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ACCELERATED TESTING OF PAINTS

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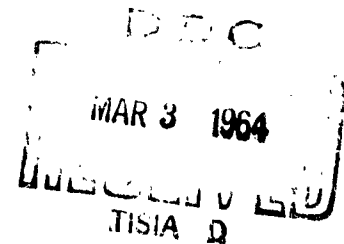
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ACCELERATED TESTING OF PAINTS

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by

Peter J. Hearst, Ph.D.

ABSTRACT

Results of a literature search of accelerated methods of testing paints are presented and discussed. Emphasis is placed on coatings applied to steel surfaces. No accelerated test methods are available for predicting reliably the service performance of paints. Some methods have limited usefulness in indicating probable performance.

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to be as meaningful as possible, the standard test methods do not cover the interpretation or the validity of the results. In addition to the methods of testing, the standards also list methods of rating to insure uniformity in specific types of rating, but different types of rating may be used for a given test method.

The Federal Test Method Standard No. 141,⁸ for methods of inspection, sampling, and testing of paint, varnish, lacquer, and related materials, lists two methods for accelerated weathering, a salt spray test, and a humidity test. These accelerated test methods are closely paralleled in Canadian Specifications, 1-GP-71,¹⁰ and in the ASTM Standards.⁷ Related methods for testing of plastics are given in Federal Test Methods Standard No. 406,⁹ as indicated in Table I.

Table I. Some Presently Specified Accelerated Test Methods

<u>Type of Test</u>	<u>Methods of Various Standards^a</u>			
	<u>141</u>	<u>1-GP-71</u>	<u>ASTM</u>	<u>406</u>
Weathering Apparatus, Open Arc	6151	---	E 42-57 ^b (Type E-G)	6022
Weathering Apparatus, Enclosed Arc	6152	122	E 42-57 ^b (Type A-D)	---
Salt-Spray Test	6061	129	B 117-62	6071
Humidity Test	6201	113.5	D 1735-60T	6011

a. The methods, which are tabulated according to the test method number, are discussed in the text and are given in references 8, 10, 7, and 9, respectively.

b. More specific instructions for testing paint, varnish, lacquer, and related products are given in method D 822-60 and for testing plastics in method D 1499-59T.

Weathering Apparatus

The accelerated weathering apparatus consists essentially of a drum within which samples are suspended and revolved about a central source of light and a provision for spraying of the samples with water once during

each revolution of the drum. Cyclic changes in the duration of the light exposure and of the water spray produce radiation, heating, cooling, wetting, and drying, which cause deterioration of the coating or other specimen.

The weathering apparatus may have an open arc or an enclosed arc. The open arc apparatus employs specially impregnated carbon electrodes in a free flow of air and the light is filtered by Correx D filters surrounding the source. The enclosed arc apparatus employs a single carbon arc or two carbon arcs burning simultaneously, with each arc being enclosed in a pyrex globe. The latter method is more generally employed.

Although both methods state that the spectral distribution of the light should be similar to that of mid-day June sunlight,^{7,8} the spectral distribution of the radiant energy of the two artificial sources is actually quite different. The violet enclosed carbon arc produces predominantly ultraviolet light, whereas the open arc produces light which is intermediate between that of the enclosed carbon arc and natural sunlight.¹¹ The newer xenon arc which more closely approximates natural sunlight¹¹ is not yet adopted in a specified method.

The cyclic exposure to light and water in the weathering apparatus can be controlled and different cycles may be specified. The Federal Standard states that, unless otherwise specified, two-hour cycles of 102 minutes without water spray, followed by 18 minutes of water spray, shall be employed. During the spray period the specimens are sprayed once during each one-minute revolution of the drum. This cycle is repeated 5 days per week under continuous irradiation, and the samples remain undisturbed during the other 2 days. The water spray at 60° F hits the panels mounted on the inside of a revolving drum, and the temperature is controlled so that the maximum black panel temperature is 145° F.

The Canadian Specification (1-GP-71) gives only one method employing an enclosed twin arc apparatus. The operating cycle in this method is somewhat different: the 5 days of each week are divided into a schedule consisting of 8 hours of light only, ten hours of light and water spray, and six hours of spray only.

