NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

REPORT 1166

RELATION BETWEEN ROUGHNESS OF INTERFACE AND ADHERENCE OF PORCELAIN ENAMEL TO STEEL

By J. C. RICHMOND, D. G. MOORE, H. B. KIRKPATRICK, and W. N. HARRISON

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National Bureau of Standards

National Advisory Committee for Aeronautics

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RELATION BETWEEN ROUGHNESS OF INTERFACE AND ADHERENCE OF PORCELAIN ENAMEL TO STEEL [1]

By J. C. Richmond, D. G. Moore, H. B. Kirkpatrick, and W. N. Harrison

SUMMARY

Porcelain-enamel ground coats were prepared and applied under conditions that gave various degrees of adherence between enamel and a low-carbon steel (enameling iron). The variations in adherence were produced by (a) varying the amount of cobalt-oxide addition in the frit, (b) varying the type of metallic-oxide addition in the frit, keeping the amount constant at 0.8 weight percent, (c) varying the surface treatment of the metal before application of the enamel, by pickling, sandblasting, and polishing, and (d) varying the time of firing of the enamel containing 0.8 percent of cobalt oxide.

Specimens of each enamel were given the standard adherence test of the Porcelain Enamel Institute. Metallographic sections were made on which the roughness of interface was evaluated by counting the number of anchor points (undercuts) per centimeter of specimen length and also by measuring the length of the interface and expressing results as the ratio of this length to the length of a straight line parallel to the over-all direction of the interface.

The following conclusions were drawn from the data:

(1) A positive correlation was found between the adherence of a porcelain-enamel ground coat and the roughness of the interface.

(2) In general, adherence correlated better with anchor points per centimeter than with the increase in interfacial area (interface ratio).

(3) The method of metal preparation had a marked effect on the relation between roughness of interface and adherence of porcelain-enamel ground coats to enameling iron. In general, better adherence was associated with enamels applied to pickled iron than to sandblasted iron for the same degree of roughness of interface.

(4) Most of the roughness that was associated with good adherence between a porcelain-enamel ground coat and iron developed during the firing process.

(5) Roughness of interface is a necessary, but not a sufficient, condition for the development of good adherence between a porcelain-enamel ground coat and iron.

(6) One or more factors other than roughness of interface also influence the adherence between a porcelain-enamel ground coat and iron.

INTRODUCTION

One of the first explanations advanced for the adherence of vitreous-base coats to steel was that of mechanical gripping. This hypothesis is based on the observation that when adherence is good there is a rough interface between the coating and the metal, as shown in figure 1. The coating penetrates into cavities or undercuts in the metal surface and, when the coating hardens on cooling, the two materials are interlocked and thus mechanically bonded.

While previous investigators (see appendix for review of literature) have noted that rough interfaces are associated with good adherence, there has been no quantitative study of this relationship reported, probably because a method of evaluating adherence quantitatively has only recently become available. This study was undertaken with the hope that it would throw additional light on the mechanism of adherence of porcelain-enamel ground coats to iron. It constitutes one phase of an investigation on the general subject of adherence that was undertaken at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics. It should be emphasized that this phase of the investigation was concerned only with a study of the relationship between adherence and roughness of interface between enamel and iron. The mechanism by which this roughness is developed is covered in a second paper (ref. 1).

EXPERIMENTAL PROCEDURE

One basic frit composition and one mill-batch formula were used for all of the enamels prepared in this study. The frit composition given in table I is the same as that for frit 109–0 reported previously (ref. 2) and the mill batch (table II) is the same as that used for enamels I 2 and I 2 R in an earlier study (ref. 3). Variations in adherence were produced by (a) varying the amount of cobalt-oxide addition in the frit, (b) varying the type of metallic-oxide addition, keeping the amount constant at 0.8 weight percent, (c) varying the surface treatment of the metal before application of the enamel, and (d) varying the time of firing of the enamel containing 0.8 percent of cobalt oxide.

Each frit, with the appropriate metallic-oxide addition, was batched, smelted, and prepared as an enamel slip according to standard procedures. Table III lists the metallic oxides added to the base frit batch to produce the various frits.

The oxides indicated in table III were chosen for several reasons. Cobalt, nickel, and manganese oxides are commonly used as adherence-promotion oxides in commercial

[1] Supersedes NACA TN 2934, "Relation Between Roughness of Interface and Adherence of Porcelain Enamel to Steel" by J. C. Richmond, D. G. Moore, H. B. Kirkpatrick, and W. N. Harrison, 1953.

