CIRCULAR #791 FEBRUARY, 1964

Scientific Section

National Paint, Varnish and Lacquer Assn

1500 RHODE ISLAND AVE., N.W.
WASHINGTON 5, D. C.

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# INSTRUMENTAL TECHNIQUES APPLIED TO PAINT FILM DETERIORATION

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## Introduction

The Joint Paint-Lumber Industry Steering Committee in one of its early recommendations suggested that an acute need of both the paint and lumber industries was a suitable laboratory method for predicting the performance of paint systems on exterior wood.

It was recognized that much effort has been expended in developing "accelerated weathering" methods, but in spite of the time and energy that has gone into this development work, few paint manufacturers are prepared to predict the behavior of a given paint system without extensive practical tests. The necessity for these makes product development in this field slow and makes the specification or certification of paint systems by performance standards impossible.

It was felt that modern instrumentation which has developed since World War II, applied to paint systems of this type, might yield better results and results which would correlate with known performance.

To carry out this investigation, a joint project was undertaken with Armour Research Foundation* of Chicago, Illinois, to study the application of modern instrumentation to a series of paints of known performance in the hope that one or more methods which correlated reasonably well with this known performance might be uncovered.

The results of the first year's work on this project are now available. While a method which is suitable for adoption by the industry did not result from this effort, several methods show promise and these will be explored further by a second contract with the Armour Research Foundation, also jointly sponsored by the National Lumber Manufacturers Association and the National Paint, Varnish and Lacquer Association.

In order to keep Association members abreast of developments, the report of the first year's work at Armour as prepared by Dr. Kurt Gutfreund is given herewith.

* Now the I I T Research Foundation.

# INSTRUMENTAL TECHNIQUES APPLIED TO PAINT FILM DETERIORATION

*by* KURT GUTFREUND

## I. Introduction

Over a period of many years, paint manufacturers have acquired extensive information on the behavior of house paints under different conditions of use. Much of this information has been obtained by empirical methods involving exposure of test panels to environmental influences. The panels are tested under widely differing climatic conditions. The extent of deterioration of paint samples in this process of "normal" weathering is determined from changes in appearance. Particular consideration is given to gross manifestations of paint failure, such as checking, formation of deep cracks and fissures, flaking, and chalking.

Although this method of evaluating paint quality is directly related to performance criteria established by industry on the basis of consumer requirements, it has obvious disadvantages. Rather than the subjectivity of the tests, the main disadvantage is the amount of time required for their completion. Advances in paint technology, spurred on by the extensive use of new constituents in improved formulations, underline the necessity of determining performance characteristics of paint by less time-consuming methods. In this manner information could be obtained sooner for further development of coating systems.

The difficulty of selecting a successful laboratory method for determining the behavior of paints results in great measure from three factors. These factors include the chemical diversity of coating systems now in use, the inadequate knowledge of the mechanisms of paint deterioration, and the interplay of environmental conditions which bear directly on the performance of the paints in use.

Many factors undoubtedly contribute to the degradation of protective coatings under outdoor exposure conditions. However, the final effects of the degradation process invariably involve mechanical failure in one form or another. Thus, for instance, checking and cracking of house paint represent a visible loss in structural integrity of the coating. These defects could have resulted from embrittlement and subsequent failure in the film to conform to dimensional changes of the substrate. Since viscoelastic effects play a particularly important role in the mechanical behavior of high-molecular-weight polymers, it could be expected that the deterioration of paints would also be associated with changes in their viscoelastic behavior.

This aspect of paint degradation was considered in an investigation of instrumental techniques. Attention was di-

rected toward developing a method to correlate a measured property of selected paints with their known quality rating as established by conventional weathering tests. The study conducted at Armour Research Foundation was supported jointly by the National Paint, Varnish, and Lacquer Association, Incorporated, and the National Lumber Manufacturers' Association. The work discussed in this report covers the period of March 20, 1962, to March 20, 1963.

## II. General Considerations of the Behavior of Paints and Methods to Determine Their Properties

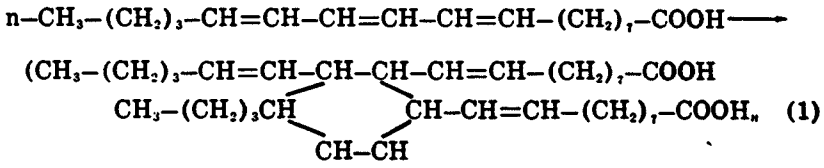
The reactions which potentially can take place in multiphase systems greatly complicate the picture of degradation in house paints. A thorough study of this subject would involve the thermally or photochemically induced decomposition and absorption, that is applicable to the various constituents (vehicle, pigment, extender and additives), and interactions between these components as well as between the main ingredients and the substrate. Interactions between pigment and vehicle could lead to embrittlement of protective coatings (1),* while adhesion and blistering problems were attributed to interactions between the paint system and water (2, 3). The moisture is supplied by the environment as well as the substrate, which in the case of certain woods could also promote migration of exuded organic compounds to the surface of the coating (4, 5). Although all these factors undoubtedly play a role in the deterioration of coating systems, the degradation of paints in prolonged service is generally considered from the viewpoint of changes which occur in the paint, particularly in regard to high-molecular-weight binders.

The opposing processes of polymerization and degradation are important in the "aging" of paints. Particular importance can be attributed to (1) loss of flexibility associated with polymerization and cross-linking and (2) deterioration of the structural integrity of paint films due to extensive bond scission in the polymer binder.

### A. Polymerization of Oil-Base Binders

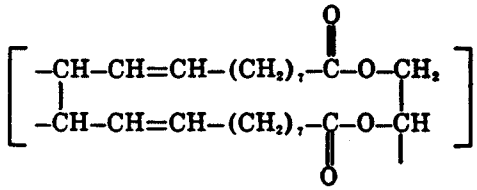
Drying oils have been used for many years in the paint industry. In modified form with polymer resins (alkyds, polyamides), they represent the most widely used base for house paints. Thermal polymerization of drying oils is considered to involve a Diels-Alder condensation of double bonds with formation of six-membered ring structures (6, 7). Ring formation through interaction of fatty acid groups on neighboring glycerides is involved as well (8).

* Numbers in parentheses refer to literature references on page 60.



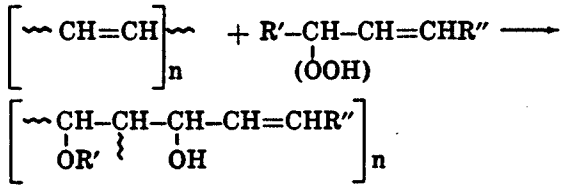
(1)

Ring formation through interaction of fatty acid groups on neighboring glycerides is involved as well (ref. 8)



In the presence of oxygen, reactions of conjugated systems generally proceed through a free radical mechanism with the formation of a hydroperoxide, such as the primary oxidation product of ethyl linoleate (9).

Further oxidation can lead to the breakdown of the compound and formation of aldehydes and ketones. Alternatively, under suitable conditions such as elevated temperatures, polymerization and cross-linking could be favored.



(2)

Formation of high- and low-molecular-weight products in the oxidation of conjugated fatty acid derivatives suggests competition between polymerization and degradation in oil-base coating systems. These reactions appear to be responsible in great measure for the mechanical behavior of paint films.

## B. Polymer Degradation

The general rate equations which describe the degradation of polymers are based on the concept that decomposition processes represent the inverse of chain polymerization. Thus, they are characterized by initiation, propagation, chain transfer, and termination (10). The mechanism of initiation plays

a particularly important role in the decomposition of polymers. If initiation occurs at specific sites, e.g., at the end of the chain as in poly-alpha-methylstyrene, then the chain unzipping process is likely to result in the degradation of the macromolecules to monomer units (11). On the other hand, if the sites of initiation are distributed randomly along the chains, then the degradation products consist of higher-molecular-weight fragments. Random degradation is the more feasible mechanism for the decomposition of polymers used in paints. However, the residual unsaturation of oil-base binders offers specific sites for oxidative degradation which could produce low-molecular-weight fragments.

In the degradation of derivatives of linoleic acid, the carrier chain appears to be a resonance-stabilized free radical which produces a peroxide upon oxidation (9).

$$\mathrm{R{-}CH{=}CH{-}CH{-}CH{=}CHR' \rightleftharpoons R{-}CH{-}CH{=}CH{-}CH{=}CHR' \xrightarrow{O_2}}$$

$$\mathrm{R{-}\underset{\displaystyle O_2}{\underset{|}{CH}}{-}CH{=}CH{-}CH{=}CHR'} \qquad (3)$$

On reacting with unoxidized linoleate, the peroxide regenerates the free radical and forms a hydroperoxide.

$$\mathrm{R{-}\underset{\displaystyle O_2}{\underset{|}{CH}}{-}CH{=}CH{-}CH{=}CHR' + R{-}CH{=}CH{-}CH_2{-}CH{=}CHR' \longrightarrow}$$

$$\mathrm{R{-}\underset{\displaystyle (OOH)}{\underset{|}{CH}}{-}CH{=}CH{-}CH{=}CHR' + R{-}CH{=}CH{-}CH{-}CH{=}CHR'} \qquad (4)$$

Further oxidation of the conjugated hydroperoxide results in scission of double bonds and formation of fragments with oxygenated ends.

$$\mathrm{R{-}\underset{\displaystyle (OOH)}{\underset{|}{CH}}{-}CH{=}CH{-}CH{=}CHR' \xrightarrow{1/2\ o_2} R{-}CH(OH){-}CHO +}$$

$$\mathrm{\left\{ OCH \xrightarrow{3/2\ o_2} R{-}COOH + HCOOH + HOCO{-}\right.} \qquad (5)$$

In the early stages of oxidation, polymerization and cross-linking reactions could conceivably outweigh polymer fragmentation. The result of cross-linking would be an apparent

improvement of mechanical properties of paint films in regard to hardness and tensile strength. Such effects are observed in some paints during the first phase of aging. However, progressive bond scission should weaken the structural integrity of the coating, thereby making it susceptible to environmental influences of moisture and to effects of differential thermal expansion of the substrate and of the coating.

These considerations suggest that the problem of paint deterioration could be approached from the viewpont of changes in intrinsic properties of the coating systems. However, a thorough study of this nature would require isolation of a single component and determination of its behavior under selective conditions.

A compromise between the fundamental and the practical approaches can be made by considering phenomenological aspects of paint deterioration for the whole system within the framework of well-designed experimental measurements. Although results thus obtained cannot be interpreted rigorously in terms of a mechanism of degradation, they can provide quantitive information which could possibly correlate with the behavior of paints in use. Such correlation is the ultimate objective of this program.

### C. Investigation of Paint Properties

The lack of suitable methods for investigating paint performance and durability is responsible for large-scale field experimentation. The foundation for many tests and evaluation procedures in the paint industry is provided by this work.

The durability of a paint is defined as the ability of the coating to retain the properties required for continued service. It is usually related to the time lapse associated with the occurrence of visible defects under outdoor-exposure conditions (12). The severity of these defects can be determined by comparison with graded photographic standards suggested by the American Society for Testing Materials. These tests include blistering (ASTM D 714-56), checking (ASTM D 660-44), flaking (ASTM D 772-47), chipping resistance (ASTM D 913-51), and efflorescence and chalking (ASTM D 1848-61). Mechanical properties are also being evaluated in regard to hardness (ASTM D 1474-52), abrasion resistance (ASTM D 1398-58), elongation (ASTM D 522-60), and toughness (ASTM D 1649-59). Toughness is determined by visual inspection of supported films after bending.

Similar methods of paint evaluation are used in other countries, notably in Great Britain and Germany. German tests, specified by Deutsche Industrie Norm, include flexibility measurements (DIN 53152), abrasion tests (DIN 53155), impact resistance (DIN 53154), and adhesion tests (DIN 53151). Impact resistance is evaluated from the susceptibility of coatings to fail when subjected to the impact of falling steel balls. In adhesion tests the tendency of paints to delaminate

from the substrate is determined by means of a line-inscribing method, similar in principle to the Arco microknife test (13).

Most of these tests are concerned with single-value or point measurements, i.e., measurements of a given property under constant test conditions. Although this does not necessarily diminish the value of the data, more comprehensive information, particularly in regard to mechanical behavior, can be derived from data representing a function of a variable such as stress, deformation, and time. This approach was utilized in studies of the effect of pigments (14). The influence of gamma and ultraviolet and infrared absorption studies were applied in investigations of oxidative degradation (16). The possibility of characterizing organic coatings in regard to polymerization and bond scission was explored by magnetochemical methods (17).

Although these methods of investigating paint properties have greatly contributed to the development of new and better paints, a clear picture of the property-performance relationship for coatings subjected to outdoor conditions has not been established. This research represents a part in the continuing efforts made in different laboratories toward a successful solution of this problem.

## III. Materials and Methods

The search for an instrumental method for the characterization of paint performance under use conditions is handicapped by the possibility that a well-defined correlation between practice and a selected laboratory procedure could prove to be highly specific for a given set of circumstances. This situation can easily occur in investigations of materials greatly differing in chemical nature and physical properties, such as in the paints submitted for consideration in this study. To minimize the danger inherent in the specificity of a given approach, a broader base was adopted by considering several instrumental techniques.

Concurrent with investigations of the applicability of instrumental methods, attention was given to the selection of appropriate environmental conditions which enhance paint deterioration. In this way, the rate of change of the measured property, whose correlation with outdoor exposure was sought, could be followed on a relatively short time scale.

Pertinent to the study are the arguments advanced in Section II in regard to possible effects of cross-linking and bond scission on the behavior of polymeric materials. Consideration was given to mechanical properties as determined by stress-strain, stress-relaxation, attenuation, and friction measurements. Methods used to increase the rate of change of the measured properties included exposure to ultraviolet radiation, high-energy light flashes, ozone, and changes in temperature and humidity.

### A. Paints and Substrates

House paints differing in composition and rated by the manufacturer in regard to their performance have been submitted by the Sherwin-Williams Company for consideration in this study. The label analyses of these paints follow.*

OJ 641; Code, 641 WFM

| | |
|---|---|
| Pigment—66% by Weight | |
| Zinc Oxide | 36.0% |
| Basic Sulfate White Lead | 19.0% |
| Basic Carbonate White Lead | 36.0% |
| Silicates | 9.0% |
| | 100.0% |
| Vehicle—34% by Weight | |
| Raw Linseed Oil | 90.0% |
| Thinner | 10.0% |
| | 100.0% |

Drier (metal) 0.17% Pb, 0.011% Mn, 0.12% Ca.

OJ 642; Code 642 WGP

| | |
|---|---|
| Pigment—61% by Weight | |
| 18/82 Leaded Zinc | 40.0% |
| Titanium Dioxide (Rutile) | 5.0% |
| Titanium Dioxide (Anatase) | 11.0% |
| Silicates | 44.0% |
| | 100.0% |
| Vehicle—39% by Weight | |
| Raw Linseed Oil | 44.5% |
| Bodies Linseed Oil | 28.5% |
| Mineral Spirits | 27.0% |
| | 100.0% |

Drier (metal) 0.33% Pb, 0.015% Mn.

OJ 643; Code 643 WG

| | |
|---|---|
| Pigment—65% by Weight | |
| 35/65 Leaded Zinc | 47.5% |
| Titanium Dioxide (Rutile) | 12.5% |
| Basic Carbonate White Lead | 12.5% |
| Silicates | 27.5% |
| | 100.0% |
| Vehicle—35% by Weight | |
| Raw Linseed Oil | 75.0% |
| Bodies Linseed Oil | 9.0% |
| Mineral Spirits | 16.0% |
| | 100.0% |

Drier (metal) 0.32% Pb, 0.03% Mn

* Obtained from Mr. M. Van Loo, Director of Paint Research, Sherwin-Williams Research Center, Chicago, Ill.