The corresponding recommended practice of ASTM lists seven types of apparatus which are variations of the single and twin enclosed carbon arc and the open arc machines. The chief differences involve the presence or absence of automatic temperature control and the dimensions and rotation speeds of the specimen racks. Unless otherwise specified, a 102-18 cam (which provides 102 minutes of light followed by 18 minutes of light and spray) and a schedule of 5 twenty-hour periods per week are recommended.

Salt Spray Test

The salt spray tests listed in Table I are all essentially the same as the ASTM method. In this test, the painted test panels are exposed

continuously to a fine salt fog at a temperature of 95° F. The salt fog is produced by atomization of a 5% sodium chloride solution, and direct spraying of the panels is prevented by baffles. The panels are inclined 15° from the vertical, and the humidity is kept above 95%. Federal Standard 141 allows use of either 5% or 20% sodium chloride, preferring the latter concentration, and Federal Standard 406 specifies the 20% solution.

Humidity Test

In the humidity tests for paints the test specimens are exposed to a moisture saturated atmosphere with continuous condensation taking place on the panels. In the Federal Standard and in the Canadian specification the temperature of the cabinet is maintained at 120° F, and in the ASTM procedure, a temperature of 100° F is suggested.

III. OTHER TEST METHODS

In addition to the specified methods discussed above, there are other test methods which are or have been specified in the United States or in other countries, or which are or have been used by limited numbers of investigators. In a review of various accelerated test methods which have been published in seven countries, Kutzelnigg presents in tabular form a total of 229 methods, of which approximately 70 are applicable to the testing of coatings.¹²

Some methods which have been published recently or which are of particular interest are listed below.

Electrical Resistance

Since corrosion is an electrochemical process, it appears logical that the electrical resistance of a coating would be related to its protective ability. Bacon and co-workers¹³ measured the change in resistance versus time for coatings on steel immersed in sea water. The D. C. resistance of the coating was essentially considered to be the internal resistance of the cell: metal/coating/aqueous environment/HgCl/Hg. This internal resistance, R_i , was calculated from the open cell potential, E_o , and the closed cell potential, E_c , when the circuit was closed with a resistance R_c , by the following equation:

$$R_i = R_c \left(\frac{E_o - E_c}{E_c} \right)$$

The logarithm of the resistance of the immersed coating was plotted versus the time of immersion and this curve was correlated with the degree of rusting of the same panels. For good coatings, the resistance changed

slowly but for poor coatings the resistance dropped more rapidly. Rusting generally was not noted on the test panels until the D. C. resistance fell below 10^6 ohms per square centimeter. The effect of variations in surface preparation, in coating thickness, and in coating composition on the performance of these submerged panels could thus be measured long before there were any visual differences. In one instance, a trend established in the resistance curve after one month, which became definite after two months, gave a visual indication in six months.

Wormwell and Brasher¹⁴ determined the A. C. resistance of protective coatings and also the capacitance. These values at 1000 cycles were measured with a simple bridge circuit in which a resistance and a capacitance in parallel were balanced against a cell containing two painted plates in artificial sea water.

Resistance measurements on coated panels immersed in sea water were also recorded by Brown¹⁵ who used this method for the evaluation of protective coatings for ships' bottoms. Brown worked with D. C. resistances because there appeared to be a limiting value above which the A. C. resistance could not be measured. Resistance measurements for two paint systems showed differences within 5 days, whereas differences in rusting were not apparent for 150 days, and in ships' trials fourteen months were required to show a difference between these coatings. A third coating system which was still better required 125 days to give a clear difference in the resistance-versus-time curve but did not yet show any difference on visual examination after 465 days. Differences in surface preparation and exposure prior to painting gave strong differences in the resistance-versus-time curves but no correlation with performance was presented.¹⁶

Capacitance

Wormwell and Brasher¹⁴ demonstrated that the breakdown of paints and the resultant rusting of the steel substrates was accompanied by a strong increase in the capacitance of the film. Thus, for three different thicknesses of a coating on steel panels exposed in salt water, the decreases in resistance were followed by increases in capacitance, and the latter were then followed by rusting. For panels sprayed under various adverse conditions and for panels in aerated or moving sea water, earlier increases in capacitance correlated with increased rusting. Of four different paints, the one which had shown excellent qualities in exposure tests had a capacitance curve which rose much more slowly than the capacitance curves of the others.