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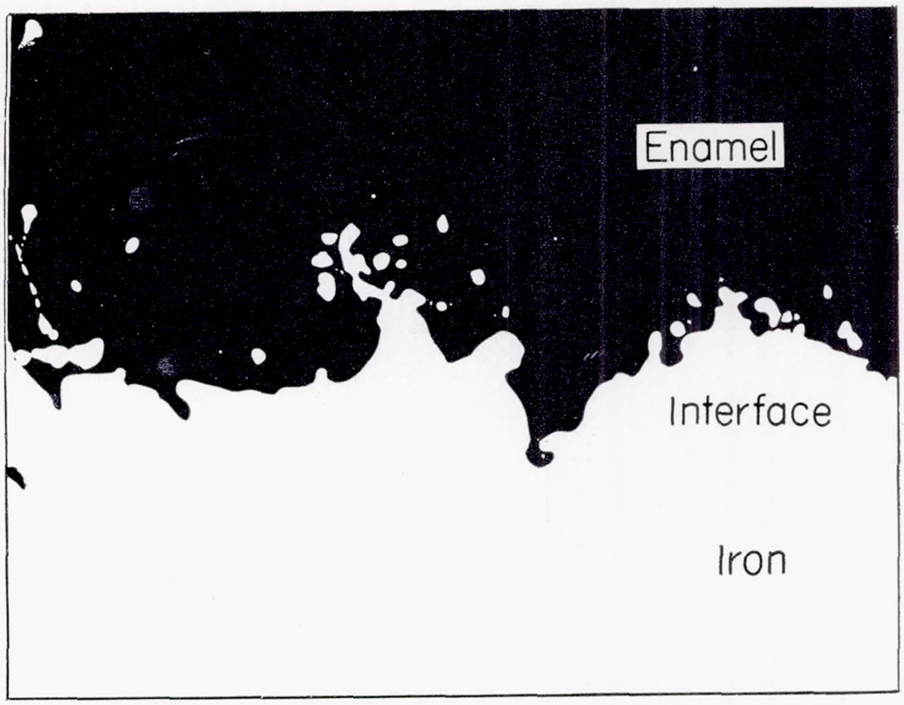


FIGURE 1.—Photomicrograph (X1,000, unetched) of metallographic section of porcelain-enamel ground coat containing 0.8 percent cobalt oxide applied to sandblasted enameling iron, showing rough interface between enamel and iron. This specimen had excellent adherence.

ground coats, although manganese oxide is of no value when used alone and of questionable value when used in combination with the other two oxides. Antimony and molybdenum oxides have been reported in the literature (refs. 4 and 5) to promote adherence to some extent. The other oxides were included because of the position of the metal in the electromotive-force series of the elements[2] in relation to iron and cobalt. In this series Cr^{+++} is above Fe^{++} (which is considered the active iron ion at the enamel-metal interface); Cd^{++} is between Fe^{++} and Co^{++}; and As^{+++} and Cu^{++} are considerably below Co^{++}.

