NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

January 1 through March 31, 1970

DEVELOPMENT OF METHODS OF TEST FOR QUALITY CONTROL OF PORCELAIN ENAMELS

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
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[3] Located at 5285 Port Royal Road, Springfield, Virginia 22151.

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DEVELOPMENT OF METHODS OF TEST FOR QUALITY CONTROL OF PORCELAIN ENAMELS

by
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National Bureau of Standards

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INTRODUCTION

A considerable portion of the porcelain enamel appliance industry monitors the quality of adherence of cover coats direct-to steel through the use of deformation-type tests. The extent and appearance of the glass coating that remains attached to the metal substrate within the deformed area serves as an indicator of bonding between coating and substrate. One of the widely used methods of producing controlled deformed areas for examination employs a drop-weight device. A hemispherical indenter impacted by a falling weight deforms an enameled piece into a circular die cavity. Experienced observers evaluate the bond quality based on the extent of oxidized metal exposed as well as on the configuration of glass slivers remaining attached to the base metal.

The experiments described in this report have suggested a testing procedure to obtain an instrumental determination of adherence without further dependence on the somewhat subjective judgements of experienced observers.

RESULTS & DISCUSSION

A. An Industry Consensus of Visual Rating.

It was desired to look at the present state-of-the-art of adherence evaluation by drop-weight testing. Three laboratories which depended on this type of adherence monitoring in their plant, volunteered to take part in these comparative tests.

1. Specimens used

A series of ten direct-on cover coats was described in the previous report. Each enamel system was designated by two code letters; the first identified the five different enamel compositions: A, B, C, D and X (including two colors and white); and the second letter identified four levels of pickling treatment: "normal" (N), "intermediate" (M), "poor" (P) and no pickling (O). Thus, AM represented enamel A applied to a substrate prepared by an intermediate pickling with a normal nickel flash. This group of enamel systems included a variety of steels, metal treatments and enamel compositions and seemed appropiate for use in these industry-wide tests of visual rating after drop-weight deformation.

2. Comparison of Results Obtained

Table 1 gives the ratings assigned by the cooperating laboratories together with the number of "counts" obtained with the PEI Adherence

Meter for these deformed specimens. Some of the values for meter counts were measured and reported by the rating laboratories. Others were obtained by "counting" the specimens after their return to NBS. The visual rating was reported in five levels of quality - numbers from 1 to 5. The ratings given in Table 1 used the scale of 1 to 5 with 1 representing the highest level of adherence and 5 representing the poorest grade. One laboratory used the 1 to 5 rating with 1 representing the poorest. Their ratings were reversed, 1 for 5; 2 for 4; etc. before entering in Table 1. It can be seen that the best agreement between ratings was obtained for grades 1 and 5 where the quality was obviously very good or very poor. A line dividing satisfactory from unsatisfactory must then fall somewhere among the ratings of 2, 3 and 4. It was among these intermediate ratings that the poorest agreement was obtained. Laboratory D rated seven of the systems grade 5 (poorest) while Laboratory B found only one system (BO) which they rated 5. System BO was an enamel applied to an unpickled substrate with no nickel applied. All laboratories were in agreement that BO had poor adherence!

3. Analysis of Results of Rating

Several steps were followed to determine a relationship between meter counts and visual ratings, if any existed.

a) A plot of "average" meter counts of deformed specimens of each enamel as a function of the average assigned rating showed a marked linear, or nearly linear relationship. This offered encouragement to proceed to the next step.

b) The individual assigned ratings were plotted against the meter counts for that indentation. The stressed area of a specimen, deformed by a drop weight device, divided by the needle density within the adherence meter cluster yields a maximum of 75 needles within the stressed area. All counts over 75 were considered to have occured in areas adjacent to the stressed area and were disregarded. A point was plotted as though the count had been 75. This plot, shown in the top portion of Figure 1, illustrates the wide variation in meter counts associated with ratings of 3, 4 and 5. Neither the least squares solid line nor a polynomial fit (dashed curve) could be considered a good fit because of the wide scatter. Several other plots and curves with their associated "F" ratios (see Table 2) led to the selection of the log-log plot shown at the bottom of Figure 1. This plot compressed the data in such a way that the scatter was materially reduced, the "F" ratio was maximized and the relationship appeared to be a linear one.

c) Solutions of the Curve of Best Fit. Table 3 gives solutions of the log-log relationship, expressed in Table 2, to serve as a guide for rating the adherence of direct-on porcelain enamel systems.

