2 may retard the embrittlement of PVA paint but hasten the embrittlement of linseed oil paint.

At the conclusion of the report period, only preliminary work had been done on the exposure of the above materials to 0.5ppm ozone.

II. Materials and Sample Preparation

Four unpigmented plastics, listed in Table 1, were evaluated in this program. The choice of these materials was based primarily on availability. The choices were fortuitous, however, as the variety of chemical types and film thicknesses has provided direction to areas of potential success for future investigations.

TABLE 1

Plastic Materials

	Film Thickness, mils
Polypropylene	1
Polyvinyl chloride-vinyl acetate	2
Polycarbonate	6
Polyvinylfluoride	6

Table 2 lists the combinations of paints and substrates that were used to prepare test panels for exposure to air pollutants. The paints were very high quality white exterior types, primarily intended for residential applications.

TABLE 2

Paints & Substrates

Paint	Aluminum	Substrate Wood	Masonite	Transite
Alkyd enamel	X	X	X	
Linseed oil		X	X	X
PVA latex	X	X	X	X
Acrylic latex	X	X	X	X

Two asphalts were used in this study, one with a softening point of 180°F and the other with a 163°F softening point.

Three aluminum sidings were chosen for inclusion in this program. The coatings were all white and of the following types:

1. Alkyd enamel
2. Polyvinyl chloride
3. Polyvinyl fluoride

All of the materials listed above were prepared in two different panel sizes: 3" x 9" for exposure in the Weatherometer and 3" x 12" for exposure outdoors on weathering racks.

The plastic materials were cut from large sheets into 3" x 9" and 3" x 12" specimens and then taped to similarly sized aluminum panels. After exposure these specimens were again cut into samples appropriate for testing.

The painted panels were prepared by spraying. A semi-automatic spray apparatus was built such that the panel was moved at a constant and controlled rate through the spray of a permanently mounted spray gun. The paints were thinned with the appropriate solvent to give a dry film thickness of 2.5 mils for the finish coat.

The wood and transite panels were preprimed with a spray applied latex base sealer-primer. The dry film thickness of the primer was 1.5 mils.

Although all of the paints were sprayable, the latex paints were particularly difficult to control due to clogging of the gun nozzle. Considering the large number of panels that were prepared, however, spraying produced more uniformly finished specimens more rapidly than could be obtained by brushing or roller-coating.

Asphalt samples were prepared by hot pressing. A bead of asphalt was placed between an aluminum panel and a water-wettable plastic sheet. After pressing and cooling, the plastic was removed. The asphalt remained adhered to the aluminum panel which then served as the supporting substrate.

Aluminum siding samples were cut from large sheets into the appropriate sizes for accelerated and outdoor exposures.

III. Experimental Conditions

Two basic approaches have been followed in studying the effects of air pollutants on the properties of materials: accelerated weathering in a Xenon Arc Weatherometer in which air contamination was controlled, and outdoor weathering at exposure sites where air quality was monitored.

The three following experiments were run in the weatherometer:

1. 1000 hours Xenon arc radiation in an atmosphere containing 0.5 ppm O_3 in air at 100°F and 65% RH.

2. 750 hours Xenon arc radiation in an atmosphere containing 2ppm SO_2 in air at 100°F and 65% RH.

3. 1000 hours Xenon arc radiation at 100°F and 65% RH without the inclusion of air pollutants.

Sulfur dioxide and ozone were monitored coulometrically as described in Report 9927. Specimens were taken from the weatherometer for testing and evaluation at 100, 250, 500 and 750 hour time intervals and finally at 1,000 hours.

Table 3 lists the ranges of the experimental parameters that were maintained over the major part of the experiments. There were occasional failures of equipment, but the duration of those failures was minor compared to the total exposure time and most likely did not contribute to the final results.

TABLE 3

Ranges of Experimental Parameters

Ozone	0.5 ± 0.1 ppm
Sulfur dioxide	2 ± 0.4 ppm
Temperature	38° ± 2°C
Relative Humidity	65% ± 5%
UV Radiation	2.2mWhr./hr.

The exposure sites at Fort Holabird in Baltimore, Maryland and at NBS in Gaithersburg, Maryland were used for the outdoor weathering of materials. A sufficient number of samples were placed on exposure racks, directed south at a 45° incline, to permit sampling at one month intervals for one year.

Fort Holabird is located in a heavily polluted urban industrial area which is high in sulfur dioxide content. The NBS is in a rural location basically free of SO_2 but high in ozone content. The Air Pollution Effects Package designed and supplied by the National Air Pollution Control Administration was used to monitor SO_2, Ozone and a number of other air pollutants including particulate matter. Data from the Package was taken monthly to correlate with the material samples taken from the exposure racks.

IV. Test Methods

Previous experience has shown that the tensile testing of free paint films presents a number of difficulties. In addition to the very poor precision obtained with the testing of limited numbers of samples, there is a major limitation to the validity of the experimental results due to the fact that exposure on a flexible tin foil substrate does not simulate a real exposure condition. The tensile testing of free paint films was abandoned, therefore, in favor of more conventional and, perhaps, more significant test methods.

Table 4 lists the test methods and evaluative techniques used in this program and the materials to which they were applied. The large number of samples involved and the manpower availability were the limiting restrictions on the extent of testing. The choices were based on the potential sensitivity of the methods to observe changes in the surfaces of the materials.

The following sections of this Report will describe the test methods in detail as well as the successes and failures associated with them. In some cases the testing procedures were modified to accomodate particular needs related to sample preparation and some of the methods were found not to be applicable to the substrates that were used.

In addition to the test methods, the Air Pollution Effects Package and the monitoring of ultraviolet radiation will be described.

An air pollution factor which was originally neglected has appeared as a major concern as to the properties and performance of coatings. Particulate matter adhering to the surfaces of materials exposed outdoors is an outstanding effect and will be discussed in the following section on Color.

TABLE 4

Test Methods and Materials

	Test Method						
COATINGS	Color	Gloss	Scratch Resistance	Scrape Adhesion	Tensile Strength	Thermo-mechanical analysis	Infrared Spectral analysis
Paints							
Alkyd enamel	X	X	X	X		X	
Linseed oil	X	X	X	X		X	
Acrylic latex	X	X	X	X		X	
PVA latex	X	X	X	X		X	
Plastics							
Polypropylene					X	X	X
PVC-VA					X	X	X
Polycarbonate					X	X	X
PVF					X	X	X
Asphalts							
180°F S.P.						X	X
163°F S.P.						X	X
Aluminum Siding							
Alkyd	X	X	X	X		X	
PVC	X	X	X	X		X	
PVF	X	X	X	X		X	

V. Discussion and Experimental Results

A. Gloss

Gloss is a measure of the amount of light reflected in a particular direction.

A Hunter Photometric Unit with a 60 degree gloss attachment was used to measure 60-degree Specular Gloss according to Method 6101 of Federal Test Standard 141a. The following modifications were made in the Standard Method with reference to sample preparation and conditioning. 1) The panels were sprayed to give a dry film thickness of 2.5 mils instead of being drawn down with a Doctor blade, 2) Aluminum, wood, masonite and transite were used as substrates in place of glass, 3) The panels were not conditioned according to the method. After the paint films were dry, the panels were placed either in the Weatherometer or on the outdoor exposure sites. At specified time intervals, the panels were removed from the Weatherometer; the tests conducted, and the panels were replaced in the Weatherometer for continued exposure. For the panels on outdoor test sites, a panel was removed each month and not returned. 4) Only two measurements, not three, were made - these being at 180 degree rotation from each other.

When the panels were removed from the outdoor test sites, some dirt and grit remained on them which could have caused a decrease in gloss. For comparisons, all panels should have been primed, to prevent penetration of the paint into the substrate, which would result in lower gloss readings. If the panels were not thoroughly dry when the readings were taken, some fluctuations in gloss measurements could have been caused. In cases where the substrate was not smooth, some unevenness in the surface caused a scattering of light and a variation in the readings. This was particularly evident in some cases where wood grain was noticeable beneath the coating.

The total film thickness on all substrates should have been equal. An "equilibrium" time should be allowed after the panels are removed from the Weatherometer or from an outdoor test site. This would permit panels to dry out and reach room temperature prior to testing or measurement.

Gloss measurements were made on all siding samples and on the paint samples applied to aluminum, masonite, transite and wood. Tables 5 and 6 summarize the data obtained for paints.