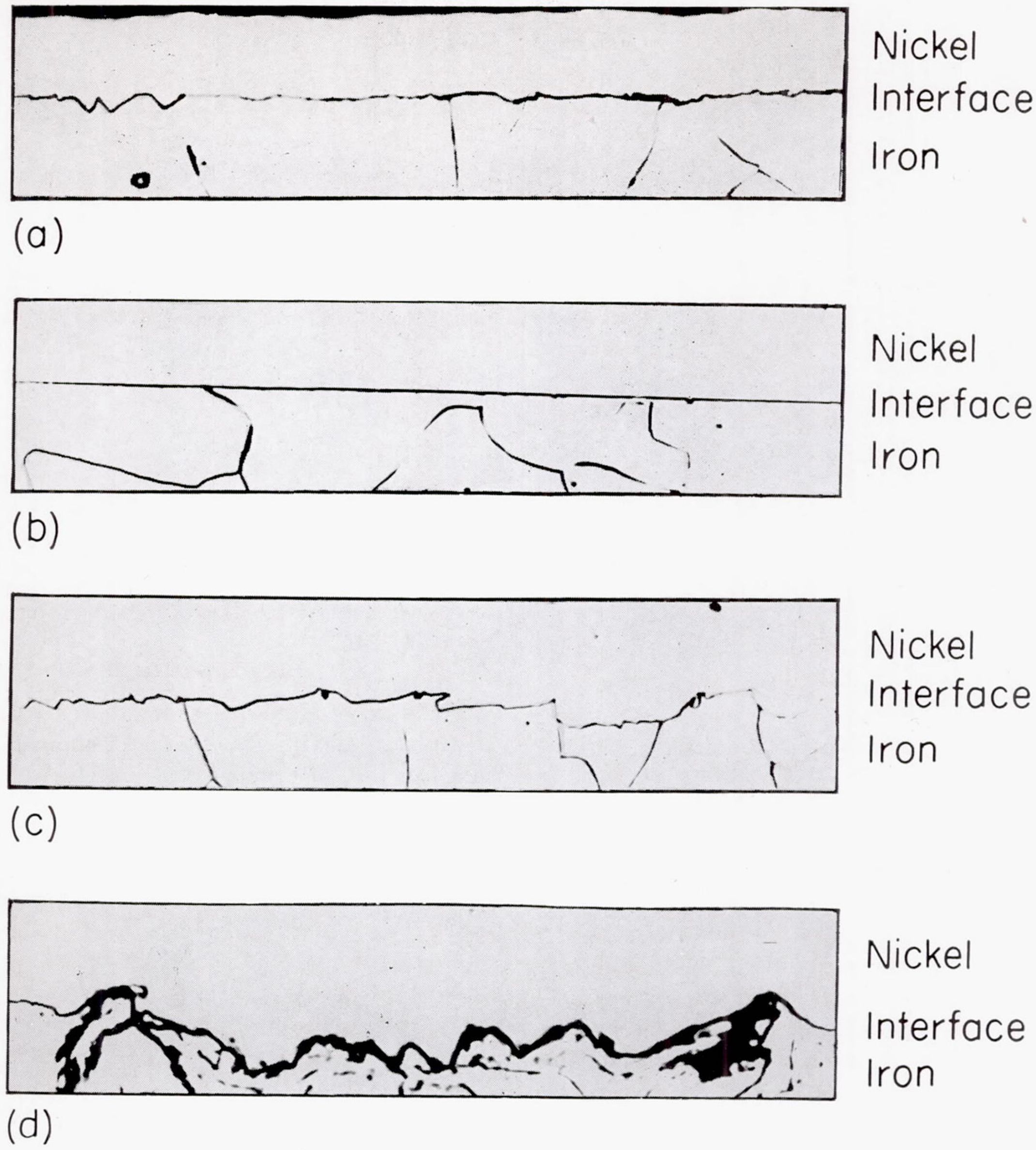
Twenty-gage enameling-iron blanks, 4 by 4 inches, were sheared to size, marked for identification, and punched to provide hanging holes. The metal blanks were prepared for enameling (a) by sandblasting, (b) by pickling, using standard procedures not including the nickel dip, or (c) by grinding and polishing. Photomicrographs of typical uncoated metal blanks are shown in figure 2 to indicate the degree of surface roughening produced by these various treatments.

The enamels were applied by dipping, and each slip was adjusted to give a fired enamel coating 5 ± 1 mils thick. Specimens of all enamels were fired at 1,575° F for 4 minutes, except that a temperature of 1,550° F was used in that part of the study in which adherence was varied by changing the firing time.

The adherence of specimens of each enamel prepared under each condition was evaluated by the standard Porcelain Enamel Institute test (ref. 6) using seven specimens for each determination. This test evaluates the degree of adherence of a porcelain enamel to metal in terms of the amount of metal exposed by a standard deformation treatment, expressed as a percentage of the total deformed area. An adherence index of less than 50 by this test is usually considered so poor as to be commercially unacceptable. Although there is no standard classification of adherence indices, values of 50 to 75 were considered fair, 75 to 90 good, and 90 or above excellent.

A metallographic section was made of the specimen of each enamel having the adherence value nearest the average for

[2] The electromotive-force series of the elements listed in standard textbooks was prepared from measurements of the potential developed between the element and an aqueous solution of the ion involved in which the ion was at unit activity (approximately one normal for most ions). Under these conditions the ions used in this study fall in the following order: Mn^{++}, Cr^{+++}, Fe^{++}, Cd^{++}, Co^{++}, Ni^{++}, Mo^{+++}, Sb^{+++}, As^{+++}, and Cu^{++}. It is known that molten glass acts as an electrolyte and that electrode potentials are developed in it, but the measurement of such potentials involves serious experimental difficulties. While the magnitude of the potentials may be considerably different, it is to be expected that the order of the elements will be about the same whether the electromotive force is developed in water or a glass, provided there are no complicating side reactions in the glass.



(a) As received.
(b) Polished.
(c) Pickled.
(d) Sandblasted.

FIGURE 2.—Photomicrograph (X1,000, nital etch) of metallographic sections of enameling iron before coating, showing degree of roughness of surface after various treatments. Nickel was chemically plated onto iron before sectioning to preserve surface contour.

the group, and evaluations of roughness of the interface were made on this section. For the first few specimens roughness was evaluated by examining the section microscopically and counting the number of anchor points (undercuts) per centimeter. Figure 3 shows the criteria used in counting anchor points. These counts correlated well with adherence, as is shown in figure 4, but the counting operation was very tedious since many fields had to be counted to obtain a statistically reliable mean value for each section.