B. Comparison of Visual and Instrumental Rating.

The data given in Table 4 allow a comparison of the visual and instrumental rating (see Table 3) of the adherence of ten enamel systems. The average ratings by the three laboratories illustrate the apparent bias of laboratory D in assigning visual ratings. The instrumental ratings on the other hand, show a good agreement between laboratories. The average standard deviations show a marked reduction when the instrumental procedure is used. More careful methods for analyzing collaborative tests 1/ are available to separate random errors (precision within a single laboratory) between laboratories. Calculations, not given here, show that both random and systematic errors are reduced by a factor of 0.6 through the adoption of the instrumental technique.

Phase II of this cooperative testing, which is underway, employs a separate group of cover coat enamels direct-to-steel. The second group of specimens was prepared with the same steel, the same pickling treatment, the same enamel composition but with controlled nickel deposits to achieve different levels of adherence quality. The second phase involves visual rating of already deformed specimens by the cooperating laboratories, in sequence. By this modification of the procedure used in Phase I it is hoped to avoid specimen-to-specimen variation as well as variability due to the use of drop-weight devices with different die sizes and conditions of wear, indentor geomtries and impact energies.

Preliminary measurements on the specimens used for Phase II are shown in Figure 2 and Table 5. The composite stnadard deviation of meter counts for specimens deformed over 5/8-inch die were 1.6 times that found for the 3/4-inch die. This was probably associated with the fact that the 5/8-inch die was well-worn while the 3/4-inch die was previously unused.

C. Conclusions from this Experiment

It has been shown that the instrumental rating system:

1. Results in increased precision within a laboratory

2. Achieves better agreement between laboratories and,

3. Does not depend on the subjective judgment of an experienced observer.

REFERENCE

1. Statistical Techniques for Collaboorative Tests, W. J. Youden, published by the Association of Official Analytical Chemists, Box 540, Benjamin Franklin Station, Washington, D. C. 20044 (1967).

PLANS FOR THE NEXT REPORT PERIOD.

A program of evaluation using the recently obtained DOAAC series of specimens of cover coats direct-to-steel, will be undertaken using a motorized adhesion tester. Parameters which will be recorded are: (1) stress at failure; (2) The appearance and location within the system, of the fracture surface monitored, at high and low magnification, under the scanning electron microscope; (3) the amount of nickel deposition applied during the metal preparation, as well as other parameters which seem relevant. Electron microprobe traces across polished sections near the ceramic-metal interface will be obtained if exploratory tests appear to justify this type of study.

MISCELLANEOUS ACTIVITIES

A series of Image Gloss standard specimens was calibrated with the cooperation of ten NBS observers. A supply of these calibrated standards is maintained for users of the Distinctness-of-Image gloss test.

A new office space for the Research Associates was assigned and occupied during the period.

A publication appearing as NBS Building Science Series No. 29 entitled "1964 Exposure Test of Porcelain Enamels on Aluminum, Three Year Inspection" by Margaret A. Baker, became available for distribution by NBS and the Porcelain Enamel Institute.

A paper entitled "High Voltage Tests Porcelain Enamel Coatings" by Margaret A. Baker appeared in Appliance magazine, February, 1970, and a short summary of the same paper appeared in Materials Engineering for February 1970. This paper was presented at the 1969 PEI Forum and will soon be available in the Proceedings of that Forum.