Dissipation Factor

Obtaining of significant results from the above resistance or capacitance-versus-time curves may take from about 10 days for poor coatings to over 150 days for good coatings. According to Okamoto and co-workers¹⁷ it is possible to make rapid predictions of the resistance-versus-time curve

by measurement of the dissipation factor of the coating at various frequencies. The dissipation factor, or $\tan \delta$, was calculated at these frequencies, f , according to the equation:

$$\tan \delta = 1/2\pi fRC$$

The resistance, R , and the capacitance, C , were determined a few hours after immersion with a simple bridge circuit. Curves of the dissipation factor versus frequency were obtained over a frequency range of 0.2 to 10 kilocycles per second. Paints with low dissipation factors which were not greatly affected by frequency gave resistance-versus-time curves characteristic of good coatings, and conversely, paints with high dissipation factors that were strongly dependent on frequency gave resistance-versus-time curves characteristic of poorly performing paints. The correlations were qualitative and no correlations with actual rusting or performance were made.

Underrust Test

The performance of coated steel panels in corrosive atmospheres was investigated by Van Laar.¹⁸ Twenty-seven paint systems with different formulations or different surface preparations were exposed in various atmospheres, including a sea atmosphere, while similar panels were immersed in water, subjected to the ASTM salt spray test, and subjected to an under-rust test. In the latter test, panels with scribe marks previously moistened with salt solution, were exposed at 85% relative humidity and slightly elevated temperature. The time required for underrusting a distance of 1 millimeter was compared with that required for similar underrusting in atmospheric exposure. The correlation of the natural exposure with the underrusting obtained in the laboratory was considered good and, according to a graphical presentation of the results, it was somewhat better than the correlation with the undercutting obtained in ASTM salt spray tests.

Photodegradation

The above tests measure the protective ability of the coatings under particular sets of conditions, but they do not measure any loss in the protective ability due to the effect of sunlight on the degradation of the coating. Degradation due to sunlight and general weathering is most evidenced by loss of gloss, chalking, cracking, fading, or yellowing. A box with two germicidal thirty-watt light sources has been described by Sawyer¹⁹ and similar boxes have been employed in a number of laboratories. The loss of gloss of three alkyd enamels exposed in this box correlated better with results of outdoor exposure than did exposure in a weathering apparatus. Although it was felt that the instrument could differentiate between films of good gloss retention and of poor gloss retention, it was felt that further investigation and correlation with outdoor exposures was necessary.

The effect of sunlight can also be accelerated by outdoor exposure in a device developed by Caryl²⁰ and called the EMMA. This device employs 10 aluminum mirrors which focus sunlight on small test panels. It is on an equatorial mount and follows the sun during the day. The samples thus receive approximately 5,000 langleys of light energy per day, almost twice as much as is obtained in a twin arc Weather-Ometer. (One langley is one calorie per square centimeter.) A similar device equipped with periodically operated water sprays, the EMMAQUA, produced chalking on house paints approximately 6 times as fast as normal exposure. These devices have been used in a desert atmosphere. They would probably deteriorate rapidly in a sea atmosphere and, therefore, could not be employed in a sea atmosphere.

Miscellaneous Methods

Manufacturers of industrial paints must employ screening tests in the development of new coatings. Very often chemical resistance is of importance, and it is usually determined by immersion of a coated specimen in the chemical or in a solution of the chemical in question. A slightly elevated temperature is generally employed to accelerate the immersion tests. For determining the approximate resistance to salt water or to salt atmosphere, immersion in aerated sea water appears to be a preferred method.