TABLE 5

Paints-Weatherometer Exposures

Paint	Substrate	Comments: Extent of Gloss Decrease
Alkyd	Aluminum	control $>$ SO_2 $>$ O_3
	Masonite	control $>$ O_3 $>$ SO_2
	Wood	control $>$ SO_2 $>$ O_3
Linseed Oil	Masonite	SO_2 $>$ O_3 = control
	Transite	SO_2 $>$ O_3 = control
	Wood	SO_2 $>$ control $>$ O_3
Acrylic	Aluminum	SO_2 $>$ control $>$ O_3
	Masonite	SO_2 $>$ control $>$ O_3
	Transite	SO_2 $>$ control $>$ O_3
	Wood	SO_2 $>$ control = O_3
PVA	Aluminum	SO_2 $>$ control = O_3
	Masonite	control $>$ SO_2 = O_3
	Transite	SO_2 $>$ control $>$ O_3
	Wood	SO_2 $>$ control $>$ O_3

TABLE 6

Paints - Outdoor Exposures

Paint	Substrate	Comments: Extent of Gloss Decrease
Alkyd	Aluminum	NBS > Baltimore
	Masonite	Baltimore = NBS
	Wood	Baltimore > NBS
Linseed Oil	Masonite	Baltimore = NBS
	Transite	Baltimore > NBS
	Wood	Baltimore = NBS
Acrylic	Aluminum	Baltimore > NBS
	Masonite	Baltimore > NBS
	Transite	Baltimore > NBS
	Wood	Baltimore > NBS
PVA	Aluminum	Baltimore > NBS
	Masonite	Baltimore > NBS
	Transite	Baltimore > NBS
	Wood	Baltimore > NBS

For all exposures to air pollutants, the gloss of the PVC siding was greater than the Tedlar siding which in turn was greater than the Alkyd siding. The PVC started with the highest gloss and retained it over time better than the other sidings. Originally, the Alkyd coating had a higher gloss than the Tedlar, but when exposure was started the Alkyd immediately lost its edge and continued to decrease at a faster rate.

For the Tedlar and Alkyd coatings, SO_2 caused the greatest change, whereas, for PVC the control samples exhibited the maximum change. Ozone caused the least change in all three sidings. Gloss appears to be affected less at the outdoor sites than in the artificial weathering machine.

TABLE 6

Aluminum Siding
Weatherometer Exposures

(Gloss of all samples decreased with time of exposure)

PVC - Decrease in gloss: controls $> SO_2 > O_3$

PVF - Decrease in gloss: $SO_2 >$ controls $> O_3$

Alkyd - Decrease in gloss: SO_2 controls $> O_3$

Outdoor Exposures

PVC - Very little change in gloss with exposure time

PVF - No significant changes

Alkyd - Samples at Baltimore site decreased in gloss; data for NBS unavailable.

Gloss decreased over time and exposure to both pollutants for all of the paint and siding samples. For the most part, Ozone seemed to cause the least change and Sulfur Dioxide the greatest. The Washington exposure was not as severe on the samples as the Baltimore site.

B. Scratch Resistance

The Scratch Resistance Test described in Federal Test Method Standard 501a-7711 is, in fact, a shear hardness test. The flat edged tool used in the method simulates shear stresses such as digging and scraping. A round diamond tool was used, therefore, to measure "the degree of resistance of a surface to be scratched or engraved."

The need for conserving undamaged surface space on samples being exposed necessitated revision of the test method such that a single scratch undera 1000 gram load was made and measured rather than making multiple scratches to establish a standard end point width.

The preponderance of scratches made with the diamond tool ranged from 0.1mm to 0.5mm in width. In some cases, however, scratch widths on aluminum substrates reached very high values indicating major adhesion loss.

The scratch test method was particularly unsuccessful when performed on materials covering wood substrates. The grain of the surface caused gouging and uneven motion. Tests on materials covering masonite, transite and aluminum gave clear cut scratches which appeared to be consistent. Figure 1 is an example of the data plots for scratch widths obtained on a variety of materials and substrates. Each data point represents an equivalent exposure time of two similar samples to two different exposure conditions. The 45-degree line indicates equal scratch widths for equal exposure times.

Examinations of the data showed that with minor exceptions, the scratch widths obtained with samples exposed to SO_2 or at Fort Holabird, Maryland were wider than those obtained with samples exposed to ozone or at Gaithersburg, Maryland. The data showed considerable consistency relevant to the accelerated SO_2 exposure and the high concentrations of SO_2 at Fort Holabird, Maryland.

The scratch test appears to be of value in examining changes in the surface properties of coatings exposed to varying exposure conditions. Individual plots of scratch width changes as a function of exposure time are encouragingly consistant in spite of the lack of replication of samples. The extreme ease and rapidity in performing the test further justifies the inclusion of this procedure in subsequent research programs.

TABLE 8

Summary of Data for Scratch Width

Paint	Substrate	Outdoor Exposures	Accelerated Exposures
Acrylic	Masonite	Baltimore = NBS	$SO_2 > O_3$
	Transite	Baltimore = NBS	$SO_2 > O_3$
	Aluminum	Baltimore > NBS	$SO_2 > O_3$
PVA	Masonite	Baltimore = NBS	$SO_2 > O_3$
	Transite	Baltimore = NBS	$SO_2 > O_3$
	Aluminum	Baltimore > NBS	$SO_2 \gg O_3$
Alkyd	Masonite	Baltimore = NBS	$SO_2 > O_3$
	Aluminum	Baltimore > NBS	$SO_2 \gg O_3$
Linseed Oil	Masonite	Baltimore = NBS	$SO_2 \gg O_3$
	Transite	Baltimore = NBS	$SO_2 \gg O_3$

Aluminum Siding

Tedlar . . . . $SO_2 = O_3$

Alkyd . . . . $SO_2 = O_3$

PVC . . . . $SO_2 = O_3$

C. Adhesion

If an organic coating is to serve as protection for the substrate to which it is applied, it must firmly adhere to the surface. Therefore, an attempt was made to determine whether certain air pollutants effect this adhesion.

A Balanced Beam Scrape Adhesion Tester was used to measure the adhesion of paint and siding samples. The method as described in Adhesion of Organic Coatings, Method A (ASTM Designation D-2197-68) was followed with the following modifications: 1) The entire test panel was coated, leaving no area free from the film on which to place the stylus at the start of each test. Thus, the test was performed over the film until it ruptured or peeled back; 2) Only one panel of each sample was tested; 3) The panels were not conditioned as described in the method. After the paint film was dry, the panels were placed either in the Weatherometer or on the exposure sites. At specified time intervals, the panels were removed from the Weatherometer, the test conducted and the panels were replaced in the Weatherometer for continued exposure. For the samples on outdoor test sites, a panel was removed each month and not returned.

This instrument did not prove to be applicable to coatings on wood substrates because the stylus indented the wood surface before the film ruptured.

After a large number of tests, the stylus gradually becomes flattened, thus, cutting less sharply into the film as it slides over it. Therefore, before the loop is reversed, the readings have a tendency to be high.

After removal from the Weatherometer, samples were usually tested within a few hours. A specific period of time should have been set aside for the panels to equilibriate to room temperature. A lack of uniformity between the time the panels were removed and tested may have been responsible for some scatter in the results.

The panels taken from outdoor sites did have sufficient time to dry and adjust to laboratory conditions. Much more uniform results were obtained from them.

The transite panels were primed with a white paint, with the top-coat also being white. The use of two coats with the resultant film thickness increase could have been the reason for high adhesion values.

Some modifications in the way the sliding plate is moved would increase the reproductibility of results. Since the transite and masonite surfaces were not perfectly smooth, it is difficult, if not impossible, to move the plate both smoothly and at a controlled rate. The arm with the stylus has a tendency to skip over the samples, thus, making the rate of advance uneven. As it skips, when the arm comes down, it indents the film surface unevenly making it difficult to determine the adhesion. A slower rate of pushing decreases the skipping, but under a heavy load it is difficult to move it slowly and smoothly. Mechanization seems to be the answer.

All substrates should be primed in a color different than the topcoat. This would facilitate determining when the top paint film has been removed.

Each panel should have an area on which there is no coating, as described in ASTM Method. Otherwise, it is doubtful whether adhesion between the film and the substrate or the cohesion of the film itself is being measured.

Adhesion measurements were made on the siding samples and on the paints applied to aluminum, masonite and transite substrates. The apparatus had a maximum load of 11,000 grams, therefore, all panels with adhesion greater than that were simply classified maximum. The following is a summary of the findings:

TABLE 9

Scrape-Adhesion

Aluminum Siding - Weatherometer Exposures

PVC	Controls $>$ SO_2 exposed samples $>$ O_3 exposed samples.
PVF	Controls - data too scattered to generalize.
PVF	SO_2 exposed samples - adhesion unchanged with time
	O_3 exposed samples - adhesion decreased with time
Alkyd	SO_2 exposed samples $>$ O_3 exposed samples $>$ controls.

