NATIONAL BUREAU OF STANDARDS REPORT

8688

PROGRESS REPORT

January 1 through March 31, 1965

PORCELAIN ENAMEL INSTITUTE RESEARCH ASSOCIATESHIP
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C.

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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SUMMARY

A Hunter multipurpose reflectometer was extensively modified to permit its use for detecting the amount of fluorescent soils that remain on specimens after standard cleaning treatments. The major modifications involved substituting an ultraviolet source for the regular lamp source and the introduction of special filters to prevent unwanted radiation from reaching the photocells. Preliminary trials with the modified instrument indicated that it will perform satisfactorily over a wide range of fluorescent intensities.

A survey of the literature was made for tests of coating continuity. As many as 13 different tests have been used for this purpose. Investigation of five of these suggested that the high voltage spark-test showed the most promise for porcelain enamels.

Specimens representing the new "Nature Tone" series of mat porcelain enamels on steel were installed on the weathering racks at the Kure Beach 80-foot site. Since no rack space was available for these new specimens it was necessary to remove several enamel types already under test. These enamels had shown such large changes in color and gloss after eight years that further testing would have furnished little, if any, information on their weathering properties.

The initial measurements on specimens of porcelain enamels for aluminum were completed and the exposure of these enamels is now under way at three of the selected sites.

A comparison was made between the citric acid spot test and the boiling acid weight changes for a large group of enamels in the PEI-NBS weathering program. These data showed the type of agreement that can be expected from the two types of tests.

I. CLEANABILITY

INTRODUCTION

The report for the previous period outlined the need for an experimental method to evaluate the "aesthetic" cleanability of porcelain enamels. A review of the literature indicated some research concerned with "bacterial" cleanability of various surface finishes, but little work was found to provide guidelines for the present effort.

The work with conventional soiling agents, previously reported, emphasized the problems involved when porcelain enamels in a wide range of colors and surface textures were to be evaluated. These problems have focused attention during the present report period on the use of a soil that would fluoresce in the visible when exposed to ultraviolet radiation. The method would be based on (1) applying the soil, (2) subjecting the surface to a standard cleaning treatment, and, finally, (3) determining the amount of soil remaining on the surface after cleaning by measuring the intensity of the residual fluorescence when the surface was exposed to a standard ultraviolet source.

Before the use of fluorescent soils could be fully investigated, it was first necessary to develop a quantitative technique for the estimation of the intensity of fluorescence which could be utilized in a cleanability test precedure.

The phenomena of fluorescence has been extensively studied. Many applications are found in biological pharmaceutical, medical and agricultural research. Methods for observing and measuring fluorescence have been used in testing paints, varnishes and laquers, fuels, detergents, and foods, as well as in criminology. Radley and Grant[1/], in 1939, and, more recently, Udenfriend[2/], have reviewed many of the instrumental systems in past and current use for fluorescence measurements. A majority of these instruments estimate materials in solution and some have been designed or modified to measure fluorescence from solids. Gardner and Sward [3/] report use of the Hunter Multipurpose Reflectometer in fluorescence analysis, and a kit is available for conversion of the instrument for this use. The Hunter instrument was originally designed at the suggestion of the Standards Committee of the Porcelain Enamel Institute for the measurement of reflectance and gloss properties of porcelain enameled specimens. The specimens required are of a convenient size. The equipment is commercially available and, in addition, some of these instruments are undoubtedly in current use in the porcelain enamel industry. For these reasons, the Hunter instrument was selected for some of the preliminary trials.

RESULTS AND DISCUSSION

1. Initial Experiments.

The first attempt at measuring the residual fluorescence of soiled specimens was made using the somewhat crude device shown schematically in figure 1. Specimens soiled with anthracene $[C_6H_4(CH)_2C_6H_4]$ were irradiated with ultra-violet light to excite fluorescence. A cadmium-sulphide photocell, fitted with a filter holder, was provided to respond to the visible radiation emitted by the soiled specimens. A DC voltage which was applied to the photocell generated a "dark current" which corresponded to the voltage drop across the potentiometer. When the soiled specimen was radiated with ultraviolet, visible light struck the photocell. This in turn caused a change in resistance of the cell which was measured as a voltage drop.

Experiments with this device showed that responses of between 0 and 8 millevolts could be generated from various specimens. However, these responses could be attributed only partly to the fluorescence of the anthracene that was present on the enameled specimens.

These early experiments led to the following conclusions: a) a more intense source of ultra-violet light was needed, b) suitable filters should be provided between the source and the specimen, as well as between the specimen and the light-sensitive cell, c) a more sensitive photocell and measuring circuit should be sought, d) adequate ventilation or cooling should be provided because the photocell response was dependent on temperature, e) light-tightness should be improved, particularly if a more sensitive cell and circuit was incorporated, and f) fluorescence measurements could not be made with the required precision unless a more sophisticated measurement system was used.

2. Modification of Hunter Multipurpose Reflectometer.

A schematic drawing of the Hunter Reflectometer is shown in figure 2. Light from a single source is split into two beams, the reflectance beam and the gloss beam. The reflectance beam strikes one barrier-layer photocell and the gloss beam strikes a second matched photocell. These two cells are connected, with opposing polarities, to a sensitive galvanometer which is used to indicate a null balance. The reflectance beam is incident upon the reflectance surface at 45°, and the reflectance photocell views the surface normally. This cell is on a movable mount so that it can be moved to a position where the light reaching it is the same as that reaching the gloss cell. The gloss path involves reflection from a specimen (or a mirror when measuring reflectance) placed horizontally on an opening in the instrument top. This beam, after passing an adjustable semi-diffusing mirror, terminates on the gloss photocell which is mounted at a fixed position.

