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Marshall Laboratory
July 17, 1952

MEMORANDUM REPORT NO. M-480

LITERATURE SURVEY ON ACCELERATED WEATHERING

Introduction:

This report consists of two parts; the first is a critical summary of the literature on accelerated weathering published since about 1922, with special emphasis on the more recent papers; the second consists of a brief summary of each of the more interesting papers. A complete list of references follows the report.

At present a paint product is evaluated by exposure to the elements in one or more localities for an extended period of time, usually at least six months. The importance of shortening this time between formulation and evaluation need hardly be emphasized in this discussion.

Summary:

Beginning in 1922, H. A. Nelson, at times in collaboration with F. C. Schmutz and D. L. Gamble, published the results of some of the first systematic work on the subject of accelerated weathering. Since then many papers on the subject have appeared, but the problem has not yet been solved completely.

It is difficult to arrive at any basic conclusions from the extant literature. The procedures have to a great extent been necessarily empirical, particularly with respect to the measurement and evaluation of film deterioration.

There are hardly any ways of measuring appearance variables quantitatively, except for gloss. Consequently the attempt to correlate the results of outside exposure with accelerated exposure has been handicapped not only by the intrinsic difficulties of

weather duplication but also by the lack of the proper tools for evaluation. This fundamental difficulty probably accounts in large part for the disagreement among authors presumably working in the same way.

Another fundamental difficulty is the lack of reliable information on the results of outside weathering. This information is difficult to obtain for a number of reasons, the most important being the fact that the results vary with season and year. It appears necessary to settle on some average weather, or perhaps an extremely deleterious weather as a standard, and the weathering apparatus should be designed to duplicate the effects of such weather. This might be done for several localities.

Films fail in several ways, the principal ones being loss of gloss, checking or cracking and blistering. Loss of gloss is perhaps best considered as an erosion, whereas checking and blistering are associated with physical or mechanical failure. The film may crack because the accumulated stresses in the film have exceeded its cohesive forces; it may blister or flake away because of the failure of the adhesive forces between film and substrate. The stresses to which a film is subject are due to such things as volume changes caused by physical and chemical reactions involved in drying and weathering, swelling of the film and differential swelling between film and substrate, and the differential expansion of film and substrate due to temperature changes.

Since fresh paint films are quite distensible the weathering process must modify, chemically or physically, by agents such as water, light and heat, the elastic properties of the film. When the film is thus modified further stresses are applied which cause breakdown.

To devise a satisfactory laboratory accelerated procedure it is first necessary to identify the variables of the natural weathering process and so increase their intensity so that breakdowns will occur in the same way as in natural weathering. Some authors have attempted to do this by a careful determination of the intensity of the natural factors and then intensifying all the artificial one proportionately. This is very difficult and has probably never been accomplished; the fact that there is no artificial light source at present which has exactly the same spectral distribution as sunlight is one reason why exact duplication is difficult. But even if exact duplication were possible it still might not be satisfactory. The consecutive stages of the overall reaction of weathering will probably not respond linearly to variation in intensity of the weathering factors, or perhaps one stage may be so much slower than the rest that it becomes rate controlling, thereby distorting the entire breakdown process. Consequently it will probably be necessary to arrive at the correct combination of weathering agents principally by trial and error.

The main discernible variables in the process of natural weathering are:

(a) Radiation of the sun of which the ultraviolet portion (down to about 2900 A) is most significant.

(b) Water

(c) Temperature and temperature changes

There are other probably less important factors involved such as acidic gases (in industrial atmospheres), dust and dirt, mildew, etc.

Gay (57) has summarized some conclusions deduced from a survey of previous work on accelerated weathering. It is evident that although numerous cycles have been devised, there is no systematic data available regarding the behavior in the various cycles of a common range of paints of defined outside behavior. Thus there is no firm basis of judgement as to the usefulness of the different cycles. The general conclusions follow:

1. The dominant wavelengths for film breakdown lie in the ultraviolet region between 2900 A and 3100 A. In industrial atmospheres, since wavelengths below 3400 A do not penetrate, an important part of the breakdown must occur by wavelengths greater than 3400 A.