Insufficient data was available for the outdoor exposures of aluminum siding samples for any major trends to be found. The Alkyd siding had the highest adhesion of the three sidings that were exposed to SO_2. For other exposures, it was the lowest, with PVC coated siding consistantly higher in adhesion than Tedlar.

TABLE 10

Scrape-Adhesion

Paints-Weatherometer Exposures

Paint	Substrate	Comments
Alkyd	Aluminum	Controls and SO_2 exposed samples - data very scattered; O_3 exposed samples - decrease in adhesion with time.
	Masonite	All samples increased in adhesion with time; controls $>$ $SO_2 = O_3$
Linseed Oil	Transite	Controls maintained high adhesion; SO_2 and O_3 exposed samples - decrease in adhesion.
	Masonite	All samples increased in adhesion; Controls $> SO_2 > O_3$.
Acrylic	Aluminum	Ozone exposed samples unchanged in adhesion; Controls and SO_2 exposed samples increased in adhesion; Controls $> SO_2$
	Masonite	All samples increased in adhesion; Controls $> SO_2 = O_3$
	Transite	Both pollutants caused decreases in adhesion; Controls $> SO_2 \simeq O_3$
PVA	Aluminum	All samples greatly increased in adhesion; Controls $> SO_2 > O_3$
	Masonite	All samples greatly increased in adhesion; Controls $> O_3 > SO_2$
	Transite	All samples decreased in adhesion; Controls $> O_3 > SO_2$

TABLE 11

Scrape-Adhesion

Paints - Outdoor Exposures

Paint	Substrate	Comments
Alkyd	Aluminum	Baltimore/NBS adhesions similar over time
	Masonite	Baltimore/NBS adhesion similar over time
Linseed Oil	Transite	Baltimore > NBS
	Masonite	NBS > Baltimore
Acrylic	Aluminum	Samples at both sites increased in adhesion NBS > Baltimore
	Masonite	Samples at both sites increased in adhesion NBS > Baltimore
	Transite	Samples at both sites decreased in adhesion; data was too scattered to rate one vs. the other.
PVA	Aluminum	Samples at both sites increased slightly in adhesion - Baltimore > NBS
	Masonite	Samples at both sites increased in adhesion NBS > Baltimore
	Transite	NBS > Baltimore

In general, it appears as if the substrate in these tests controls the measurement of the adhesion properties. Coatings on transite usually started with a high adhesion and through the course of the exposures either remained constant or decreased. Adhesion on aluminum was generally low and remained constant or increased gradually. On masonite, the adhesion always increased after having started at a moderate level.

Under the conditions of the exposures, ozone seemed to exhibit the least effect on the adhesion, whereas, SO_2 undoubtedly was most severe. The panels exposed at the outdoor sites usually produced very similar results although those from Washington often had slightly higher adhesion.

On the basis of the data which was obtained with this scrape-adhesion test, it is not recommended that this method be used in evaluating the effects of air pollutants.

The test is not sufficiently sensitive to measure small changes. Under any circumstances the test should be performed only on primed, metal substrates.

D. Color

The analysis of color changes as a function of exposure time is a popular technique used in studies of materials durability. Color change can result from pigments bleaching, binders yellowing and film thickness losses, all of which are manifestations of film deterioration.

All color measurements were made using a differential colorimeter which gives the tristimulus values of the Adams Coordinate System. The total color difference, "E", in NBS units was calculated for each set of measurements using the "Color Coordinate Tables" computed by Glasser & Troy. Samples exposed in the Weatherometer were allowed to reach equilibrium with laboratory conditions prior to measurement. Samples that had been exposed outdoors were washed gently in a stream of distilled water, dried, and also allowed to reach equilibrium.

Table 12 lists the data obtained for samples exposed to the three different accelerated exposure environments (control, ozone, and sulfur dioxide) for totals of 750 hours in each case. The exposure to ozone results in no major color differences with reference to the control samples. The exposures to sulfur dioxide do, however, result in definite positive trends with reference to both the control samples and those exposed to ozone.

A major cause of color change which may have no relationship at all to film decomposition is the surface adherence of solid and liquid particulates which, in fact, appears to be the case with the paint samples exposed outdoors at the NBS and Fort Holabird sites.

Figures 2, 3, 4 and 5 are the plots of the total color differences of the materials exposed outdoors. The color changes of the acrylic and PVA latex paints are significantly greater for those exposed at Fort Holabird. The alkyd enamel color changes are greater for the samples exposed at the NBS and the linseed oil samples show no significant pattern at all.

Visual examination of the samples provides striking confirmation of the optical measurements. The latex paints exposed at Fort Holabird retain a great deal more surface dirt than the samples exposed at NBS in spite of the washing procedure. Solid particulates of dark color are deeply embedded in the surface and rust colored spots or stains are generally distributed over the panels. The alkyd enamel samples exposed at the NBS site exhibit a darkening or graying due to the adherence of very fine dirt particles. This effect is not as pronounced on the samples exposed at Fort Holabird. The linseed oil paint chalked very badly at both outdoor sites and within a short time presented a surface that was essentially clean. This is confirmed by the bunching of the color difference data indicating that beyond a short exposure time there were no major changes in color.

The esthetic qualities of a surface coating may be the most significant factor in decisions relating to the refinishing of residential siding. If that is indeed the case, atmospheric dust and dirt may be the primary air pollutant from an economic point of view. Color differences due to dirt retention appear to be the most striking changes observed in this study and an economic analysis of losses due to these effects is warranted.

Correlation of data on air quality, (as obtained from the air pollution effects package), dirt retention and film surface properties, preceeded by the development of an accurate procedure for measuring dirt retention and the preparation of visual standards would be a logical and worthwhile program to follow up this preliminary effort.

TABLE 12

Total Color Difference - 750 Hours Exposure

Material	Substrate	Xe Arc Control	Xe Arc + O_3	Control Difference	Xe Arc + SO_2	Control Diff.
Acrylic	Aluminum	1.5	1.0	-0.5	5.5	+4.0
	Masonite	1.0	2.0	+1.0	1.0	0
	Transite	1.0	0.5	-0.5	10.0	+9.0
	Wood	2.5	2.5	0	2.0	-0.5
Alkyd	Aluminum	0.5	0.5	0	1.5	+1.0
	Masonite	1.5	0.5	-1.0	2.5	+1.0
	Wood	1.5	1.0	-0.5	3.5	+2.0
PVA	Aluminum	2.0	1.5	-0.5	2.0	0
	Masonite	2.5	2.0	-0.5	4.0	+1.5
	Transite	1.0	1.5	+0.5	2.5	+1.5
	Wood	1.5	2.5	+1.0	4.0	+2.5
Linseed Oil	Masonite	1.5	2.0	+0.5	5.0	+3.5
	Transite	3.5	4.0	+0.5	2.0	-1.5
	Wood	2.5	4.0	+1.5	2.5	0

E. Strength

Four types of plastic materials were evaluated by tensile testing after Weatherometer and outdoor exposures. The plastics included in the test program were a polycarbonate, a polyvinyl fluoride, a polyvinyl chloride and a polypropylene. The Weatherometer cycles were Xenon Arc control, xenon arc plus ozone and xenon arc plus sulfur dioxide. Specimens were subjected to outdoor exposure cycles at Fort Holabird, Maryland and at the NBS site in Gaithersburg, Maryland. Tensile tests were performed after Weatherometer exposures at 100, 250, 500, 750 and 1,000 hours. Tensile tests of the naturally weathered specimens were performed at one month intervals for seven months on the polycarbonate, four months on the polyvinyl chloride and two months on the polypropylene.

The tensile tests were accomplished on a Tinius Olsen universal testing machine. Specimens were cut 100mm long by 12mm wide. Smooth faced grips were used with the distance between jaws of the machine being 50mm. A rate of loading of 2mm per minute was used.

The results of accelerated weathering are shown in Figure 6. The polyvinyl fluoride and polyvinyl chloride show no effects resulting from any of the exposure conditions. The polycarbonate shows a trend toward reduced tensile strength due to xenon arc and xenon arc plus ozone exposures. The most marked effect involved the xenon arc plus SO_2 exposure condition, where a reduction of approximately 17 percent in tensile strength was realized after 250 hours exposure.