In later experiments, photomicrographs at 1,000 diameters were taken of 20 areas selected at random on each section. The negatives of these photomicrographs were then pro-

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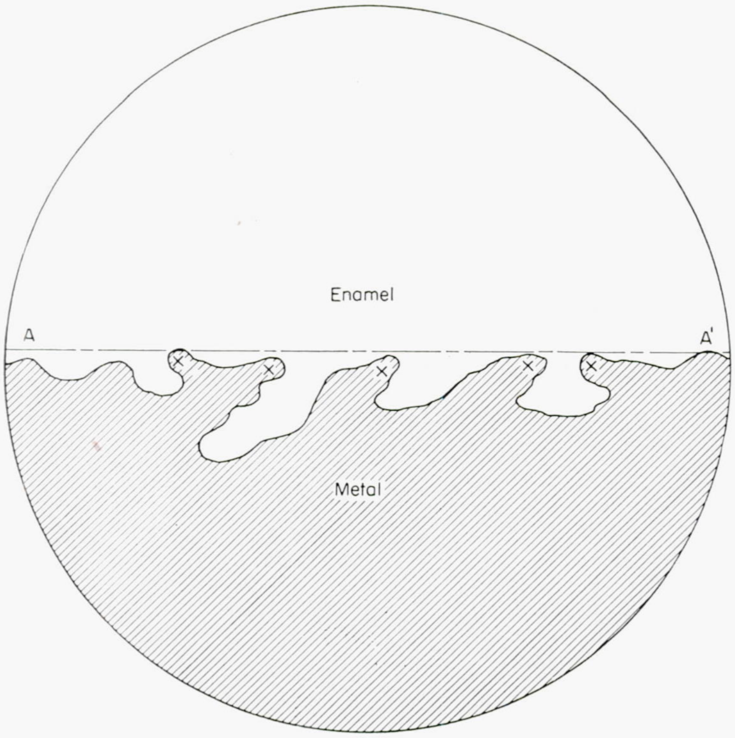

FIGURE 3.—Schematic section of enamel-metal interface, showing methods used to evaluate roughness. Anchor points (undercuts), indicated by X, were counted and expressed as number per centimeter of specimen. In the second method, length of line representing interface was measured with a map measure and expressed as a ratio of length of straight line AA′, parallel to interface.

jected onto a sheet of thin paper supported by a ground-glass screen to produce a total magnification of 10,000 diameters, and a tracing was made with a soft pencil of the enamel-metal interface. Such a tracing is illustrated in figure 3. Roughness was evaluated on these tracings by counting the number of anchor points and converting this value to the number per centimeter length. An anchor point was taken as a definite undercut in the metal, except that an undercut overshadowed by another undercut was not counted. In figure 3 the locations to be counted as undercuts are indicated by crosses. Vertical lines, normal to the interface, were used to determine whether or not a definite undercut occurred. As a second method of evaluating roughness, the length of the line representing the interface was determined with a map measure. Results were expressed as the ratio of the interface length to the length of a straight line parallel to the interface (line AA′ in fig. 3). This value was called "interface ratio."

If adherence is due to the "keying-in" action of the rough interface, the best correlation between adherence and roughness of interface should be obtained when roughness is evaluated in terms of anchor points per centimeter. On the other hand, if adherence is due to a chemical bond between enamel and metal, the bond strength would be expected to be a function of area of contact, and better correlation should be obtained between adherence and roughness when roughness is evaluated in terms of the interface ratio.

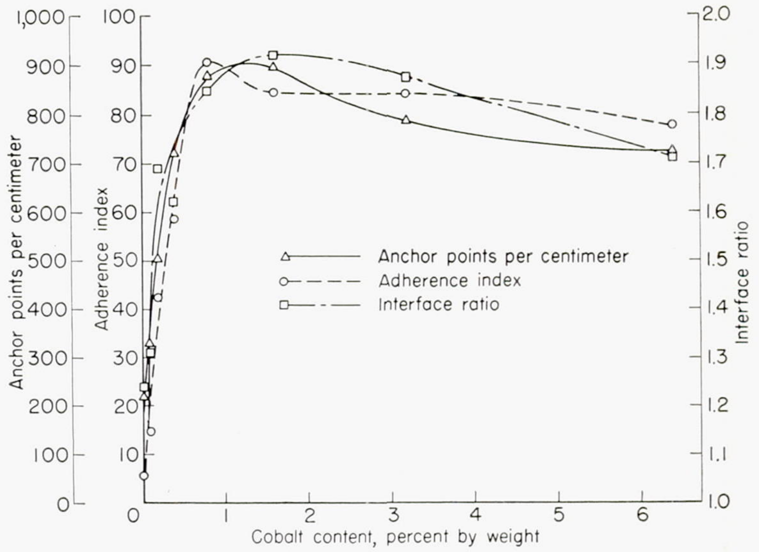

FIGURE 4.—Adherence, anchor points per centimeter, and interface ratio plotted as a function of cobalt content of a porcelain-enamel ground coat.