2. Ultraviolet radiation at zero or low humidity produces less deterioration than at higher humidities or in the presence of spray. Spray is more effective than high humidity.

3. Failure by checking or cracking is rarely observed at zero or low humidity, but there is evidence that water treatment after irradiation may increase fine checking.

4. Low pressure oxygen treatment in combination with exposure in the weathering apparatus gave promising indication of correlation in mode of breakdown by chalking, checking and cracking. No systematic work has been reported on this variable.

5. The application of water is most effective when it is applied so as to penetrate the film and cause swelling for a long enough time. The purity of the water used in many tests is usually unknown; this may account for many of the variations in the results.

6. There is some evidence that high humidity with dew deposition is more effective than direct spraying of panels, but fine water spray seems to be the best compromise in practical apparatus.

7. The rate of film deterioration attained in combined ultraviolet radiation, water spray cycles increases with increasing panel temperature over a certain range. The temperature must be controlled to avoid heat polymerization, which with some media

Light is a 30 inch mercury arc.

3. V. G. Jolly

Journal Society Chemical Industry 41, 329 (1933)

In the weathering machine used here, the light source consisted of a 30 ampere carbon arc at 75 volts. The cycle consisted of eighteen minutes of light, then 2 minutes of light and cold water, for 14 hours per day and 10 hours of rest. For a wide variety of clean and pigmented oleoresinous products, it is claimed that the test gave failure of the same kind and order as with outside exposure. However, no quantitative relationships existed for nitrocellulose formulations, and no correlation of the results was possible.

4. Sward and Hart

Scientific Section, American Paint and Varnish Manufacturing Association Circ 375 Jan. 1931

The results of this work have been mentioned previously in Part I. The low wavelength arcs (therapeutic carbon and uviarcs) did not cause checking with checking formulations as did the "Weatherometer" 13 ampere carbon arc and the "Sunshine" carbon arc, (and outside exposure) but the paint seemed to erode with chalking. This could be caused by continual washing away of the chalk as it is formed. For materials which fail by chalking the therapeutic and uviarcs cause more rapid failure than the other light sources.

5. Cincinatti-Dayton Indianapolis Club

Scientific Section, American Paint and Varnish Manufacturing Association October 1930

The authors found that there is a certain correlation between various sets of outside exposures (same groups of materials exposed in different sections of the country) and attribute the discrepancies mainly to individual differences and localized climatic conditions. It was also found that some materials tested under various types of accelerated weathering showed a certain corrleation. However, there was very little or no correlation in breakdown between the outside exposure and the accelerated exposure.

Five different tests were used, none of which were very similar. The usual cycle consisted of various combinations of light, water temperature and humidity. One cycle included immersion in sodium chloride solution.

6. Cincinatti-Dayton Indianapolis Club

Scientific Section, Paint and Varnish Manufacturing Association January 1, 1932

Numerous cycles of water spray, light, temperature and humidity were tried. Very many contradictions and unexpected results were found, but a few general results were observed.

may greatly improve durability or cause decomposition. 55°C. has been suggested as a maximum working temperature.

8. Rapid temperature changes of wide amplitude result in stresses which cause breakdown after elasticity has been reduced by weathering. Sometimes this induces failure by checking and cracking.

9. Refrigeration alone has relatively little effect on film deterioration.

The main problem in the design of a satisfactory accelerated weathering cycle is to obtain the correct balance of intensity among the various weathering agents so that overall breakdown is accelerated without distorting the form of breakdown. It is hoped that with increased knowledge and experience this balance will eventually be reached.