The results of natural weathering at the Fort Holabird and NBS sites is presented in Figure 7. No significant difference occurs in tensile strength of the polyvinyl chloride and polypropylene samples. The tests were discontinued after 4 and 2 months, respectively, due to embrittlement of the samples to the point where they could no longer be placed in the testing machine. The polycarbonate exhibited little effect through 5 months. The samples from the NBS site exhibited a reduction in tensile strength of approximately 45% in the 7th and 9th months. Present thoughts are that this reduction in strength is the result of biodegradation due to a source as yet undetermined.

F. Thermomechanical Analysis

A device designed to measure the change in mechanical properties of materials as a function of temperature was employed to detect the effects of weathering in this study. The schematic diagram in Figure 8 shows the basic design of the apparatus.

The linear transducer is capable of sensing displacement of the probe of the order 1/100th of one mil. The y ordinate on the x, y recorder at maximum sensitivity represents the order of 1 mil displacement for full scale.

The samples were preapred by cutting small pieces from the test panels, about $20 mm^2$ area. Previous tests indicated the proper starting temperature for each type of material. The heating rate and load, w, on the specimen was also determined from earlier work. The load was 10g and the heating rate 12°C per minute for all samples. The starting temperature was -40°C unless otherwise indicated.

A typical TMA curve is shown in Figure 9 with the method of determining the glass transition temperature, Tg, shown on the intersection of two tangents to the curve. In some of the samples Tg was vague because the curve shape was very irregular. Some of the variability in the TMA data was undoubtedly due to the uncertainty in the position of the tangent lines to the curve but other variabilities could have resulted from semi-micro changes in the consistency of the same surface, i.e., soft spots, dirt inclusions, load hardening, etc. The probe area of contact is very small (less than $1 mm^2$) and so will respond to small local changes in the sample. Some materials also exhibit "memory" effects, i.e., previous strain or temperature stress may leave areas of the material in an unstable state sensitive to later temperature effects. Plastics are particularly good examples of such effects as in evident with the shrinking observed for calendared or pre-stretched films on subsequent heating to temperatures in the vicinity of the glass transition temperature.

The experimental results are described as follows:

1. Alkyd Paint on Aluminum

The glass transition temperature (Tg) of the alkyd paint used in this study was 11°C for the unaged paint on aluminum. The weatherometer control sample showed an initial decrease in Tg followed by a progressive increase to 15°C after 750 hours. Ozone in the atmosphere caused an increase in the Tg of almost 10° with a plateau as if the surface of the paint became saturated or reached an equilibrium. Sulfur dioxide showed erratic behavior with a final Tg at 750 hours identical with the control.

2. Linseed Oil Paint on Transite

Starting with an original Tg of 44°C for the linseed oil paint on transite, the control exposure gave a smoothly increasing Tg up to 77°C at 750 hours exposure. Both O_3 and SO_2 gave higher Tg than the controls, 95° and 82°, respectively.

3. Acrylic Paint on Aluminum

The Tg of the original paint film was -3°C with the control samples giving a slow increase to +4°C. An increase of 7°C overall. Both SO_2 and O_3 in the atmosphere increased the Tg more rapidly than the control and to a higher value of 13° and 8°C, respectively.

4. PVA Latex on Aluminum

Little change in Tg for this material was noted from the initial presence of 21°C for 750 hours of exposure in the Weatherometer in the presence of O_3 and SO_2. The control sample showed an immediate decrease and finally reached a value of 15°C after 750 hours. The Washington site changed the Tg drastically to 5°C in three months while the Baltimore site showed little or no change from the original.

5. Asphalts

The two roofing asphalts used in this study showed greatly different Tg values initially with drastic changes appearing almost immediately for both laboratory and outdoor exposures. The initial Tg values of -5 and +11°C jumped to 26 and 31°C, respectively, after only 100 hours weatherometer $+O_3$ exposure and 22°C for both after 100 hours exposure to SO_2 in the weatherometer. The changes to subsequent exposures to O_3 were small with final values being approximately the same as the first 100 hours. Exposure to SO_2 continued to raise the Tg to values of 62 and 80°C, respectively, after 750 hours; not very different from the control exposures. Outdoor exposures jumped from the original values given above to +7 and +10°C after one month in Washington and +4 and +7°C after one month in Baltimore. No great differences were noted between the two outdoor sites as the Tg increased to +29 and +36°C for the Washington site and +33 and +42°C for the Baltimore site.

6. Polycarbonate

The sample of polycarbonate studied here showed little or no change in Tg from the original value of 152°C regardless of exposure conditions both in the laboratory or the two outdoor sites.

7. Polyvinyl Chloride-Vinyl Acetate Film

The initial Tg for this material was 68°C. Only a slight change to a higher Tg value of 71.5°C was noted on exposure to SO_2 for 750 hours in the weatherometer. No other conditions altered the Tg from the original value.

8. Polypropylene Film

This material degraded so rapidly under all the exposure conditions that only one or two measurements could be made by this technique. The initial value of Tg of 161°C remained relatively constant for 250 hours exposure to O_3 and SO_2 in the weatherometer, but then the sample decayed to the point that the measurements were impossible or meaningless. Similarly, slight decreases in Tg were noted over the first 2 months of outdoor exposure and then complete failure of the material occurred at both sites.

9. Fluoro-polymer

The value of Tg for this material showed little or no change from 175°C for the original material for all exposure conditions.

10. Polyvinyl Chloride Coated Aluminum Siding

Very little, if any, change was observed from the original Tg value of 45°C for any of the exposure conditions used.

11. Alkyd Coated Aluminum Siding

The inital drop in the Tg value from 41°C to about 35°C occurred under all test conditions and remained at about this value over the rest of the test period for all conditions.

12. Fluoro-polymer (PVC) Coated Aluminum Siding

The value for Tg for this material showed little or no change from the original 195°C. The higher value for Tg for this sample than for the free film shown above is probably caused by the bonding to the substrate slowing down the relaxation of calendaring stresses in the film.

G. Infrared Analysis

Infrared absorption measurements were made on the plastic films and on the asphalts used in this study. The coatings and paint samples could not be measured due to the pigmentation which prevented direct observation of changes in the binder.

The carbonyl index or ratio of the absorbance of the samples at 5.8 microns to the absorbance at 6.9 microns was measured on each of the asphalt samples. The samples were prepared by dissolving a small portion of the previously exposed sample in a few drops of carbon tetrachloride and evaporating the solvent from some of this solution placed on a rock salt window. This technique of solution casting of a film eliminated the chance that the sample might be changed by the usual heating and pressing methods previously employed.

The plastic films required no special handling for the infrared measurements and specimens were used as cut directly from the exposed sheet material.

The absorbance in the 5.8 micron region was measured for PVF and propylene films with no corrections made for film thickness. In both cases the absorbance in this region was very small in the initial samples. The hydroxyl index was measured for both the polycarbonate and polyvinyl chloride - vinyl acetate plastics using the absorbance at 2.8 - 2.9 microns in both cases. However, the absorbance at 3.4 microns as used in the PVC film could not be used for polycarbonate because it was too strong in the polycarbonate spectrum. Therefore, the absorbance at 4.45 microns was used for the calculation of the hydroxyl index for polycarbonate.

These numbers used to characterize certain chemical changes in the materials investigated should not be evaluated as quantitative. The indices given are certainly related to the quantity of certain structures present, but the methods of measurement used are not calibrated and no conversion factors are known at this time. However, they do represent changes in trends in the reactions involved and should be so interpreted.

1. Poly (vinyl chloride-vinyl acetate)

The hydroxyl index measured on this material indicated that SO_2 in the Weatherometer resulted in higher concentrations of hydroxyl groups than did the control exposure while O_3 gave lower concentrations than the control. No appreciable difference in rates of hydroxyl generation was noted between the two outdoor sites.

2. Polycarbonate

Again, SO_2 + Weatherometer resulted in large increases in the hydroxyl content of this material while O_3 and the control condition appeared similar and showed much smaller changes.

After the first month of outdoor exposure, this material showed more rapid hydroxyl increases in samples exposed at the Washington site than those exposed at the Baltimore site.

3. Polypropylene

The carbonyl index measured on the propylene film increased very rapidly after the first 100 hours of exposure and the samples were so badly decomposed after 250 hours that they were not suitable for study. No obvious distinction could be made as to the effects of O_3 and SO_2 as the general degradation was so severe.

The samples exposed outdoors showed a slight increase for the first two months at the Washington site.

4. Fluoropolymer

Exposure in the Weatherometer + SO_2 caused a more rapid increase in carbonyl index for this material than the control or O_3 conditions of exposure. No appreciable effect of O_3 over the control was observed.