OJ 645; Code, 645 WFG

| | |
|---|---|
| Pigment—62% by Weight | |
| 12/88 Leaded Zinc | 29.0% |
| Basic Sulfate White Lead | 27.5% |
| Titanium Dioxide (Anatase) | 15.5% |
| Silicates | 28.0% |
| | 100.0% |
| Vehicle—38% by Weight | |
| Raw Linseed Oil | 61.0% |
| Bodied Linseed Oil | 19.0% |
| Mineral Spirits | 20.0% |
| | 100.0% |

Drier (metal) 0.43% Pb, 0.22% Mn

OJ 646; Code 646, WP

| | |
|---|---|
| Pigment—63% by Weight | |
| Titanium Dioxide (Anatase) | 9.0% |
| Barium Sulfate | 21.0% |
| Basic Carbonate White Lead | 30.0% |
| Zinc Oxide | 30.0% |
| Silicates | 10.0% |
| | 100.0% |
| Vehicle—37% by Weight | |
| Linseed Oil (Alkali Refined) | 75.5% |
| Vacuum Bodied Linseed | 5.5% |
| Mineral Spirits | 19.0% |
| | 100.0% |

Drier (metal) 0.88% Pb, 0.011% Mn

OJ 644; Code, 644 WXGP

| | |
|---|---|
| Pigment—39% by Weight | |
| Titanium Dioxide (Anatase) | 69.5% |
| Mica | 14.0% |
| Silicates | 16.5% |
| | 100.0% |
| Vehicle—61% by Weight | |
| Alkyd Solids | 53.0% |
| Thinners | 45.5% |
| Phenyl Hg Oleate (10% Hg) | 1.5% |
| | 100.0% |

Drier (metal) 0.42% Pb, 0.068% Mn

OJ 639; Code, 639 BGP

| | |
|---|---|
| Pigment—34% by Weight | |
| 35/65 Leaded Zinc | 21.5% |
| Brown Oxide | 52.0% |
| Ferrite Yellow | 5.5% |
| Cuprous Oxide | 6.5% |
| Litharge | 1.5% |
| Silicates | 13.0% |
| | 100.0% |
| Vehicle—66% by Weight | |
| Silicone Modified Alkyd Solids | 65.0% |
| Mineral Spirits | 35.0% |
| | 100.0% |

Drier (metal) 0.63% Pb, 0.03% Mn, 0.033% Ca.

EM-7338; Code, 338 WLA

| | |
|---|---|
| Pigment by Weight—34% | |
| Titanium Oxide | 68.0% |
| Calcium Carbonate | 19.0% |
| Silicates | 13.0% |
| | 100.0% |
| Vehicle by Weight—66% | |
| Synthetic Latex, 46% NVM | 64.0% |
| Water | 36.0% |
| | 100.0% |

EM-7339; Code, 339 WLB

| | |
|---|---|
| Pigment by Weight—34% | |
| Titanium Oxide | 53.0% |
| Calcium Carbonate | 29.0% |
| Silicates | 18.0% |
| | 100.0% |
| Vehicle by Weight—66% | |
| Synthetic Latex, 47% NVM | 57.0% |
| Water | 43.0% |
| | 100.0% |

*Explanation of Code*

The first letter indicates the color of the paint. Thus, W is white and B is brown. The letters that follow indicate the quality of the paint: FM is fair minus; GP, good+, FG, fair to good; P, poor; LA, latex first quality; and LB, latex second quality.

These formulations represent oil-base, alkyd, and emulsion paints of different quality, as established by their resistance to checking, cracking, blistering, and flaking. The applicability of a given method for correlating measured properties with

performance ratings had to be determined. For this study it appeared desirable to limit the comparative evaluation of some paints to formulations similar in chemical properties but representing extremes in quality. Thus oil-base paints 641 WFM and 642 WGP, representing poor and superior formulations, respectively, received particular attention in this investigation.

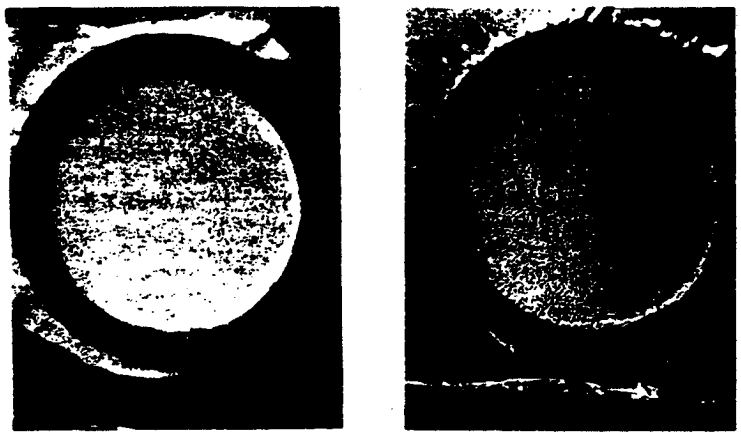
Among the substrates used for preparation of supported paint samples were cedar wood siding panels that were cut in planed rectangular sections of 3¼ x 5⅜ x ¼ inch and in ¼-inch thick disks of 2¾ inch in diameter. The cedar disks and similar supports made of stainless steel and aluminum were used in friction studies.

**B. Preparation of Test Specimens**

To obtain suitable test samples for stress-strain and stress-relaxation measurements, film specimens were cast on 9 x 9-inch glass plates by the drawing method. A good casting surface was obtained by applying tin foil with a squeegee to the plate which was already coated with dimethyl phthalate. The paint was spread by means of a Gardner applicator whose blade was adjusted to provide a dry film of approximately 0.003-inch in thickness. After 72 hours of drying at 50% r.h., the paint film and the adherent tin substrate were cut in 1 x 4-inch strips. The tin foil was removed by amalgamation in a mercury bath. Masking tape grips were used to reinforce the unsupported paint samples to prevent damage when they were inserted in the jaws of the tensile-testing machine.

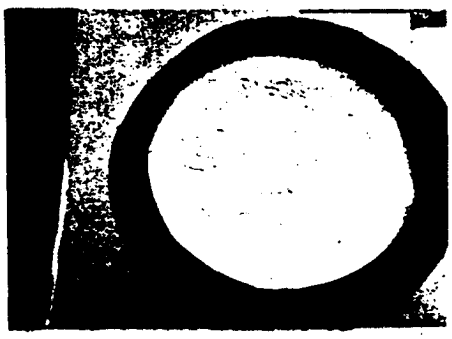
Prepared test samples individually mounted on a supporting rack were stored in a temperature-humidity cabinet or in a ozonization chamber, as required for the particular experiment. Stress-strain and stress-relaxation measurements were performed with an Instron testing machine whose isolated work area was maintained at constant humidity by saturated salt solution. Relative humidities of 20 and 93% were provided at 20°C by saturated aqueous solutions of potassium acetate and sodium sulfate decahydrate, respectively.

In an effort to prepare test samples supported on different substrates, a film-casting method was employed. In this method, a known volume of paint, diluted with turpentine to provide a concentration of volatile solvent of 40% was delivered through a calibrated syringe onto the substrate. The area of the substrate was delineated by a rubber-ring template of 5.6-cm internal diameter. After 2 days at 50% r.h. some of the deposited film wrinkled appreciably due to their particular response to solvent evaporation. The extent of wrinkling appeared to correspond to the over-all rating of paint performance as established by the manufacturer. Thus an alkyd-base film and oil-base paints with good quality ratings (Figures 1a, 1b, and 1c), showed little surface imperfection, while paints with ratings of poor, fair to good, and fair exhibited



a
(OJ 646)

b
(OJ 645)



c
(OJ 641)

Figure 2
Surface Appearance of Films Prepared from Fair and Poor Quality Paints

pronounced wrinkling (Figures 2a, 2b, and 2c). However, these surface irregularities disappeared when the dry thickness of films was changed from 0.012 inch, obtained in the casting method to 0.002 to 0.003 inch obtained in the drawing method. The film-drawing procedure was therefore adopted for coating aluminum, cedar wood, and tin foil substrates. The circular shape and small size of supports employed in friction studies necessitated accommodation of the substrate in an appropriately cut metal plate to fit the specimen and provide a larger coating surface.

### C. Mechanical Properties

In amorphous polymers the ultimate stress and elongation depend on the physical state of the polymer, its molecular structure, and experimental conditions under which tests are conducted. Therefore, it appeared desirable to determine stress-strain properties of paint films and follow possible change in mechanical behavior as a function of exposure to environmental influences. Measurements were performed with the Instron testing machine at a span length of 2 inches. Specimens ranged in thickness from 0.002 to 0.005 inches. The rate of elongation was maintained at 0.1 inch/minute for all but latex paints, which were tested at 1.0 inch/minute.

The dissipation of applied mechanical energy, which is characteristic of viscoelastic materials, was studied. Rate of stress decay was measured at constant strain on samples extended 5% beyond their initial unstrained condition. The duration of each experiment was 10 minutes.

Constant temperature and humidity conditions were maintained during stress-strain and stress-relaxation measurements. The results obtained from triplicate specimens, were averaged and appropriate curves were reconstructed from the data. Samples which failed near the jaws of the instrument or otherwise represented accidental failure were not considered.

### D. Friction Measurements

The interrelationship between surface and bulk mechanical properties of high polymers has been demonstrated in friction and wear studies of polyvinyl chloride, polymethyl methacrylate, and Teflon (18, 19). Viscoelastic effects were particularly important in regard to surface damage. The basic relationship governing friction in solids is represented by:

$$F = As + P \qquad (6)$$

where F is the frictional force, A is the area of contact, s is the shear strength of the adhesive junctions formed between the two surfaces at the areas of contact, and P is a "plowing factor" which depends on the geometry of the contacting surfaces and the visoelastic nature of the softer material.

The possibility of detecting changes in surface properties of paint films in the early stages of deterioration made the

friction method particularly attractive for the study of coating systems under different exposure conditions. The apparatus used consisted of motor-driven disk fixture which accommodated test specimens on appropriate circular substrates, a load-reaction spindle serving as the mechanical transducer of frictional force, a variable-speed drive coupled to a synchronous motor, and a spherical stainless-steel rider 0.25 inch in diameter which established sliding contact with the films. Bonded wire SR-4-resistance strain gages were used as sensing elements for converting frictional effects into equivalent electrical responses. In the course of the experiments, paint films supported on metal or cedar wood substrates were subjected to progressively increasing loads, while the surface remained in sliding contact with the rider. The normal load, frictional force, and humidity at which incipient failure of the film occurred were noted. These data were used to compare the surface behavior of different films. A comparison of frictional behavior of oil-base paints subjected to different doses of ultraviolet radiation was also performed.

### E. Acoustical Methods

The ability of acoustical waves to produce small stresses in coatings when applied to film-substrate systems suggested the investigation of elastic and dissipative properties of paints. The general relationship between acoustical and mechanical properties of materials is given by the equation:

$$Z=E\,\frac{\rho\ (1-\sigma)}{(1+\sigma)\ (1-2\sigma)} \qquad (7)$$

where Z is the acoustic impedance (a measure of the sound energy which enters the material investigated), E is Young's modulus, $\rho$ is the material density, and $\sigma$ is Poisson's ratio.

The dissipation of sound energy in paint samples has received particular attention since attenuation measurements were expected to correlate with changes in viscoelastic properties of coatings exposed to conditions promoting their degradation. The method involved the use of 4 x ¾ 1/16 inch aluminum specimens which vibrated in flexure as a cantilever beam. Paint films of 0.003-inch thickness were applied to these specimens by the film-drawing procedure. The dimensions of the substrate were modified, as necessary, to obtain a resonant frequency of 5 to 10 kc/sec. The system was excited electrostatically, and vibration amplitudes were measured by a capacitative probe in conjunction with a frequency-modulating system. Before the paint coating was applied, the aluminum strips were set into oscillations with a pulse carrier of the natural frequency of the strip. Adjustment of the frequency for maximum amplitude provided resonance conditions and permitted determination of the decrement from measurements

of rate of decay of forced vibrations. The dissipative constants of the paint were evaluated from data obtained for the clean substrate and for the substrate with the deposited paint film.

### F. Attenuation Measurements at Microwave Frequencies

Interaction between an electromagnetic wave and an isotropic medium through which it propagates depends on the permitivity of the material, its magnetic permeability, and the corresponding loss angles. These parameters represent material constants which reflect intrinsic properties of the dielectric in regard to its chemical nature and molecular configuration. Consideration was given to the attenuation of microwave signals in paint films supported on a short-circuiting brass flange. Standing wave ratio measurements were made at frequencies ranging from 8.5 to 12.5 kmc/sec.

The standing wave ratio (VSWR) is determined according to:

$$\text{VSWR}= \frac{1+|\Gamma|}{1-|\Gamma|}\,\frac{1+e^{-2\alpha d}}{1-e^{-2\alpha d}}=\text{ctgh}\alpha d=\frac{1}{\alpha d} \quad (8)$$

where $\Gamma$ is the reflection coefficient, $\alpha$ is the attenuation constant, and d is the thickness of the dielectric medium.

A Hewlett-Packard sweep oscillator (model 686 A) was used as a variable-frequency signal generator, while a Hewlett-Packard broad-band detector was employed as the traveling probe. The attenuation of 1 x 0.375 x 0.010-inch paint samples deposited on the short-circuiting brass flange was determined for freshly prepared and heat-treated specimens.

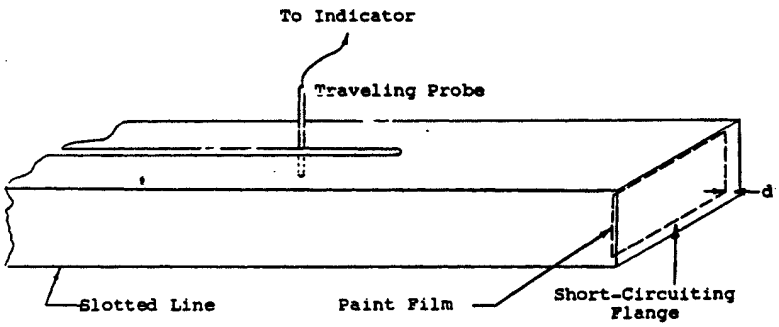



Figure 3

TEST ARRANGEMENT FOR ATTENUATION MEASUREMENTS

## G. Differential Thermal Analysis

Differential thermal analysis (DTA) is based on measurements of temperature differences between a system under study and a thermally-inert reference compound such as aluminum oxide. This technique was perfected by Duval and reported in this classic treatise (20). In essence the procedure involves continuous recording of the temperature differential between the sample investigated and the reference standard while heating proceeds at a predetermined rate. In endothermic processes, which are associated with the absorption of heat as in dehydration, desolvation, and thermal decomposition, the temperature of the sample lags behind that of the standard. This lag leads to distinct minima on the curve. On the other hand, exothermic reactions such as oxidation, polymerization, or condensation exhibit characteristic peaks in the DTA curve. Thus a thermogram, representing a "fingerprint" of the material investigated, is obtained. From this thermogram valuable qualitative and quantitative information can be derived on the physical and chemical changes occurring at progressively increasing temperatures. Since paint degradation is undoubtedly accompanied by chemical and structural changes in the organic coatings, differential thermal analysis appeared to offer a convenient method for determining differences in the behavior of paints subjected to outdoor weathering conditions. Thermograms of oil-base paints exposed in Florida for 4 years were compared with freshly prepared samples. The heating rate was programed at 3°C/minute over a temperature range of 25 to 600°C.

## IV. Exposure Conditions

The applicability of a given instrumental technique to studies of paint deterioration depends not only the sensitivity of the method to detect changes in measured properties, but also on the selection of suitable environmental conditions to promote the rate of paint degradation. In this way the observed effects were amplified. No particular effort was made to devise an "accelerated-aging" test which would simulate outdoor exposure. However, several methods were considered to enhance the rate change of measured properties.