MARSHALL LABORATORY

H. L. Wagner

H. L. WAGNER

HLW:cms
7/16/52
7/17/52

Abstracts of Important Papers

1. H. A. Nelson, F. C. Schmutz, D. L. Gamble

A. S. T. M. Proceedings - Vol. 26, p. 563 (1926)

Accelerated Weathering: Further Development of Apparatus and Exposure Cycles

Summary:

Conclusions from the study of accelerated weathering have indicated that a flexible exposure system is desirable for obtaining the most satisfactory results. The equipment described in this paper is "designed to obtain the maximum of flexibility and still be practical for routine testing". The different types of exposure cycles thus made possible are limited only by the number of practical combinations that can be made of the following:

1. Light (Mercury or Carbon Arc)
   - (a) At controlled, slightly elevated temperatures (140°F.)
   - (b) With 100 percent relative humidity
   - (c) With less than 5% relative humidity
   - (d) In an atmosphere charged with active gases as, for example, oxygen.
2. Water Spray
3. Refrigeration (Temperature Changes)

The introduction of silica gel as a dehydrator, which provides for humidity control without necessitating air conditioning by refrigeration, is interesting.

The use of additional oxygen in the light exposure chamber has facilitated the reproduction of the checking type of failure.

The average weather of a given locality is used to determine the weathering machine cycle.

The decrease in the intensity of the quartz mercury arc with use varies the effectiveness of the accelerated test.

No actual results are presented in this paper.

2. H. A. Nelson and F. C. Schmutz

Ind. Eng. Chem. 18, 1222 ('26)

The authors discuss their apparatus (See Proc. A. S. T. M. 26, 563 (26)) and then go into a consideration of some fundamentals governing its applications.

(1) Heat as an auxiliary to light

Too high a temperature reduces distensibility too greatly for correlation with normal weathering. Low temperatures reduce rate too greatly.

(2) Humidity

Light acting upon water soaked film is the most destructive weathering combination. Nevertheless, most failure is accelerated by high humidity followed by low humidity exposures. Weakening in film caused by high humidity shows up when it has less distensibility in less humid situation.

(3) Special Atmospheres with Light Exposures

Increasing oxygen content from 21 to 30 percent increased checking markedly. In addition generalized acceleration was found. In pure oxygen the acceleration was extremely marked.

(4) Water Spray Washing

Not much actual acceleration of the deterioration process can be obtained in the water spray washing exposures representing rain. The author distinguished this from effect of humidity.

(5) Temperature Changes

Materials of low original distensibility are very severely affected by stresses and strains resulting from temperature change. Any system involving an excessive number of temperature changes is especially severe on finishes of low distensibility. Small temperature changes may be effective if a critical distensibility is reached.

Weathering Cycle Used

Monday	Refrigeration 0°F.	2 hrs.
	Water 90°F.	3 hrs.
	Light 140°F. (30% O_2)	18 (16 wet, 2 dry)
Tuesday	Water	3
	Ref.	2
	Light (30% Oxygen atmos.)	18 (16 wet, 2 dry)
Wednesday	Ref.	2
	Light (30% oxygen atmos.)	3 (wet)
	Water	16
Thursday	Ref.	2
	Water	3
	Light (30% O_2 atmos.)	20
Friday	Ref.	2
	Water	3
	Light (30% O_2 atmos.)	18 (wet)
Saturday	Ref.	2
	Water	3
	Light (30% O_2 atmos.)	15
Sunday to Monday	Light (30% O_2)	27 (24 dry, 3 wet)

A brief historical review of accelerated weathering development is given and the limitations and valuable uses of the accepted methods of testing are described.

An apparatus has been built with which some of the more important features of "weather" can be varies e.g., intensity and time of ultraviolet irradiation, amount of water treatment and period of revolution of the test drum. Attempts to increase the rate of polymer degradation by treatment of paint films with oxygen at elevated pressures to accelerate its diffusion into the films have given promising results. Films subjected to the oxygen pressure treatment described have broken down in a manner comparable with that obtained outdoors. There are indications that a study of the oxygen concentration variable will provide one of the most hopeful developments in durability testing procedure for paints.