A Hunter instrument was modified to test its suitability for fluorescence measurements. The following changes were made:

a) A General Electric AH-4 mercury arc lamp together with a special lamp holder and a transformer was substituted for the projection lamp normally used.

b) An ultra-violet transmitting filter glass was substituted for one of the tri-stimulus colored glass filters normally used in the instrument. This primary filter passes the UV but filters out most of the unwanted visible light that is generated by the GE AH-4 lamp.

c) A holder for a 2" x 2" filter glass was installed in front of, but attached to, the movable reflectance photocell. This secondary filter was required to eliminate any ultraviolet radiation reflected from the specimen surface. Unfortunately, the photocell responds to this radiation as well as to the visible.

d) A centimeter scale was substituted for the gloss and reflectance scales normally used with the instruments. When a null balance is achieved, this centimeter scale is used to measure the distance from the reflectance photocell to the vertical specimen surface on the instrument front which, in turn, is an indication of the light intensity from the specimen. The photocell is adjustable between 10 and 33.8 cm. from the specimen.

e) The black, porcelain enameled comparison surface supplied with the instrument was replaced with a front-surface aluminum mirror. This mirror is a part of the gloss path and rests horizontally on the top opening of the instrument.

f) The semi-diffusing adjustable mirror in the gloss path was replaced with a flat piece of fluorescent uranium glass (Corning CS 3-73).

3. Experiments with the Modified Reflectometer.

a) Present Concept of Instrument Use.

Present plans call for measuring fluorescence by a substitutional method. A bare specimen, before soil application, would be balanced on the instrument with the reflectance cell in the front position, 10 centimeters from the specimen. The balance would be obtained by adjusting the angular position of the fluorescent glass with adjusting screw to allow the proper fraction of light to fall on the fixed photocell. After soiling and cleaning the specimen, residual soil would be measured by replacing the treated specimen in the test position and reestablishing a null balance, this time by moving the reflectance photocell away from the specimen (if fluorescence was detected). The distance of the cell movement would then be indicative of the residual soil on the specimen.

This concept of use is only one of several by which the instrument could be used to measure residual fluorescence on specimens. One advantage of the presently contemplated method, however, is that all measurements would depend on an initial balance at the front position of the movable photocell, which is the most sensitive portion of the scale. The technique would also insure equal sensitivity when making intensity measurements on specimens of different colors.

b) Filter Selection.

Numerous filters have been evaluated for use in the instruments. Both the percentage transmission and the wavelength selectivity (band pass) must be considered. In the case of the primary filter located between the source and the specimen, a relatively low transmission is not serious because of the high intensity of the UV source; however, it is important that the filter pass little or no visible radiation. The secondary filter, on the other hand, should have a transmission as high as possible to permit sensitive measurement of low intensity fluorescence and at the same time it should selectively exclude UV radiation reflected or strayed from the source.

The best results obtained so far, based on these considerations, and confirmed by experiment, have been with a Corning CS 7-60 primary filter and a Wratten Number 3 gelatin filter in front of the movable photocell. No filter was required in front of the fixed photocell. Several filters, now on order, may lead to even better filtering.

c) Adjustment of Reflectometer for Sensitivity Equalization.

A selection of white and colored porcelain enameled specimens was made to include the extremes of photocell response for the initial balance. As explained above, it is desirable that all colors be balanced in the front position of the reflectance cell. Because the filters are not 100% efficient, some light from the UV source will be reflected by the specimen and reach the photocell. The amount of this light will be less for black specimens than for high reflectance white specimens. It was found that a suitable initial balance could not be achieved with the original diffusing mirror; hence, the fluorescent uranium glass was used for this purpose.

d) Sensitivity of Multipurpose Reflectometer.

Experiments were performed to determine the response of the modified instrument to the wide range of anthracene intensities that might conceivably be encountered in a cleanability test. Both black and white specimens were used. The specimens, which were in the "as manufactured" condition, were washed with a tri-sodium phosphate solution prior to soiling. A different amount of anthracene was applied to the surface of each specimen. This was done by first applying the material in excess and then cleaning the specimens by light or hard rubbing either with dry or wet disposable paper tissues. Visual ratings of the amounts of anthracene that remained were made by inspecting the specimens under a laboratory ultra-violet lamp. The visual ratings varied from a "large amount" to "a very slight amount." The results of the experiment, given in table 1, show good agreement between visual and instrumental readings. There were differences in surface texture between the black and the white specimens, which might, in fact, contribute to a difference in cleanability. The results obtained with the reflectometer suggest that this method was more sensitive than the visual ratings and could provide a numerical basis for assigning differences in cleanability.

FUTURE PLANS

Work for the next report period will be concerned with:

a) Development of a reproducible abrasion pretreatment for cleanability specimens.

b) Determination of most suitable fluorescent "soil."

c) Selection of effective and reproducible mechanical methods for soil application and cleaning.

d) Improvement in the filtering of ultra-violet light to exclude all visible wavelengths.

e) Development of an index to express cleanability results.

f) Investigation of the degree of correlation between test results with fluorescent soils and the cleanabilities as determined from qualitative estimates of volunteers.

II. CONTINUITY OF COATING

INTRODUCTION

One of the more important reasons for applying a porcelain enamel coating to appliances, architectural panels, or sanitary ware, is to protect the base metal from corrosion. Thus, to insure the highest quality, any discontinuity or defect, either on the surface or within the layer of porcelain enamel, that might lead to early corrosion of the base metal should be detected before an enameled part is placed in service. It is believed obvious that a continuity of coating test that would detect these defects would be beneficial to all parties concerned.

The first phase in the development of a continuity of coating test was to analyze the defects that might lead to early failure of an enameled part. Figure 3 is a schematic drawing of such defects. These include:

1. Holidays. Holidays are the largest of these defects. A holiday may be caused by tearing, crawling, jumping, fishscaling, or chipping. Holidays are relatively large defects and they can be detected easily by visual observation.

2. Burnoff. Burnoff is also easily detected visually. However, it is rarely considered a serious defect, when considering continuity of coating, because the exposed edges, where burnoff usually occurs, are not normally subjected to corrosive conditions. Therefore, burnoff does not ordinarily shorten the life of a porcelain enamel part.