### A. Temperature and Humidity Variations

Temperature is greatly responsible for structural changes in high-molecular-weight materials since it influences polymerization and degradation processes. It was therefore considered desirable to subject paint samples to elevated temperatures in order to produce changes in measured properties within a relatively short time. Cyclic exposure to high and low temperatures appeared to offer additional advantages for mechanical degradation because of thermally-induced dimensional changes. Also, the possibility of microcrack formation in embrittled paints subjected to thermal stresses suggested further magnification of observed degradation effects through exposure of paint films to high-humidity conditions.

Therefore, paint films were placed in a controlled temperature and humidity environment. Changes in their mechanical properties were determined over a period of several weeks. Initial experiments were conducted in an environmental chamber maintained at 71 and 4°C and 90 and 20% r.h., respectively. The total exposure of paint specimens to these cyclic conditions was 30 hours. This time was divided into alternating high and low temperature-humidity intervals. Each was 5 hours long. Additional tests made over a period of 25 days involved exposure of paints to the following conditions which were repeated after a cycle of 24 hours: 4 hours 60°C and 3% r.h., 1 hour at 21°C and 90% r.h., 3 hours at 60°C and 95% r.h., and 16 hours at 21°C and 90% r.h.

### B. Flash Irradiation

Intense flashes of light have been used to bring about chemical and thermal reactions which take months or years under ordinary conditions. Such intensities are readily produced by comparatively small electronic flash units of about 2500-joule capacitor storage energies. Photolytic reactions, which cause the yellowing and hardening of polymeric materials, are greatly accelerated by intense light flashes. Also, thermal expansion and contraction of a coating can be simulated by flash exposure. For these reasons flash photolysis was considered among other exposure methods intended to produce a rapid change in properties of house paints.

A 4000-microfarad unit, capable of delivering 100,000 joules/millisecond was used with a xenon flash tube for irradiation of unsupported paint films and paint coatings deposited on metal substrates. Since some paints exhibited a pronounced tendency toward charring when subjected to high-intensity flashes, the output of the unit was decreased to 23,000 joule/flash. To dissipate the heat generated by consecutive discharges and thereby eliminate thermal effects, the paint films were mounted on copper plates which were cooled on one side with ice water. The properties of paints exposed to different doses of flash irradiation (20 to 450 x $10^3$ joules) were investigated by optical and mechanical methods.

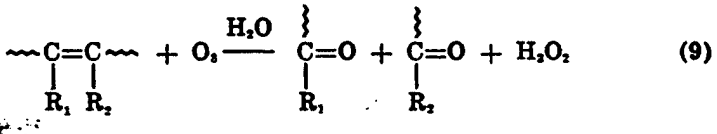
### C. Ultraviolet Irradiation

The photoinitiated depolymerization of high-molecular-weight materials has received considerable attention in recent years, because of the growing interest in stable coatings for space applications. However, the deteriorating effect of solar and ultraviolet radiation on the performance of paints has been recognized by the paint industry for a long time. It was therefore suggested that ultraviolet radiation be used in accelerating the degradation of paint films investigated in this program.

The ultraviolet source employed was an AH-6 mercury arc located 10 cm above a plate which served as a support for the irradiated specimens. The samples were cooled by a stream of air which was flushed across the paint surface. After exposure to different doses of ultraviolate radiation coatings and unsupported films were subjected to visual inspection, spectrophotometric analysis, and measurements of surface properties by friction methods.

### D. Ozonization

The severe conditions imposed on unsaturated organic compounds by ozone in regard to double bond scission and oxidative attack in a peroxide environment appeared to make ozonization a particularly good method for promoting degradation of house paints.



(9)

Accordingly, a Welsbach ozonizer, capable of delivering $O_3$-enriched oxygen up to an ozone concentration of 5% was employed. Unsupported paint films cut in 4 x 1 x 0.003-inch strips were suspended from a wire in a closed glass container. Into this container a mixture of oxygen and ozone in propor-

tion of 25:1 was continuously admitted. The duration of exposure was approximately 100 hours. During this time samples were removed periodically from the conditioning chamber, so that stress-relaxation and stress-strain measurements could be made at different stages of ozonization. To magnify the effects of ozonization on the mechanical properties, individual film samples were subjected to a tensile load of 45 g during exposure. Externally imposed stresses, known to greatly increase the susceptibility of rubbery materials to failure in an ozone environment, were expected to exert a similar influence on paints, particularly on those with an appreciable residual unsaturation.

## V. Experimental Results and Discussion

### A. Stress-Strain Relationships

Preliminary investigations of stress-strain properties of oil-, latex-, and alkyd-base paints were made at 45 and 20% r.h. on films ranging in thickness from 0.0025 to 0.0035 inches. The results shown in Figure 4 indicate that, with the exception of paint 646 WP, the stress-strain properties of oil-base paints correlate fairly well with the original quality rating. Thus films 642 WGP and 643 WG rated good + and good, respectively, have a relatively high ultimate strength (300 psi) when compared with 645 WFG and 641 WFM, which were considered fair-to-good and fair-. The films prepared from 645 WFG and 641 WFM formulations exhibit strengths of 200 to 260 psi and have correpondingly lower moduli of elasticity as indicated by the slopes of the curves.

The average elongation for oil-base paints of 14 to 20% at 45% r.h. is comparable with the ultimate deformation of 644 WXPG alkyd-base paints (Figure 5). However, films prepared from alkyd formulations have relatively high ultimate strengths (650 to 750 psi) and high moduli of elasticity. Unlike their oil and alkyd counterparts, emulsion polymer films are characterized by a high ultimate elongation (150 to 160%) as shown in Figure 6. The equilibrium stress which was maintained at 300 psi over two-thirds of sample elongation, suggests typical flow behavior of latex films. The deformability of latex films and their capacity to absorb a considerable amount of energy indicates an inherent resistance of this material to brittle fracture. However, the initial stress-strain conditions do not warrant conclusions about the long-term behavior of emulsion polymer paints without further considering their behavior upon exposure to selected environmental conditions.

One of the first exposure variables investigated was relative humidity. Samples equilibrated at the selected humidity were subjected to the stress-strain measurements described in Section III. It should be noted that measurements of mechanical properties of paints exposed to cyclic conditions

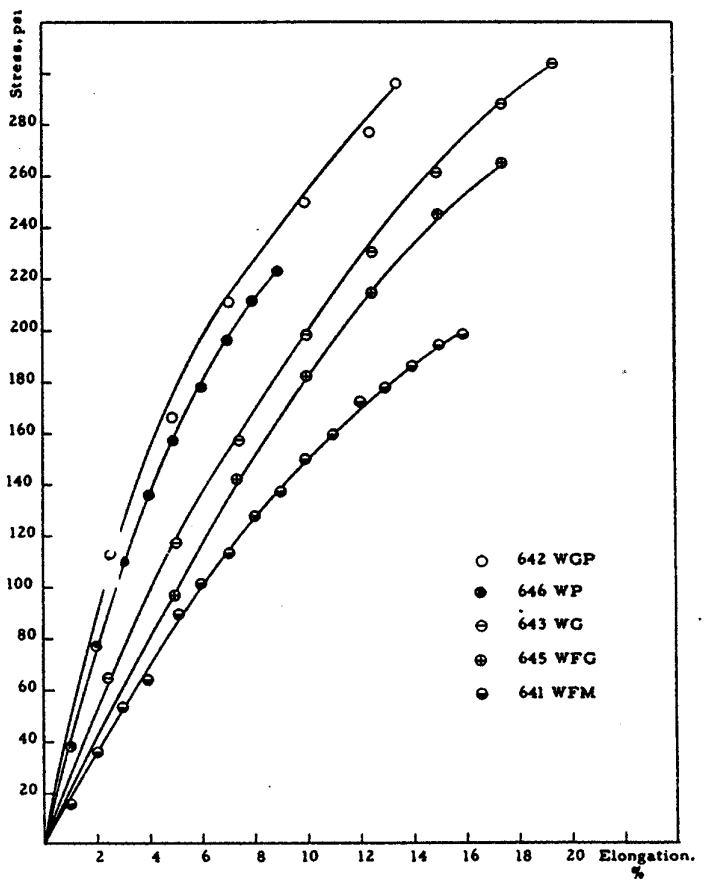



Figure 4
Stress-Strain Behavior of Oil-Base Paint Films at 45% r.h.

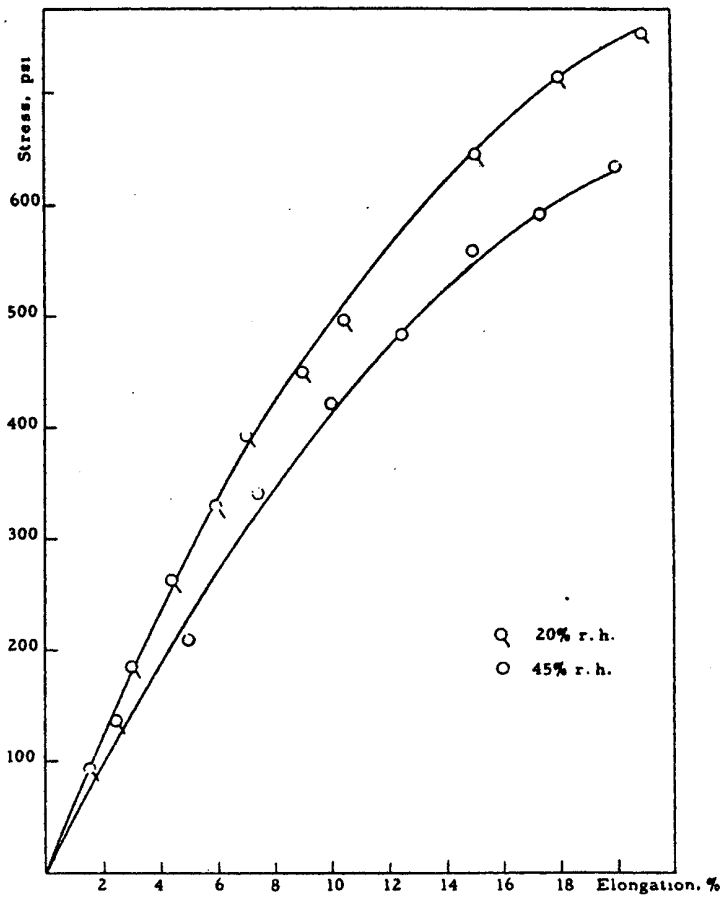



Figure 5
Stress-Strain Behavior of Alkyd-Base Paints at 20 and 45% r.h.

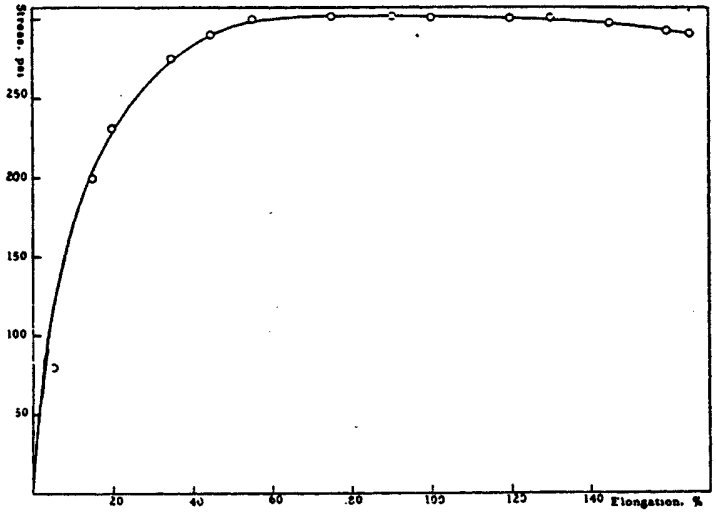



Figure 6

Stress-Strain Behavior of 7338 WLA Paint

(71°C at 90% r.h. and 4°C at 20% r.h.) were performed at 23°C and 20% r.h. which emphasizes the importance of the lower humidity level in these tests. The results are presented in Figures 7, 8, 9, and 10.

It is apparent that paint films exposed to high humidity exhibit a lower ultimate strength than films conditioned at lower humidities. Also, oil-base paints seem to be more susceptible to plasticization by moisture than alkyd- and latex-base paints. This susceptibility was indicated by the relative changes in stress-strain curves at different humidities. Short-duration cyclic conditioning of unsupported paint films seems to exert little influence on their mechanical properties. Consistent decrease in ultimate strength is noticeable for most films when compared with those tested at 20% r.h. without cyclic exposure.

The effect of moisture was analyzed more closely by comparison of apparent moduli of elasticity and consideration of the change of this property upon transition from 45 to 93% r.h. and from 45 to 20% r.h. Table 1, summarizing the data, indicates a relatively small effect of environmental humidity on the modulus of alkyd-base paint. This effect is evidenced by the small departure from unity of the ratios arbitrarily related to the base condition of 45% r.h.

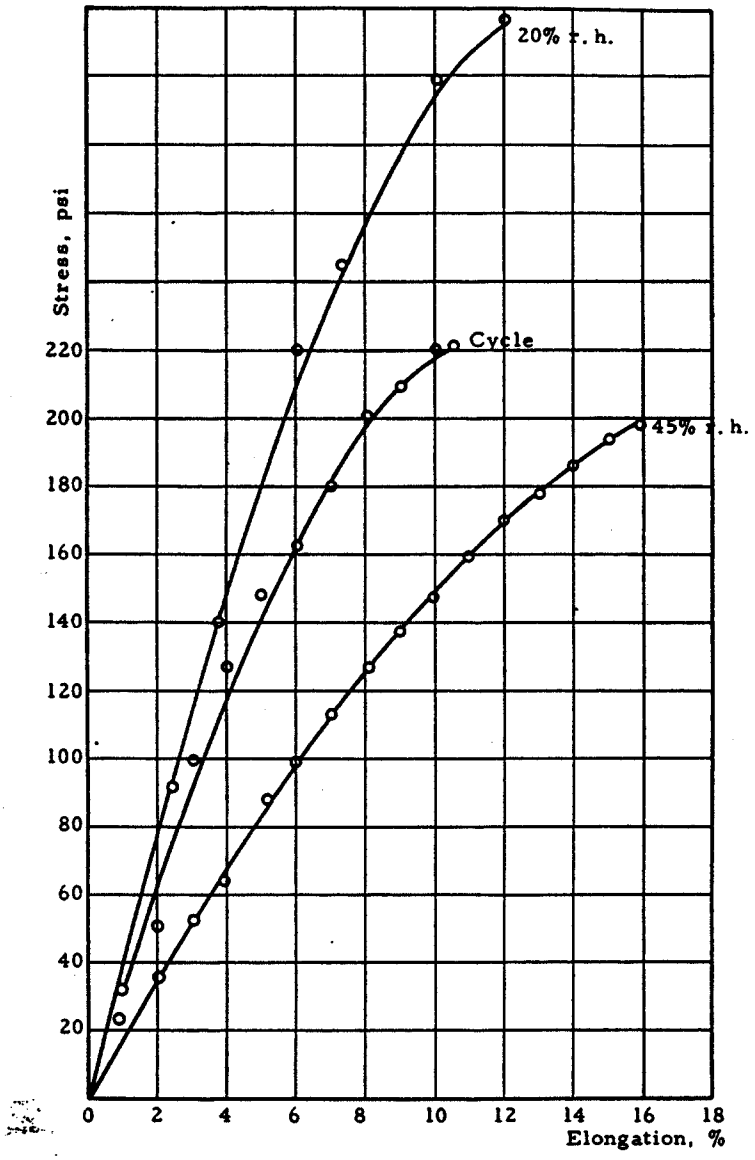



Figure 7

Stress-Strain Behavior of 641 WFM Oil-Base Paint
at Different Exposure Conditions