This film was not exposed at either outdoor site.

5. Asphalts

Exposure to ozone in the Weatherometer did not result in any increase of carbonyl generation in either of the asphalts as compared to the weatherometer control condition. Sulfur dioxide, on the other hand, appeared to increase the carbonyl content faster than the control for the first 500 hours for both asphalts and then slowed down to the control rate.

Outdoor exposure showed a difference in the two asphalts. Asphalt "A" developed more carbonyl when exposed at Holabird than at the NBS and then remained relatively constant.

Asphalt "B" started out faster at Holabird than at NBS and then leveled off while the samples at NBS eventually overtook the Holabird samples and increased rapidly to higher carbonyl contents than the Holabird samples.

VI. Ultra Violet Radiation Monitoring

The total UV radiation at each site was measured using a device* designed and constructed by Warren D. Hayes, Jr. of the Materials Durability and Analysis Section of the Building Research Division. The device integrates the incident radiation from 300mm to 400mm and, thus, gives a measure of the actual total UV radiation for the period indicated. The results are given in the following table:

UV Radiation (milliwatt hours)

	April	May	June	July**	August
NBS	629	929	845	788	799
Holabird	620	798	808	773	752

**During the month of July, both areas were in heavy smog cover for about one week.

+The data were normalized to 30 days/month by dividing the total observed radiation for the month of observation by the actual number of days exposure and then multiplying by 30 days as a standard.

*This apparatus will be described in detail in a paper presently in preparation.

VII. Pollution Monitoring At Outdoor Sites

The NAPCA Effects Package was used to monitor pollutants at the two sites. The sulfation was measured by the lead dioxide petri dish method, the wind-blown particulates by the adhesive paper method, ozone by the rubber strip, hydrogen sulfide by the silver plate, and oxides of nitrogen by the nylon screen. The results are shown in the following tables:

Effects Package Analyses

Sulfation rate: ug $SO_2/cm^2 \cdot$ day

	April	May	June	July	August
Washington	5	4	4	4	4
Holabird	6	5	9	10	11

Wind-blown Particulates: multiply by 10^3 to obtain particulates/sq. in.

Sample	Month*	N	NE	E	SE	S	SW	W	NW
Holabird	April	45	10	10	5	3.5	3.5	30	60
	May	10	2	20	45	45	20	20	30
	June	1	1	2	5	10	3.5	5	5
	July	1	2	2	10	20	20	5	1
	August	1	3.5	5	5	5	5	3.5	1
Washington	April	1	1	1	1	1	2	3.5	2
	May	2	1	1	1	1	1	2	3.5
	June	1	1	1	1	1	1	1	1
	July	1	1	1	1	1	1	1	1
	August	1	2	2	1	1	1	1	1

*Samples are only in the field for 1 week

Rubber Deterioration

Sample	Month	Average Crack Depth
Holabird	April	none
	May	none
	June	111 microns
	July	96 microns
	August	237 microns
Washington	April	none
	May	117 microns -- only 6 cracks, some of these were away from the center
	June	142 microns
	July	88 microns
	August	112 microns

Nylon Deterioration: Number of breaks developed in the nylon in one month.