The test procedures of three laboratories involved primarily in testing of pipeline coatings have recently been described.²¹⁻²³ All three laboratories reported some accelerated tests to determine the effect of cathodic protection, by applying a potential to a coated steel pipe placed in a conducting medium. One of the laboratories²¹ also added a coating deformation test and an impact adhesion test for hot-applied enamels. In the latter test, two discs held together by the enamel were separated by a dropping weight. Good correlation with these various properties and field exposures, and poor correlations with unspecified accelerated tests and standard ASTM tests, were claimed.

At another laboratory the preferred accelerated test was immersion of scribed panels in water at 105° F for 25 days.²⁴ The panels were rated before and after stripping of the coating. It was claimed that the data was almost identical with that of the standard salt spray test.

Other investigators²⁵ measured the change in flexibility of coatings on panels after exposure in a weathering apparatus, but no correlations of time to failure with actual performance were presented.

Accelerated tests with free films have been reported by MacDonald,²⁶ who obtained stress-strain curves and retardation spectra for films, with or without water leaching or ultraviolet radiation. MacDonald also studied various other properties of free films and related some of these to in-service observations, but no actual correlations with exposure results were given.

In another study,²⁷ a comparison of rusting and blistering for 7 types of coatings on steel panels with their oxygen permeability, water transmission, adhesion, and content of water extractibles, gave only limited correlations.

A probe has been designed for measuring corrosion under paints and coatings.²⁸ The probe consists of a thin metallic layer on a non-metallic backing, and the paint is applied to the metal surface. Corrosion of the metallic layer causes increased electrical resistance in the probe. Results to date appear to be very preliminary, and the potentiality of this method is not yet known.

IV. DISCUSSION

A large number of laboratories all over the world spend considerable funds and energy in the testing of paints. Coatings manufacturers and raw materials producers maintain laboratories to improve or develop products, and most major users in industry and at all levels of government, maintain laboratories to determine which of the available products are best suited for their purposes. The tests employed include tests on the original paint, physical tests of applied coating films or free films, service trials, exposure of test panels to representative environments, and accelerated tests. Methods employed have been described in many articles and in many volumes, ranging from detailed descriptions²⁹ to well illustrated brochures.³⁰

A number of physical tests of applied coating films are useful in predicting performance. Such characteristics as hardness, abrasion resistance, adhesion, flexibility, impact resistance, tensile strength, permeability, and gloss may indicate upper limits of performance that might be expected. However, a paint showing good characteristics initially may deteriorate rapidly and, therefore, tests which give any indication of expected service life must also consider performance after aging.

It would appear at first thought, that in spite of the considerable time required, actual service exposures or field tests would be the best method of testing a paint. However, many authors have pointed out that valid comparisons under service conditions are very difficult to obtain, because of the many variables involved.^{5,15}

These factors include surface preparation, method of handling and damaging, different climatic conditions, etc. Thus, results with test panels which can be more uniformly prepared and more uniformly exposed, are considered to be much more valid.

Test panels can be uniformly exposed under conditions similar to those which will be encountered in practice or they can be subjected to accelerated tests. Deterioration in natural atmospheres can be accelerated by selecting those atmospheres which produce the most rapid deterioration. Thus, panels exposed at Kwajalein, Marshall Islands, deteriorate much faster than those exposed at Kaneohe, Hawaii, which in turn deteriorate faster than those exposed at Port Hueneme, California.³¹

At Kwajalein, panels facing south and inclined 9 degrees from the horizontal position should show still faster any deterioration dependent primarily on sunlight. According to calculations, and also according to other authors,^{32,33} maximum average solar radiation is received at an inclination from the horizontal which is approximately the same as the angle of the latitude. However, sunlight is not necessarily the chief deteriorating factor, and absorbed radiation may be less important than other cumulative effects. Thus, it has been reported that in general panels exposed to a 45 degree angle rust more at the back of the panel than on the surface exposed to sunlight.³⁴