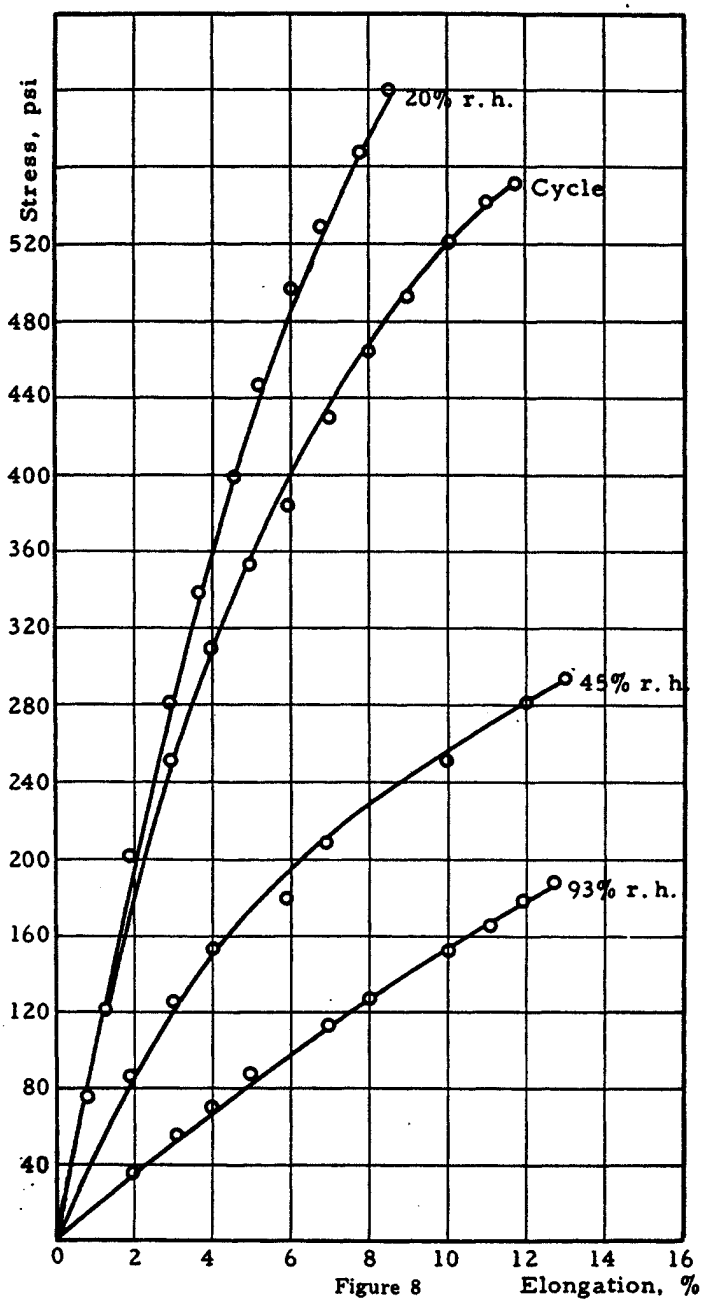



Figure 8

Stress-Strain Behavior of 642 WGP Oil-Base Paint at Different Exposure Conditions

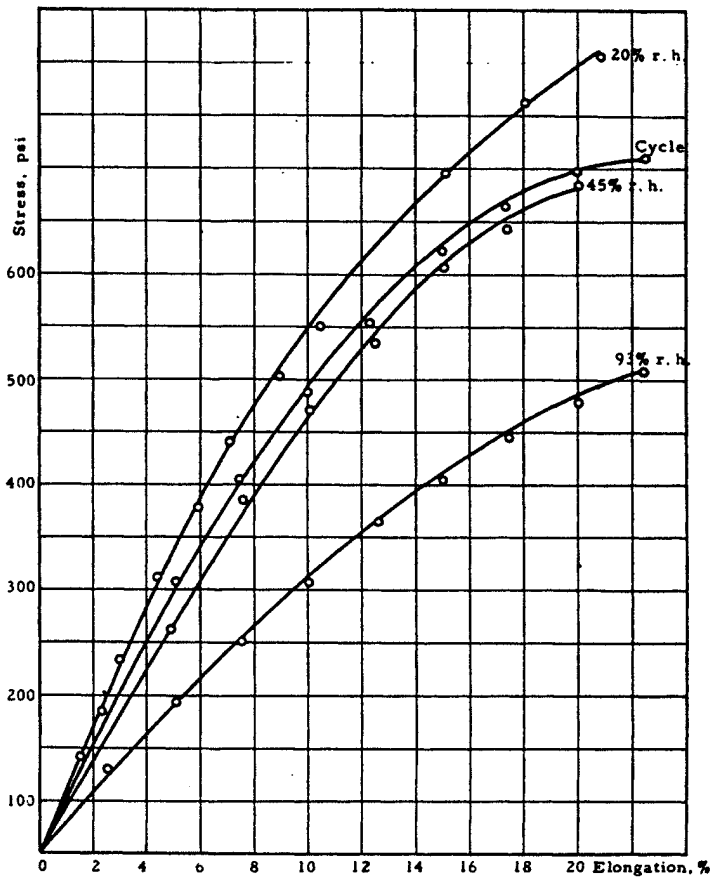



**Figure 9**

**Stress-Strain Behavior of Alkyd-Base Paint at Different Exposure Conditions**

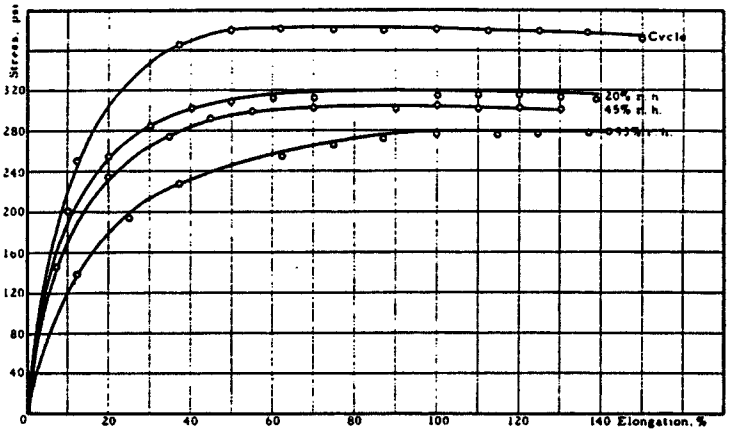



Figure 10

Stress-Strain Behavior of Emulsion Paint
at Different Exposure Conditions

Table 1
APPARENT MODULUS OF ELASTICITY OF PAINT FILMS
AT DIFFERENT HUMIDITY CONDITIONS

| | Modulus of Elasticity psi × 10⁻³ | | | | Normalized Modulus of Elasticity $E/E_{r.h.\ 45\ r.h.}$ | | |
|---|---|---|---|---|---|---|---|
| | Exposure Conditions, % r.h. | | | | | | |
| Sample | 20 | 20,cycle | 45 | 93 | 20/45 | 20,cycle/45 | 93/45 |
| 642 WFM | 4.4 | 3.3 | 1.7 | — | 2.6 | 1.9 | — |
| 642 WGP | 10.0 | 9.0 | 4.2 | 1.8 | 2.4 | 2.1 | 0.4 |
| 644 WXGP | 6.0 | 5.0 | 4.7 | 3.3 | 1.3 | 1.1 | 0.7 |

The greater sensitivity to moisture of oil-base paints in comparison with alkyd paints is indicated by the ratios in the last column of Table 1. Since the differential response to humidity is undoubtedly the result of gross differences in chemical nature, it appeared desirable to determine the effect of exposure conditions on paints similar in composition but different in performance. Special attention was therefore given to 641 WFM and 642 WGP.

Stress-strain measurements on two oil-base paint films exposed to cyclic temperature and humidity variations between 60°C at 3% r.h. and 60°C at 95% r.h., were made over a period of 25 days. The results shown in Figure 11 and Figure 12 indicate an increase in the apparent modulus of elasticity with increasing exposure, while under the same conditions ultimate elongation remained essentially unchanged. A plot of the secant modulus at 1% elongation (normalized with respect to initial conditions) against exposure duration (Figure 13) suggests that 641 WFM films undergo a greater change in the measured property over a longer period of time than do 642 WGP films.

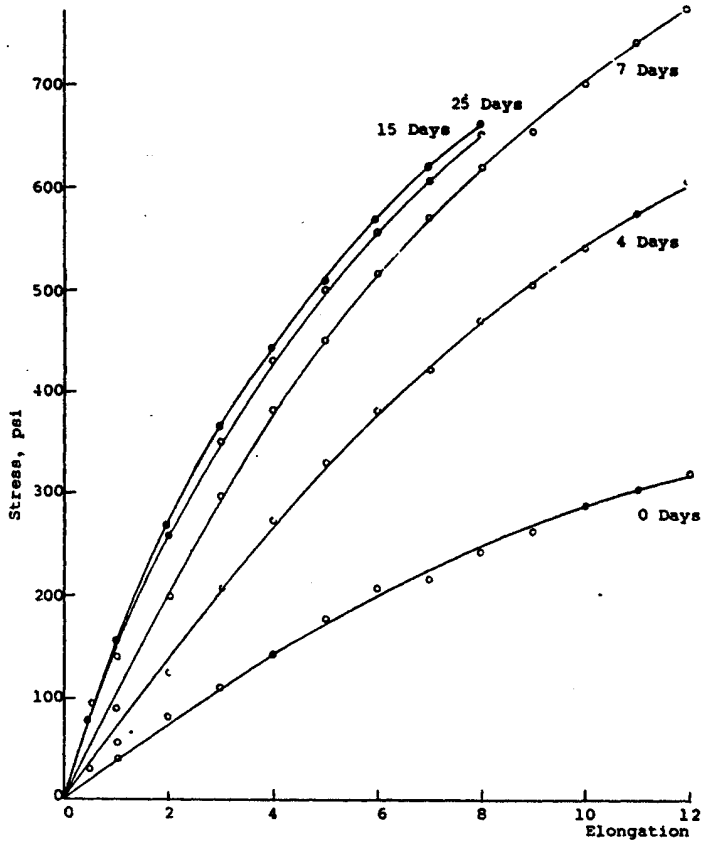



Figure 11
Stress-Strain Behavior of 641 WFM Films on Cyclic Exposure

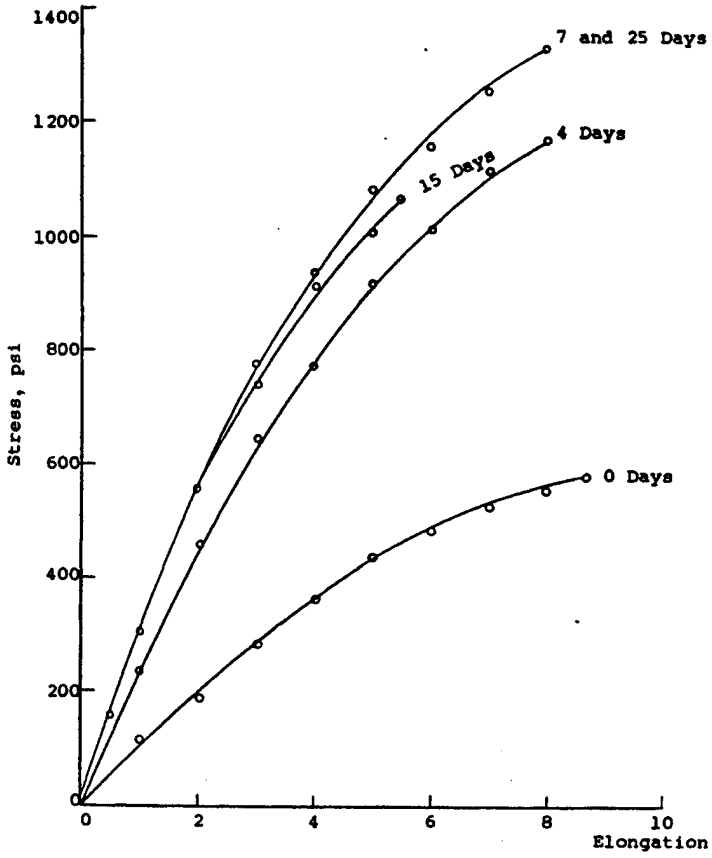



Figure 12
Stress-Strain Behavior of 642 WGP Films on Cyclic Exposure

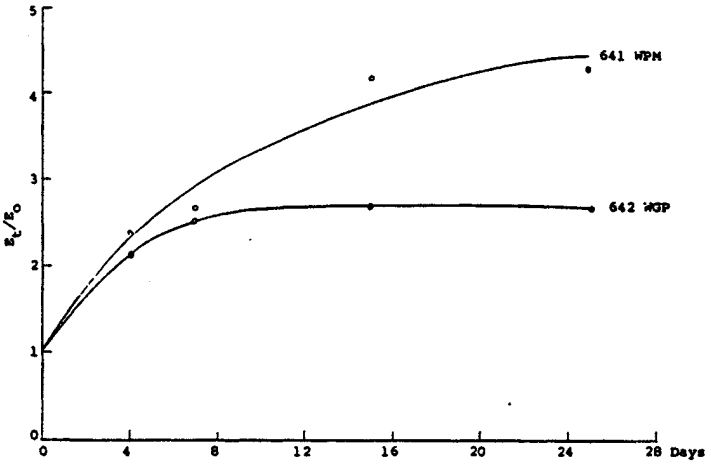



Figure 13
Effect of Cyclic Exposure on Secant Modulus of Oil-Base Paints

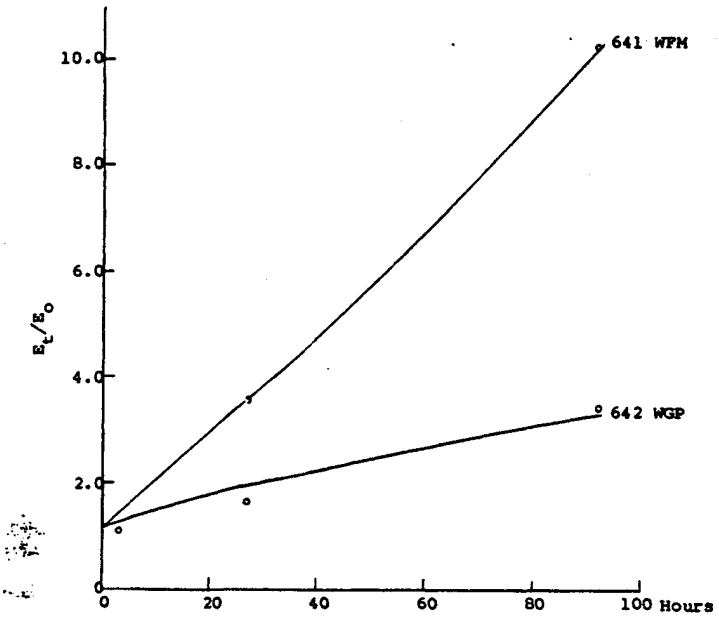



Figure 14
Effect of Ozone Exposure on Secant Modulus of Oil-Base Paints

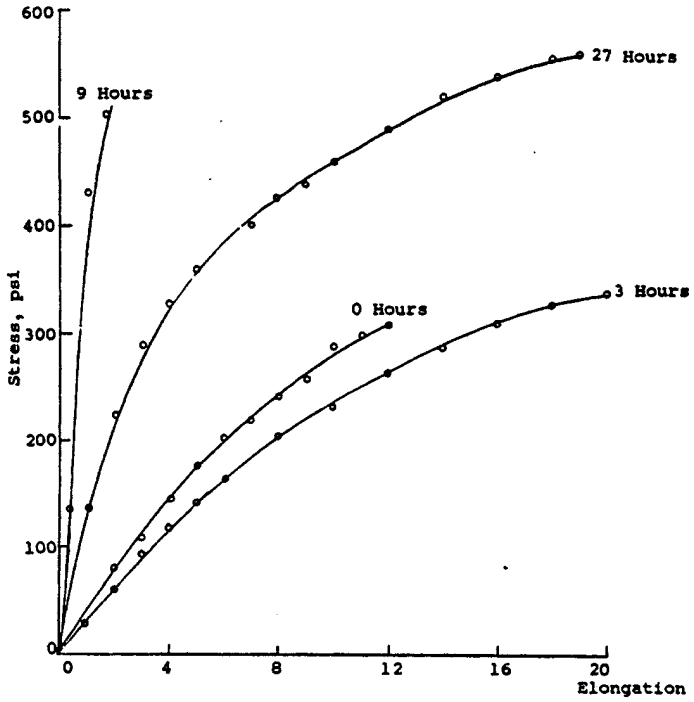



Figure 15

Stress-Strain Behavior of 641 WFM Films on Exposure to Ozone

A similar but more pronounced effect was also noted during exposure of oil-base paints to ozone (Figure 14). Here the reduced secant modulus for 641 WFM exhibits a continuous and relatively steep rise on exposure to an ozonizing atmosphere, while 642 WGP changes at a more moderate rate. Stress-strain curves presented in Figure 15 and Figure 16 indicate a general "hardening" effect of samples conditioned in ozone, although little change is observed in elongation up to 93 hours of exposure. Both samples, and particularly 642 WFM, became embrittled after this 93-hour exposure. The apparent inconsistency in the stress-strain behavior of the reference standard and ozonized 641 films in regard to elongation and the apparent modulus of elasticity cannot be interpreted at this time.