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TABLE 1 RESULTS OF A COLLABORATIVE TEST ON THE ADHERENCE OF COVER COATS DIRECT-TO-STEEL.

PEI Adherence Meter Counts and Visual Rating of Drop-Weight Deformed Companion Specimens in Three Laboratories.

Code	PEI Designation	PEI Meter Counts Lab B	Lab C	Lab D	Visual Rating by: Lab B	Lab C	Lab D
1	AM	53	75	56	3	4	5
2	BO	152	134	132	5	5	5
3	CP	85	102	74	4	5	5
4	DM	26	15	36	2	1	4
5	XP	67	64	60	4	4	5
6	AN	13	9	15	1	1	1
7	BN	52	35	40	3	3	3
8	CM	59	67	52	3	4	5
	CM	77	--	--	4	-	-
9	DN	78	84	76	4	4	5
10	XN	75	32	54	4	3	5

TABLE 2 VARIOUS CURVES TO DETERMINE THE BEST FIT TO PLOTS OF NUMBER OF COUNTS AND AN INDUSTRY CONSENSUS OF ADHERENCE QUALITY RATINGS ON A SCALE OF 1 TO 5.

Plot 1/	Equation of Curve	"F" Ratio 2/
y vs x	$y = 0.88519 + 0.05081\ x$	72
log y vs x	$\log y = 0.03756 + 0.00881\ x$	88
y vs log x	$y = -3.9224 + 4.51306 \log x$	97
y vs x	$y = -0.5577 + 0.1341\ x - 0.00090\ x^2$	104
log y vs log x	$\log y = -0.85368 + 0.81084 \log x$	175

1/ y is the visual rating on a scale of 1 to 5
x is the number of counts on a PEI Adherence meter

2/ "F" ratio is the ratio of "explained variance to the unexplained." A maximum ratio indicated the best fit.

TABLE 3 AN INSTRUMENTAL GUIDE FOR RATING THE ADHERENCE OF COVER COATS DIRECT-TO-STEEL 1/

PEI Meter Counts	Adherence Rating	PEI Meter Counts	Adherence Rating	PEI Meter Counts	Adherence Rating
1	0.1	28	2.1	55	3.6
2	0.2	29	2.1	56	3.7
3	0.3	30	2.2	57	3.7
4	0.4	31	2.3	58	3.8
5	0.5	32	2.3	59	3.8
6	0.6	33	2.4	60	3.9
7	0.7	34	2.4	61	3.9
8	0.8	35	2.5	62	4.0
9	0.8	36	2.6	63	4.0
10	0.9	37	2.6	64	4.1
11	1.0	38	2.7	65	4.1
12	1.0	39	2.7	66	4.2
13	1.1	40	2.8	67	4.2
14	1.2	41	2.8	68	4.3
15	1.3	42	2.9	69	4.3
16	1.3	43	3.0	70	4.4
17	1.4	44	3.0	71	4.4
18	1.5	45	3.1	72	4.5
19	1.5	46	3.1	73	4.5
20	1.6	47	3.2	74	4.6
21	1.7	48	3.2	75	4.6
22	1.7	49	3.3	76	4.7
23	1.8	50	3.3	77	4.7
24	1.8	51	3.4	78	4.8
25	1.9	52	3.4	79	4.8
26	2.0	53	3.5	80	4.9
27	2.0	54	3.6	81	4.9
				82	5.0

1/ Based on the relationship:

$$\log y = -0.85368 + 0.81084 \log x$$

Where x = PEI Meter counts on a drop-weight deformed specimen

y = an instrumental adherence rating equivalent to the currently used visual rating on a scale of 1 to 5. (1 is the best and 5 is the poorest).

TABLE 4 A COMPARISON OF TWO METHODS OF EVALUATING DIRECT-ON ADHERENCE BASED ON DROP-WEIGHT DEFORMATIONS.