RESULTS AND DISCUSSION

Preliminary data on the adherence, anchor points per centimeter, and interface ratio for enamels A to H are plotted as a function of cobalt-oxide content in figure 4. It can be seen that the two measures of interfacial roughness correlate well with adherence.

The data on adherence, anchor points per centimeter, and interface ratio for the various specimens are presented in tables IV, V, and VI. Some interesting data on the effect of metal preparation, cobalt content of ground coat, and metal-oxide content of the ground coat on adherence are presented in figures 5, 6, and 7.

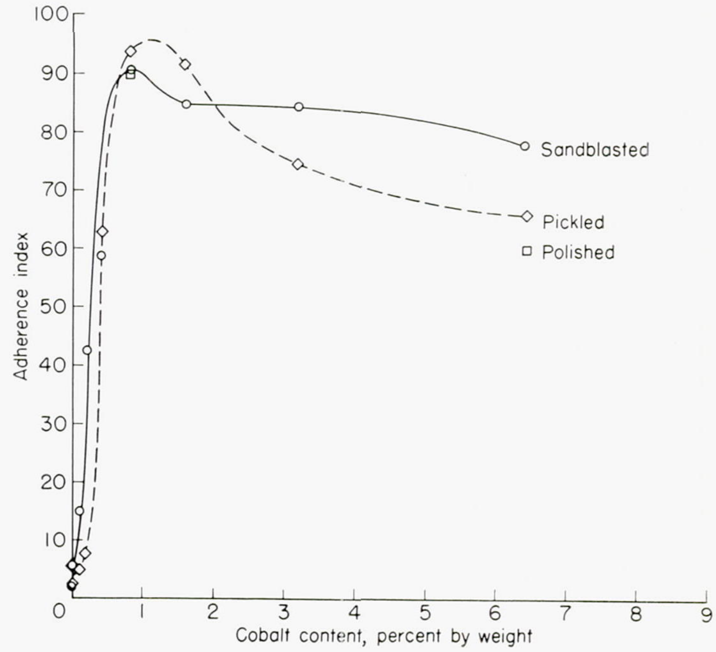

FIGURE 5.—Adherence as a function of cobalt content of a porcelain-enamel ground coat. showing effect of metal preparation.

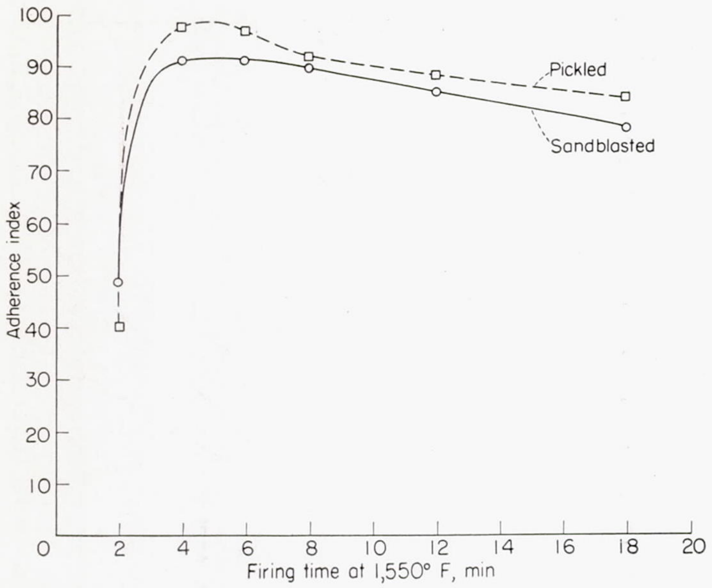

FIGURE 6.—Adherence as a function of firing time for a porcelain-enamel ground coat containing 0.8 percent cobalt oxide, showing effect of metal preparation.

