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NATIONAL BUREAU OF STANDARDS REPORT

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PROGRESS REPORT

October 1 through December 31, 1967

Development of Methods of Test
For Quality Control of Porcelain Enamels

by

M. D. Burdick and M. A. Rushmer

Porcelain Enamel Institute Research Associateship

National Bureau of Standards

Washington, D. C.

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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FOR QUALITY CONTROL OF PORCELAIN ENAMELS

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SUMMARY

A method of wet cleaning was developed which gave reproducible results when a water soluble soil was used in the cleanability test development.

A round-robin test for the calibration of high-voltage test equipment has been completed. These data indicate that each piece of equipment has a distinct calibration curve. Part of the round-robin indicated that the overvoltage necessary to puncture virgin enamels was not the same for all instruments.

An investigation of the effect of abrasion time on the correlation of the PEI and proposed Mechanical abrasion techniques indicated that the two methods correlated for abrasion times less than three minutes.

I. CLEANABILITY

INTRODUCTION

Many different materials must be integrated into a building specification to permit the achievement of structural stability, a safe, useful and aesthetic building design and a maximum life expectancy consistent with overall cost.

Many surface finishes must also be evaluated and specified for use on floors, interior and exterior walls and roofing systems. The final selection of surface finishes often depends on the use of performance type testing procedures to compare, not the individual properties of the various materials but their ability to achieve the performance level necessary and desirable in the service for which they are considered. The equitable selection of performance levels for a bath tub, a floor or wall covering or an appliance finish rests squarely on the existence and use of testing procedures which both simulate service use and are equally applicable to many quite different candidate materials.

The research effort of the Porcelain Enamel Institute research associates is attempting to develop and emphasize the need for testing procedures of the performance type as well as test methods useful within the industry in connection with quality control during production, and reliability estimation.

One project has been concerned with a testing procedure to numerically evaluate the ease or difficulty of cleaning a surface finish. A method has been evolved and previously described which permitted the comparison of the cleanability of porcelain enamels, ceramic tile and glass surfaces. Modifications of this procedure are under study to permit its valid application to a wider variety of finishes which may be considered in performance testing of building and appliance systems.

RESULTS AND DISCUSSION

The previous method for cleanability employed an oily soiling agent which was extracted with an organic solvent. It was found that the small amounts of retained soil were proportional to the time of mechanical cleaning treatment. Porcelain enamels, for instance, were characterized by different cleaning rates and this fact was utilized in the testing procedure developed to assign numbers to the cleaning characteristics of these surfaces. This proportionality of soil retained and cleaning time depended on the oily nature of the standard soil used and its film-thinning tendencies. The method was not applicable to those surfaces affected by the aggressive organic solvent used for extracting the residual soil after the cleaning operation.

Numerous reagents were tried as a base for a soiling agent which could be extracted with water. The dry-wiping technique, used for cleaning the non-drying oily soil did not give reproducible results with the water-soluble soils. The results of experiments with a wet cleaning method have shown some promise of reproducibility and typical results are given in Tables 1 and 2. One cleanability determination was made on each of six specimens of an enamel on each of four days. These data permitted an analysis of variance to separate the variability found from day-to-day from that between specimens. The contribution of all other variables was accumulated as an error variance. The ratio of the day-to-day variance to that attributable to experimental error was indicated as an F ratio. A significance statement was based on a comparison of this ratio with a critical value selected to reflect the sample size and the desired confidence level. If the F ratio exceeded the critical value, the day-to-day variability was considered to be statistically significant at the confidence level selected. Examination of the F ratios associated with "specimens" and "days" in both Tables 1 and 2 leads to the statement that no significance, at the 95 percent confidence level, should be attached to the differences in average results, either from day-to-day or between specimens within the lots tested.

Some of the details of the method used are given below:

Standard Soil

The soiling agent agent used in the tests reported in Tables 1 and 2 had the following composition:

Polyethylene glycol	98.0	percent
Water-soluble dye	1.0	
Uranine	1.0	

Method of Soiling

One drop of the soil was distributed mechanically over an area centrally located on a specimen.

Method of Wet Cleaning

One drop of water was placed on the soiled specimen which was then cleaned mechanically for 15 seconds with a wiping tissue. One more drop of water was added and the cleaning continued for 15 additional seconds with a clean tissue.

This cleaning method was thought to simulate the round-and-round hand cleaning action of a housewife with a damp rag.

Extraction of Retained Soil

The soil remaining on a known area of the specimen was extracted with distilled water. The fluorescence of the extract allowed the calculation of the soil retained, in micrograms per square centimeter.

The results of these cleaning experiments showed a marked difference in retained soil between Enamel 5 with a glossy surface ($0.60 \mu g/cm^2$) and Enamel 3F which had a matte finish (1.16 $\mu g/cm^2$). These results were considered to show a satisfactory degree of reproducibility and were in qualitative agreement with results obtained on the same enamels using the oily soil.

PLANS FOR THE NEXT REPORT PERIOD

Trials of the wet-cleaning method will be made on other porcelain enamels and on other types of finishes to make sure that a cleaning method is selected which will be non-destructive to the softer finishes and also gives results which agree with visual estimates of cleanability.

It is possible that other modifications of the cleaning, soiling or extraction methods will be found which will permit greater reproducibility of results to be obtained.

II. CONTINUITY OF COATING

INTRODUCTION

One of the prime reasons for using a porcelain enamel coating on a metal is to protect the base metal from corrosion. In the past, the application of two to three coats of enamel almost always assured continuity of coating. However, the use of thinner coatings and matte coatings have led to the need for a test for continuity of coating for procelain enamels. Exploratory work indicated that the high-voltage test method offered the most promise of being developed into a test method. A method of calibrating different pieces of test equipment was developed and a round-robin test was initiated among four laboratories that had high-voltage test equipment. The goals of the round-robin test were 1) to determine the calibration curves for the different test equipments and 2) to determine the average overvoltage necessary to puncture virgin enameled specimens. This round-robin testing has been completed and the results are reported below.

RESULTS AND DISCUSSION

The same 150 pre-punctured specimens of 65 different enamels were sent to each of the four laboratories participating in the round-robin test. Each laboratory was asked to measure the thickness of these enameled specimens and to probe their surface to determine the voltage necessary to arc across the previously punctured defects. After these two steps were completed, a calibration curve of the air-gap voltage vs the thickness was calculated. The fitted curve as well as the individual points for Laboratory A's dc test equipment are illustrated in Figure 1 while the fitted curves for all four laboratories are illustrated in Figure 2 (Note that Laboratory A had borrowed Laboratory B's ac test equipment to determine this curve).

The second part of the round-robin test consisted of puncturing virgin porcelain enameled specimens and determining the voltage in excess of the air gap voltage necessary to puncture the specimens. This voltage will be referred to as overvoltage. The overvoltage curves are presented in Figure 3. It was felt that these curves would be similar for the three laboratories using ac test equipment. Although a statistical analysis of the slope and intercept values of these three curves indicated that no significant differences existed among them, it was still felt that better agreement would be desirable particularly when specifying overvoltages necessary if this test method were ever to be incorporated into product specifications.

It was initially thought that differences in input voltages at the various laboratories might affect the results. However, close perusal of the literature about the ac test equipment indicated that the high voltage meter on the instrument was connected directly across the high-voltage output. Therefore it should be accurate regardless of the input voltage. The dc test equipment literature did not indicate this, but checks of the output voltage showed no difference when the input voltage was varied from 90 to 124 volts. Therefore, the effect of input voltage was eliminated from further consideration as a variable that might have caused Laboratory B's overvoltage curve to differ from those obtained at Laboratories C and D.

Upon careful survey of the results it was recalled that the calibration procedures at Laboratories A and B were carried out using older probes that were beginning to show wear while Laboratories C and D were given new probes. It is possible that the differences in the condition of the probes could account for the differences in the overvoltage curves.

PLANS FOR NEXT REPORT PERIOD

During the next report period, it is planned to recalibrate Laboratory B's high-voltage test equipment using a new probe and to redetermine the overvoltage curve to see if this instrument will agree with those at Laboratories C and D. It is also planned to check the wave form of the output voltage of Laboratory B and D's instruments to see if they differ.

III. SCRATCH ABRASION

INTRODUCTION

Almost all products designed for use in the home are subjected to some type of abrasion. There have been many types of abrasion tests developed, but few of these have given quantitative results or have agreed with the results of field exposure.

One of the current goals of the Porcelain Enamel Institute Research Associateship is to develop a performance oriented scratch-abrasion test.

RESULTS AND DISCUSSION

Work on the development of a performance oriented abrasion test has closely followed the development of the cleanability test work. It was found that the change in dirt retained on a specimen before and after abrasion gave an indication of the abrasion damage of porcelain enamels that not only agreed with the way people ranked the damage, but it also ranked the enamels in the same way, regardless of the method used to cause the abrasion.

Specimens of a porcelain enamel on steel and a porcelain enamel on aluminum were abraded for periods of 1, 2, 4, and 8 minutes using both the PEI and the proposed Mechanical Abrasion techniques. This was done to determine 1) the effect of abrasion time and 2) to determine a suitable abrasion time. After these enamels were abraded it was noted that a change in the relative severity of attack occurred after approximately four minutes of abrasion with the PEI abrader, as illustrated in Figure 4. This was not considered objectionable since visual observation by four observers indicated that an enamel appears unsightly after it had been subjected to two minutes abrasion by either the PEI or Mechanical abrading techniques.

PLANS FOR NEXT REPORT PERIOD

Since both the PEI and the Mechanical abrasion techniques rank different enamels in the same order and are reproducible, it is planned to see if either of these two methods can be used on competitive organic materials and, if not, to modify the method of abrasion to make it applicable to the organic finishes as well as porcelain enamel.

Table 1. Four Independent Determinations on Each of Six Specimens of Glossy Enamel No. 5 Using Soil XIV and Wet Cleaning. The Values in the Body of the Table are in $\mu g/cm^2$.

Specimen No.	Days				Ave.
60	0.43	0.61	0.52	0.72	0.57
140	.50	.64	.68	.74	.64
51	.83	.61	.62	.55	.65
54	.51	.68	.44	.54	.54
55	.65	.54	.72	.50	.60
56	.43	.75	.55	.52	.56
Ave.	0.56	0.64	0.59	0.59	0.60±0.04

Analysis of Variance

Variance Associated With:	Degrees of Freedom	Sum of Squares	Variance	F Ratio	Critical Value
Specimens	5	0.03918	0.00783	0.53	2.90
Days	3	.01933	.00644	.44	3.29
Error	15	.22164	.01477		
Total	23	.28015			

Conclusions: There is no significant difference between the specimens.

There is no significant difference between the individual determinations on different days.

Table 2. Four Independent Determinations on Each of Six Specimens of Matte Enamel 3F Using Soil XIV and Wet Cleaning. The Values in the Body of the Table are in μg/cm^2.

Specimen No.	Days				Ave.
2	1.21	1.20	1.39	0.83	1.16
3	1.38	0.92	1.51	.90	1.18
4	1.01	1.10	1.04	.89	1.01
5	1.52	0.90	1.10	1.31	1.21
6	0.85	1.13	1.48	1.02	1.12
8	1.30	1.44	1.51	0.82	1.27
Ave.	1.21	1.12	1.34	0.96	1.16±0.08

Analysis of Variance

Variance Associated With:	Degrees of Freedom	Sum of Squares	Variance	F Ratio	Critical Value
Specimens	5	0.15264	0.03052	0.62	2.90
Days	3	0.45474	0.15158	3.07	3.29
Error	15	0.74035	0.04935		
Total	23	1.34773			

Conclusions: There is no significant difference between the six specimens.

The difference between the different days approaches significance.

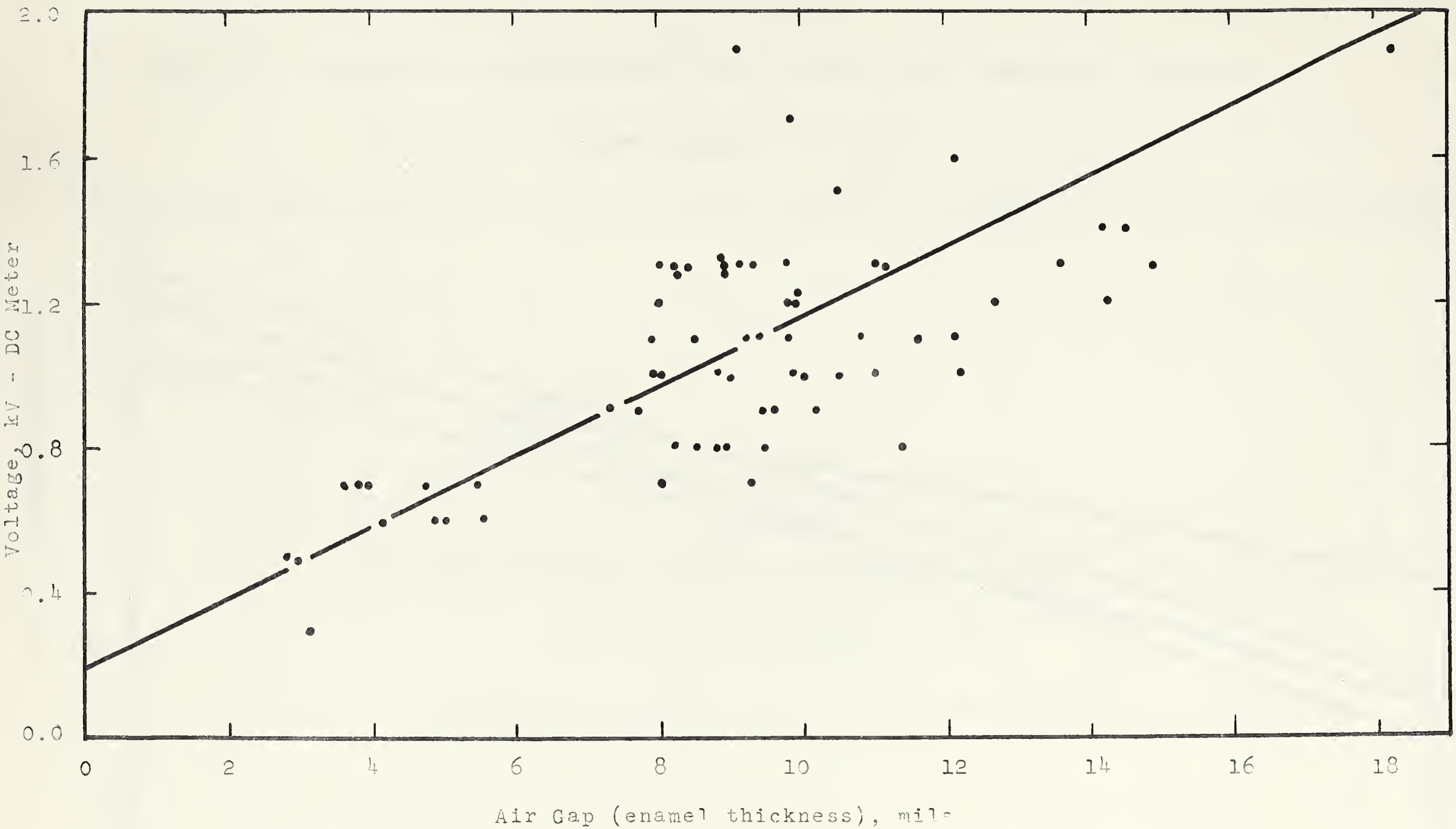

Figure 1. Calibration Curve for **Uvral**, DC Test Equipment

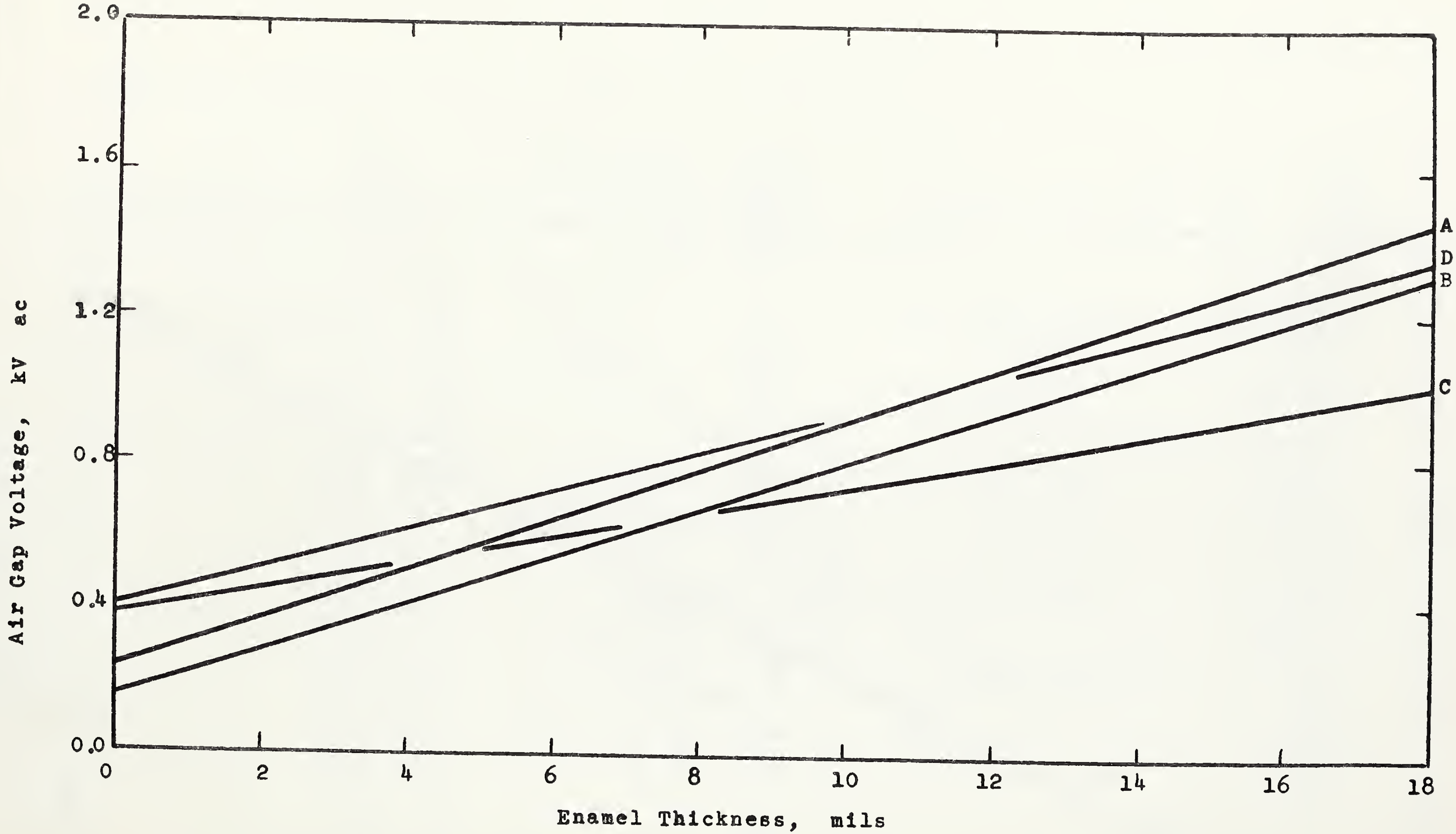

Figure 2. Comparison of Calibration Curves for the Four Cooperating Laboratories.

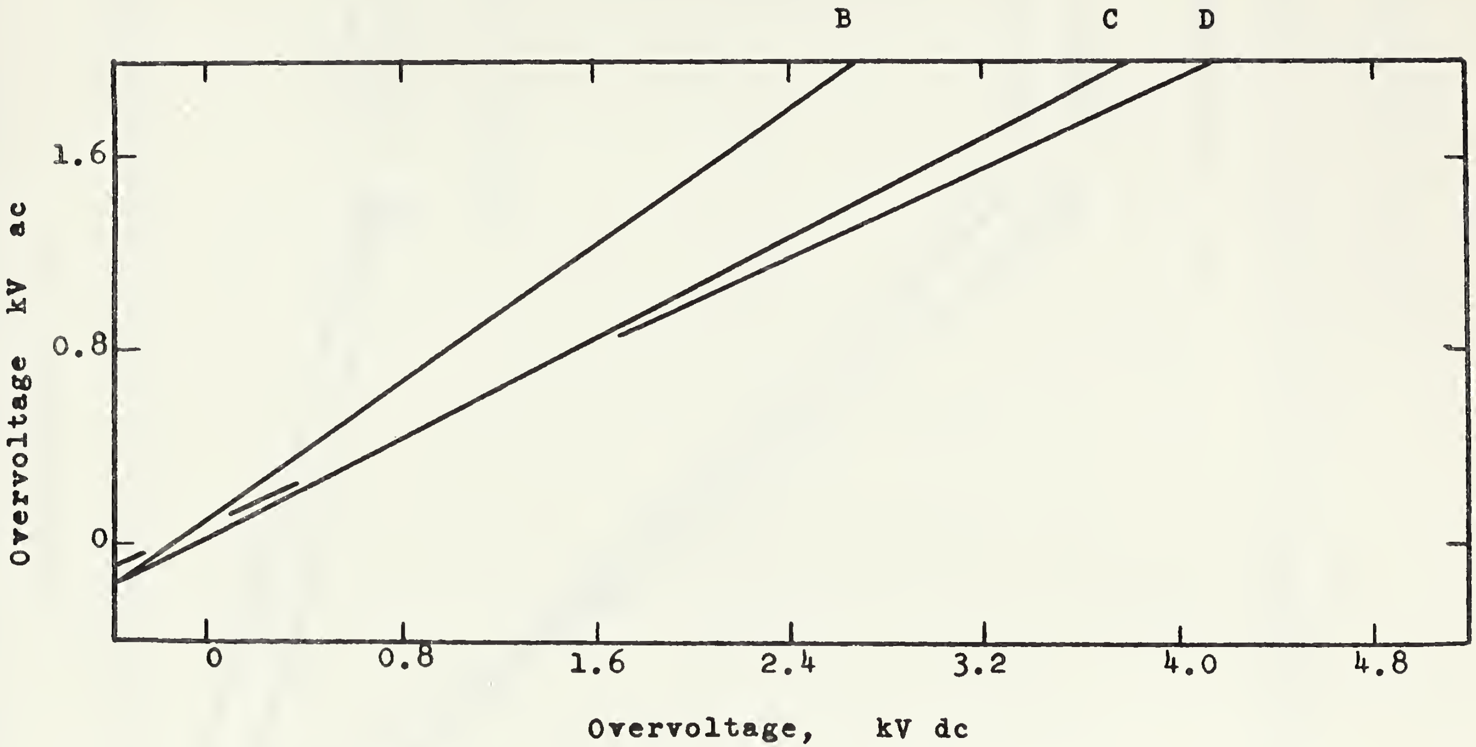

Figure 3. Comparison of Overvoltages for all Laboratories Participating in the Round-Robin Test.

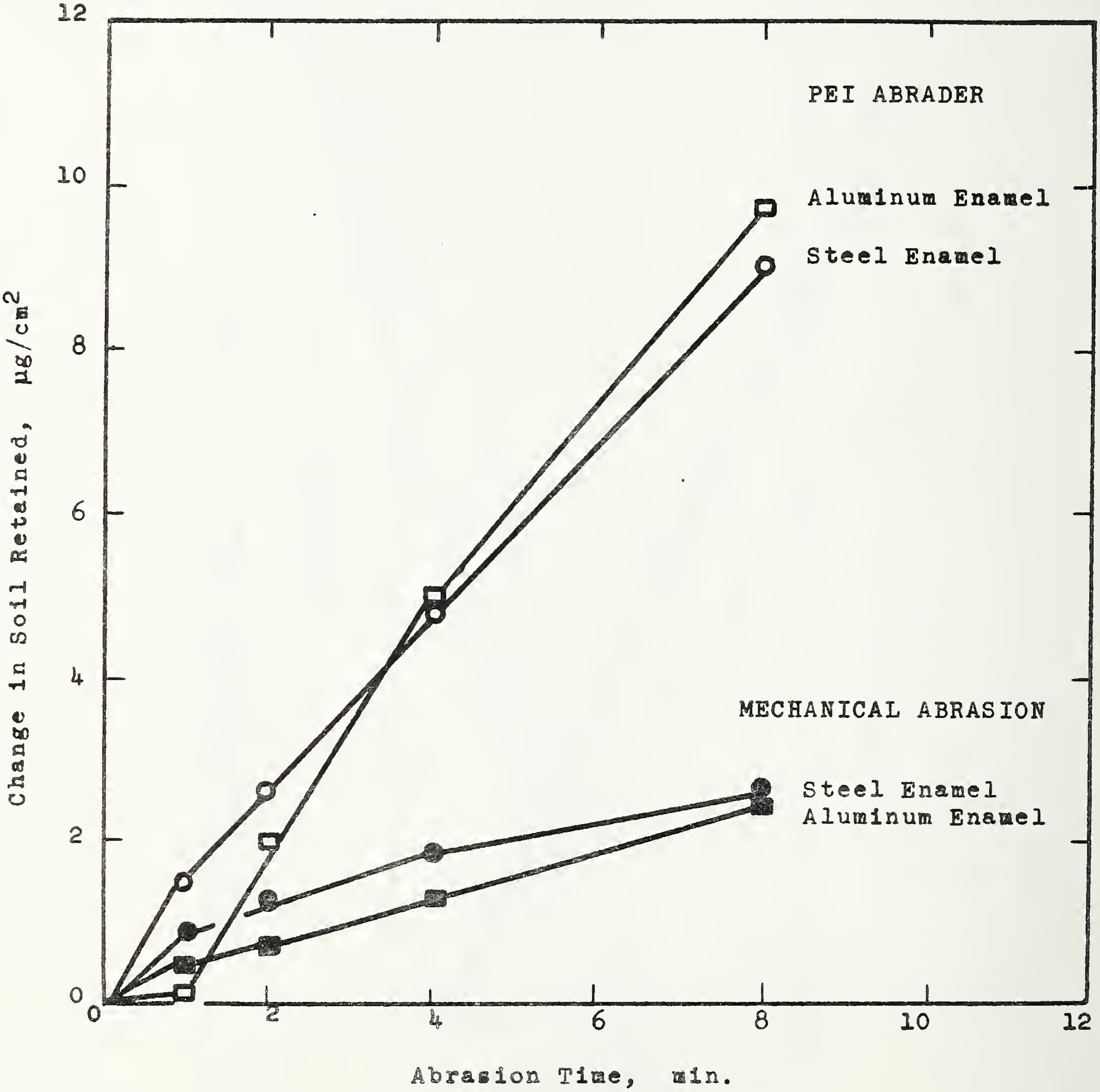

Figure 4. Comparison of Change in Soil Retained for Enamels Abraded Mechanically and with the PEI Abrader.

MISCELLANEOUS ACTIVITIES

The Hoover Instrument Service at Mansfield, Ohio has expressed an interest and shown a capability of serving as a manufacturing source for the PEI alkali test equipment. A trip to Mansfield was made by M. D. Burdick to familiarize them with the present equipment design and to discuss possible changes in the equipment which might be desirable from a manufacturing viewpoint and to make sure that the operating characteristics of the equipment would not be altered. This company has several industry requests for alkali equipment. It was desirable that the above dialogue take place before they start the production of any units for industry use.