	April	May	June	July	August
Washington	0	0	failed	1	4
Holabird	0	0	0	3	1

FIGURE 1

SCRATCH RESISTANCE

ALKYD ENAMEL PAINT

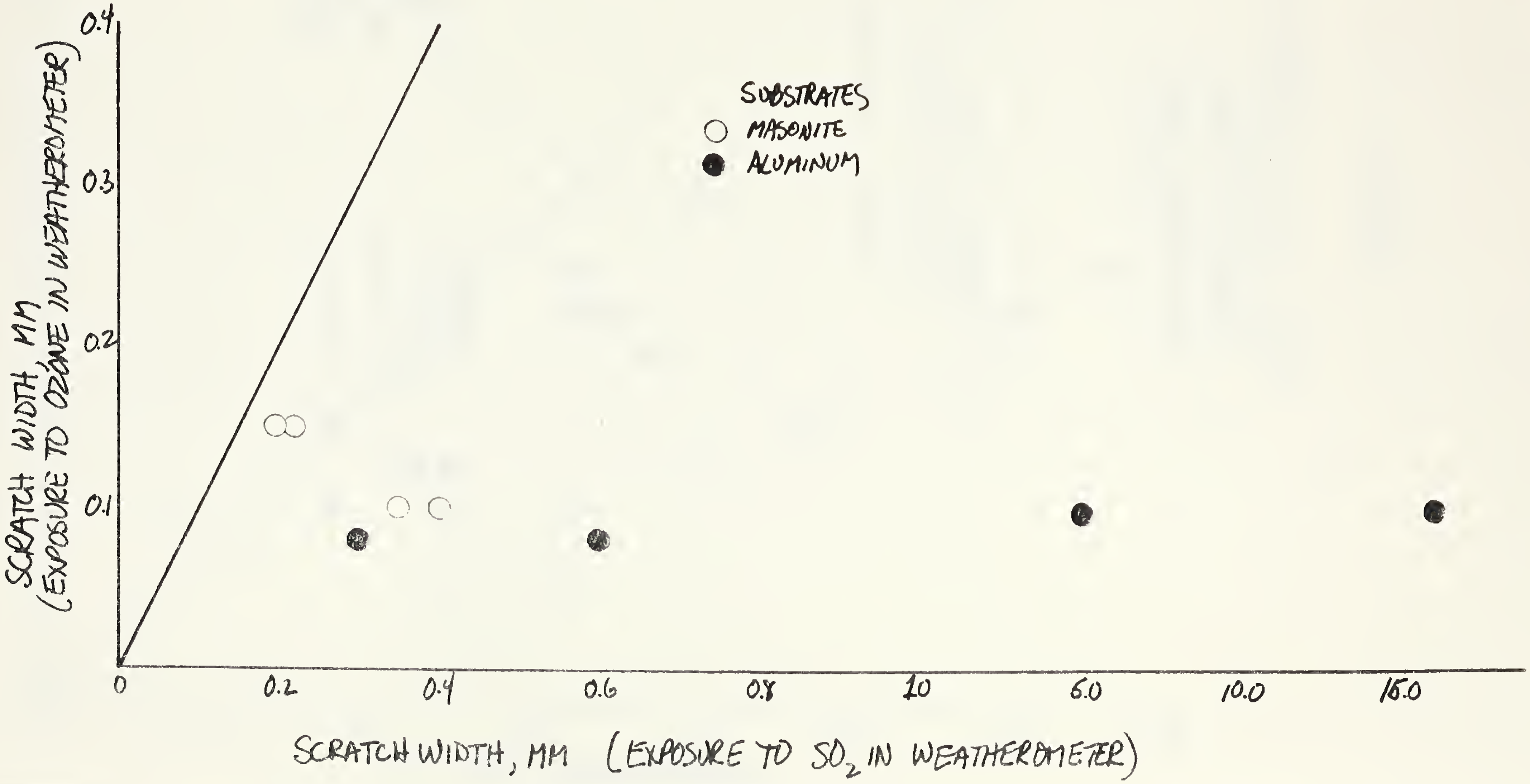


FIGURE 2

TOTAL COLOR DIFFERENCE, ΔE
OUTDOOR EXPOSURES
ALKYD ENAMEL PAINT

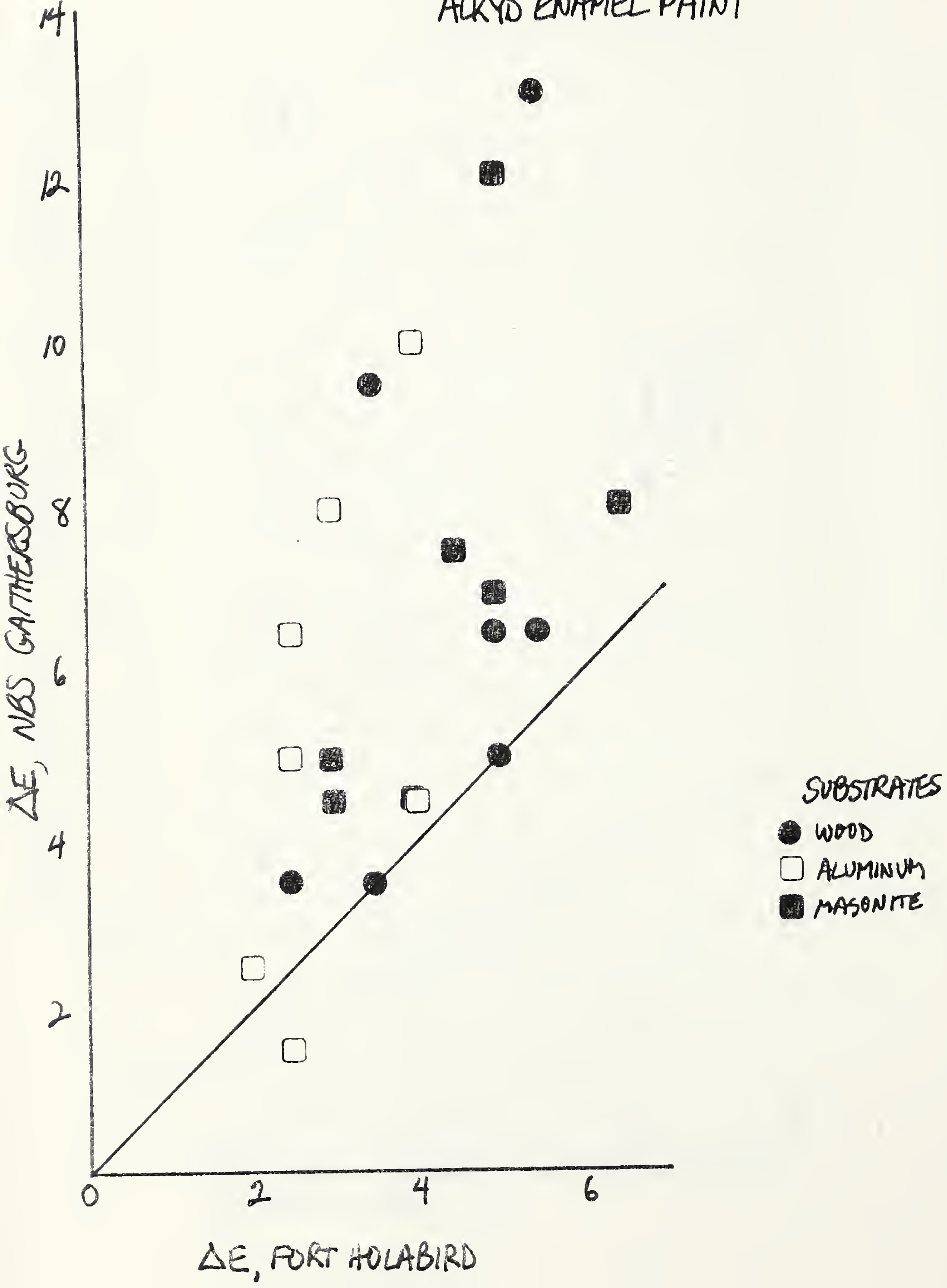


FIGURE 3

TOTAL COLOR DIFFERENCE, ΔE
OUTDOOR EXPOSURES