3. Cracking. Cracking or crazing can oftentimes be detected by visual inspection. The depth of the crack is an important factor in determining whether or not it will cause early corrosion of the base metal.

Unfortunately it is difficult to determine visually the depth to which the crack penetrates. Any continuity of coating test should provide this information.

4. Pinholes and Blisters. These can oftentimes be detected visually, but it is difficult to determine how far they penetrate into the enamel. Pinholes and blisters which do not penetrate deeply should not cause any special difficulties from the corrosion standpoint. However, those that penetrate almost to the metal may well lead to an early failure; hence, a continuity of coating test should detect this type of defect.

5. Subsurface Pores. Subsurface pores can not be detected visually and it is also difficult to determine whether or not they can cause early corrosion of the base metal. It seems likely that large pores might be detrimental. These, therefore, should be detected by a continuity of coating test.

6. Copperheads. Copperheads of the type often times observed in ground coat enamels may not be serious defects with respect to corrosion protection, but more information is needed in this area.

A review of this list of defects shows that pinholes, blisters, large sub-surface pores, and cracks are the main types that can cause corrosion difficulties. Hence, at least the preliminary work on a continuity of coating test should concentrate on these four defects.

RESULTS AND DISCUSSION

A review of the literature revealed that several test methods have been used for locating discontinuities in either porcelain enamel or organic coatings. Preliminary investigations of a few of these test methods have been made. Attention was focused on ease of performing the test, types of defects located, and reproducibility of the test method. A brief description of the five methods investigated follows:

1. High-Voltage Methods.

An instrument for continuity testing with a high voltage probe is the Porosity Detector, produced by Uvral.[5/] The voltage on the probe can be adjusted at any desired level from 0-5 KV. Because of the low amperage the high voltage is harmless to humans. The operation of the equipment is quite simple. The ware to be tested is grounded and a wire probe searches the surface for discontinuities. When the probe passes over a discontinuity, a discharge occurs to the base metal. The completion of the circuit is then indicated by a bell ringing and a light that flashes in the handle of the probe and is recorded on a counter. The type of results obtained with the high-voltage tester are dependent both on the thickness and the dielectric strength of the enamel.

The Porosity Detector was obtained for the present study and it was used for several preliminary tests. The resulting data indicated that the instrument is capable of locating a wide range of discontinuities depending on the voltage setting. It is not possible, however, to use the whole range of voltage settings and then to repeat the same test and duplicate the results because the higher voltages used in the first probing apparently create new discontinuities. However, the results are fairly reproducible when several passes of the probe are made at one voltage setting only.

It was also found that if a piece of carbon paper was placed over the specimen prior to the test, the discharges resulted in a "map" of the discontinuities on the carbon paper. When the number of discontinuities recorded by the instrument was compared with the number of discontinuities on the "map," there was good agreement, except at the highest voltages where an almost continuous discharge occured.

This high-voltage instrument seems to be capable of locating subsurface defects, as well as those that are open to the surface. A similar instrument is also available from Pfaudler.[6/]

The main disadvantage of the instrument is that a spark discharging through a subsurface pore will create a tiny hole to the base metal which may later lead to corrosion. This puncture will not occur, however, if the voltage is not excessive.

2. Wet Chemical Test.

This test, which has been used by Western Electric,[7/] consists of soaking a filter paper in a solution consisting of 1900 ml of distilled water, 100 ml concentrated sulfuric acid, and one gram of potassium ferricyanide. The wet filter paper is placed on the surface to be tested for fifteen seconds, after which it is removed and examined visually. Areas showing dark blue discolorations represent discontinuities in the enamel.

Besides being messy to perform, this test was found to be sensitive only to very large discontinuities, most of which could have been located by visual examination.

3. Electrographic Printing.

This method [8, 9/] consists of first soaking a sheet of photographic dye transfer paper and blotting paper in a solution of 5% by weight of potassium nitrate for 30 minutes. The method is quite involved. The excess potassium nitrate is removed by placing the papers between a sheet of dry blotting paper and a sheet of plastic after which they are pressed at 300 psi. The dye transfer paper is next placed on the specimen to be tested and the blotting paper containing the potassium nitrate is used to back it up. The specimen and blotting papers are then placed between two sheets of aluminum, the one under the specimen is the cathode while the one on top of the blotting paper is the anode, and six volts are placed across the specimen. The specimen sandwich is then placed between two sheets of rubber and pressed at 300 psi for 15-20 seconds. The dye transfer paper is next developed in a solution containing 2.5% potassium ferricyanide and 2.5% potassium ferrocyanide for 30 minutes. Finally, the dye transfer paper is washed in warm water until the background color of the paper is white. The discontinuities appear as dark blue spots on the white background.

Several difficulties were encountered in using this test with porcelain enamels. The first occurred with specimens which were not completely flat. When these specimens were pressed at 300 psi, the enamel would chip or crack. The second difficulty was that while two successive tests on the same specimen often yielded approximately the same number of defects, the defects were not always in the same location. Therefore, the reproducibility was poor. Also, it is difficult to detect the small dark blue spots which indicate the discontinuities.

One point to remember when considering this particular test for continuity of coatings, is that it could not be applied to most production parts.

4. Swab Tests.

Swab tests[10,11] consist of connecting a low voltage source to either a sponge or felt probe which has been dampened with an electrolyte. This probe then scans the specimen surface and changes in either amperage or voltage indicate discontinuities. It has been found in some brief exploratory experiments that the test lacks sensitivity, in that either no discontinuities or one continuous discontinuity was indicated. However, after a meeting with the Standards Committee it was disclosed that many people are now using this test with satisfactory results. Therefore, a more careful look will be given to the swab testing approach.

5. Electrified Particle Method.

The electrified particle method was developed and licensed by the Statiflux Corporation[12]. The method consists of spraying the surface with charged particles of calcium carbonate. These particles are attracted to the base metal where a discontinuity exists. This test seems to be more sensitive for small discontinuities, expecially cracks, than it is in locating relatively large discontinuities. Again it is relatively hard to see the powder deposit that forms on the top of a pin hole.