The data show a greater time dependence of mechanical properties with 641 WFM than with 642 WGP films. This dependence indicates some correlation with the rated durability. As previously mentioned, 641 WFM represents a paint of inferior quality.

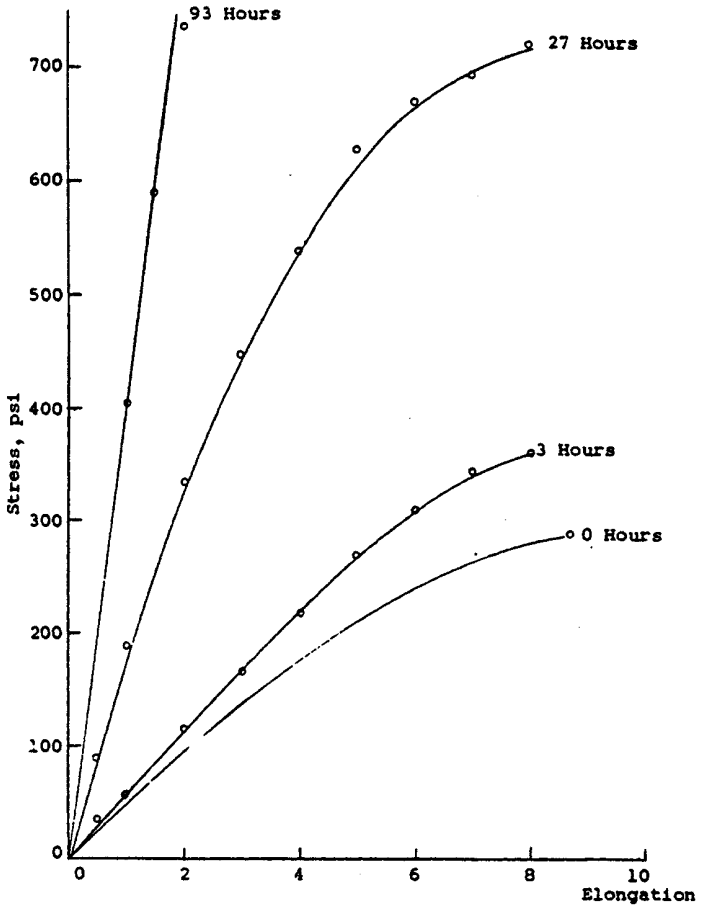



Figure 16
Stress-Strain Behavior of 642 WGP Films on Exposure to Ozone

## B. Stress-Relaxation

Stress-relaxation in polymeric materials is closely related to the energy dissipated through bond scission and viscous flow. As such, stress-relaxation represents irreversible processes which could take place in paint films under conditions of use.

Measurements performed on an alkyd-base paint and a series of oil-base paints at 45% r.h. are presented in Figure 17. Paints with a good quality rating (644 WXPG, 643 WG) exhibit a lesser initial rate of stress-relaxation than paints with a poor quality rating (646 WP, 641 WFM). A similar relationship was observed for emulsion paints (Figure 18). It

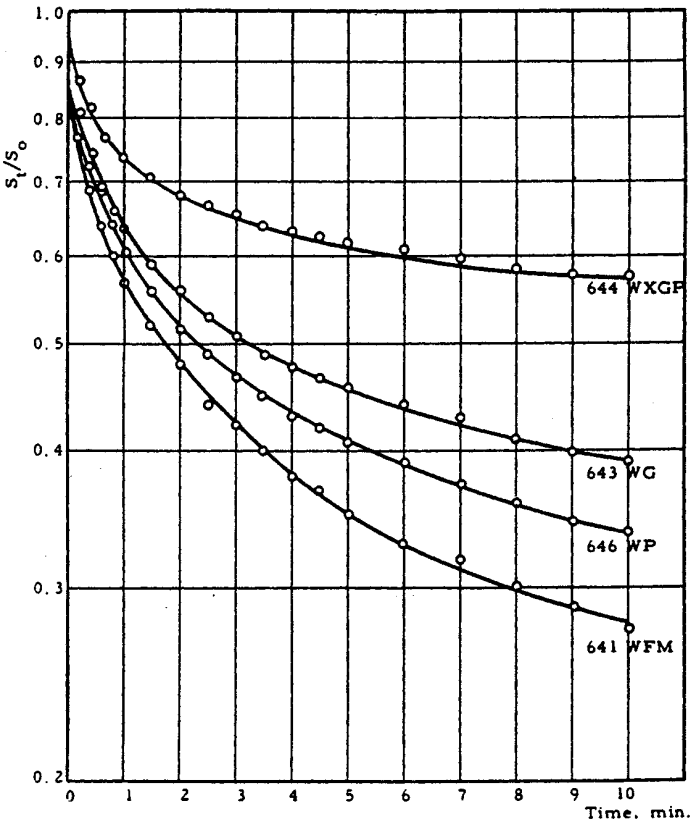



Figure 17
Stress-Relaxation of Paint Films at 45% r.h.

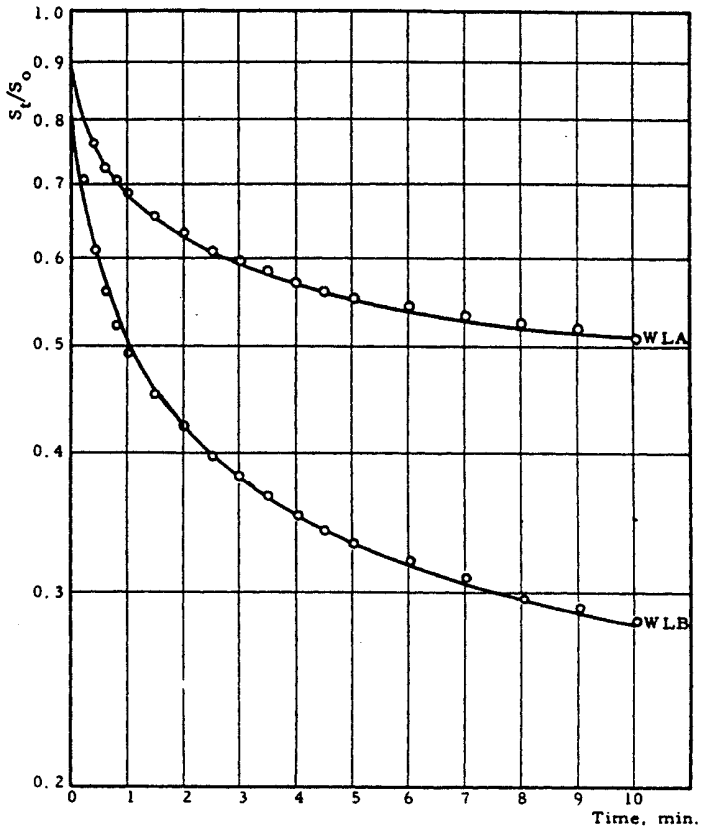



Figure 18

Stress-Relaxation of Emulsion Paints at 45% r.h.

would appear that the greater rate of energy dissipation in samples maintained at constant strain could be correlated with performance rating. However, it would be fortuitous indeed, if measurements based on initial properties would correlate with the performance of paints. The results obtained could not predict the behavior of paints in regard to hardening, cross-linking, and embrittlement under outdoor exposure conditions.

Certainly, initial stress-relaxation properties of alkyd-base paints should not be directly compared with those obtained for oil-base paints, if significant information about the property-performance relationship of these coatings is to be derived. The diverse chemical nature of both formulations could easily dominate the mechanical behavior of freshly prepared

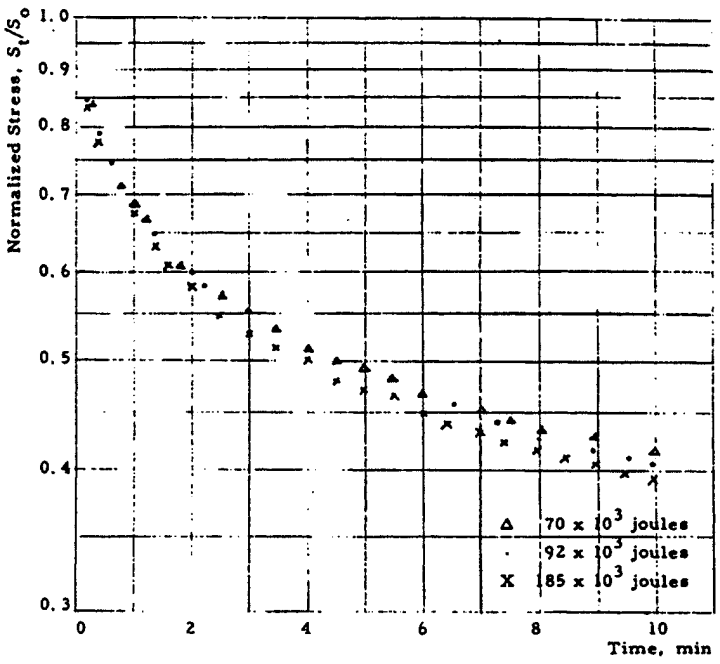



Figure 19

Stress-Relaxation of 641 WFM House Paint
at Different Flash Exposures

paint films although the measured properties of samples subjected to conditions promoting their degradation could drastically change. For this reason, the stress-relaxation behavior was followed at different stages of exposure to environmental influences.

One of those conditions involved exposure to flash irradiation. Exposure changed the surface appearance of some paints but did not produce perceptible changes in the stress-relaxation of 641 WFM and 642 WGP films (Figure 19 and Figure 20). Exposure to cyclic temperature and humidity variation according to the scheme adopted in stress-strain measurements (Section IV) affected the stress-relaxation behavior of oil-base paints to a greater extent (Figure 21 and Figure 22). The data were plotted semi-logarithmically according to the following relationship,

$$(1 - S_t/S_o) = a \log t + B \qquad (10)$$

where $S_t/S_o$ represents the ratio of the stress at time t and the stress at the end of the straining phase, a is a measure of the rate of stress-relaxation, and B is a constant. As indi-

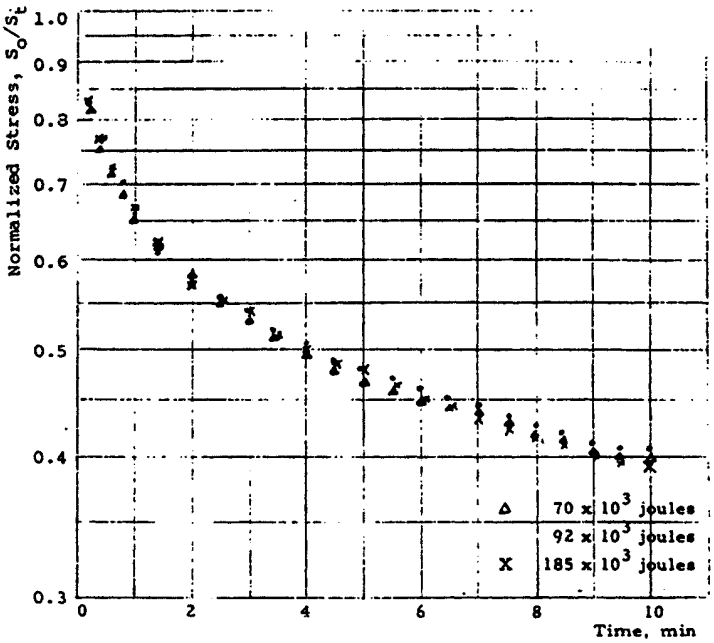



Figure 20

Stress-Relaxation of 642 WGP House Paint
at Different Flash Exposures

cated in Figure 21 and Figure 22, 641 WFM films show a greater change in the stress-relaxation curves when exposed to cyclic temperature and humidity conditions than do 642 WFP paints. A similar but more pronounced relationship was also observed for paints subjected to ozone for 5 to 98 hours (Figure 23 and Figure 24). Extrapolation of the essentially linear semilogarithmic curves to zero time provided intercepts on the ordinate which increased with the time of exposure. Since these intercepts depend on the nature of the material investigated, it appeared desirable to use the "constants" as parameters for determining changes in paint films subjected to oxidative degradation. Figure 25 shows a greater change in extrapolated relaxation values of 641 WFM upon ozonization than 642 WGP, thus suggesting a potential correlation between the measured property and the performance of these paints in use. Significant changes in the stress-relaxation behavior upon exposure to ozone were also noted for an emulsion-base paint (Figure 26).

In view of these conditions, a more detailed study of the stress-relaxation behavior of house paints exposed to ozone merits consideration.