LINSEED OIL PAINT

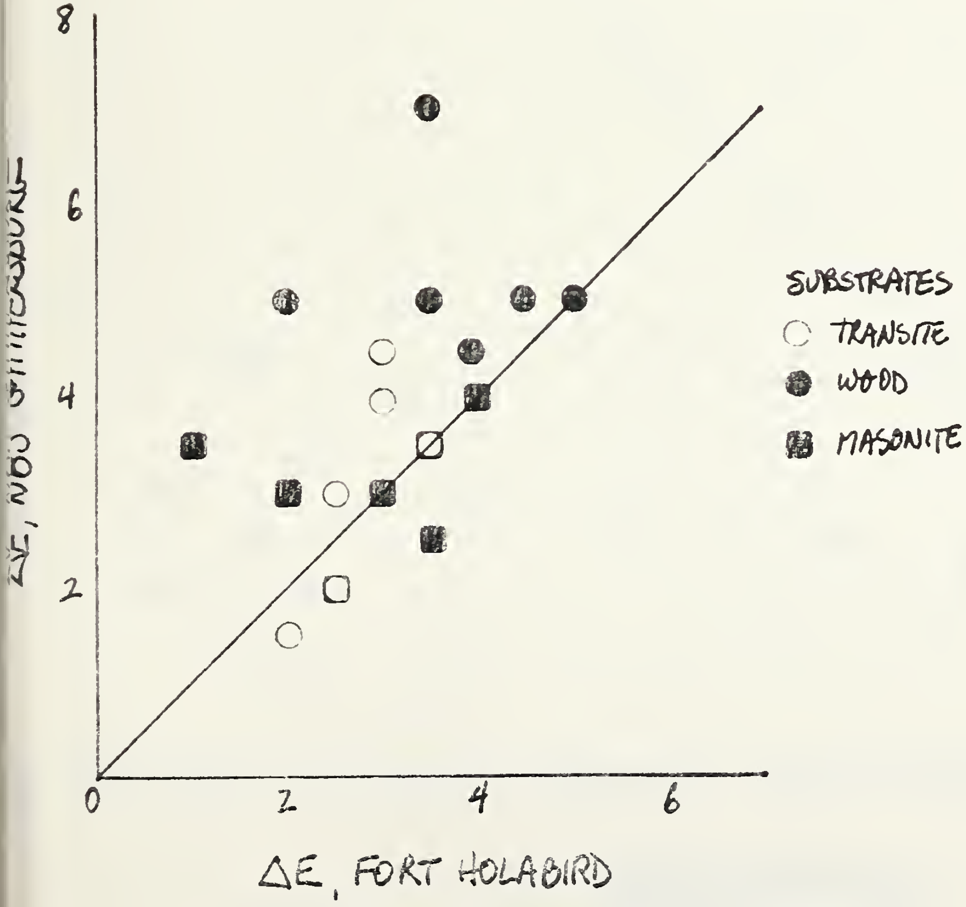


FIGURE 4

TOTAL COLOR DIFFERENCE, ΔE
OUTDOOR EXPOSURES
ACRYLIC LATEX PAINT

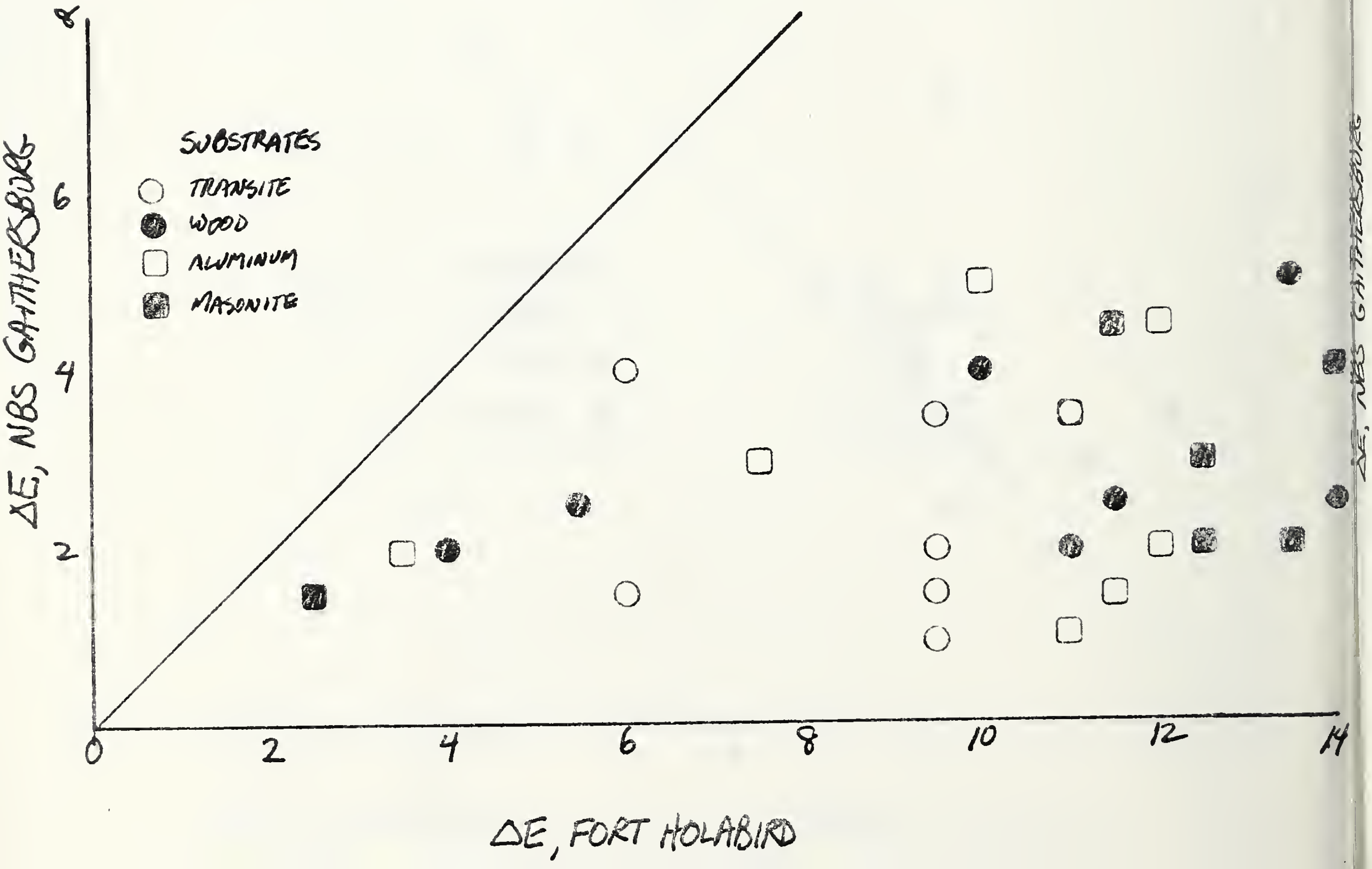


FIGURE 5

TOTAL COLOR DIFFERENCE, ΔE
OUTDOOR EXPOSURES
PVA PAINT

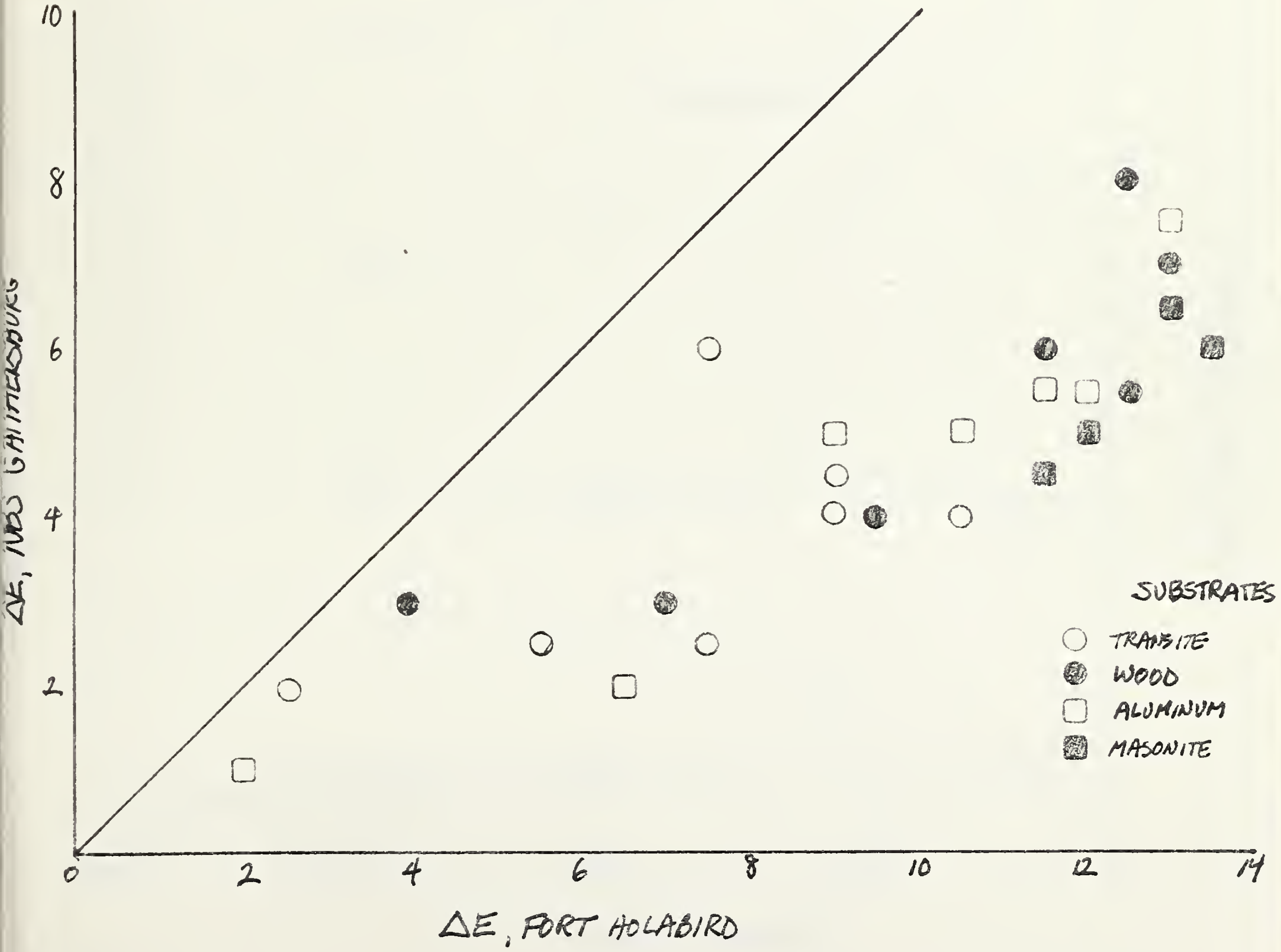


FIGURE 6

TENSILE STRENGTHS OF PLASTICS EXPOSED TO ACCELERATED WEATHERING