Company Literature

10. Dennington, R. F.

Imperial Chemical Industries, Lmt.
Research and Development Dept., Report
No. 86, Issued 9/23/46

The machine consists essentially of a board moving vertically to which the panels under test are fixed and which faces in turn a cold box, moist hot box and an ultraviolet lamp. As set up at the time, the panels were subjected to the same period in each condition. The results indicate that long periods in each condition (50 minutes at each station in the order cold-hot and moist-ultraviolet) emphasized chalking while short periods (7 minutes, same order of stations) in each condition emphasizes cracking. When the order of the conditions were changed (order ultraviolet, hot and moist-cold) the type of cracking changed.

11. G. H. Wescott

Du Pont Co. Finishes Division, Phila. Lab. 11/22/39
Evaluation of Accelerated Weathering Machine II Research
Report #680

Work with carbon-arc instruments has been so limited that no definite conclusions can be drawn. The earlier work showed that they offer possibilities for obtaining relative checking resistance. The present study has shown that differences in the chalking characteristics can be detected and appear in the same general order as produced by normal exposure, but are not of the same magnitude. Possible uses for the carbon arc instruments are (1) indication of color retention or chalking characteristics where time is a factor, (2) breakdown of short oil enamels where sales needs require urgent action (3) evaluation of material from new sources of supply versus an established standard (4) check on customers' or competitors' claims based on information obtained with accelerated units.

1. Mercury arc caused faster breakdown than carbon arc, particularly chalking.

2. The mercury arc alone causes chalking and dulling, but no checking.

3. Salt spray alone is not a very useful indication of overall durability. The same may be said for infrared exposure.

4. The combination of salt spray, light and water does result in checking.

7. Cleveland Paint and Varnish Production Club

Official Digest, Federation of Paint and Varnish Production Clubs 276, 44-63 (1948)

This report may best be summarized by the conclusions the authors arrived at concerning the operation of weathering machines to obtain check results between exposures for a known time in Miami and the machines. Four basic recommendations are made. The water supply must be treated for purity, comparatively long water exposure is necessary, and a maximum temperature of 145°F. must be maintained for at least one-half of the total radiation hours to duplicate results of Florida exposure. The machines used in the test were generally of the commercial variety. At the time this report was written, a good correlation had not yet been found among the machines or between any of the machines and Florida.

8. Fancutt, F.

Paint Technol. 14, 159, 106-11 (1949)

The author claims that better correlation between actual and accelerated weathering of paints and varnishes has been achieved by means of a new test cycle. Earlier discrepancies were reduced or eliminated by the use of $NaHSO_3$ spray, and this was later replaced by a procedure involving SO_2 in the humidified test chamber. The machine ultimately evolved exposed the paint to ultraviolet light, water, and a warm saturated atmosphere into which SO_2 is passed. Different cycles are used to correspond with rural, industrial, and highly corrosive conditions.

9. Gay, P. J.

Journal of Oil and Colour Chemists Ass'n. 34-43 (51)
"Accelerated Weathering of Paint and Varnish Films"

The breakdown of paint films during weathering is due to degradation of their polymer structure so that they can no longer accomodate the physical stresses resulting from temperature changes and water absorption. Accelerated weathering seeks to hasten the polymer degradation and impose physical stresses of a high order.

The disadvantages are (1) limited space (2) unable to produce low temperatures which are likely to cause flaking and peeling as on galvanized metal finishes. They do not yield information on mildew and dirt collection, stain resistance, which is especially necessary for house paints.

12. R. E. Pike

Results of Exposure Study Series No. 9144
August 1, 1946

No report issued.

13. Baltimore - Pigments Dept. Work

The Pigments Department finds that the commercial type of instrument gives good correlation with Florida results except in a small percentage of the cases. Without further work it is impossible to say what these discrepancies are due to -- iron contamination in the water is a possibility. The data are now on file with us.

Appendix

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