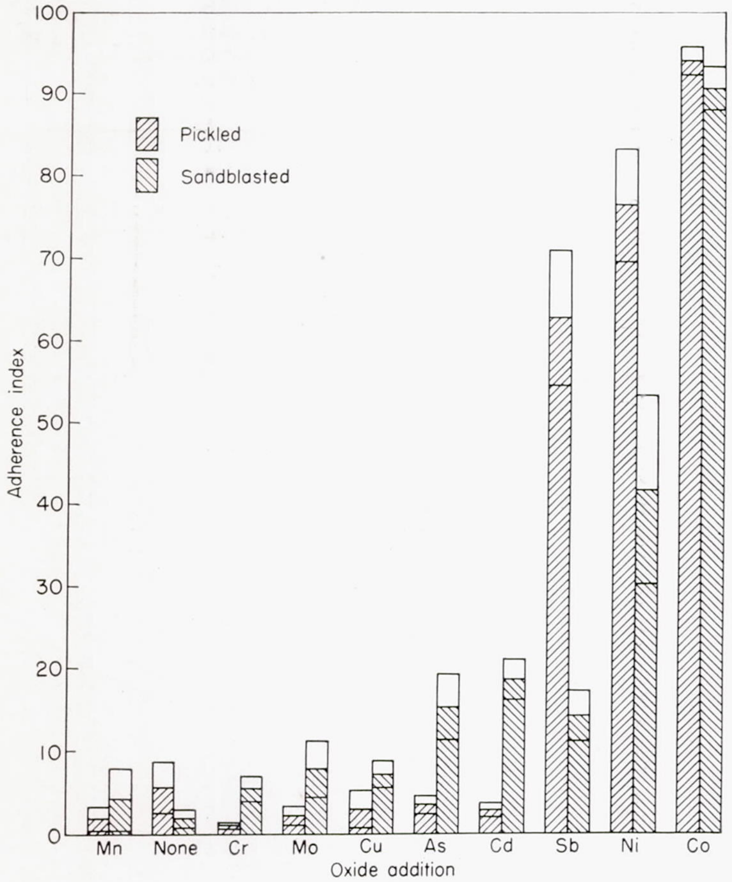

FIGURE 7.—Adherence as a function of metallic oxide smelted into a porcelain-enamel ground coat, showing effect of metal preparation. Horizontal lines above and below cross-hatched portion represent 95-percent confidence limits for average in each case. (See table V.)

In figure 5 adherence has been plotted as a function of the cobalt-oxide content of the enamel frit for enamels applied to polished, pickled, and sandblasted metal. In each case, maximum adherence was obtained with enamel E containing 0.8 percent of cobalt oxide. Type of metal preparation did not significantly affect the adherence of this enamel, the values being 90.5 ± 4.80 for polished, 93.9 ± 1.86 for pickled, and 90.7 ± 2.67 for sandblasted metal, respectively. When the complete curves are examined, however, there seem to be some definite trends. Where adherence is excellent (90 or better), the enamels adhere better to pickled metal, and, where adherence is fair or poor, the enamels generally adhere better to sandblasted metal. As shown in figure 5, better adherence was obtained on pickled or sandblasted metal than on polished metal, especially for enamel H containing 6.4 percent of cobalt oxide.

In figure 6 adherence has been plotted as a function of firing time, all specimens having been coated with enamel E (containing 0.8 percent cobalt oxide) which was found in the previous test to give maximum adherence. These curves show that adherence went through a maximum at some time between 4 and 6 minutes. Except for the specimens fired for 2 minutes, on which adherence was poor, better adherence was obtained in every case on pickled metal than on sandblasted metal.

Figure 7 is a bar chart showing the degree of adherence obtained with enamels containing the various metallic oxides applied to both pickled and sandblasted iron. The effect of metal preparation on adherence noted in the previous figures again appears in these data. If adherence is poor, the enamel adheres better to sandblasted iron; if adherence is good, the enamel adheres better to pickled iron. No adequate explanation was found as to why the antimony-bearing enamel adhered so much better to pickled iron than to sandblasted iron.

When interface ratio was plotted against anchor points per centimeter for all specimens, as in figure 8, a good correlation was indicated. The two lines shown on the figure are the least-squares regression lines, one having the ordinate and the other the abscissa as the independent variable. The angle between these two lines is a function of the correlation coefficient, which is a statistical measure of the interdependence of the two variables. If the correlation were perfect, the two lines would coincide, all points would lie on the line, and the correlation coefficient would be ± 1.00. If the two lines intersect at right angles, there is no linear relation between the variables, and the correlation coefficient is zero. For the conditions prevailing in these experiments, a correlation coefficient above 0.95 is regarded as indicating excellent correlation, 0.85 to 0.95 very good, 0.70 to 0.85 good, 0.50 to 0.70 fair, and below 0.50 poor. In the data presented in figure 8, the correlation coefficient of 0.923 indicates very good agreement between the two methods, especially when the high scatter of the values, from which each plotted average (point) was obtained, is considered.