Enamel System	Visual Rating by Experienced Observer				Instrumental Rating Based on Meter Counts			
	Lab B	Lab C	Lab D	Standard Deviation	Lab B	Lab C	Lab D	Standard Deviation
1 AM	3	4	5	1.0	3.5	4.6	3.7	0.59
2 BO	5	5	5	0.0	5.0	5.0	5.0	0.0
3 CP	4	5	5	0.59	5.0	5.0	4.6	0.23
4 DM	2	1	4	1.53	2.0	1.3	2.6	0.65
5 XP	4	4	5	0.59	4.2	4.1	3.9	0.16
6 AN	1	1	1	0.0	1.1	0.8	1.3	0.25
7 BN	3	3	3	0.0	3.4	2.5	2.8	0.46
8 CM	3	4	5	1.0	3.8	4.2	3.4	0.40
9 DN	4	4	5	0.59	4.8	5.0	4.7	0.16
10 XN	4	3	5	1.0	4.6	2.3	3.6	1.15
Average	3.3	3.4	4.3	0.63	3.7	3.5	3.6	0.40

1/ The standard deviation among the laboratory ratings was used as a measure of the between-laboratory variability.

TABLE 5 DOAAC Specimens; Drop-Weight Deformed Using 3/4 and 5/8 in. dies and 70, 80 and 90 in-lbs - Impact Energy

Die	Enamel No.	Individual Values				Ave.	S.D.
		70 in-lbs					
3/4"	1	59.7	56.7	58.0	66.7	60.3	4.46
	2	48.0	52.7	41.7	43.3	46.4	4.96
	3	21 7	41.3	33.7	25.7	30.6	8.70
	4	19.0	28.7	16.0	19.0	20.7	5.53
	5	23.0	9.3	11.7	14.7	14.7	5.97
						mean	5.92
5/8"	1	85.0	55.7	76.0	65.7	70.6	12.68
	2	7.7	18.0	42.7	27.3	25.2	27.02
	3	9.3	28.7	17.3	2.7	14.5	11.19
	4	11.7	24.3	11.7	12.3	15.0	6.21
	5	9.0	5.3	6.0	1.0	5.3	3.30
						mean	12.1
		80 in-lbs					
3/4"	1	62.0	65.7	58.3	54.0	60.0	5.01
	2	56.3	48.0	48.3	49.7	50 6	3.89
	3	38.7	47.0	34.7	40.7	40.2	5.13
	4	28.7	27.3	17.0	27.7	25.2	5.48
	5	20.7	13.7	24.0	17.3	18.9	4.43
						mean	4.79
5/8"	1	79.0	55.7	65.3	75.3	68.8	10.49
	2	51.3	43.3	10.3	44.3	37.3	18.35
	3	16.3	14.3	23.0	33.3	21 7	8.57
	4	10.0	17.7	11.7	8.3	11.9	4.09
	5	5.7	5.7	4.7	7.3	5.8	1.08
						mean	8.52
		90 in-lbs					
3/4"	1	38.7	60.7	54.0	55.0	52.1	9.41
	2	48.0	45.7	46.3	47.0	46.8	0.99
	3	61.7	21.7	41.7	33.7	39.7	16.81
	4	34.7	27.7	43.0	24.3	32.4	8.27
	5	23.7	18.7	19.7	17.7	20.0	2.63
						mean	7.62
5/8"	1	88.3	60.3	68.7	70.3	71.9	11.78
	2	27.0	20.7	22.3	24.7	23.7	2.76
	3	66.3	21.7	20.7	24.3	33.2	22.09
	4	7.7	12.0	11.7	15.7	11.8	3.27
	5	13.0	9.3	9.3	12.3	11.0	1.96
						mean	8.37