Although exposures in natural environments (but not service conditions) are considered to be the most reliable methods of comparing coatings, the comparisons are not absolute. The faster results from one location cannot be used to predict comparative performance for other locations. Even results at the same location but from exposures started at different times may not give useful comparative data. Reference has been made to the considerable climatic changes in one location from year to year which may make performance predictions based on such comparisons invalid.¹ It has also been claimed that panels which are first exposed during the summer months will generally last longer than panels first exposed in the winter:⁵ the samples exposed in summer age more rapidly and thus become more resistant to swelling and contraction resulting from moisture changes; the samples exposed during the winter months age more slowly and meanwhile are subjected to large moisture and volume changes and resultant stresses. On the other hand, in central India, it was found that panels exposed in July failed more rapidly than those exposed in May or October.³⁵ Thus, seasonal effects are different in various climates. It has also been found that for underrusting at a scribe mark, the rate of subsequent rusting may depend on the atmospheric conditions at the time of initial rusting.³⁴

Test conditions can be more uniform and results can be obtained more rapidly in accelerated exposures of test panels. However, the results of accelerated exposures and of exposures in natural environment often show only limited correlation, and the accelerated test methods may, therefore, be of limited value in predicting the service life of coatings. One difficulty in assessing correlations is that the properties of the coating or the degree of deterioration often cannot be measured with sufficient accuracy and precision.³ In some instances, the lack of validity of accelerated tests in predicting service performance may be due to too great

a change in the artificial environment or to differences in the surfaces coated or in the manner of paint application for the accelerated and natural exposure tests.³⁵

There are a number of different types of accelerated tests. The test which first comes to mind, especially when interest lies in the atmospheric exposure of the paint to be tested, is exposure in an accelerated weathering apparatus. Accelerated weathering machines intensify those factors which have been claimed to be the primary cause of natural weathering: (1) absorption of energy from sunlight, (2) elevated temperature and thermo-shock caused by temperature changes, and (3) water in contact with the paint film.¹ Atmospheric contaminants are also of importance, and some of these, such as sulfur dioxide, have been introduced into accelerated weathering machines.^{1,29} The introduction of a salt atmosphere in a weathering apparatus apparently has not been found practical because of difficulties with corrosion of the apparatus. A Weather-Ometer which had been converted to produce a salt water spray on the panels gave such trouble and maintenance problems that its use was discontinued.³⁷

The three factors enumerated above (light, heat, and water) can be varied in accelerated weathering machines in cycles of varying combinations. Some cycles have been mentioned above and various other cycles have been employed by different investigators. However, in the original articles and in a number of recent review articles there appears to be little discussion of the reasons for choosing the various cycles nor a discussion of comparisons of various cycles.

According to many investigators, one weathering test cannot give correlation with outdoor exposure for different types of coatings. Even for paints of different colors, the agreement with actual exposures has been reported to vary.¹ Various authors have reported good correlation between accelerated and outdoor weathering of a small number of coatings, whereas others have reported poor correlation. No article has come to the attention of the author which describes good correlation between accelerated and natural weathering for a large number of different coatings. Although for bituminous roofing materials accelerated weathering appears dependable,² the accelerated weathering results of one investigator have been reported to give less correlation for bituminous paints than they did for oleo-resinous varnishes or for alkyd varnishes.¹ A claim for accurate reproduction of tropical failure of a variety of coatings in ten days of exposure, based on the analysis of 3200 panels, has been cited by one reviewer, but the degree of correlation is not given.¹ Each day's exposure consisted of an 8-hour irradiation with a mercury vapor arc and a 16-hour shut down period. The first and last three hours of the irradiation period were under a water spray at 140° F, and the center two-hour period was without water at a temperature of 180° F.

Accelerated weathering data is often used to establish a minimum performance standard in specifications.^{11,38} For this purpose correlation of results with actual exposure is not quite so important as for a direct comparison because the test is not used as a method of selection but rather to eliminate substandard paints. On the other hand, if the correlation is poor some otherwise acceptable paints will be eliminated together with the substandard paints.