Correlation coefficients were computed for the relation between (1) adherence and anchor points per centimeter and (2) adherence and interface ratio for each group of specimens,

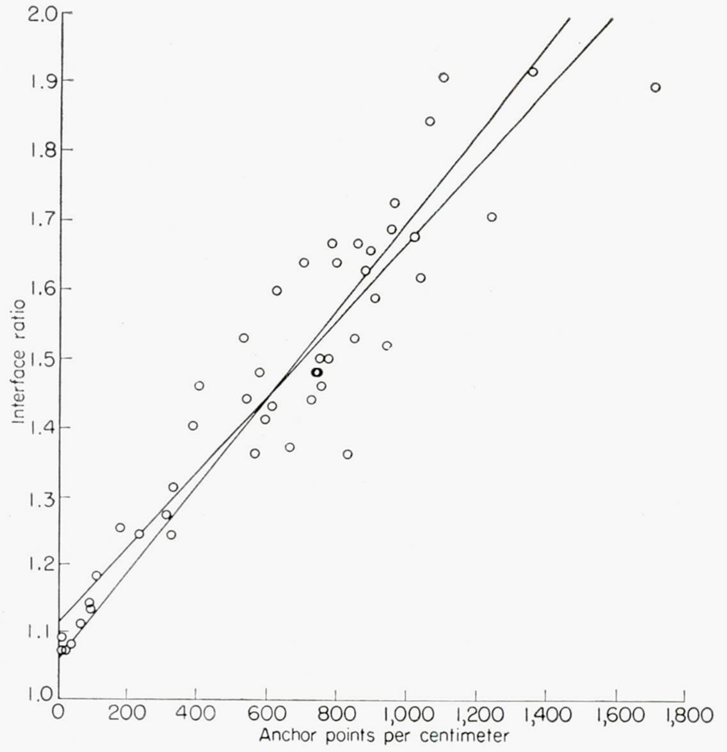

FIGURE 8.—Interface ratio plotted as a function of anchor points per centimeter for all samples tested. Correlation coefficient, 0.923.

with the results indicated in table VII. With but two exceptions, where the differences are slight, adherence correlated better with anchor points per centimeter than with interface ratio. This finding indicates that the keying-in action of the rough interface is probably more important than the effect of the increased area of contact between enamel and metal.

When anchor points per centimeter are plotted against adherence index for all 48 specimens, as in figure 9, it is found that the correlation is fairly good, the coefficient being 0.786. Close examination of this chart discloses that enamels applied to sandblasted metal generally have more anchor points per centimeter at the same adherence values than do the same enamels applied to pickled metal. When the data are plotted separately for sandblasted and pickled specimens, as in figures 10 and 11, there is much better correlation, as indicated by the higher correlation coefficients and smaller angles between regression lines.

The observation that lines with different parameters are obtained for enamels applied to sandblasted and pickled iron indicates that one or more factors other than roughness of interface also affect adherence. Since good adherence was in all cases associated with values of roughness above 500 anchor points per centimeter, one may conclude that this degree of roughness is necessary for the development of good adherence. On the other hand, values of roughness up to 1,000 anchor points per centimeter were sometimes associated with poor adherence; hence it appears that roughness alone is not a sufficient condition for adherence.

Under optimum conditions no significant difference was found between the adherence obtained on polished metal, which was completely smooth before coating, and that

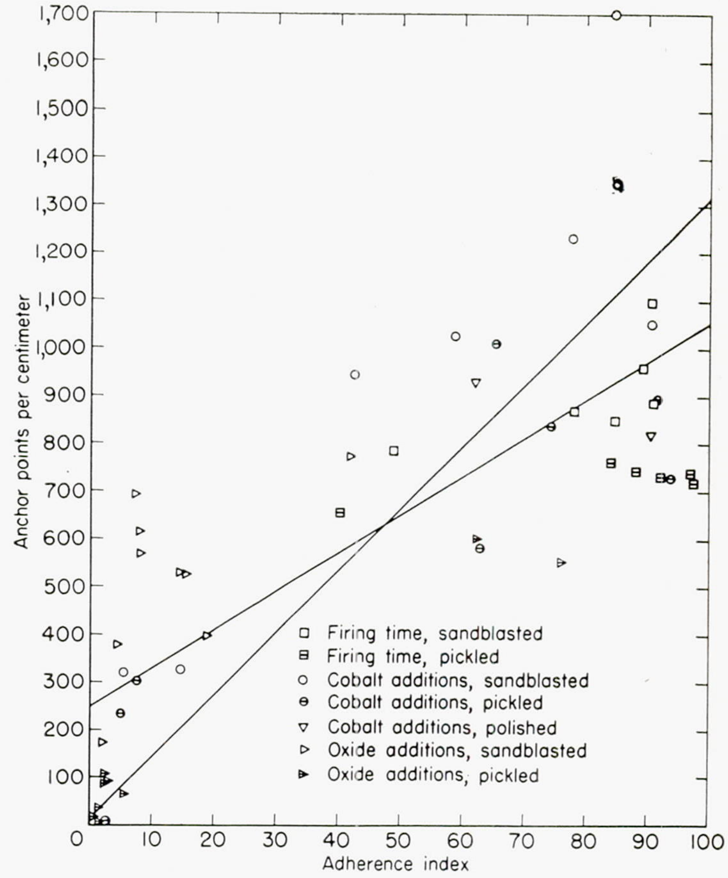

FIGURE 9.—Anchor points per centimeter plotted as a function of adherence for all samples tested. Correlation coefficient, 0.786.

