NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

October 1 through December 31, 1969

DEVELOPMENT OF METHODS OF TEST FOR QUALITY CONTROL OF PORCELAIN ENAMELS

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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DEVELOPMENT OF METHODS OF TEST FOR QUALITY CONTROL OF PORCELAIN ENAMELS

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I. The Adherence of Porcelain Enamels Direct-to-Steel

INTRODUCTION

The objective of this study is to develop a new method or to modify existing methods for measuring the quality of adherence in direct-on porcelain enamel production.

A number of plant visits have been made to survey existing adherence methods and to assess industry needs in this area of quality control.

The work described in this report was intended to compare, quantify and correlate several existing destructive, deformation techniques related to the evaluation of adherence.

RESULTS AND DISCUSSION

A. Enamel Systems

A series of ten cover coats direct-to-steel was described in the previous report in this series. Each enamel system was designated by two code letters; the first identified the five different enamel compositions: A, B, C, D and X; and the second letter identified the pickling treatment: N, M. P and O described in Table 1. The enamel systems in the above described series were used in the present evaluations.

B. Deformation Methods Employed

1. A "stretch" test described by J. E. Sams[1/] produced a flat, uniformly deformed specimen area which was thought to contribute to a more objective visual or instrumental rating than did the concave surface obtained from an indentation-type of deformation. Strip specimens, about 3/4 inch in width and 4 to 6 inches long were de-enameled at each end by sand blasting to provide uniform gripping in a tensile machine. Load was applied beyond the yield point of the steel to provide an elongation of between 8 and 10 per cent. When adherence was poor, after the bulk of the enamel layer chipped away, mainly bare metal of a light grey color was exposed in the stretched area. With improved adherence, greater amounts of glass were left attached to the substrate which resulted in darker grey colors and decreased reflectance. Those enamel systems showing the best adherence (estimated by other methods) appeared dark grey after stretching and the reflectance of the pulled specimen area was thought to be influenced more by the adherence than by the color of the original glass coating.

2. Impact Deformation Test

A conventional drop-weight test was used to estimate adherence of the direct-on systems for comparison with other estimates. A five pound weight falling through a distance of 16 inches impacted a one-half inch diameter ball indenter resting on the specimen and centered over a 5/8 inch bottomless die. The indentations were evaluated with a PEI adherence meter to obtain numerical results. The adherence index was calculated as: $AI = \frac{75 - X}{75} \times 100$ where X was the average number of counts obtained for each indentation. This modified method of calculation was intended to compensate for a smaller area of indentation than that obtained with a one inch ball indenter in the PEI press. This method of calculation was previously used by Afflerbach. [2/]

3. Adherence Tests with the PEI Equipment

All of the direct-on systems were evaluated with deformations obtained with the 20 gage and Research dies, with and without water immersion after deformation, and after immersion in still and ultrasonically agitated water. The amount of bare metal was estimated in the usual way with the PEI counter.

C. Relative Severity of the Deformation Methods

A compilation of all adherence estimates is given in Table 2. The use of the 20 gage die, with a depth of 0.156 inch, produced mild deformations. The enamel layers were cracked in six of the ten systems tested but remained attached to the substrate in such a way that no bare metal was found by the needle probes. The remaining four systems, obviously with poorer adherence, had lowered adherence indices. It is not unreasonable, in view of later results, to assume that there may be differences in adherence among the six systems which were not resolved with the 20 gage die deformations. It was desired to use a modified die form or other treatments which would increase the severity of the test procedure and resolve differences in adherence which might be expected to obtain within a series of systems deliberately designed to include a wide range of adherence values. The difficulty of this operation is obvious. How can one resolve differences in adherence which are only assumed, without a referee test for adherence measurement?

Water immersion of deformed specimens before counting appeared to be an effective way to obtain increased removal of cracked enamel (increased severity of the test procedure). This is illustrated in Figures 1 and 2.

The use of the deeper research die (depth 0.190 in.) appeared to be effective in increasing the severity of the test procedure as shown in Figure 3. The adherence indices obtained with the drop weight test appeared to be still lower and are also shown in Figure 3. It may be noted, however, that the drop weight indices fail to resolve any assumed differences between systems XP, CP, and BO. Perhaps this drop weight procedure is too severe for the range of adherence values among these specimens. Even the ball peen hammer (a classical method for demonstrating lack of bond) showed a difference in adherence between BO on the one hand and the "poorly" pickled enamels X and C.

Comparison among the deformation methods shown in Figures 1, 2, and 3 suggest that the order of increasing severity was as follows:

1) (least severe) 20 gage die, dry; 2) 20 gage die, wet; 3) research die, wet, and 4) drop weight test. The mildest deformation method failed to resolve assumed differences among the good adherence enamel systems, and the drop weight deformations failed to separate several of the poor adherence systems. As shown in Figure 3 it is suggested that the research die results in intermediate deformations which, after immersion in water, give the best resolution on both ends of the quality scale of adherence for these cover coats direct-to-steel. This conclusion is based on the assumption of real differences in adherence among these systems.

Figure 4 shows a comparison between deformed specimen immersion in still water and in a water bath which was ultrasonically agitated. The small differences in adherence indices obtained following these treatments were not considered statistically significant. The difference in results as a function of immersion time (one and ten minutes) might be real for systems of intermediate adherence indices (such as AM).

D. Correlation Comparison of Several Methods

Four methods of adherence estimation can be compared in Table 3 by observing the relative order or rank in which these tests placed these enamel systems. There are minor differences in rank for the various enamels. AN, for example, ranks best by three test procedures and second best by the fourth, while CP is rated poorest by three procedures and second poorest by the fourth. The consensus of these procedures is reflected in a mean rank in the last column. The mean rank allows a comparison with the intuitive judgment based on the degree of the pickling treatment these specimens received. Enamel A was ranked superior (1.25) when applied to normally pickled steel and intermediate (4.0) when applied to an intermediate pickled steel. In the same way, XN had a better adherence than XP; and CM was rated better than CP. Enamel D, however, in all tests, exhibited better adherence when applied to a medium pickled steel than when applied to a steel which had received a normal metal preparation. This unexpected result may be associated with the marked difference in enamel thickness for DM and DN or it may result from an inadvertent mix-up of these two enamel groups.

The lower part of Table 3 gives values for correlation coefficients for the several method-pairs. In general, coefficients between 0.81 and 0.95 indicated good agreement between these destructive, deformation methods or modifications.

PLANS FOR NEXT REPORT PERIOD

A. A new bank of direct-on cover coated specimens has been ordered. The new specimens will be coated with the same (white) enamel composition applied to a single lot of decarburized steel and pickled at the same time. Six different grades of adherence will be sought through control of the nickel deposition. One hundred specimens of each grade will be prepared and several hundred steel blanks will be retained in dry storage for future use.

B. An adhesion tester (button test) designed to cover the range of 0 to 2000 psi has been purchased and its motorization has been completed with the exception of receiving the motor, delivery of which is expected momentarily. A program of testing will be undertaken with the new specimens:

1. To determine the reproducibility to be expected when using the readily available deformation tests, and...

2. To determine the reproducibility of the direct pulling button test and to seek some validity for the deformations tests through comparison with direct pulling values.

C. Explore the possibility of a modified tape peel test similar to that used for adherence of organic coatings.

MISCELLANEOUS ACTIVITIES

The second meeting of a Direct-On-Adherence Advisory Committee (DOAAC) was held at NBS on January 14, 1970. This committee consists of representatives from (1) the steel producers, (2) the frit producers, (3) the appliance industry and (4) NBS. Volunteers from among the steel and frit producers are preparing the specimen bank mentioned above. Several subcommittees have been appointed to support the Direct-On Adherence Study.

W. E. Pierce (PEI) and M. D. Burdick visited three appliance manufacturers early in January to observe presently used adherence measurement techniques, to survey the needs in the industry in the adherence testing area and to obtain suggested parameters which might be considered in designing a plant control test. Other visits may be arranged.

REFERENCES

1. Stretch Testing - A New Method of Measuring the Attachment of Porcelain Enamel to Sheet Metal, J. E. Sams, PEI Forum 5 p. 73, (1940).

2. Correlation Between Direct-On Cover Coat Adherence and Chippage, H. W. Afflerbach, PEI Forum 25 p. 69, (1963).

TABLE 1

Cover Coats Direct-to-Steel
on 20 gage decarburized enameling steel

Pickling treatment requested:

Normal	(N)	2-3 g/ft^2 metal removed plus Nickel
Medium	(M)	1.0 " " " " "
Poor	(P)	0.5 " " " " "
Zero	(O)	(not pickled)

Designation	Color	Coating Thickness mils	Pickling treatment reported: Metal Removed g/ft^2	Ni added g/ft^2
AN	White	3.6	2.7	0.14
AM	"	4.2	1.2	.13
BN	Avocado	3.5	*	*
BO	"	4.2	none	none
CM	White	4.9	*	*
CP	"	5.0	*	*
DN	Copper	4.4	2.25	0.11
DM	tone	6.6	1.0	0.10
XN	"	4.5	1.92	0.09
XP	"	4.9	0.45	0.05

*Not reported.

Specimens were supplied through the courtesy of the following firms:

Chicago Vitreous Corp.
Ferro Corporation
Glidden-Durkee Division of SCM
Ingram-Richardson, Inc.
O. Hommel Company

TABLE 2

Comparison of Several Procedures for Estimating the Adherence Index [a/]

Enamel System	AN	BN	DM	XN	CM	AM	XP	DN	CP	BO	n [b/]
Test Methods											
20 gage die, Dry [c/]	100	100	100	100	98	100	81	71	45	6	5
20 " " Wet [c/]	100	100	97	87	86	77	48	39	20	9	5
Research die, Dry	99	99	90	87	83 [e/]	84	28	26	30	1	3
Research die, Wet	97	99	85	69	36 [f/]	53	24	25	18	0	3
Research die, 30 sec. in water h/	99	100	85	64	45 [g/]	41	24	27	23	0	3
Research die, 10 min. in water h/	--	98	--	--	--	32	--	--	17	--	3
Drop Weight i/	86	62	75	31	40	41	0	19	0	0	12
Mean Value, All Methods	98	97	91	79	73	65	43	42	29	4	--
Stretch Test, Reflectance	10.5	--	8.6	12.8	16.7	14.1	16.1	16.2	21.1	--	

a/ Using PEI Adherence meter.
b/ n = number of indentations upon which Adherence Index was based.
c/ The indices indicated as "Dry" were measured on specimens at least 30 minutes after deformation. The indices by the "Wet" method were obtained after 15 minutes water immersion, followed by oven drying.
e/ Based on measurements of 23 specimens.
f/ Based on measurements of 13 specimens.
g/ Based on measurements of 10 specimens after one minute immersion in ultrasonic water.
h/ The immersion was in ultrasonically agitated water.
i/ The drop weight involved a deformation by a one-half inch round tup, energized by a five pound weight dropped through a distance of 16 inches.

TABLE 3

Comparison of Results Obtained for Estimating Adherence by Four Deformation Methods

20 ga. die Wet			Research die Wet			Drop Weight			Stretch Test			Enamel System	Mean Rank
	AI	Rank		AI	Rank		AI	Rank		Refl	Rank		
AN	100	1	AN	97	1	AN	86	1	DM	8.6	1	AN	1.25
DM	97	2	DM	85	2	DM	75	2	AN	10.5	2	DM	1.75
XN	87	3	XN	69	3	AM	41	3	XN	12.8	3	XN	3.5
CM	86	4	AM	53	4	CM	40	4	AM	14.1	4	AM	4.0
AM	77	5	CM	36	5	XN	31	5	XP	16.1	5	CM	5.0
XP	48	6	DN	25	6	DN	19	6	DN	16.2	6	DN	6.25
DN	39	7	XP	24	7	CP	0	7.5	CM	16.7	7	XP	6.4
CP	20	8	CP	18	8	XP	0	7.5	CP	21.1	8	CP	7.8

The Correlation Coefficients Between the Four Methods for Estimating Adherence

	20 gage, wet	Research, wet	Drop Weight	Stretch
20 gage, wet	--	0.95	0.83	0.83
Research, wet		--	0.90	0.88
Drop Weight			--	0.81
Stretch				--

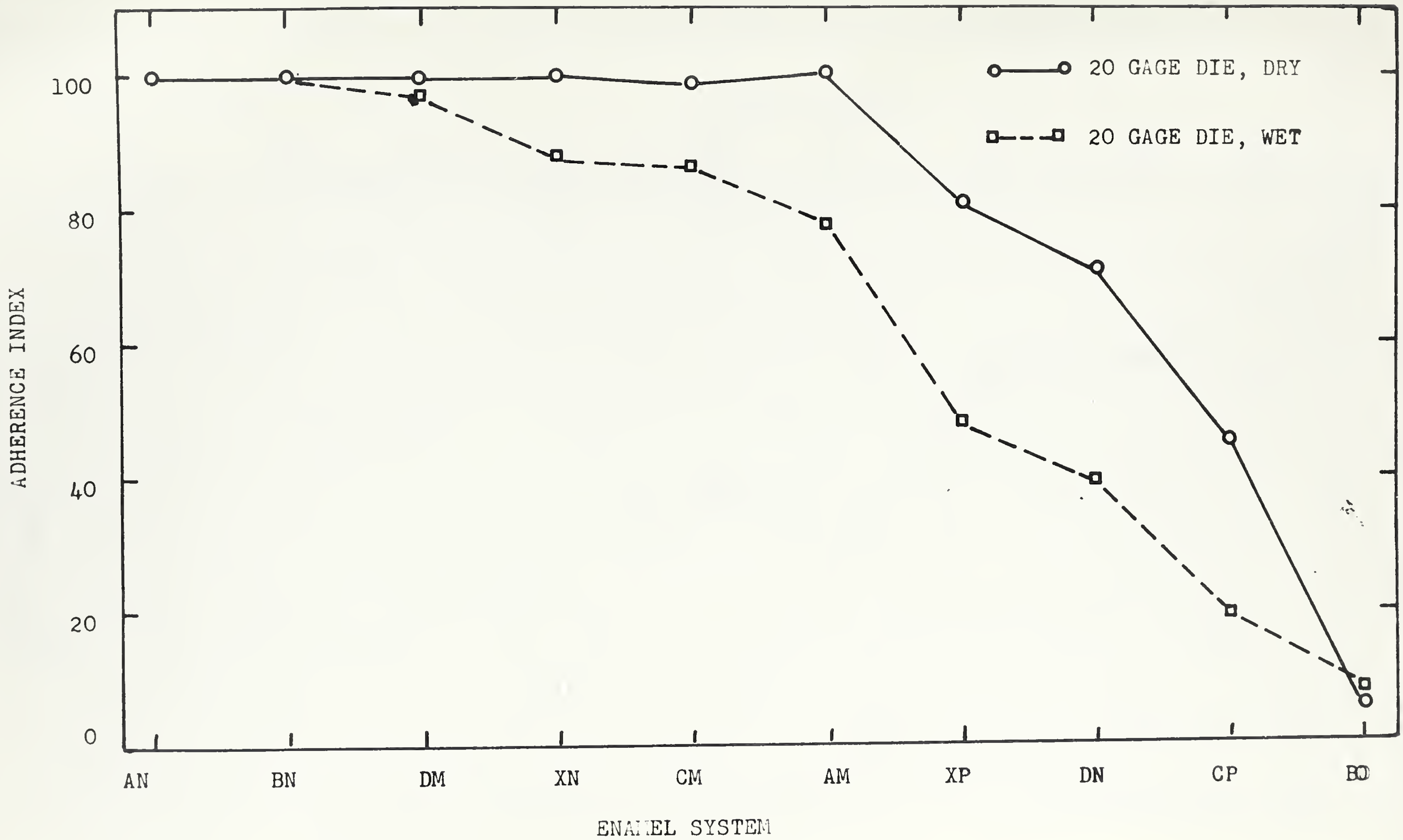

Figure 1. Comparison of Adherence Indices after various Deformation Treatments.

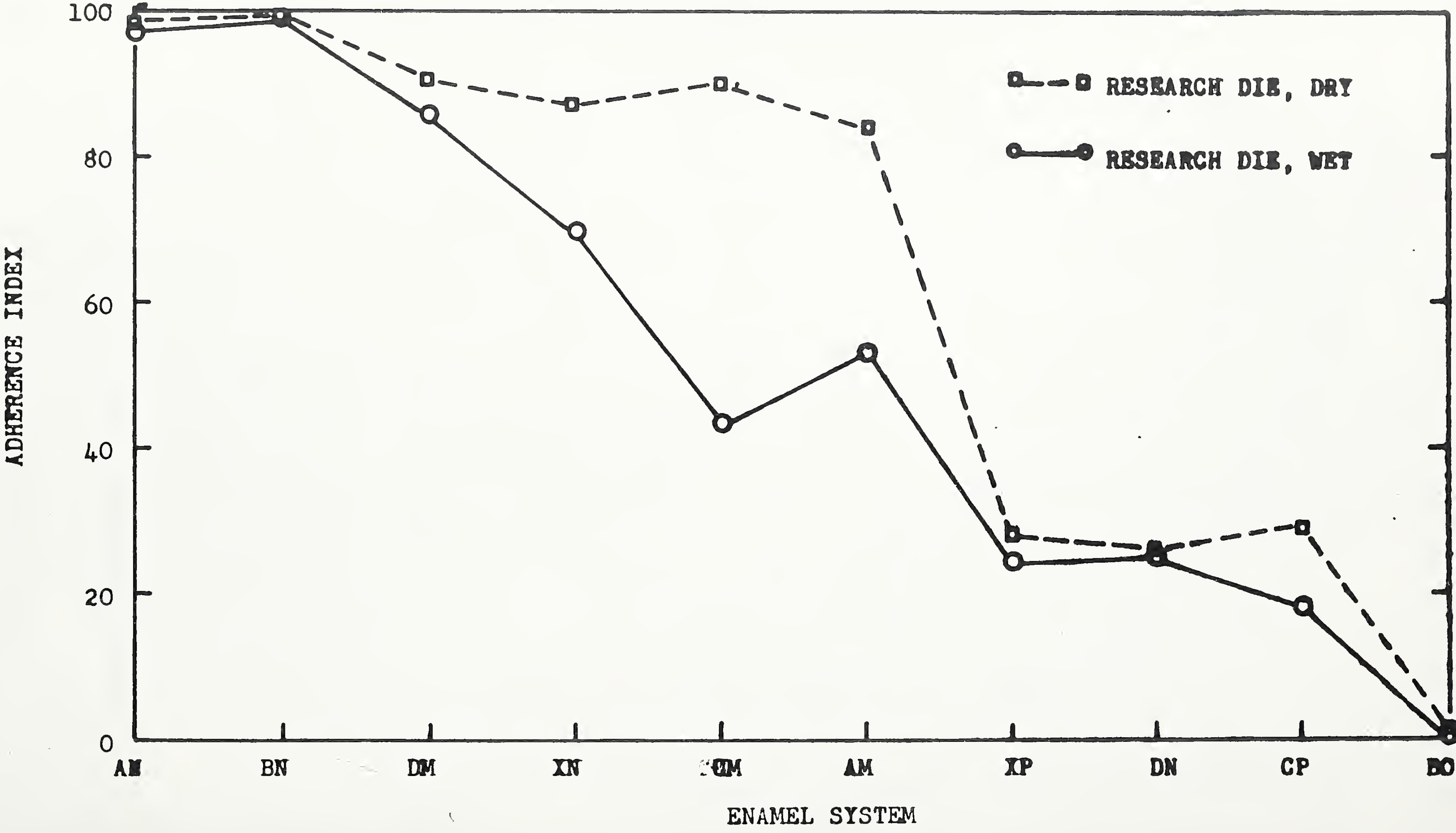

Figure 2. Comparison of Adherence Indices after various Deformation Treatments

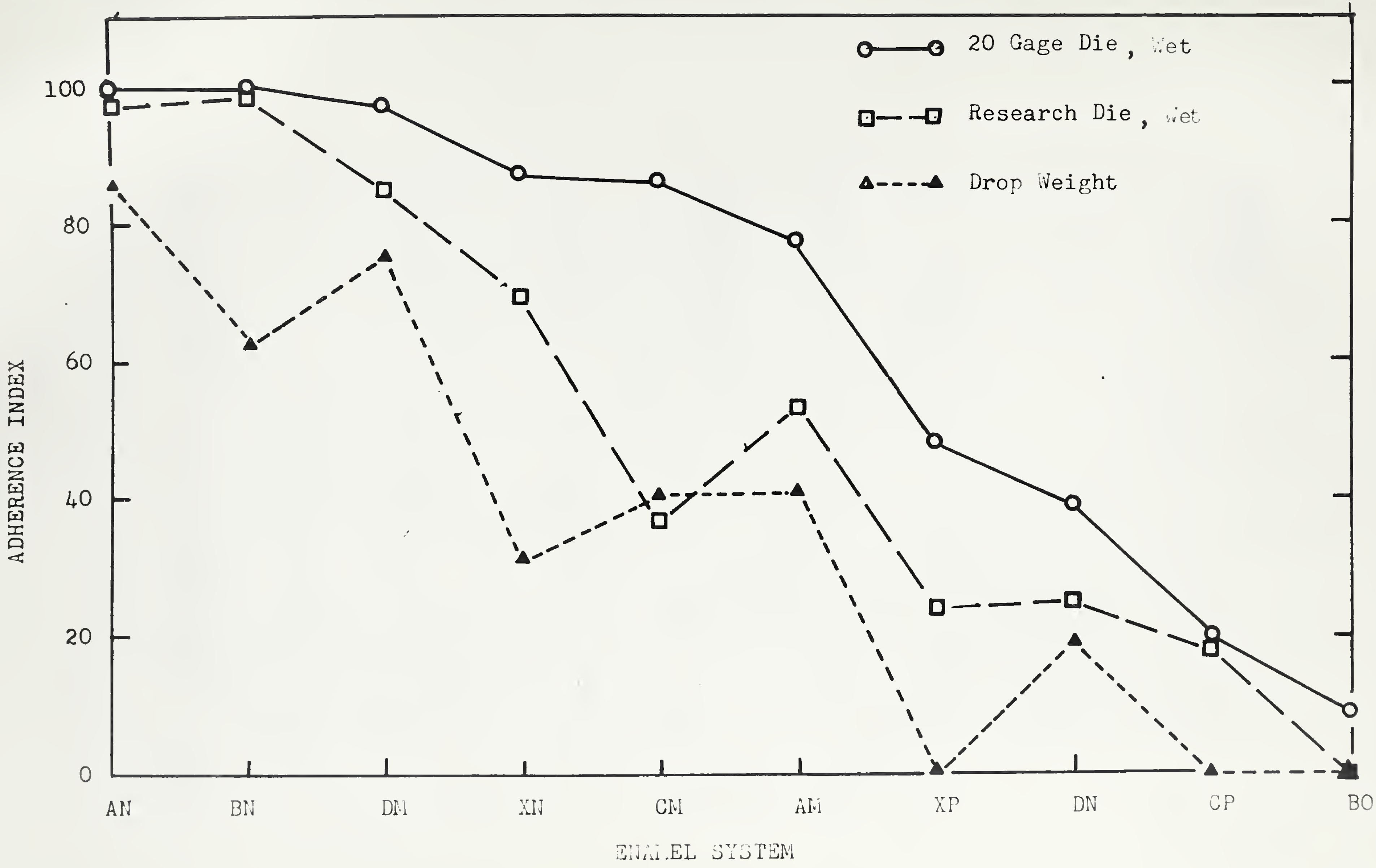

Figure 3. Comparison of Adherence Indices after various Deformation Treatments

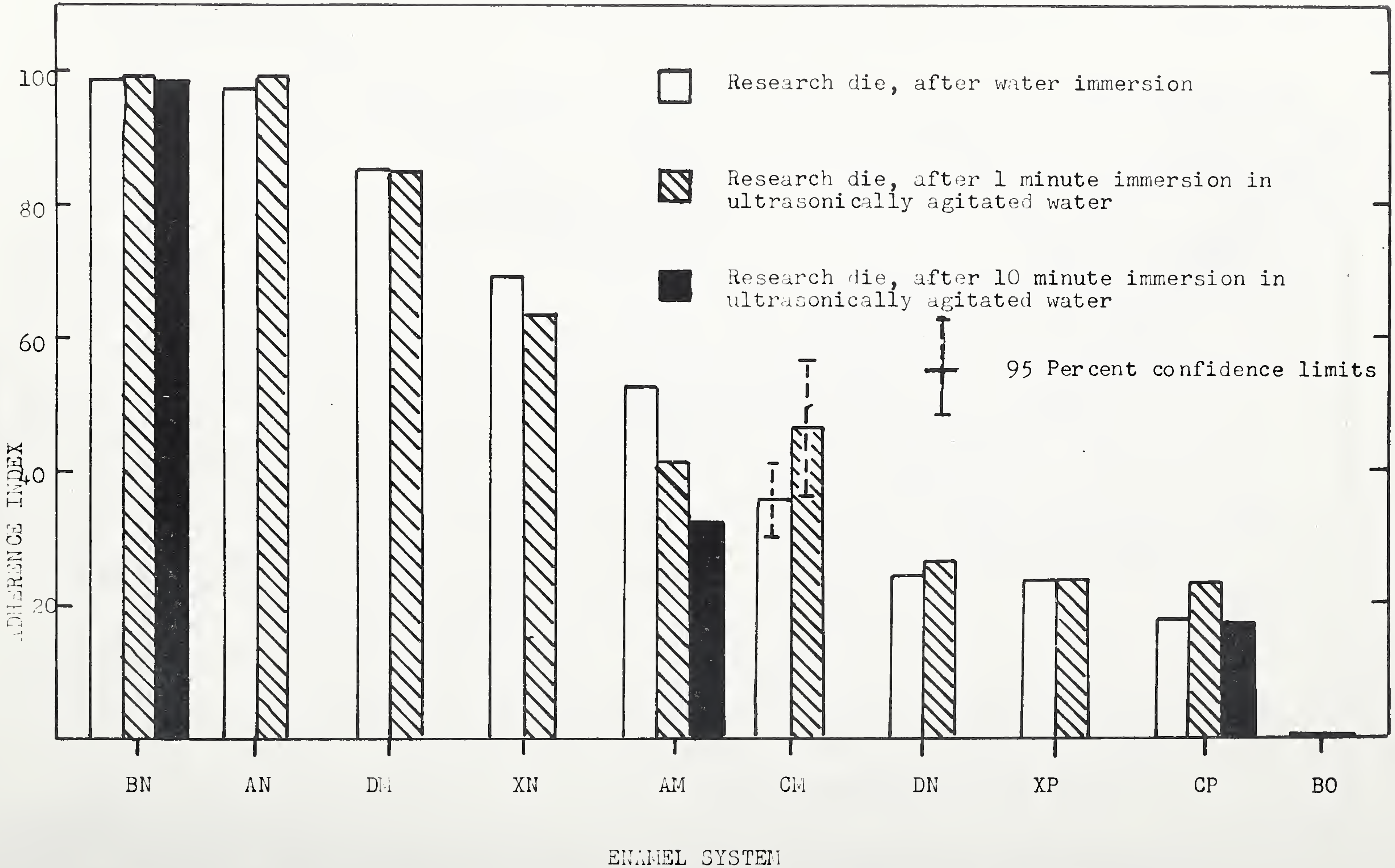

Figure 4. Comparison of Adherence Indices after various Deformation Treatments.