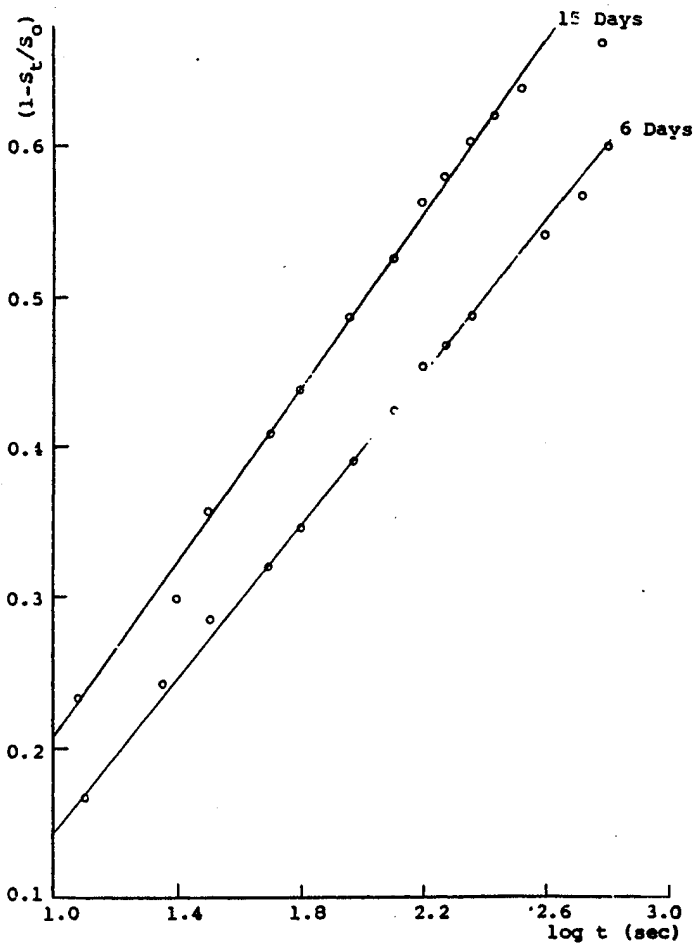



**Figure 21**

**Stress-Relaxation of 641 WFM Films on Cyclic Exposure to Temperature and Humidity Variations**

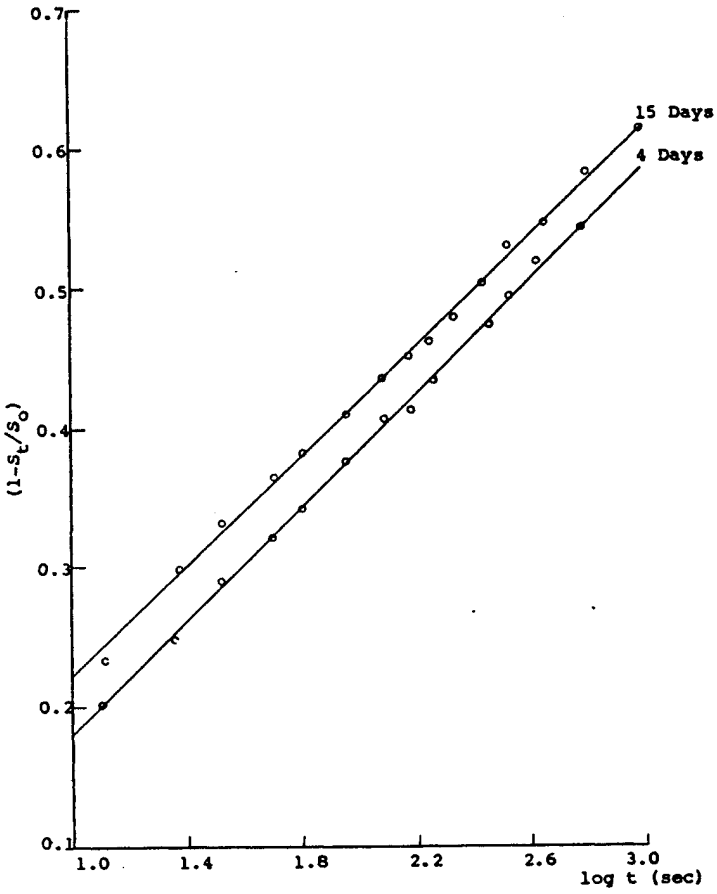



Figure 22

Stress-Relaxation of 642 WGP Films on Cyclic Exposure to Temperature and Humidity Variations

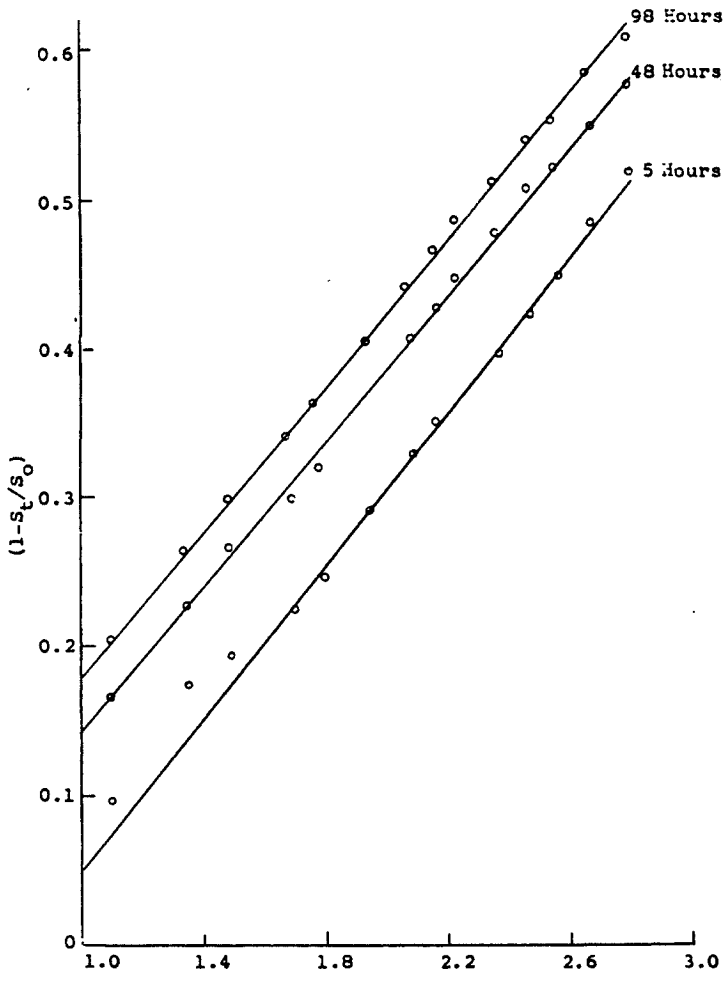



Figure 23
Stress-Relaxation of 641 WFM Films on Exposure to Ozone

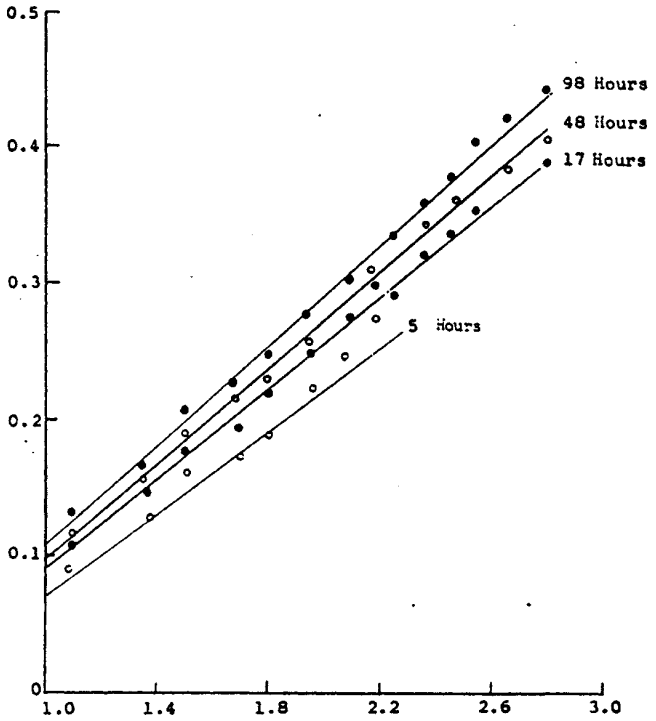



**Figure 24**

**Stress-Relaxation of 642 WGP Films on Exposure to Ozone**

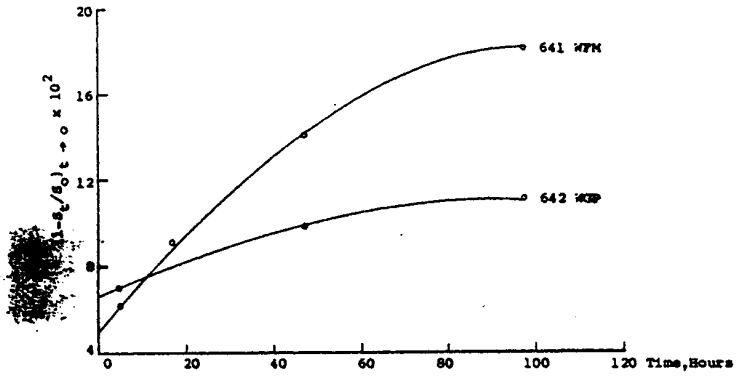



**Figure 25**

**Dependence of the Extrapolated Stress-Relaxation Ration on Ozone Exposure**

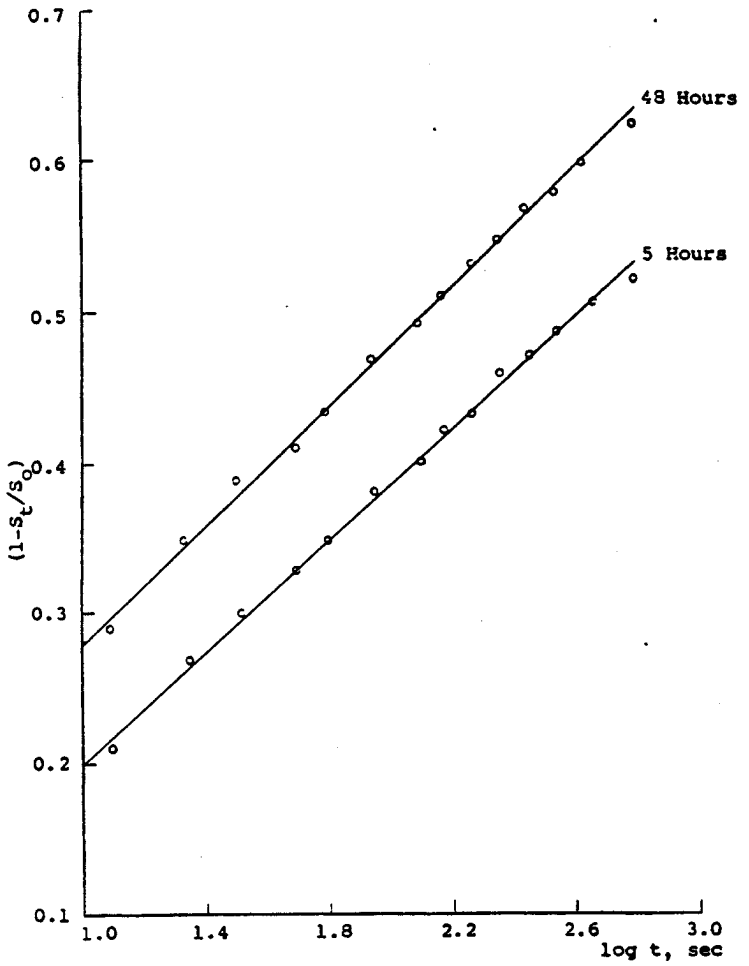



Figure 26
Stress-Relaxation of 7338 WLA Films on Exposure to Ozone

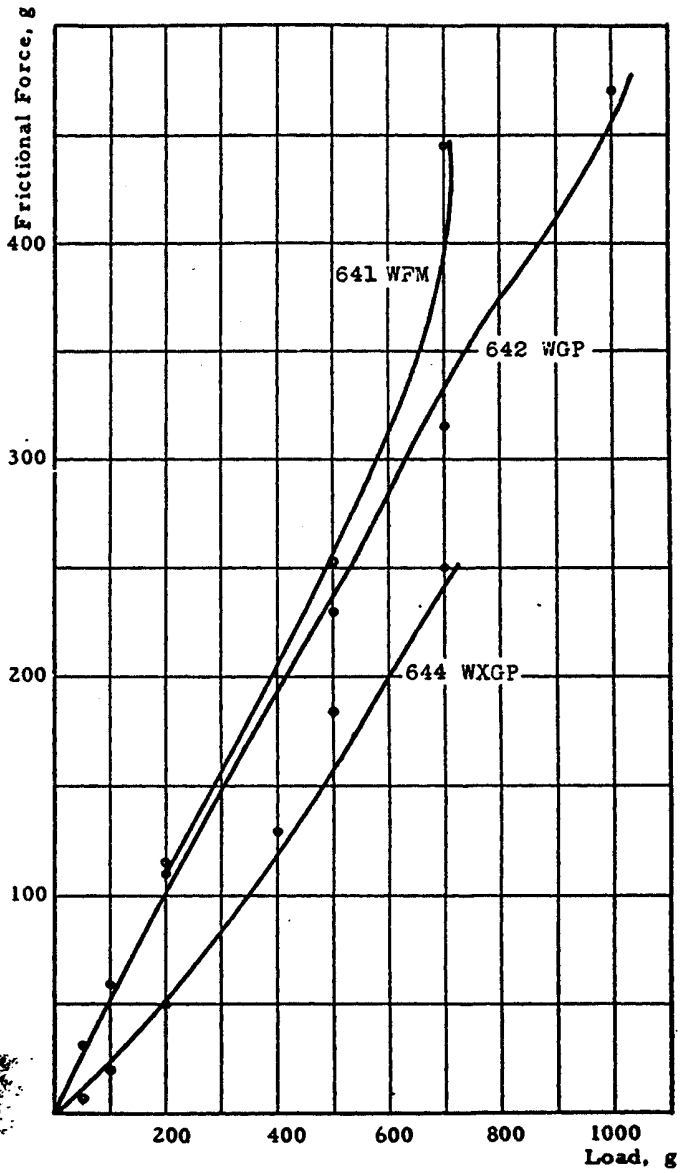



Figure 27
Frictional Resistance of House Paints Supported on Cedar Wood Panels

## C. Friction Studies

The possibility of determining surface and mechanical properties of films supported on different substrates by friction measurements suggested application of this method to house paints.

Initial measurements were made at 45% r.h. on oil- and alkyd-base paints deposited in approximately 0.003 inch thicknesses on cedar disks. The data presented in Figure 27 indicate a greater resistance to sliding for oil-base paints than for the alkyd-base film. In view of the previously obtained stress-strain information, this behavior could be explained not so much by the high shear strength of adhesive junctions formed at the paint-rider interface of the 641 WFM coating, but rather by the appreciable viscous plowing to which the oil-base paint was subjected. The sharp rise in the friction curve of 641 WFM beyond the 300 g load was a result of accumulation of paint debris in front of the rider. Actually, as shown in Figure 28, this paint was sheared from the wooden substrate, thus exhibiting interlaminar failure, unlike 642 WGP and 644 WXGP which retained their integrity during the test. Inconsistencies in some frictional measurements were attributed to the pronounced dependence of results on the grain orientation of the wooden panels. To eliminate this interference of the substrate, aluminum disks were employed


**Figure 28**

**Appearance of Oil-Base Paints After Exposure to Sliding Friction**

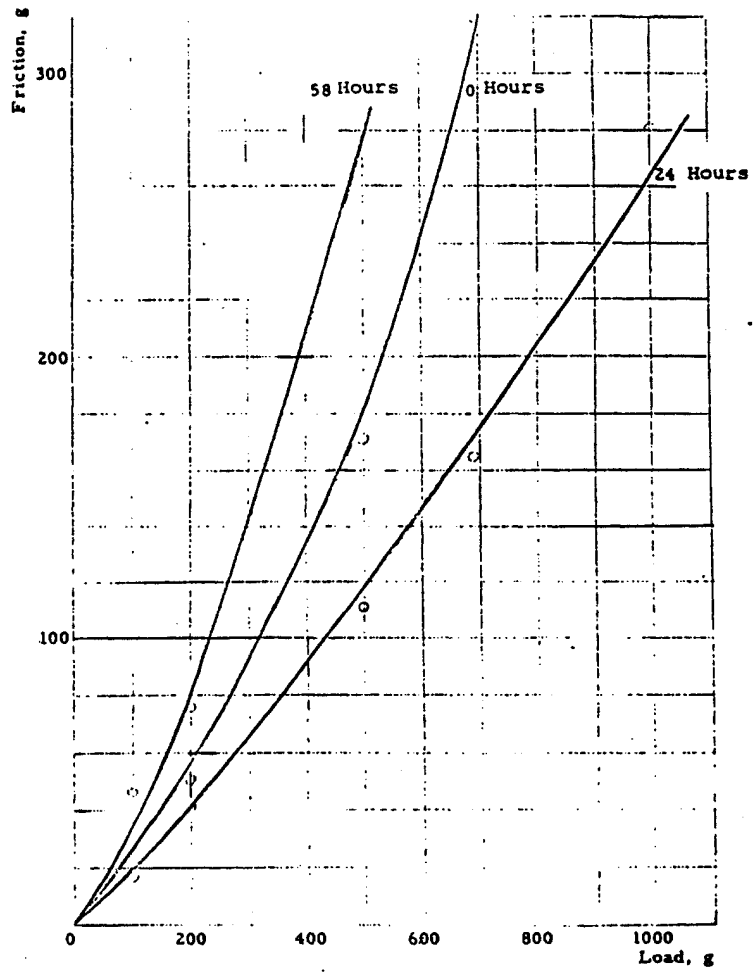



Figure 29

Frictional Resistance of 641 WFM House Paint
Before and After Exposure to Ultraviolet Radiation

as supports for films deposited from 641 WFM and 642 WGP formulations. After exposure to ultraviolet light for 24 and 58 hours, frictional force measurements were made on these films at a sliding speed of 0.05 inch/second. The results are presented in Figure 29 and Figure 30. It is interesting to note the pronounced decrease in the frictional force of films irradiated for 24 hours and the subsequent increase in friction on further exposure to ultraviolet light. This behavior, also demonstrated at sliding speeds of 0.4 inch/second, could be attributed to the initial surface hardening of films due to cross-linking and the later degradation of the polymer due to excessive bond scission. Further studies will be required to determine the relationship between the extent of ultraviolet irradiation, the change in frictional behavior, and the quality rating of films investigated.