Some of the differences between accelerated and natural weathering may have been due to the differences between the light distribution in the carbon arcs and mercury vapor arcs which have been employed, as compared to the spectral distribution of sunlight. This may be one reason why better results have been observed with simple light boxes containing germicidal lamps, than with weathering machines employing carbon arcs.¹⁹ The newer xenon source may thus improve the results obtained with a weathering machine. Some work on xenon arcs, especially with respect to fading, has been published in Europe.³⁹

In a recent study, the open arc and the enclosed arc Weather-Ometers were compared with a Weather-Ometer having the newer xenon arc source.⁴⁰ The twin-arc Weather-Ometer in general caused greater fading whereas the xenon arc and the sunshine arc (or open arc) gave greater loss of gloss and chalking. The relative performance of the paints exposed under the three different sources was quite different, and it appeared that almost any coating could be made to look better than another by the proper choice of tests. Panels coated with the same twelve paints which were exposed in the Weather-Ometers are being exposed to the atmosphere. The correlation of the Weather-Ometer results with actual exposure results are not yet available.

Exposures in weathering apparatus are essentially accelerated tests of the deterioration of a coating as opposed to direct tests of the protective ability of the paints. Thus, the exposures may not be of sufficient duration to produce rusting and the results are most often expressed as loss of gloss versus exposure time. The results may also be expressed as fading, checking, or chalking, which also indicate a deterioration of the paint or the pigment. The time required to produce a specified loss of flexibility²⁵ or to produce a specified embrittlement²⁹ may also be recorded.

The degradation of the paint film is a very complicated process. Part of the degradation is due to photochemical processes initiated by light. These chemical reactions may be oxidative reactions or non-oxidative, and different products and reaction rates are obtained in the presence or absence of oxygen.⁴¹⁻⁴³ Reactions caused by ultraviolet light of a short wave length may occur entirely at the surface,⁴⁴ producing erosion and chalking; reactions caused by ultraviolet light of longer wave lengths may occur throughout the body of the film.^{41,44} The rates of these reactions are modified by pigments. The rates are considerably reduced by zinc oxide but are less strongly affected by titanium dioxide,⁴⁵ or may be

relatively unaffected by titanium dioxide.⁴¹ Other degradation is caused by physical stresses due to thermal effect and due to swelling and contracting caused by water absorption and drying. The latter effects may tend to give more cracking and checking. It has been claimed that accelerated weathering emphasizes chalking whereas normal weathering produces more checking and cracking.⁶

Accelerated weathering machines measure chiefly the durability of a paint film in changing environments and under exposure to radiation. Other methods measure the protective ability of a paint, or the change in protective ability of a paint, after prolonged exposure to a given environment. For a coating applied to steel the protective ability is the ability to prevent rust formation. The original protective ability may be due to the high electrical resistance of a coating, due to its low permeability to water and oxygen, and due to the presence of inhibitive pigments. The adhesion of the coating is also very important, especially when damage to the film has occurred or in high humidity or underwater exposures where adhesion provides resistance to blistering. The importance of good surface preparation is constantly stressed by paint manufacturers, because adhesion is very much dependent on surface preparation.

Some of the above properties have been studied individually. Thus, the permeability of even good coatings to water and to oxygen has been shown to be much greater than that needed for the corrosion processes which might occur.⁴⁶ Electrolytic conductance or capacitance were found to increase because of absorption of water or electrolyte, because of changes in film integrity, or because of ion transfer.^{47,48} A number of methods for testing adhesion of coatings are used but none of the methods appear to give sufficiently good reproducibility, except for complicated ultra-centrifugal methods.^{49,50} Furthermore, for many coatings the adhesion changes considerably upon immersion.²⁷

Among the tests designed to measure the ability of paints to prevent corrosion, the salt spray test probably is the most used. Panels exposed in the salt spray test are generally scribed so that the more rapid deterioration at the scribe mark can be noted. This deterioration may include corrosion under the coating, saponification of the coating, and loss of adhesion. Many authors have considered the salt spray test unreliable, including Van Laar,¹⁸ whose graphical data does indicate some correlation with atmospheric exposure tests. Fair correlation was reported with exposures 5 meters from the sea but little correlation with exposures 2 kilometers from the sea,⁵¹ and another study showed poor correlation.⁵² The salt spray test is often used for corrosion studies with metals, but for this purpose it has also been claimed to have strong limitations.^{12,53}

A study of the correlation of outdoor exposure at various sites with the results of a humidity test, the salt spray test, and two other similar tests providing salt atmospheres, has recently been published.⁵⁴ Except for the ASTM salt spray test, the other three tests were conducted according

to United Kingdom or Australian specifications. Identically prepared panels containing 16 primers, with or without top coat, were exposed according to the four test methods and also in seven different climatic locations. For different climatic conditions, different tests showed better correlations. At a severe marine location, none of the tests showed significant correlations. At a less severe marine location, the ASTM salt spray test with a 96 hour exposure gave the best correlation. However, the correlation coefficient was only 0.55.

The underrust test, at a relative humidity below 100%, as described in Section III, does not appear to be employed by many investigators. According to Van Laar this test gave better correlation with natural atmospheric exposure than did the salt spray test.¹⁸

Methods of measuring electrical resistance or capacitance changes of immersed coatings have been discussed in Section III. The decrease in A. C. or D. C. resistance and the increase in capacitance appeared to correlate well with the rusting which occurred under prolonged exposure.¹³⁻¹⁶ In these tests, there is no acceleration in the rate at which rusting occurs, as compared to rusting in the same immersed exposure, but rather the detection of the deterioration is accelerated. Thus, the film deterioration produces changes in electrical properties, which precede the rusting and which are detected prior to the rusting.

Observations by Okamoto and co-workers had indicated that the resistance-versus-time curve could be predicted from measurements of the dissipation factors at various frequencies.¹⁷ This method would thus constitute a very rapid method of assessing performance. However, it appears that further experimentation is needed to determine whether this method is really very promising.

In electrical measurements with alternating current, the coating is essentially the dielectric of a capacitor. For this capacitor, the dissipation factor, D, or loss tangent, $\tan \delta$, is the ratio of the loss current to the charging current. The loss current, I_1 , is the resistive component of the total current, or V/R . The charging current, I_c , is the capacitive component of the current, or ωCV . Thus,⁵⁵

$$D = \tan \delta = I_1/I_c = 1/\omega RC$$

The loss current is a function of the resistance of the coating. As a coating deteriorates and its resistance decreases, the dissipation factor would therefore be expected to increase. A poor coating or a deteriorated coating with low resistance would be expected to have a high dissipation factor. However, it is not clear why the initial dissipation factor and the curve of the dissipation factor versus frequency should be able to predict the shape of the resistance-versus-time curve or the actual performance of a paint.

The extension of resistance-versus-time measurements to panels exposed in the atmosphere has been proposed by Bacon,¹³ but no published data on such experiments has been found. A translation of a Russian article by Rosenfeld and co-workers,⁵⁶ claims that capacitance data can be used to determine the behavior of a film in an atmospheric environment. The same article also mentions other electrical measurements on paint films similar to those discussed above, and claims "complete agreement" with exposure results in natural environments; however, no substantiating data are given.

Corrosion probes which indicate corrosion by changes in electrical resistance have been used in a variety of media and atmospheres. One probe has been specifically designed for measuring corrosion under paints and coatings, but results obtained so far are very preliminary.²⁸ With other corrosion probes, especially those employing thin metallic films, considerable difficulty has been encountered in providing proper sensitivity and reproducibility.⁵⁷ Because thin steel films would have to be used to measure corrosion under coatings, and because the resulting surfaces might be considerably different from those encountered in practice, it is possible that it will be difficult to develop a reliable probe for testing coatings.

Some investigators have employed thin paint films or tapered paint films to obtain more rapid test results under natural conditions.²⁹ Although thin films do give less protection, there appears to be no definite relationship between thickness and performance. Furthermore, some believe that there is a critical film thickness below which the performance changes very strongly.

Most of the above tests for measuring the protective ability of a paint, such as immersion tests, underrust tests, and salt spray tests, as opposed to accelerated weathering machines, do not measure deterioration that may be associated with sunlight, changing temperature, or other varying environments. A number of accelerated tests for rusting of painted panels, which do include exposure to ultraviolet light, have been cited,¹² but without a discussion of their validity.

The effect of both salt spray and sunlight had been combined in a modified salt spray test for plastics,⁵⁸ but this method is no longer listed in the current Federal Standard.⁹ In this method, which appears to be similar to a method given in another specification,⁵⁹ samples are subjected to alternate 10-minute periods of spray with 5% salt solution and hot air at 55° C, while they are under continuous irradiation under a sunlamp with corex filter.

The reasons for the discontinuance of this method--whether because of poor correlation with natural weathering or for other reasons-- is not known. A related method for the accelerated testing of painted steel panels has been described.⁶⁰ In the latter method, the panels are irradiated under a carbon arc and are sprayed intermittently with a 4% salt solution. The degree of correlation with exposure is not known.

Very few of the articles in the literature which do present good correlation for accelerated test methods discuss the degree of correlation obtained for a large number of paints. Often correlations are indicated for three or four coatings and there is then no indication of the expected performance or correlation for other coatings. In most instances, only one generic type of paint is discussed, and there is no indication whether the method applies to other generic types.

In the degradation of an applied paint film, various processes, including chemical degradation, reactions to mechanical stresses, diffusion of degradation products, diffusion of metallic ions, oxygen, or water, etc., occur simultaneously. In an ideal accelerated test, all the processes which would take place in a given natural exposure would be accelerated by the same factor. For two coatings which degrade by considerably different mechanisms, it is unlikely that all processes will be accelerated by the same factor in any one cycle, and, therefore, it may not be possible to ever develop one cycle which can be used with equal effectiveness for all coatings. However, it should be possible to develop better methods if the basic mechanisms involved in the degradation of paints and the mechanisms of inhibition of rusting become better understood.

The difficulty in accelerating photochemical processes proportionately is illustrated by the observation that when the amount of radiation is increased by employing the EMMA, a device increasing solar radiation by the use of mirrors, the "efficiency" of the light in producing degradation is only 33 to 83% of that obtained in a normal exposure.⁶¹ Thus, the higher intensities of radiation did not produce a proportionately higher rate of degradation, presumably because other related processes were not speeded as much as the photochemical reactions. However, another investigator found that when a similar amount of total radiation was absorbed over a longer period of time, the higher intensity of radiation in the summer produced 8 times more degradation than was obtained in the winter.⁶²

Since it is difficult to accelerate evenly all the various factors involved, an accelerated method of detecting the deterioration, or the lack of continued protection, of a coating may be more useful and accurate than a method of actually speeding up the deterioration or the corrosion process. This is one reason why electrical methods for detecting paint breakdown in immersed panels appear to show a comparatively high degree of correlation with actual breakdown in the same environment. The extension of electrical methods for measuring the degree of deterioration to coatings exposed in atmospheric environments may thus be promising.

It would also appear desirable to investigate accelerated weathering tests with the xenon arc source. For both of the above methods correlations with actual deterioration should be made and investigation of those paints which show poor correlation might be of value. If those paints which show poor correlation have in common other properties which may be related to the rate of deterioration it may be possible to develop a better overall correlation by considering these properties together with accelerated test results.

V. CONCLUSIONS

1. Accelerated tests sometimes have been found useful for differentiating between the performance of similar paints of the same generic type or for indicating the relative performance of various paints under given service conditions which are very similar to the test conditions.
2. No accelerated tests have been proven sufficiently reliable to use as a basis for the prediction of performance of paints in service, especially when the paints differ considerably from each other. A reliable test of this nature would be of great value in the writing of paint specifications.
3. Accelerated tests may be useful in paint specifications for the elimination of coatings which are likely to be inferior.
4. Methods of accelerated detection of the normal deterioration of paints are likely to give better correlation with performance than methods using normal observation under conditions giving accelerated deterioration.
5. Further studies of some accelerated methods, including weathering with a xenon source and electrical methods of detecting deterioration, would be desirable.
6. A better understanding of the degradation of various generic coatings would ultimately lead to better accelerated tests.

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