Other test methods for continuity of coating which have not been investigated by the research associateship are:

1. X-Ray Ionization.

This method [13] was developed by Joeseph A. Finlayson as a thesis project at The State University of New York State College of Ceramics at Alfred University. The method consists of connecting two specimens, facing each other but separated by a small airgap, to a 2200 volt DC power supply. One of the specimens was a standard, while the other was a piece to be tested. A volt-meter was connected in the circuit to measure the voltage when the circuit was energized. The voltage was recorded before and after ionizing the air by X-ray radiation and the differences in voltage gave an indication of the discontinuities present. In the thesis it was noted that this method was less sensitive than the wet chemical method previously described. It is, therefore, not considered as a promising approach.

2. Salt Spray Tests.

These test methods [14,15,16] consist of exposing a specimen to a salt spray for a standard test period and then inspecting the surface for evidence of localized corrosion. Discontinuities appear as rust on the surface. This type of test would probably not be convenient as a coating continuity procedure, but it might be desirable in correlating results of a continuity of coating test with simulated service conditions.

3. Dye Penetration.

This type of test[17] consists of three steps; (1) applying a penetrant and removing the excess, (2) developing the penetrant, and (3) examining the piece for discontinuities. After the penetrant has been applied to the piece and the excess removed, the developer forms a thin porous layer on the surface of the specimen. Any penetrant in a discontinuity can return to the surface through the developer which tends to spread the dye penetrant over a larger area and thus make the defect more easily visible. This method of test reveals only those defects which are open to the surface.

4. Iodine Vapor Test.

In this test[18] iodine vapor from crystals of iodine penetrate defects and corrode the base iron making the defect visible.

5. Copper Deposition.

In this test [19] the specimens are immersed in a solution of copper sulfate and sodium chloride. Copper deposits on the surface of the specimen where a discontinuity permits the solution to contact with iron.

6. Other methods, including the resistance test, electrolytic test, and transformer test, are outlined in the 1951 Proceedings of the PEI Shop Practice Forum[20].

PLANS FOR NEXT REPORT PERIOD

The review of possible test methods as outlined above has indicated that one of the more promising approaches to coating continuity testing is the high voltage discharge. However, a large amount of additional study is required. In the work for the next report period emphasis will be placed on a further examination of the variables that affect the test results.

III. EXPOSURE TEST OF PORCELAIN ENAMEL ON ALUMINUM

INTRODUCTION

An exposure test of porcelain enamels on aluminum was authorized early in 1964. Detailed planning regarding the enamels in the test, specimen sizes, exposure sites, selection of exposure specimens, as well as the procedure to be followed when cleaning and measuring the gloss, color, and acid resistance of the enamels, has been previously reported All specimens were installed during the present report period at Kure Beach, Washington, and Montreal.

RESULTS AND DISCUSSION

1. Initial Measurements.

The 45° specular gloss, color, acid solubility, and acid spot test ratings were determined by the procedures reported previously. The results of these measurements for all fifty-one enamels are given in table 2.

2. Thickness.

The thicknesses were measured with an Elcometer Minitor Thickness Gauge. Since these values seemed low, polished cross-sections were prepared of all the enamels and the thickness was measured with a micrometer eyepiece on a metallographic microscope. While these two thickness values were not the same, there was a good correlation between the two, as illustrated in Figure 4. In this figure the microscope (or true) thickness is plotted against the thickness value determined with the Elcometer Thickness Meter. The solid line represents the least squares fit through the points, while the dashed line indicates where the points would lie if the meter gave the same thickness values as the microscope. It is planned to correct the meter readings to the microscope values by using the equation for the least squares line, $Y = 1.09X + 1.03$, where Y would be the corrected value and X would be the value determined with the thickness meter. By correcting the thickness it will be possible to follow any changes in thickness that might possibly occur during weathering. The corrected thickness values are included in table 2.

3. Distinctness of Image Gloss.

The distinctness of image gloss for each enamel was determined in accordance with PEI Bulletin T-20 [21/], with the exception that only six specimens were tested. The values for the distinctness of image gloss for all 51 enamels are given in table 2.

4. Spall Tests.

Triplicate specimens of each enamel are being spall tested in accordance with ASTM Standard Method of Test C 486-61T [22], (96 hrs. - 5% by weight NH_4Cl). Since these tests were not completed, the results will not be reported until next quarter.

5. Installation of Exposure Specimens.

The test specimens have been installed at Kure Beach, Washington, and Montreal. The specimens have been sent to Los Angeles for installation.

PLANS FOR NEXT REPORT PERIOD

It is planned to complete the spall testing and to install the exposure specimens and racks at New York City during the next quarter.

IV. EXPOSURE TEST OF NATURE TONE ENAMELS

INTRODUCTION

The interest shown by architects in mat finishes has led to the development of a series of mat enamels called "nature tones." While these enamels meet the requirements of the architects for color, gloss, and texture, they have not been thoroughly weather tested to ascertain whether or not the accelerated tests developed for glossy enamels on steel are reliable for predicting the weatherability of these new low gloss enamels.

Since a previous exposure test [23] has indicated that enamels exposed 80 feet from the ocean at Kure Beach, N. C., undergo an especially severe weathering attack, this site was selected for testing so that information on weatherability could be obtained in the shortest possible time.

RESULTS AND DISCUSSION

Four specimens of each of thirty selected nature tone enamels were received early in March. Two of these four were used for exposure, while the other two were tested by the acid spot test and by boiling acid solubility.

Before the exposure specimens were measured for either gloss or color they were washed by scouring 30 strokes with calcium carbonate on a sponge, rinsing with tap water, and wiping with a sponge moistened with trisodium phosphate followed by rinsing with tap water, distilled water, and alcohol. This method of washing was found to be effective in removing dirt films while causing only very slight changes in the gloss of the surface.

Since the enamels had low 45° specular gloss values, a gloss standard with an assigned value of 15 was used instead of the usual standard, which has a value of 54.3. The data for 45° specular gloss, image gloss, acid spot test, and boiling acid solubility are given in table 3. The initial color values; Rd, a, and b, were also determined.

The specimens were installed on the racks at Kure Beach-80 on March 19, 1965. At the same time, 60 specimens in the current PEI-NBS Weathering Test, now in its eighth year, were withdrawn from this site to provide space for testing these new enamels. All of the enamels withdrawn showed color retentions of 90 or less and/or rusting of the base metal through the enamel surface.

PLANS FOR NEXT REPORT PERIOD

The first inspection of the nature tone enamels is scheduled after six months. Therefore, no further work on this project is scheduled during the next report period.

V. CORRELATION OF CITRIC ACID SPOT TEST WITH BOILING ACID SOLUBILITY

INTRODUCTION

The acid resistance of porcelain enamels has long been measured by the citric acid spot test (PEI T-21). Although this test has proved to be a reasonably good indicator of acid resistance of glossy enamels, it is not satisfactory for low-gloss enamels. The boiling acid solubility test (ASTM C 283), however, does not suffer from this difficulty and, in addition, it provides a more quantitative measure of acid resistance. Because of these two advantages, there appears to be an increasing trend for some laboratories to use the boiling acid test rather than the spot test for evaluating acid resistance. A comparison of test results by the two methods for a large number of enamels was, therefore, believed of some interest.

RESULTS AND DISCUSSION

Recently, both the boiling acid solubility and the acid spot test ratings were obtained for a group of storage specimens of 90 enamels, which are included in the PEI-NBS weathering study. The results of these determinations are given in table 4. It will be noted that, on the average, an excellent correlation exists between the two tests. However, there is considerable scatter, as indicated by either the ranges or the high standard deviations. This high scatter suggests that conversions from one test result to the other cannot be made with any high degree of assurance. However, the comparison shows that for the 75 regular enamels, those that were rated acid-resistant (AA or A) by the spot test all had boiling acid solubilities of 7.0 mg/in^2 or less.

At the same time 10 of the 25 enamels that were rated B and C by the spot test showed acid solubilities under 7 mg/in^2. Since these 10 enamels also had good weather resistance, it seems that they might be termed acid-resistant enamels if it was not for their tendency to show slight stains on exposure to room temperature acids.

This same comparison could not be made for the low-temperature enamels, since there were no C and D enamels and only one B enamel included in the test.

PLANS FOR NEXT REPORT PERIOD:

No further work is planned.

STANDARD REFERENCE MATERIALS

The following stock of standards was on hand April 1, 1965:

Corundum abrasive, March 1960 issue, for subsurface abrasion	296 lb., 74 jars
Standard Pennsylvania Glass Sand, July 1963 issue, for Surface abrasion	300 lb., 100 jars
Distinctness of image gloss standards	20 sets
Calibrated glass plates for abrasion testing	28.5 doz.

Respectfully submitted,

M. D. Burdick
M. A. Rushmer
Research Associates

Table 1. Comparison of Visual and Instrumental Measurement of Fluorescence Intensity from Specimens "Soiled" with Anthracene.

Specimen No.	Visual Estimate of Retained Anthracene	Multipurpose Reflectometer a/ Measurement of Intensity	
		Black Enamel cm.	White Enamel cm.
1	Large amount	23.0	16.7
2	Medium "	15.1	14.4
3	Small "	12.4	11.3
4	V. slight "	10.4	10.2
5	None	10	10
6	None	10	10

a/ Modified to use AH-4 mercury lamp
Primary filter CS 7-60
Secondary filter Wratten No. 3
Technical grade anthracene (90-95 percent Purity)

Table 2. SUMMARY OF THE INITIAL DATA FOR THE ENAMELS IN THE ALUMINUM EXPOSURE TEST

ENAMEL	45° SPECULAR GLOSS	COLOR			IMAGE GLOSS	THICKNESS (mils.)	ACID SOL. (mg/in.^{2})	ACID SPOT
		Rd	a	b				
AA-A	70.1	79.8	-1.6	-0.1	3.9	4.5	5.5	A
AA-B	74.2	77.8	-1.3	-0.8	7.1	4.3	5.9	A
AA-C	71.5	75.9	-1.5	+0.4	6.4	3.4	5.0	AA
AA-D	71.9	82.5	-1.8	0.5	3.4	6.5	12.7	AA
AB-A	56.8	71.2	-1.7	0.1	3.4	4.0	7.2	B
AB-C	55.6	70.0	-1.9	-0.4	<1	4.0	4.9	A
AB-D	28.9	81.3	-0.7	1.0	<1	6.2	7.9	A
AC-A	74.5	76.1	-1.4	-1.2	9.0	3.5	6.4	A
AC-B	71.8	73.1	-1.5	-1.5	3.7	2.8	11.3	AA
AC-C	70.5	76.9	-1.6	-0.8	3.7	3.3	9.9	AA
AD-A	55.0	71.7	-1.5	-1.7	2.6	2.8	6.2	AA
AD-B	68.3	77.8	-0.8	+0.4	2.7	4.3	6.7	B
AD-C	42.4	73.0	-1.8	-1.6	<1	3.2	7.1	B
AD-D	34.9	74.8	-1.6	-1.1	<1	2.7	12.4	A
AE-A	75.6	0.3	0.2	0.0	8.1	2.4	6.5	A
AE-B	78.0	0.7	0.1	0.0	7.1	1.6	10.1	A
AE-C	78.1	0.6	0.2	0.0	9.5	2.0	12.1	A
AE-D	75.0	0.3	0.4	0.0	4.2	3.4	15.5	B
AF-A	78.4	0.3	0.4	0.0	5.1	1.5	14.2	B
AF-B	58.5	0.8	0.5	0.0	3.6	2.7	9.0	B
AF-C	76.8	0.3	0.4	0.0	6.6	3.1	10.1	C
AG-B	26.0	1.0	0.6	0.0	<1	3.0	12.5	B
AG-C	12.6	2.3	1.1	0.0	<1	2.0	7.5	A

AH-A	46.9	9.1	49.0	19.7	10.0	2.8	8.1	A
AH-B	85.3	7.0	55.5	19.7	11.8	3.1	8.8	B
AH-C	85.6	7.1	56.5	19.6	8.5	3.1	6.5	B
AH-D	82.0	9.0	44.3	22.2	5.9	1.9	10.5	B
AO-A	78.8	3.7	-12.1	2.6	7.1	3.2	19.9	A
AO-B	79.8	3.6	-13.0	2.9	8.1	1.6	10.1	A
AO-D	78.3	5.4	-10.9	7.9	6.6	2.1	17.0	A
AP-A	42.4	19.9	-17.6	1.3	< 1	6.4	12.3	B
AP-B	38.5	33.5	-14.6	1.3	< 1	4.1	6.4	A
AP-C	30.2	30.1	-15.4	-0.2	< 1	4.0	6.2	A
AP-D	45.3	30.7	-14.8	1.2	< 1	6.4	10.0	A
AR-A	9.6	26.5	-14.9	0.8	< 1	3.2	4.4	A
AR-B	7.3	28.2	-14.7	0.8	< 1	2.7	5.5	A
AR-C	5.7	28.4	-13.0	0.2	< 1	4.3	8.1	A
AS-A	64.9	41.2	-7.5	7.0	2.4	5.0	13.4	A
AS-B	61.6	17.1	-0.4	3.0	2.9	5.5	7.4	AA
AS-C	62.2	14.5	0.5	3.7	3.1	3.9	5.4	A
AT-A	30.7	32.9	-11.9	-30.0	< 1	4.4	6.2	A
AT-B	54.8	34.7	-12.5	-28.7	2.6	3.6	7.0	A
AT-C	62.4	28.1	-11.8	-28.3	2.9	2.9	6.1	AA
AU-A	50.0	35.9	15.0	13.0	1.9	7.2	5.3	A
AU-B	35.4	38.0	14.0	11.4	< 1	6.4	7.5	A
AU-C	46.6	35.6	14.2	11.7	2.1	4.4	7.6	A
AW-A	62.4	51.6	-4.8	33.5	2.2	5.8	7.8	A
AW-B	63.1	58.6	-5.4	35.3	2.7	4.1	8.7	A
AW-C	80.9	54.3	3.5	33.5	4.7	5.0	18.6	A
AZ-A	72.0	78.3	-1.5	-0.6	4.2	4.2	9.5	A
AZ-B	71.2	74.5	-1.6	-0.2	6.4	2.7	5.2	A

Table 3. Summary of the Initial Data on the Nature Tone Enamels.

Specimen	Color	Acid Resistance		Gloss	
		Boiling Solubility mg/in^2	Spot Test	45° Specular	Image
MA-3	Yellow Green	2.1	A	6.5	< 1
MA-4	Light Green	0.9	A	1.8	< 1
MA-5	Medium Gray	1.8	A	10.4	< 1
MA-6	Light Red-Brown	1.7	A	8.8	< 1
MA-12	Dark Gray	1.2	A	20.4	< 1
MB-4	Light Yellow Green	9.0	B	8.5	< 1
MB-5	Gray	7.0	A	5.3	< 1
MC-2	Light Blue	1.2	A	22.0	< 1
MC-4	Blue	1.3	A	22.0	< 1
MC-5	Light Gray	1.1	A	25.7	< 1
MC-6	Dark Gray	1.6	A	30.2	< 1
MC-9	Red Brown	1.0	A	30.1	< 1
MC-10	Black	1.1	A	22.4	< 1
MC-12	Light Blue	3.2	A	5.5	< 1
MD-1	Peacock Blue	1.2	A	20.5	< 1
MD-3	Chocolate Brown	0.9	A	25.4	< 1
MD-4	Red Brown	0.9	A	26.6	< 1
MD-5	Dark Gray Black	1.1	A	29.6	< 1
MD-6	Medium Green	0.6	A	48.4	< 1
ME-2	Chartruse	1.7	A	17.6	< 1
ME-3	Medium Gray	0.8	A	18.7	< 1
ME-4	Slate Blue	1.0	A	36.0	< 1
ME-5	Red Brown	0.7	A	21.7	< 1
ME-6	Green	0.9	A	7.2	< 1
ME-7	Dark Gray-Green	1.2	A	12.7	< 1
ME-8	Black	1.9	A	25.6	< 1
ME-9	Steel Blue	0.7	A	20.2	< 1
ME-10	Chocolate Brown	2.6	A	19.1	< 1
ME-11	Brown	0.9	A	1.2	< 1
ME-12	Black	1.3	A	17.1	< 1

Table 4. Correlation of Average Boiling Acid Solubilities with Spot Ratings.

Regular Enamels

Citric Acid Spot Test Rating	Number of Enamels	Boiling Acid Solubility Average mg/in^2	Minimum mg/in^2	Maximum mg/in^2	Range mg/in^2	Standard Deviation mg/in^2
AA	10	1.7	0.5	4.0	3.5	1.3
A	21	2.4	0.9	7.0	6.1	1.3
B	15	9.8	2.1	18.6	16.5	5.4
C	20	55.4	1.2	442.7	441.5	108.9
D	9	128.8	19.2	536.4	517.2	190.6
total	75					

Low-Temperature Enamels

Citric Acid Spot Test Rating	Number of Enamels	Boiling Acid Solubility Average mg/in^2	Minimum mg/in^2	Maximum mg/in^2	Range mg/in^2	Standard deviation mg/in^2
AA	8	7.1	2.8	12.0	11.2	2.6
A	6	14.4	6.2	21.1	14.9	6.9
B	1	11.4	11.4	11.4	---	---
total	15					

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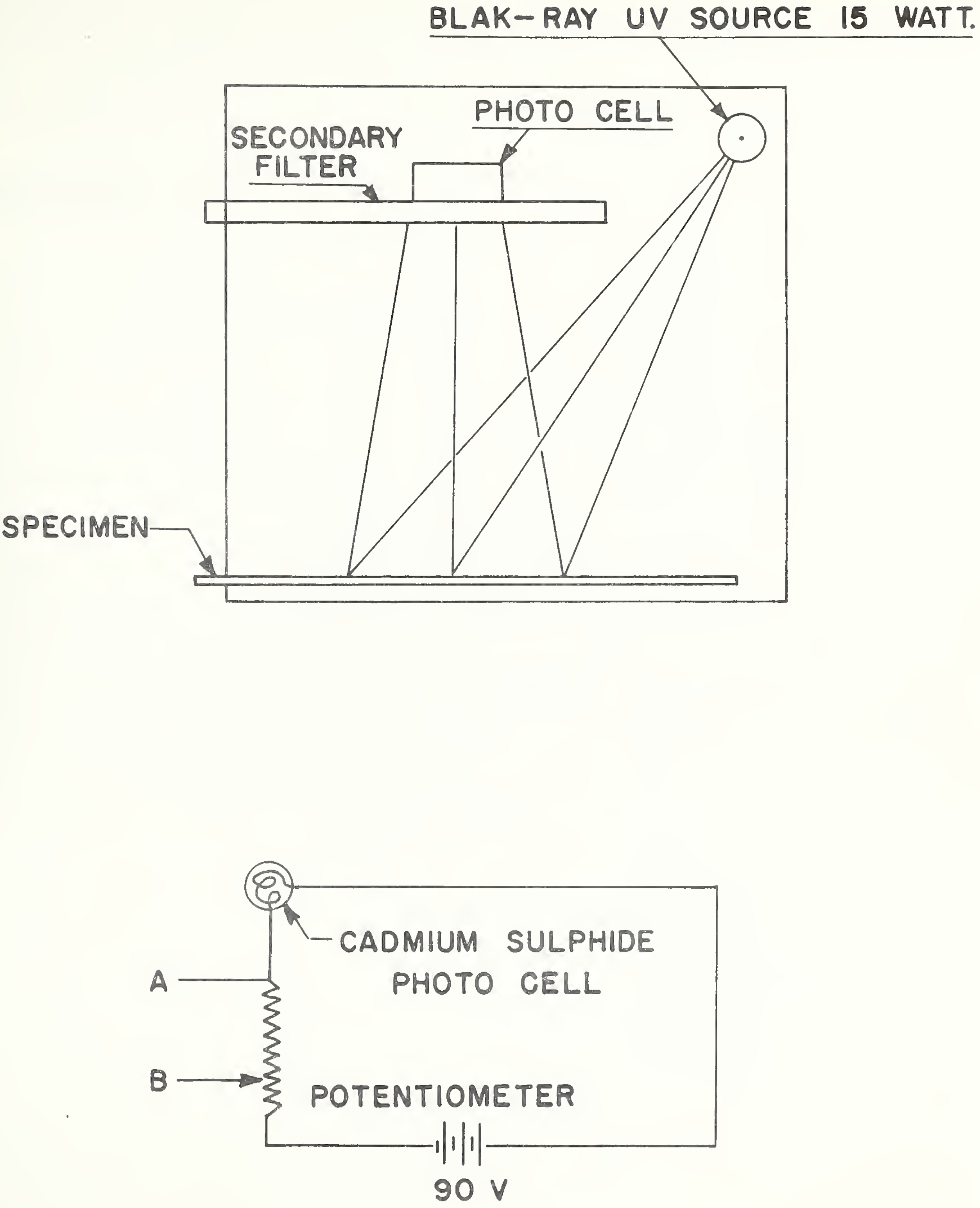


FIG. 1. PROTOTYPE FLUORIMETER AND MEASURING CIRCUIT.

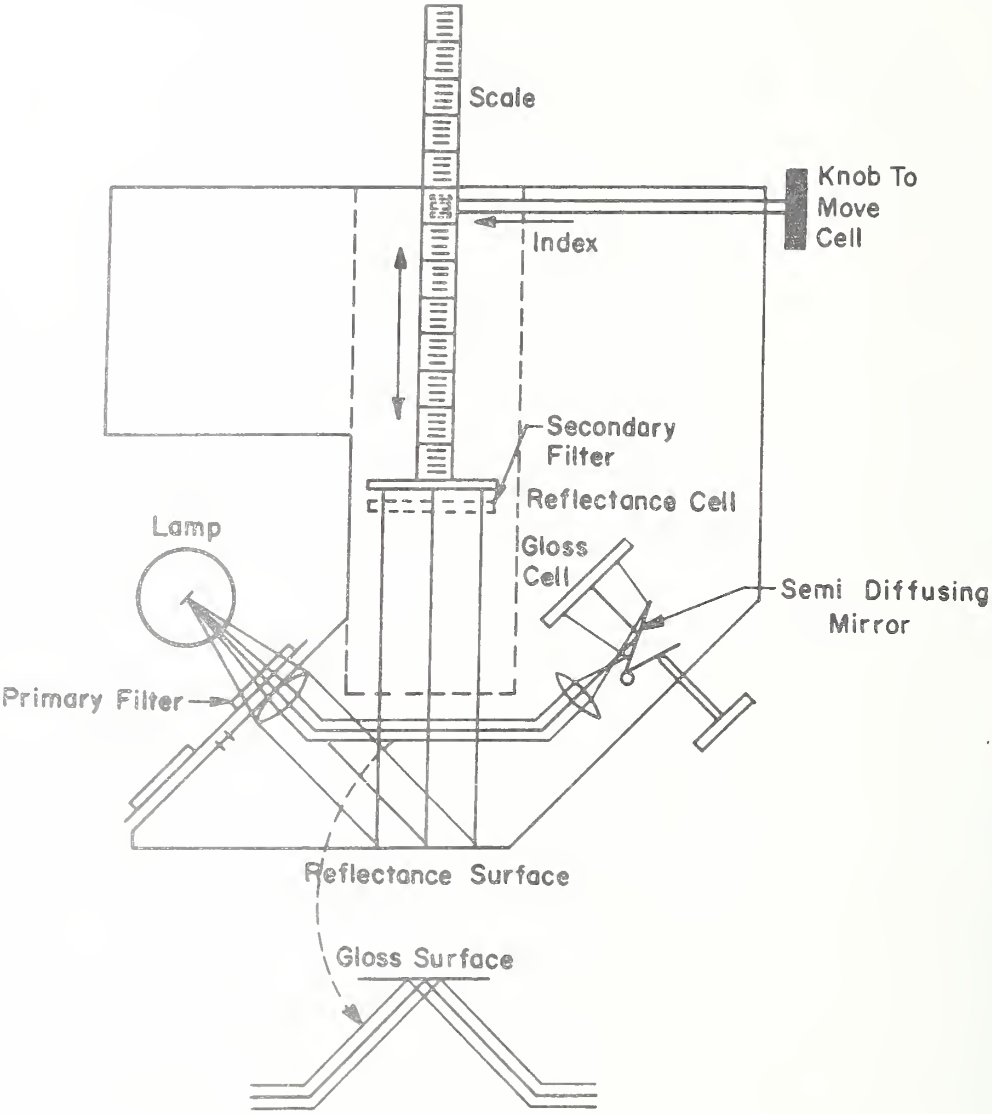
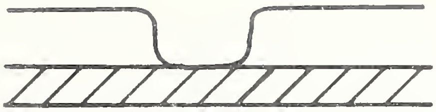


Figure 2. Diagram of Hunter Multipurpose Reflectometer



HOLIDAY

PINHOLE CRACK

BLISTER BURNOFF

SUBSURFACE PORE COPPERHEAD

Figure 3. Schematic drawing of discontinuities in porcelain enamel.

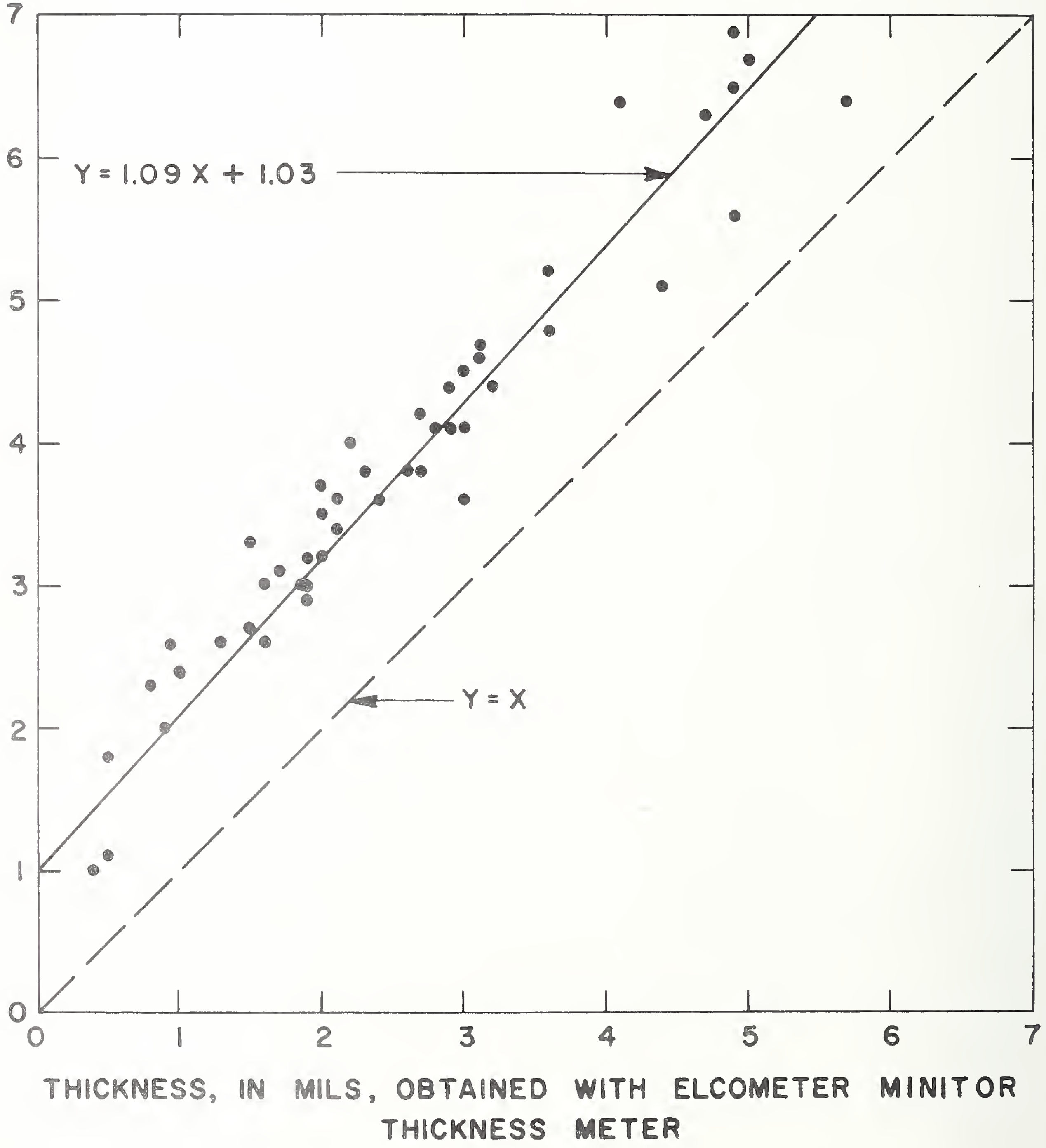


Figure 4. Correction curve for the Elcometer Thickness Meter.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