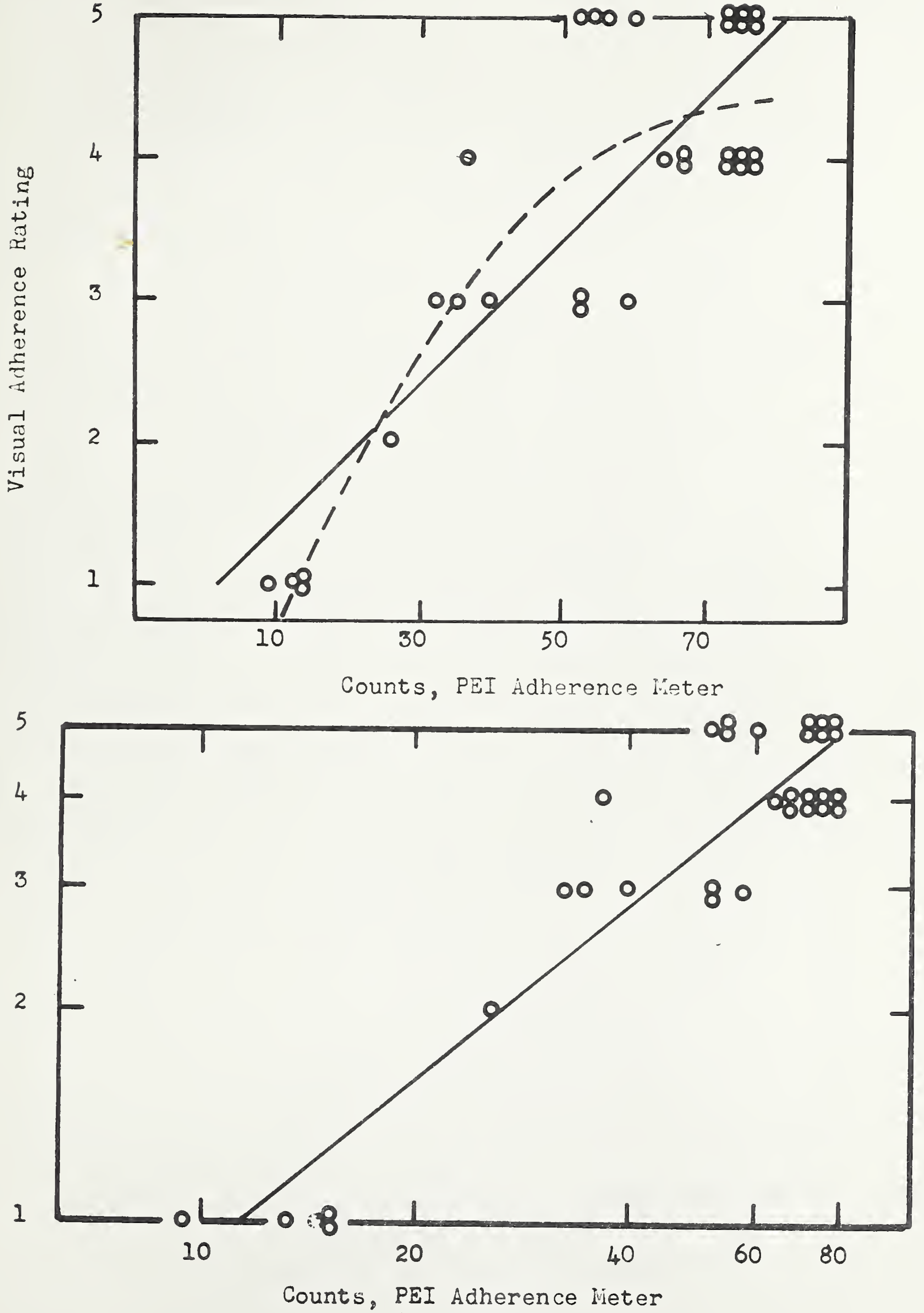

Figure 1 The Relationship Between Visual Adherence Rating And The Counts With PEI Adherence Meter for Several Porcelain Enamels. Top: Arithmetic Scales; Bottom: Logarithmetic Scales.