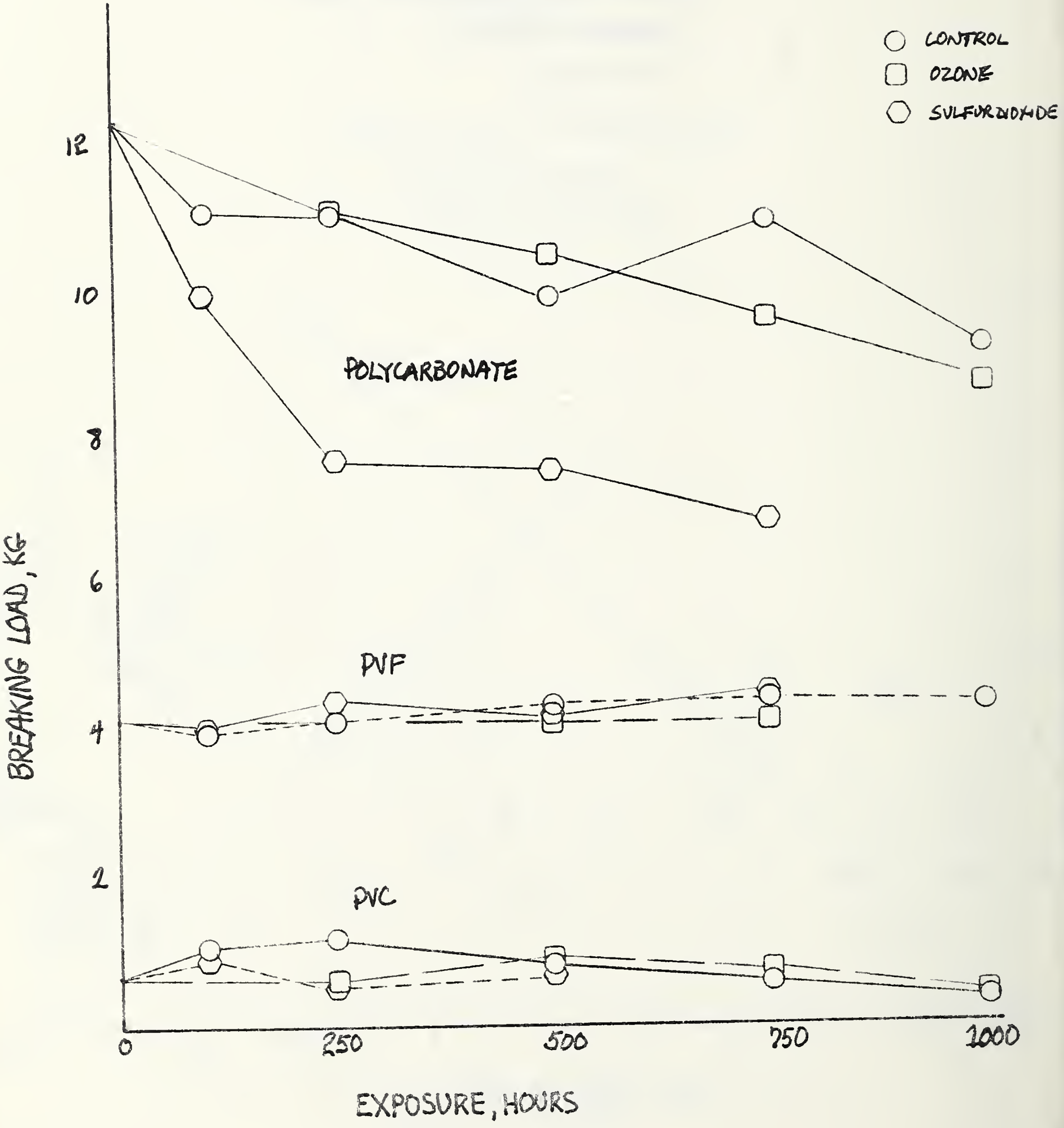


FIGURE 7

TENSILE STRENGTHS OF PLASTICS
EXPOSED AT OUTDOOR WEATHERING SITES

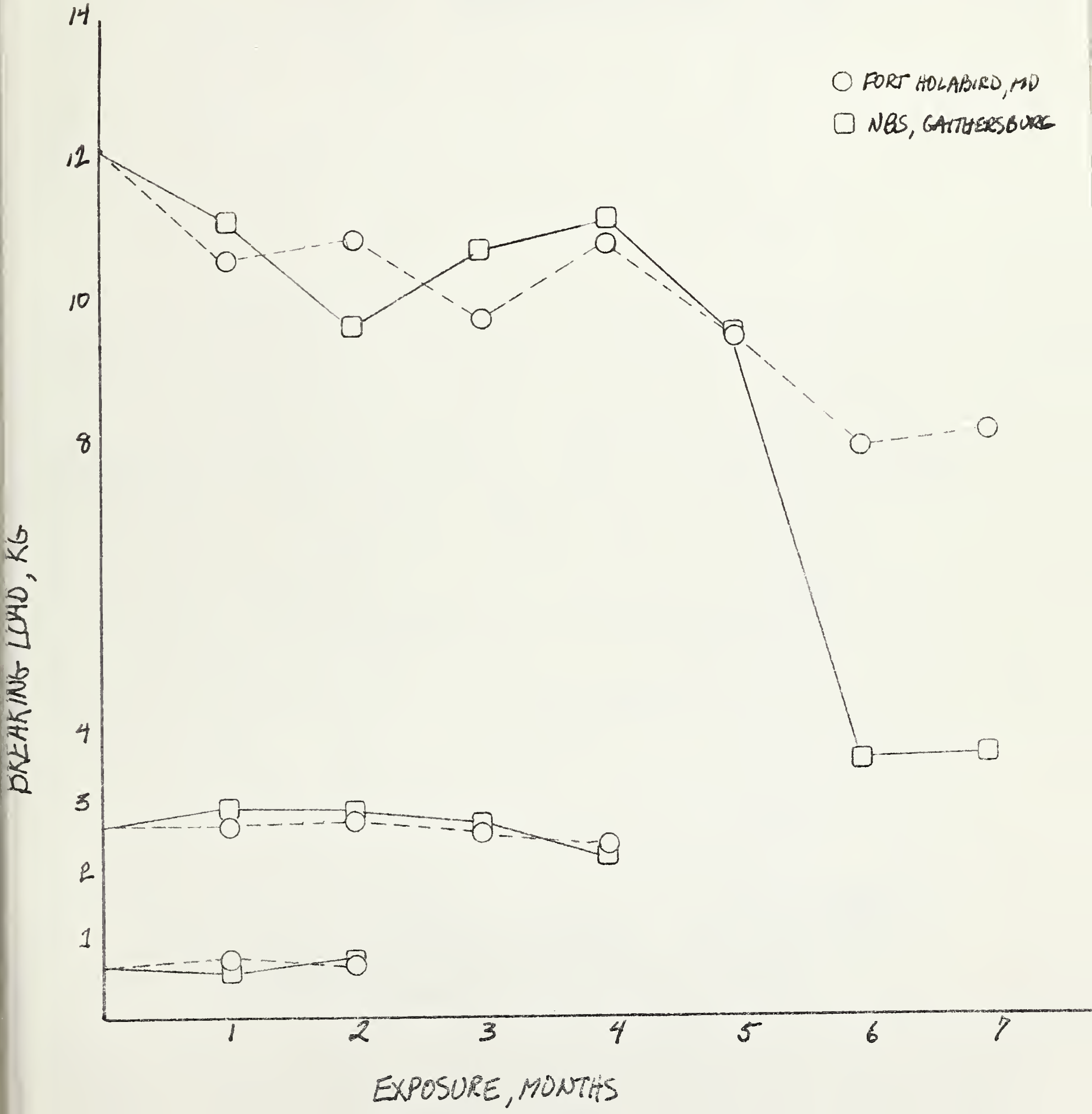
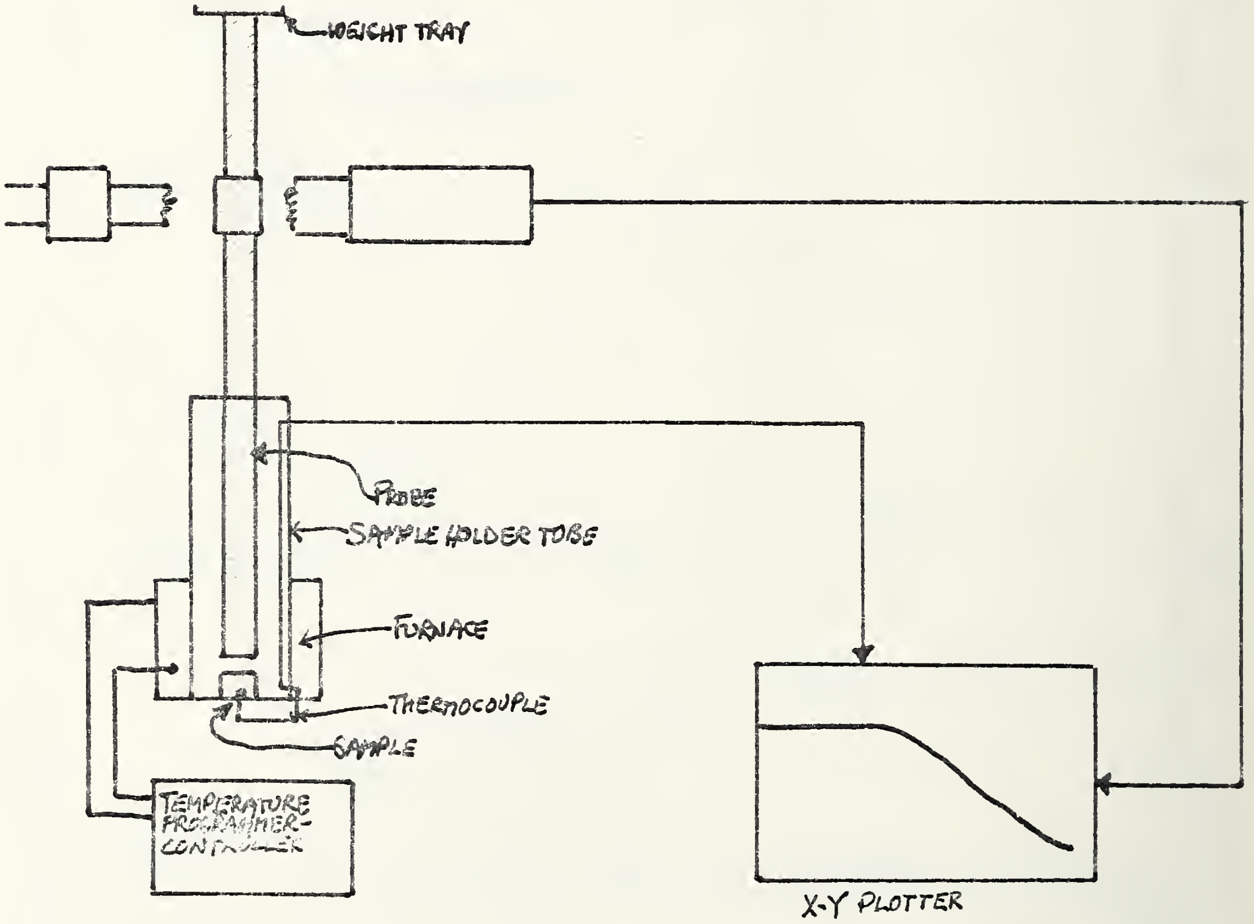
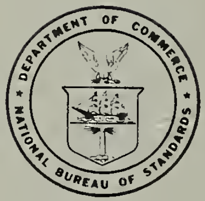


FIGURE 8

DESIGN OF TMA APPARATUS




DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS