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NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

July 1 through September 30, 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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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.
[2] Located at Boulder, Colorado 80302.
[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

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SUMMARY

Numerical adherence values for ten porcelain enamel cover coats direct-to-steel were obtained by three different test methods. The first was the PEI adherence test designed for two coat systems on steel. The other two methods had not previously been used to evaluate porcelain enamels. One of these, intended for use with organic coatings, showed some promise of being adapted to estimate the adherence of cover coats direct-to-steel.

I. THE ADHERENCE OF PORCELAIN ENAMELS DIRECT-TO-STEEL

INTRODUCTION

The application of vitreous porcelain enamel cover coats direct-to-steel has long been considered a desirable goal. The development of decarburized enameling steels and appropriate metal preparation techniques has changed the dream to reality. The adoption by industry of the direct-to-steel concept has been rapid during the past decade. In 1961 four plants were in production or closely approaching this stage for a limited number of porcelain enameled shapes. By 1965 seventeen plants had adopted direct-on enameling production. A current survey shows approximately 30 plants in direct-on production of a fairly wide variety of metal shapes, all of decarburized enameling steel.

The advent of rather extensive use of the cover coats direct-to-steel has not provided a panacea for the many defects that must be avoided in the production of top-quality ware. Experience has shown that direct-on enameling may require more rigid control of physical and chemical preparation of the substrate than was required with the two coat system.

A quality evaluation seminar at the National Bureau of Standards in October 1968, sponsored by the Porcelain Enamel Institute, described the wide variety of testing methods available for use within the porcelain enamel industry. Discussion among the industry representatives indicated the need for a production-line test method to numerically evaluate the adherence of cover coats direct-to-steel. The research associates have undertaken the development of this method as a short range goal.

RESULTS AND DISCUSSION

A. Procurement of Specimens for Evaluation

The development of satisfactory adherence of cover coats direct-to-steel depends, among many other processing steps, on suitable chemical preparation of the substrate. Before the enamel application, drawing compounds introduced during forming must be removed by cleaning and rinsing solutions. Surface metal removal by acid etching and rinsing must be controlled. The addition of an adherence promoter such as the nickel dip must be made to the cleaned and etched surfaces.

In order to obtain groups of enameled specimens with a wide range of adherence values, specimens were obtained with etching pretreatments ranging from "normal" metal removal, about 2 to 3 grams per square foot, through an intermediate amount of metal removal, about 1.0 gram per square foot, to low amount of metal removal, 0.5 gram per square foot. One set of specimens received no pickling treatment. Each supplier applied an enamel of his choice to two groups of specimens prepared by different degrees of pickling pretreatment. Table 1 gives the metal removal by pickling, the nickel added and the fired enamel thickness for the one coat enamel systems used in this work.

B. Types of Tests Used to Evaluate Adherence

1. Fracture Toughness.

This testing method was described in the previous NBS Progress Report No. 10,075. The parameter Gc was calculated as outlined in that report.

2. The PEI Adherence Test.

The PEI adherence test described in ASTM designation C-313 was used. The deforming die design and pressure for 20 gage metal was used. The adherence index, AI, was calculated for each enamel system.

3. The Adhesion Tester.

The adhesion tester is a portable, direct pulling device to measure the force required to pull the coating from the substrate. This apparatus was designed to measure the adhesion of various organic coatings. Because of the "buttons" which are attached to the coating with an epoxy adhesive and pulled off, the test is here referred to as a "button" test. Figure 1 illustrates the device ready to be slipped over the attached button, and on the left a specimen after test from which four discs of coating have been pulled off. The device has a scale which roughly indicates the stress from 0 to 1000 psi.

required to remove the button. Several undesirable features of this device were observed during its use: a) The loading, applied by the rotation of the top hand wheel was not uniform or controlled. b) Deformation of the specimen system was observed during the loading operation. This was partly overcome by resting the specimen plate on a magnetic table during the loading. c) Failures within the epoxy adhesive were sometimes observed. Several types of failure were found, often more than one type in a single failure: 1) in the epoxy glass interface, 2) within the glass layer, 3) at the interface of the glass and an "oxide rich" layer, and 4) at the interface of the "oxide layer and the bright metal."

C. Test Results

Table 2 gives individual results of fracture toughness, Gc, obtained on the ten cover coats. AN-1 is the designation for a single test piece of enamel "A" applied to a normally pickled substrate. AN-1D designates a duplicate test piece of the same specimen. In the same manner BN-1 represents enamel "B" on a normally pickled substrate while BO-1 differs in that the metal specimen was not pickled before the application of enamel "B". For each test piece at least four, and usually eight cracks were caused to propagate and were then arrested. Each crack so controlled lead to a value of Gc indicative of the fracture toughness of the area through which the crack traveled.

Table 3 gives average results for fracture toughness, Gc; adherence index, A1; and the failure stress in the button adherence tests, for the ten cover coat systems. The adherence indices were obtained from only one specimen of each enamel system. The failure stresses in the button test are averages of four tests on a single specimen in most cases. The rank correlation coefficients shown diagramatically at the bottom of Table 3, while they may lack rigorous numerical significance, indicate that the button test and adherence index correlate better with each other than they correlate with the fracture toughness.

The same test results presented in Table 3 are given in Table 4 arranged to allow comparison of the several degrees of pickling pretreatment. Enamels "A" and "D" allow comparison of normal and medium pickling treatment. Results obtained on enamels "B" and "X" allow comparison of normal and poor pretreatments. Enamel "C" results allow comparison of medium and poor treatments. For each enamel there are three parameters which may be used to aid in selecting the better of two pretreatments. The results of the tests on enamel system "A" compared by Gc and A1 did not distinguish between normal and medium pickling treatment, and the button test results were quite similar also. For three of the four remaining enamels, "B", "C" and "X", the adherence index, A1, and the button test were in agreement in the selection of the "superior" pickling treatment. This is another way of illustrating the correlation between this pair of parameters shown in Table 3.

1. The Fracture Toughness Test.

We believe this to be the first trial of fracture mechanics in an adherence situation. The test as outlined in our previous report is a rather complex one. It is believed to hold some promise as a "research method" to evaluate adherence in porcelain enamel systems. Several modifications in the technique suggest themselves as a result of this first trial, and will be applied as time permits.

2. The PEI Adherence Test

It is thought that this test method in its present form does not sensitively distinguish between porcelain enamels of good adherence. The counting system of the equipment may offer promise of a rapid test with appropriate die re-design or other changes in the deformation technique.

3. The Adhesion Tester (the Button Test)

The device is attractive for production line testing because of its extreme portability. It seems worthwhile to obtain better control of the loading rate through a modification of the device to permit motorized loading. This would undoubtedly reduce the portability of the equipment, but should improve its reproducibility.

PLANS FOR NEXT REPORT PERIOD

1. Explore adherence meter counting for the evaluation of adherence in specimens deformed by a drop-weight test.

2. Consider the use of an aggressive adhesive tape for stripping scored or cut specimens.

3. Obtain a motorized adhesion tester and evaluate its use in measuring adherence of cover coats direct-to-steel.

II. WEATHERING OF PORCELAIN ENAMELS

A paper summarizing the findings of the three-year inspection of porcelain enamels on aluminum was written to be published in the National Bureau of Standards Building Science Series and presented at the Technical Forum of the Porcelain Enamel Institute.

III. CONTINUITY OF COATING

A paper was prepared on the use of the high-voltage continuity of coating test to be presented at the PEI Forum.

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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	1.10
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

Cover Coats Direct to Steel
Individual Values of Gc, lb/inch

Enamel A

Crack No.	AN 1	AN 1D	AM 1	AM 1D
2	0.36	0.23	0.44	--
3	.27	.21	.28	0.02
4	.40	.15	.32	.02
5	.52	.12	.57	.02
6	.29	.07	.41	.02
7	.25	.09	.24	.02
8	.17	.09	.22	--
9	.17	.07	.18	--
10	.16	--	--	--
mean	0.29	0.13	0.33	0.02

Enamel B

Crack No.	BN 1	BO 1	BO 2
2	1.07	--	0.02
3	1.15	--	.02
4	2.05	0.03	.02
5	1.46	.03	.02
6	1.61	.03	.02
7	1.73	--	.02
8	1.75	.02	.02
9	2.06	.02	.02
mean	1.61	0.03	0.02

Enamel C

Crack No.	CM 1	CM 1D	CP 1	CP 1D
2	--	0.58	0.41	1.02
3	0.34	.89	.31	.88
4	.49	.18	.32	.60
5	.53	.20	.42	.55
6	.14	.17	.29	.56
7	.15	.23	.29	.58
8	.15	.17	--	.66
mean	0.30	0.35	0.34	0.69

TABLE 2 (Continued)

Cover Coats Direct-to-Steel
Individual Values of Gc, lb/inch

Enamel D

Crack No.	DN 1	DN 1D	DN 2	DN 2D	DM 1	DM 1D
2	0.12	0.11	0.27	0.08	0.39	0.17
3	.11	.18	.20	.08	.38	.16
4	.07	.13	.12	.02	.27	.10
5	.09	.08	.10	.02	.21	.09
6	.07	.08	.08	.02	--	--
7	.08	.06	.08	.02	--	--
8	.07	.06	--	.02	--	--
9	--	--	--	.01	--	--
mean	0.09	0.10	0.14	0.03	0.31	0.13

Enamel X

Crack No.	XN 1	XN 1D	XP 1	XP 1D
2	0.26	0.25	0.39	0.42
3	.15	.15	.46	.06
4	.12	.14	.81	.15
5	.11	.10	.71	.32
6	.11	.08	.07	.10
7	.10	.09	.16	.12
8	.08	.08	.13	.10
9	.07	.09	.12	.10
mean	0.12	0.12	0.33	0.17

TABLE 3

Ten Cover Coats Direct-to-Steel
(ranked in quality by three test methods)

Enamel System	Fracture Toughness Gc lb/inch	Rank	Enamel System	PEI Adherence Test Adherence Index	Rank	Enamel System	Button Test Load psi	Rank
BN	1.61	1	XN	100	2.5	CM	440	1
CP	0.54	2	AM	100	2.5	XN	325	2
CM	.32	3	BN	100	2.5	AM	295	3
XP	.26	4	AN	100	2.5	CP	290	4
DM	.22	5	CM	99.2	5	BN	270	5
AN	.21	6.5	CP	98.6	6	AN	240	6
AM	.21	6.5	DM	85.8	7	DN	235	7
XN	.12	8	XP	77.7	8	DM	220	8
DN	.09	9	DN	81.8	9	XP	210	9.5
BO	.02	10	BO	1.8	10	BO	210	9.5

Rank Correlation Coefficient, $\rho = 1 - \frac{6 \sum d^2}{n (n^2 - 1)}$

where: d = difference in ranks

n = number of items ranked

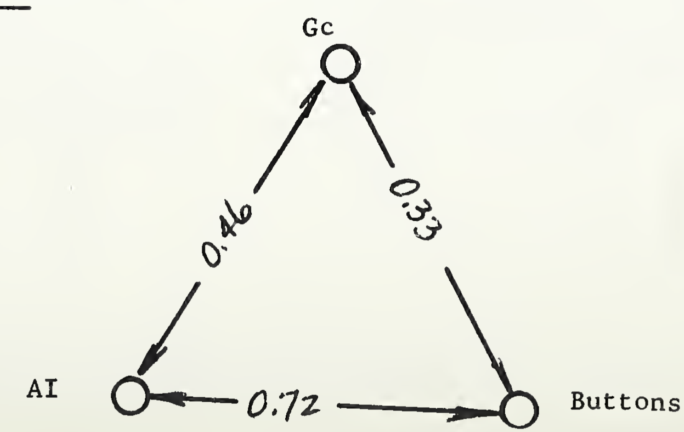
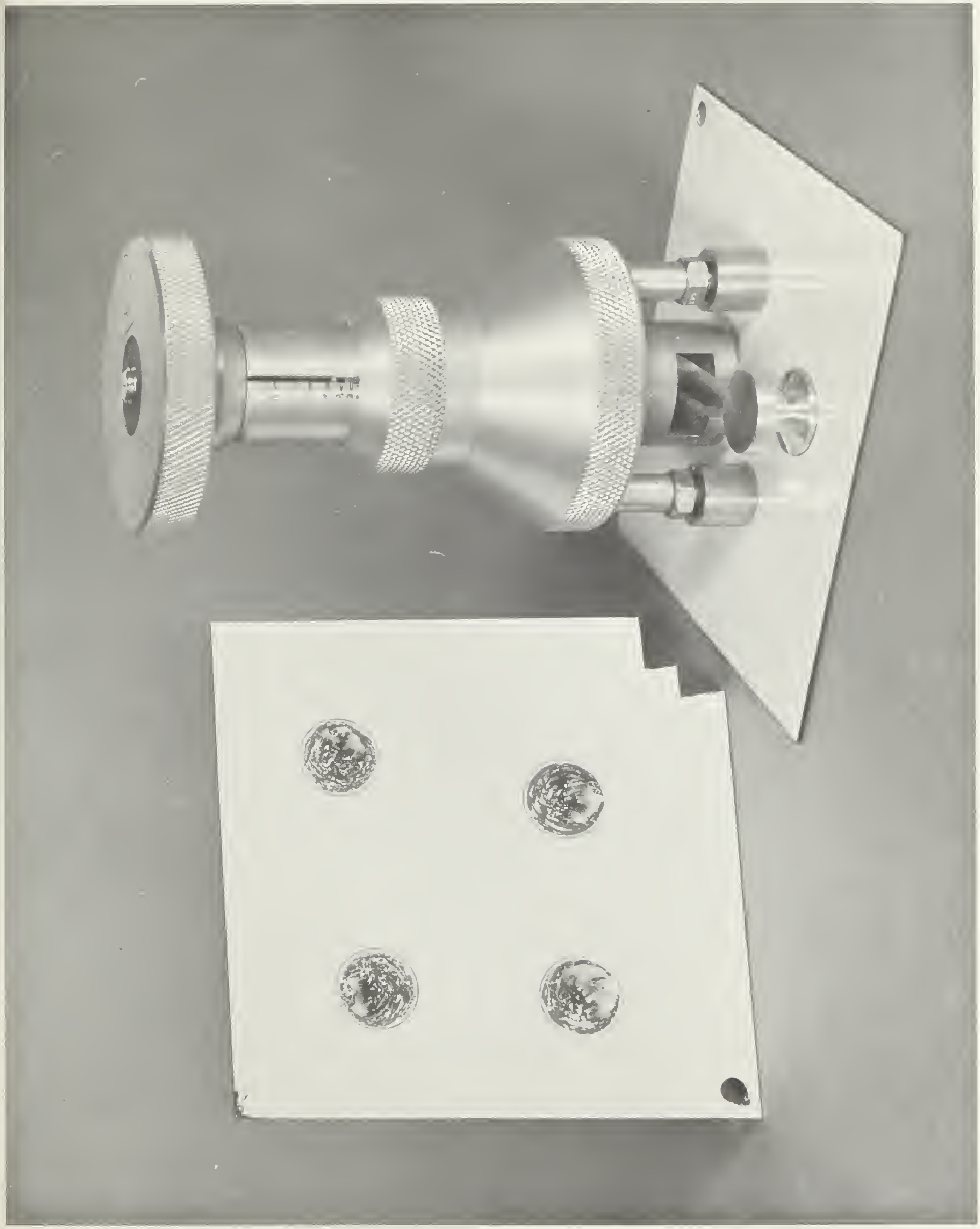


TABLE 4

Comparative Ranking of Pickling Treatments for Cover Coats Direct-to-Steel
(Substrates prepared for enameling by different degrees of metal removal)

Porcelain Enamel	Ranking Parameter a/	Degree of Substrate Metal Removal			Superior Pickling Treatment
		Normal	Medium	Poor	
A	Gc	0.21	0.21		Same
	Psi	240	295		Medium
	AI	100	100		Same
B	Gc	1.61		0.02	Normal
	Psi	270		210	Normal
	AI	100		1.8	Normal
C	Gc		0.32	0.54	Poor
	Psi		440	290	Medium
	AI		99.2	98.6	Medium
D	Gc	0.09	0.22		Medium
	Psi	235	220		Normal
	AI	71.8	85.8		Medium
X	Gc	0.12		0.26	Poor
	Psi	325		210	Normal
	AI	100		77.7	Normal

a/ Gc is the fracture toughness value.
Psi is the fracture stress in the "Button" test.
AI is the Adherence Index from the PEI Adherence Test.



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