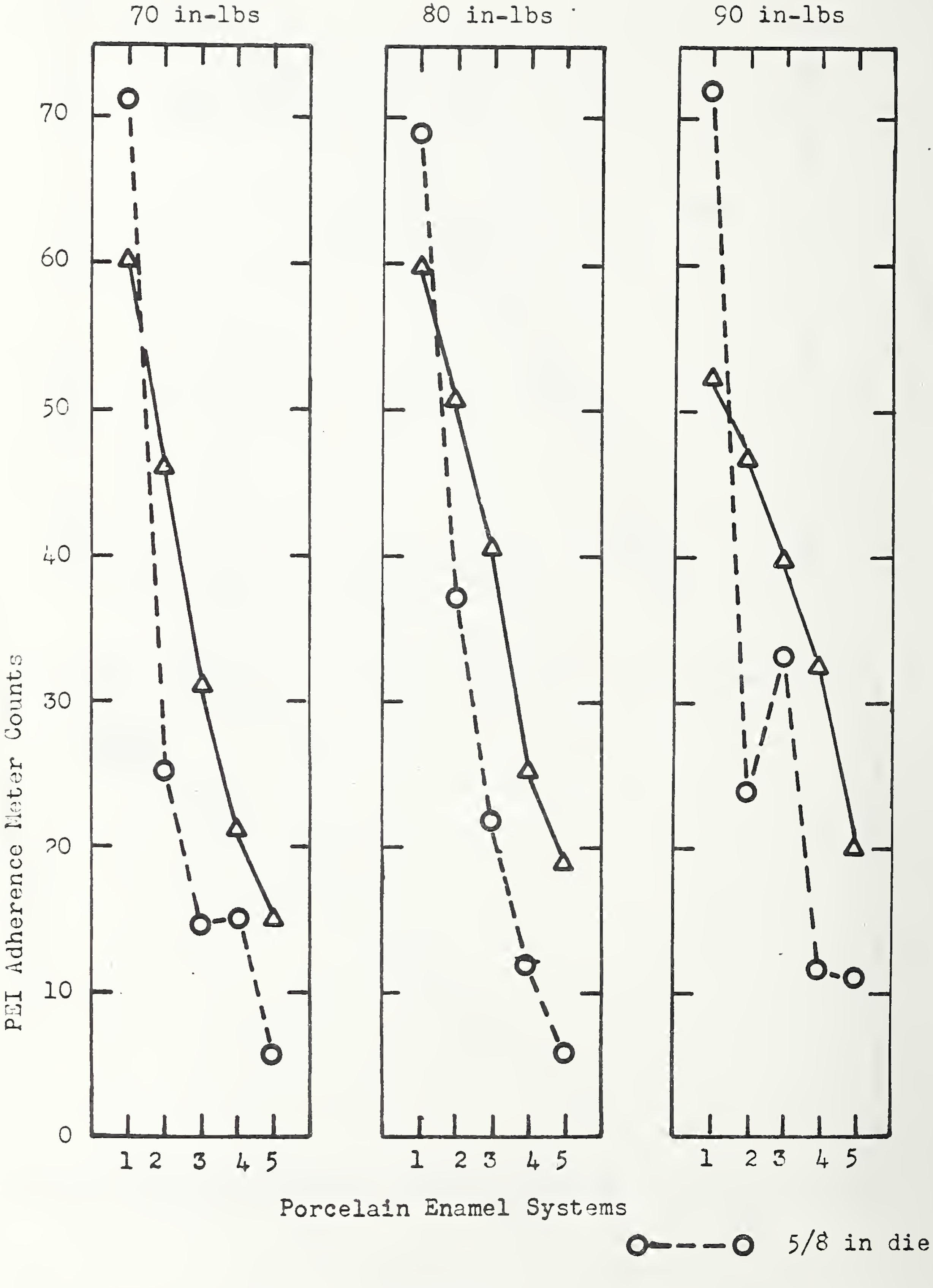

Figure 2 Effect of Die Size and Impact Energy on PEI Adherence Meter Response

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