### D. Acoustic Techniques

Acoustic methods for determining elastic properties of supported oil-base paints proved insensitive for use. This was determined by measuring the resonant frequency and mechanical loss (Q) of strips vibrating in flexure. Measurements made on paints deposited on aluminum and phosphor bronze substrates of 0.0625- and 0.010-inch thickness, respectively, provided results which were not significantly different from those obtained on the substrates alone. Since differences in effects produced by various paints were to be determined rather than the effect of a specific paint, the selected method could not be easily applied to studies of house paints.

Some consideration was given to the use of surface waves for eliminating the difficulties encountered and for selecting a method of measurement in which the perturbation introduced by the paint film would be at least of the same order of magnitude as the effect of the substrate. Preliminary investigations toward this end were made by surface wave-attenuation methods on a steel plate coated in part with a thin film of acrylic of uniform thickness. The attenuation was measured by monitoring the surface-wave amplitude as a function of path length. Figure 31 depicts the abrupt change in attenuation of the surface wave on transition from the uncoated to the coated substrate.

Since the mechanism of surface-wave attenuation is not well understood, quantitive estimates of the elastic properties of paints cannot be directly deduced from these measurements. It would be difficult to tell, for instance, whether the paint absorbs the surface wave or whether the phenomenon observed is the result of a complicated process occurring at the paint-substrate interface. Nevertheless, regardless of the mechanism of absorption, it is not reasonable to assume that the attenuation could vary for different paints or that the rate of attenuation could change for a given specimen as a result of exposure to conditions promoting paint degradation. If this is

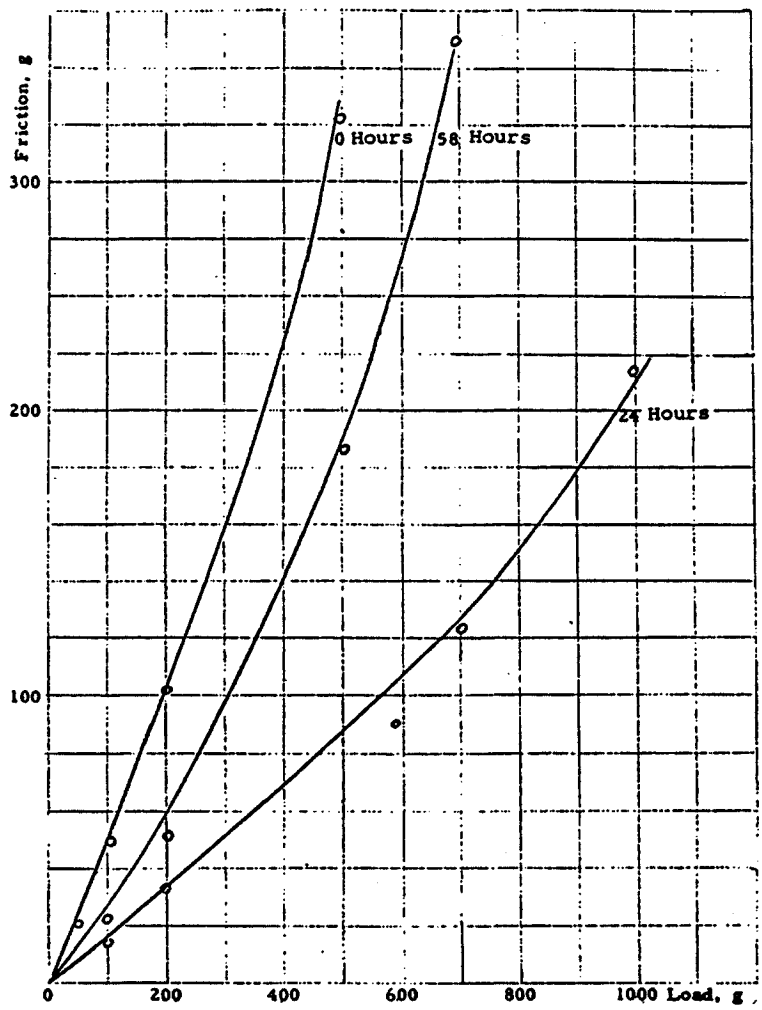



Figure 30

Frictional Resistance of 642 WGP House Paint
Before and After Exposure to Ultraviolet Radiation

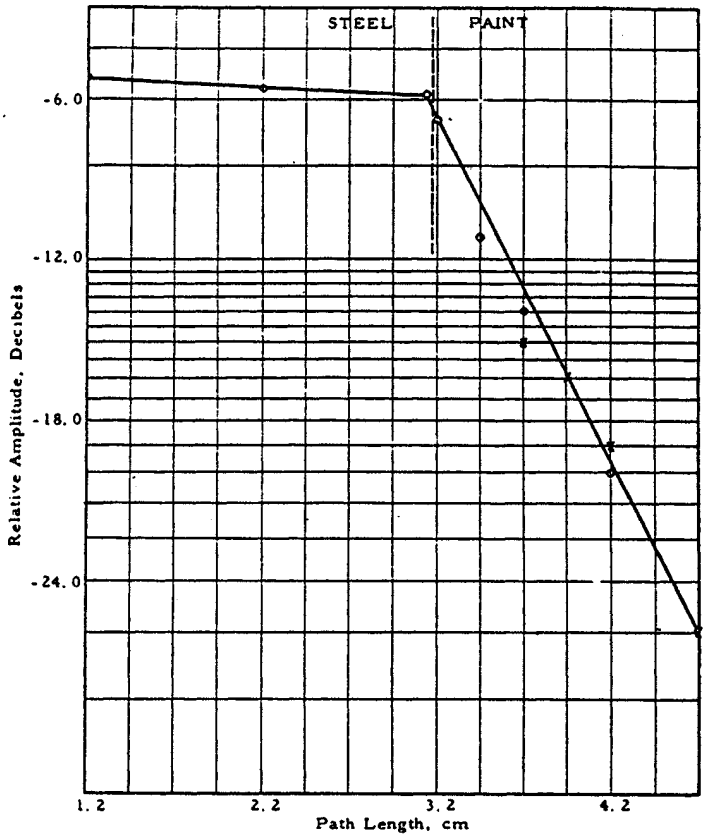



Figure 31

Attenuation of Surface Wave by Acrylic Coating

the case, a correlation may exist between surface wave attenuation and the quality of paint. The validity and relevance of data obtained from studies of surface wave relationships will have to be determined by measurements on a larger number of specimens.

### E. Energy Absorption of Paint Films at Microwave Frequencies

The power dissipated in oil-base paints at frequencies ranging from 8.5 to 12.5 kmc/sec was determined by means of a standing wave detector and a Hewlett-Packard sweep oscillator, as shown in figure 3. Measurements of the maximum amplitude of the voltage applied along the waveguide in the direction of wave propagation were performed on 641 WFM and 642 WGP films that were deposited on brass supports of the waveguide section.

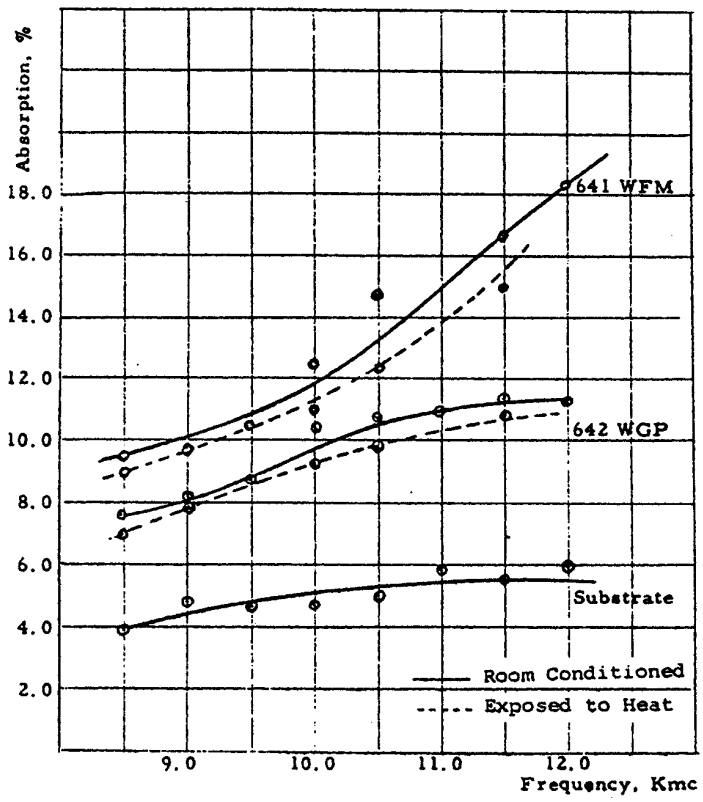



Figure 32

Power Loss in Oil-Base Paint Films

To obtain information about the sensitivity of this method, the power-absorption coefficient was determined for paint specimens before and after 35-hour exposure to heat at 55°C. Although the curves shown in Figure 32 indicate differences between 641 WFM and 642 WGP paint films in their initial state, room-conditioned and over-exposed specimens exhibit only slight differences in attenuation. Unlike acoustic measurements, at radar frequencies the attenuation of the deposited film and the energy absorbed by the substrate alone can be easily differentiated. However, the practical coincidence of curves obtained for a given paint before and after conditioning indicates the relative insensitivity of this method to detect changes in the properties of the coatings after exposure to

heat. The possibility of a resonance peak beyond the frequency range of the signal generator used in these measurements is suggested by the steep increase in the slope of the curve for 641 WFM films. If this condition should exist, the viscoelastic properties and changes in these properties as a result of exposure to environmental influences could effectively be evaluated for this film by conventional band-width measurements at ½ amplitude of the absorption maximum.

### F. Ultraviolet and Flash Irradiation

Ultraviolet irradiation was applied to oil-base paints in preliminary efforts to develop suitable exposure conditions for the degradation of materials investigated. It was observed that 642 WGP paint, deposited on aluminum plates, lost its gloss during exposure to a high-energy AH-6 source. The change in surface appearance was closely related to the duration of exposure, suggesting progressive degradation of the paint vehicle at the surface. Continued ultraviolet irradiation of unsupported paint films, that were suspended in a quartz tube flushed with either nitrogen or air to minimize temperature effects, imparted a curvature to 641 WFM and 642 WFP specimens. The extent of this curvature could be indicative of surface stresses induced in the paint by reformation of bonds under new equilibrium conditions existing in the partly degraded surface layer of the polymer. However, quantitive interpretation of these results would require parallel experiments under closely controlled conditions. The possibility of detecting changes in surface properties of irradiated paint films by the use of spectrophotometric methods was investigated. Diffuse-reflection spectrograms obtained for oil-base paints before and after ultraviolet irradiation showed very slight changes in the visible and almost none in the ultraviolet range.

The absence of significant changes in the visible and ultraviolet reflection spectrum was also noted for paint films exposed to intense light flashes in flash-photolytic experiments. Although the reflectance curves in Figure 33 show individual differences between paints, they are identical for the same specimens before and after exposure to flashes of a cumulative energy of 100,000 joules. Paint 641 WFM departs from this behavior; it shows greater absorption in the visible range after irradiation. This was attributed to the spotty discoloration of the film presumably resulting from the presence of a heat-absorbing component or impurity in the paint.

A better presentation of the visual effect of light flashes on oil- and alkyd-base films is given in Figure 34. Whereas films prepared from oil-base paints of poor quality (641 WFM) practically charred on exposure to flashes equivalent to 150,000 joules, oil-base paint films of better quality (642 WGP) showed no visible effects under similar conditions of exposure. Irradiation of alkyd-base paints with flashes total-

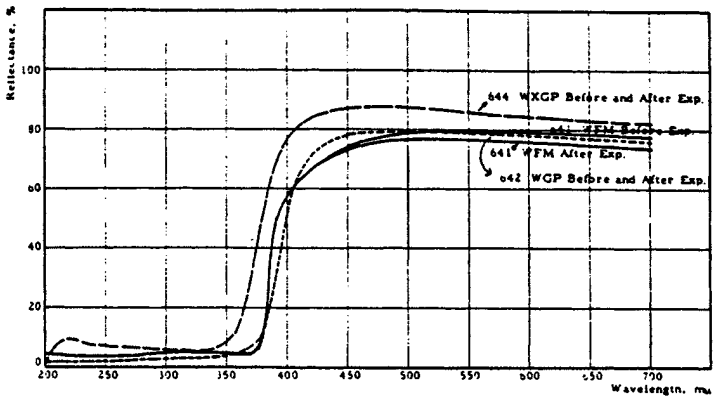



Figure 33

Specular Reflectance of White House Paints Before and After Exposure to High Energy Flashes

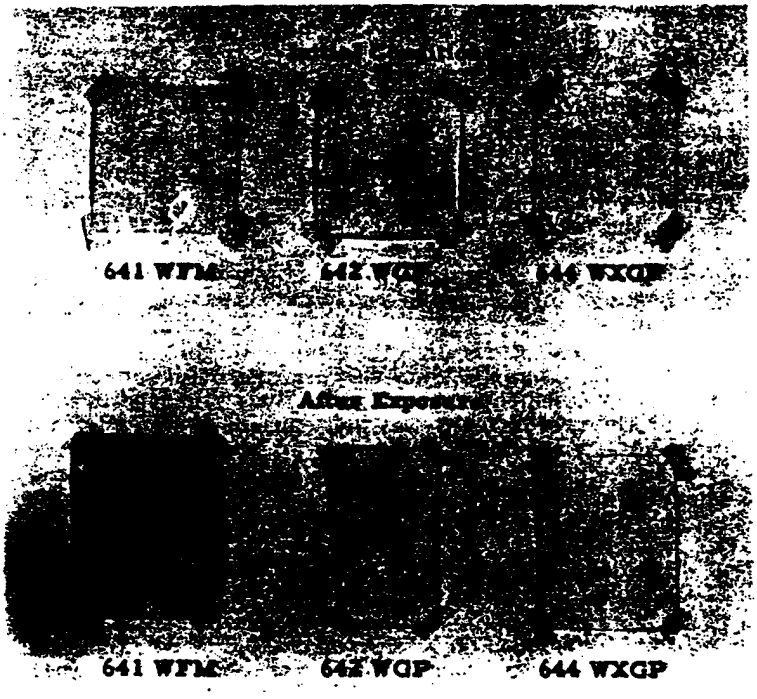



Figure 34

Change in Appearance of Paint Films Subjected to High-Energy Flashes

ling 250,000 joules did not change the appearance of test samples at all.

The possibility of inducing thermal degradation in oil-base paints by heat transfer from the base, whose temperature was undoubtedly raised during the flash experiment, was briefly investigated. It was found, however, that test specimens placed on ice-cooled blocks of copper showed the same behavior when subjected to similar doses of radiation. Therefore, photolytic effects rather than secondary heating processes appeared responsible for the observed degradation of 641 WFM paint films.

The use of the flash irradiation method for differentiating between paints with good and poor quality ratings was investigated in greater detail. 641 WFM and 642 WGP films were subjected to light flashes of high intensity (23,000 joules/flash), while the total energy incident on the samples was varied from 23,000 to 185,000 joules. The size and surface concentration (number/cm$^2$) of spots occurring after irradiation was determined under a microscope at low magnification (10X). The results summarized in Table 2 indicate a progressive increase in size and resultant decrease in concentration of spots on 641 WFM films with increasing doses of radiation. Films prepared from the 642 WGP formulation showed little change in appearance upon irradiation up to a maximum of 185,000 joules.

Table 2
SIZE AND NUMBER OF SPOTS
ON FLASH-IRRADIATED 641 WFM AND 642 WGP FILMS

| Sample | Energy, joules $\times 10^{-3}$ | Size, mm | | | Concentration, no./cm$^2$ | | |
|---|---|---|---|---|---|---|---|
| | | Min. | Avg. | Max. | Min. | Avg. | Max. |
| 641 WFM | 46 | 0.05 | 0.5 | 1.2 | 35 | 39 | 54 |
| 641 WFM | 70 | 0.04 | 0.3 | 0.8 | 104 | 131 | 136 |
| 641 WFM | 92 | 0.5 | 1.2 | 3.0 | 12 | 20 | 42 |
| 641 WFM | 185 | 1.2 | 2.5 | 5.5 | 5 | 7 | 12 |
| 642 WGP | 230 | 0.02 | 0.2 | 0.7 | 7 | 12 | 24 |

Since flash irradiation has not produced appreciable changes in mechanical properties of oil-base paints as found from stress-relaxation measurements (Figure 19 and Figure 20), this treatment appears to be essentially limited to surface effects.

In regard to the specificity of spotting which was most pronounced for the 641 WFM formulation, Mr. Van Loo of the Sherwin-Williams Company suggested that the photolytic sensitivity of this paint could have resulted from the presence of basic lead carbonate in the pigment. To verify this assumption, parallel flash experiments were performed on films prepared from 641 WFM, OJ 347A, and OJ 346A formulations. The last two paints differed only in that lead carbonate (OJ 347A) was substituted for lead sulfate (OJ 346A), while all other ingredients remained the same as shown in Table 3. The appearance of the aforementioned films after irradiation (185 x $10^3$ joules) is represented in Figure 35. It is apparent

Figure 35

Appearance of Oil-Base Films After Flash Irradiation

that the observed surface effects are greatly dependent on the presence or absence of lead carbonate in the paint formulation. For this reason the flash irradiation method may not be generally applied to distinguish between paints of good and poor quality. This, of course, does not exclude the possibility that the known poor performance of 641 WFM paint could be related to photolytic effects observed in flash experiments.

## G. Thermoanalytical Studies

The susceptibility of oil-base paint films to oxidative degradation was investigated by differential thermal analysis. Samples were prepared in powder form by grinding unsupported films in a mortar containing liquid nitrogen in order to promote brittle fracture of the elastic material. Samples weighing approximately 0.5 g were introduced in the well of the furnace while the reference sample holder was filled with aluminum oxide. The heating range of the furnace was programmed at 3°C/min over a temperature range from 25 to 600°C. Thermograms thus obtained for oil-base paints are shown in Figure 36 and Figure 37. As indicated, 641 WFM exhibits a pronounced exotherm at 200°C suggesting its relatively easy reaction with oxygen at this temperature. Gross oxidative degradation for 641 WFM and 642 WGP films ap-

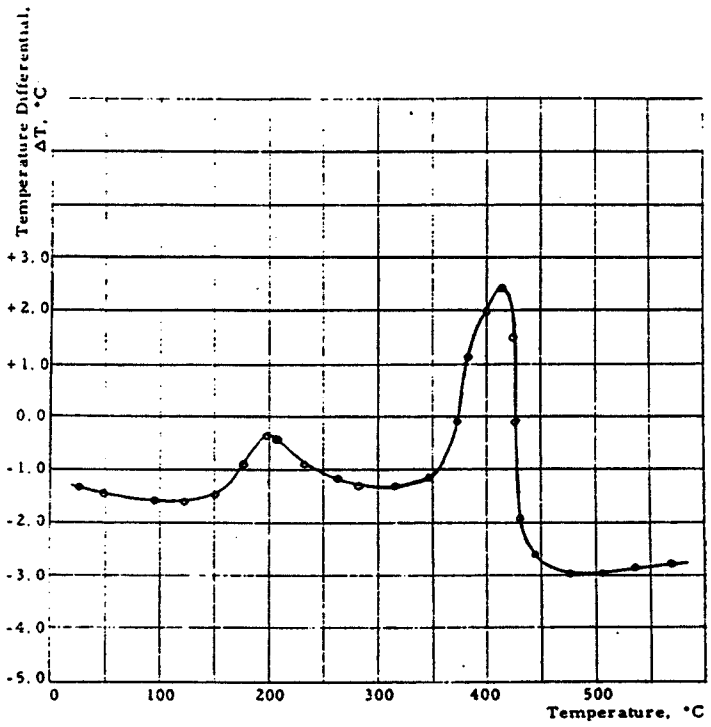



Figure 36

Differential Thermal Analysis of 641 WFM House Paint

pears to occur in the temperature range of 350 to 450°C. The two small peaks in the DTA curve of 642 WGP paint cannot be interpreted on the basis of available data.

The differential thermal behavior of paints subjected to outdoor exposure conditions in Florida for 4 years is presented in Figure 38. The correlated thermograms suggest almost complete oxidation of the aged 641 WFM paint. indicated by the absence of reaction isotherms at 200 and 400°C.

If oxidative degradation should correlate with the mechanical behavior of paints, as was suggested in ozonization experiments, then it would appear desirable to follow the oxidation of coatings by thermoanalytical methods at different stages of exposure. This could lead to a correlation between the extent of oxidation, changes in mechanical parameters, and the quality ratings of paints.

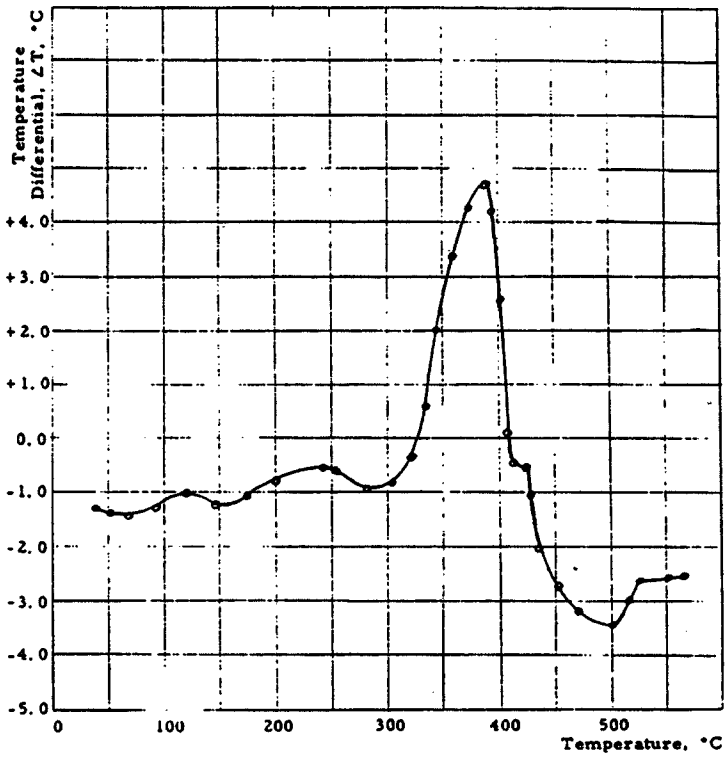



Figure 37
Differential Thermal Analysis of 642 WGP House Paint

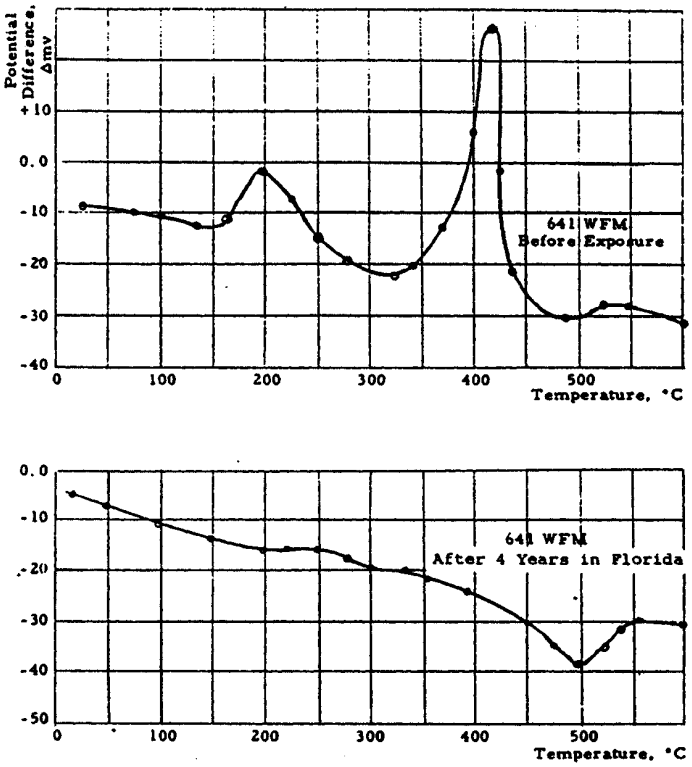



Figure 38

Differential Thermal Analysis of Oil-Base Paints
Before and After Outdoor Exposure

Table 3

LABEL ANALYSES OF HOUSE PAINTS*

| OJ 346A | | OJ 347A | | 641 WFM | |
|---|---|---|---|---|---|
| Pigment | 61% by weight | Pigment | 61% by weight | Pigment | 66% by weight |
| Basic Sulfate White Lead | 7.2% | Basic Carbonate White Lead | 7.2% | Zinc Oxide | 36.0% |
| Acicular Zinc Oxide | 32.8 | Acicular Zinc Oxide | 32.8 | Basic Sulfate White Lead | 19.0 |
| Titanium Dioxide (rutile) | 5.0 | Titanium Dioxide (rutile) | 5.0 | Basic Carbonate White Lead | 36.0 |
| Titanium Dioxide (anatase) | 11.0 | Titanium Dioxide (anatase) | 11.0 | Silicates | 9.0 |
| Silicates | 44.0 | Silicates | 44.0 | | 100.0% |
| | 100.0% | | 100.0% | | |
| Vehicle | 39% by weight | Vehicle | 39% by weight | Vehicle | 34% by weight |
| Raw Linseed Oil | 44.5% | Raw Linseed Oil | 44.5% | Raw Linseed Oil | 90.0% |
| Bodied Linseed Oil | 28.5 | Bodied Linseed Oil | 28.5 | Thinner | 10.0 |
| Mineral Spirits | 27.0 | Mineral Spirits | 27.0 | | 100.0% |
| | 100.0% | | 100.0% | | |
| Drier (metal) 0.33% Pb, 0.015% Mn. | | Drier (metal) 0.33% Pb, 0.015% Mn. | | Drier (metal) 0.17% Pb, 0.011% Mn, 0.12% Ca. | |
| Solids of paint by volume—75.4% | | Solids of paint by volume—75.4% | | | |

* Submitted by the Sherwin-Williams Company

## VI. Summary and Conclusions

Progressive deterioration of house paints due to environmental conditions is manifested by defects which are potentially related to changes in the mechanical behavior of paint films. The applicability of various instrumental techniques in studies of paint deterioration was investigated. The objective of this program was to determine the correlation between a measured parameter, based on mechanical or optical properties of selected paints, and their quality rating established by conventional weathering tests.

In the course of this study, it became apparent that the rate of change of a measured property of specimens, compared under exposure conditions promoting such change, was of paramount importance in the correlation of measurements with the performance of paints. It was therefore suggested that not only a method capable of distinguishing between films slightly differing in their behavior be selected, but also an appropriate conditioning environment be used in order to magnify observed effects.

Initial studies involving determination of elastic properties of oil-base paints by acoustic methods proved too insensitive for use since results obtained on supported test specimens were not significantly different from those provided by the substrate alone. Attenuation measurements at microwave frequencies indicated differences between oil-base paints of good and poor quality ratings when considered in their initial states. However, after conditioning at elevated temperatures, only a negligible change in the measured property could be observed. This small change indicated the inapplicability of this method for rate studies in the selected environment. A more pronounced dependence of the measured property on exposure conditions was noted in stress-strain and stress-relaxation measurements. The plasticizing effect of moisture was indicated by the decrease in the apparent moduli of elasticity of oil- and alkyd-base paints, although the alkyd paint was less susceptible to plasticization than the oil-base film.

Distinct differences in initial stress-strain and stress-relaxation properties were noted for films prepared from oil-, alkyd-, and latex paints. Oil paints had a considerably lower strength than alkyd paints, while emulsion polymer films were characterized by a relatively high ultimate elongation. However, in view of gross differences in the chemical nature of these films, a direct comparison between the initial properties and the performances could not be made.

Changes in mechanical behavior of oil-base films exposed to cyclic temperature and humidity variations were followed for formulations with good and poor quality ratings over a period of 25 days. Stress-strain and stress-relaxation data suggested a greater relative change in measured properties for films with a poor performance record. A similar but more pronounced effect was found in oil-base films subjected to the

oxidizing environment of ozone. Samples conditioned for 93 hours in an ozone-enriched atmosphere exhibited progressive "hardening." Hardening was indicated by the increasing apparent modulus of elasticity of films withdrawn from the conditioning chamber at different times. A material parameter derived from stress-relaxation measurements showed a greater dependence on the duration of exposure to ozone for films prepared from oil paints of inferior quality than for those obtained from a formulation with a good performance rating.

The importance of oxidation processes in the degradation of paints exposed to outdoor weathering conditions was implied in the thermal behavior of oil-base paints before and after 48 months exposure in Florida. A pronounced exotherm obtained in differential thermograms of freshly prepared film specimens at 200°C was missing in samples recovered from test panels subjected to prolonged weathering. Since the thermograms were obtained in an oxidizing environment, lack of an exotherm peak in the weathered specimen suggested its complete oxidation during outdoor exposure.

Flash irradiation produced noticeable changes in the surface appearance of two oil-base paints. However, the observed effects could not be attributed to differences in performance of these formulations but instead to the presence of a particular pigment constituent (basic lead carbonate) in one of them. The specificity of this method and its limitation to surface effects appeared to lessen the usefulness of this approach in studies of paint deterioration, at least in measurements related to bulk mechanical properties of paint films.

Exposure of paints to ultraviolet radiation was found to produce noticeable changes in frictional properties of supported films. The frictional resistance to sliding of oil-base paints decreased after 24-hours exposure to a AH-6 mercury arc, but further irradiation resulted in an increase in friction. This apparently inconsistent behavior could be attributed to the initial hardening of the film due to cross-linking and the later degradation of the polymer due to the pronounced effect of bond scission.

Although studies conducted thus far have not provided a simple, generally applicable laboratory method for determining the performance of house paints under conditions of use, this investigation suggested several promising approaches for correlating the property-performance relationship for outdoor paints. The progressive changes in mechanical properties of oil-base paints resulting from exposure to ozone and the relative differences in evaluated stress-strain and stress-relaxation parameters of paints with good and poor quality ratings suggest extension of these studies to other paint systems. These studies could permit determination of paint behavior at different stages of prolonged exposure to an oxidizing environment. Concurrent measurements of the extent of oxidation by methods of differential thermal analysis should supply independent data about the susceptibility of paints to oxidative

influences and also provide information about paint degradation in an ozonizing atmosphere.

In view of the observed changes in the frictional behavior of oil-base paints upon exposure to ultraviolet radiation, surface studies in frictional shear merit further attention. More severe conditioning environments, particularly those combining ultraviolet and ozone exposure should be selected for alkyd- and emulsion-polymer paints. The effect of a property-changing environment and the viscoelastic behavior of paint films should be investigated while considering the rate sensitivity of materials investigated. This could be done in stress-strain measurements at different rates of strain, attenuation studies over an appropriate frequency range, and friction measurements at different speeds and rates of load application.

It is believed that the proposed studies, conducted under controlled exposure conditions will show significant differences in the rate of change of measured properties. Thus a property-performance correlation of house paints representing a wide spectrum of quality ratings could be established.

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