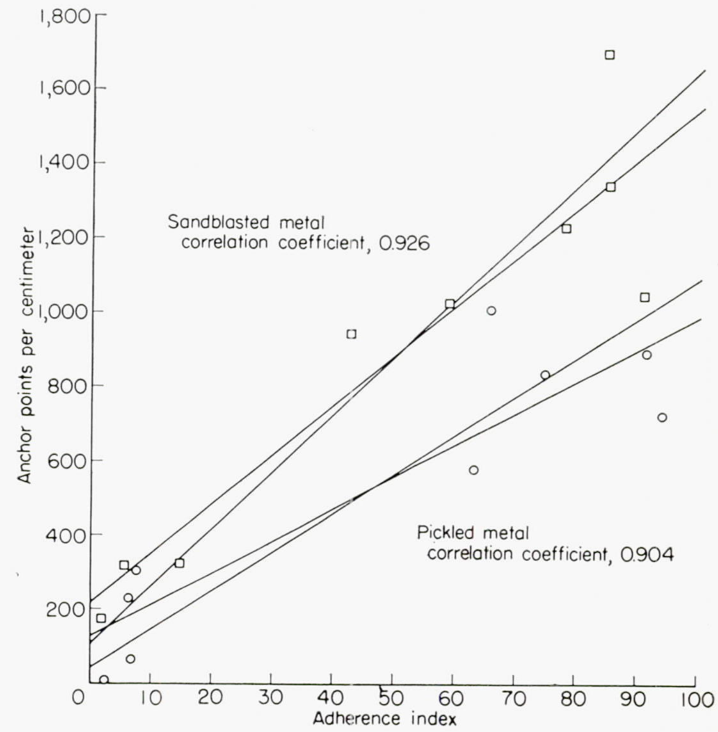

FIGURE 10.—Anchor points per centimeter plotted as a function of adherence index for enamels of various cobalt contents, showing effect of metal preparation.

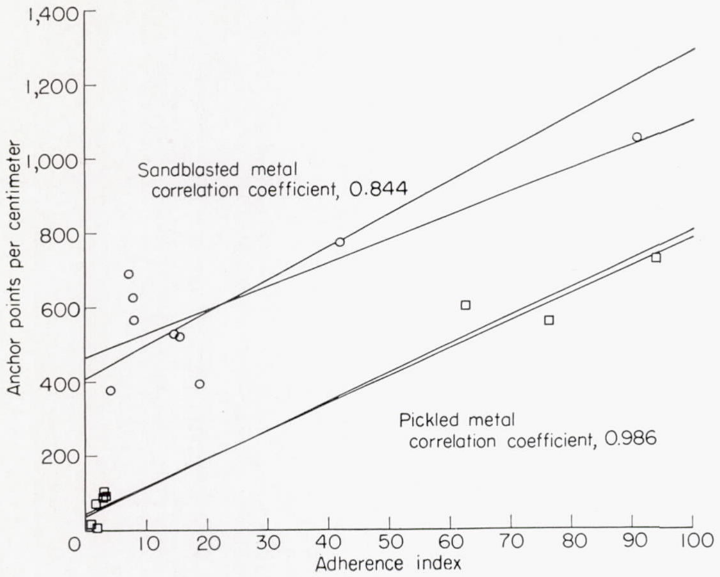

FIGURE 11.—Anchor points per centimeter plotted as a function of adherence for enamels having various metallic-oxide additions, showing effect of metal preparation.

obtained on sandblasted metal, which was initially fairly rough. This indicates that the roughness associated with good adherence must have been developed during the firing process.

CONCLUSIONS

It should be emphasized that this phase of the investigation on the general subject of adherence was concerned only with a study of the relationship between adherence and roughness of interface between enamel and iron. The mechanism by which this roughness is developed is covered in a second paper (NACA TN 2935). The following conclusions appear to be justified from the data presented here:

1. A positive correlation was found between the adherence of a porcelain-enamel ground coat and the roughness of the interface.
2. In general, adherence correlated better with anchor points per centimeter than with the increase in interfacial area (interface ratio).
3. The method of metal preparation had a marked effect on the relation between roughness of interface and adherence of porcelain-enamel ground coats to enameling iron. In general, better adherence was associated with the enamels applied to pickled iron than to sandblasted iron for the same degree of roughness of interface.
4. Most of the roughness that was associated with good adherence between a porcelain-enamel ground coat and iron developed during the firing process.
5. Roughness of interface is a necessary, but not a sufficient, condition for the development of good adherence between a porcelain-enamel ground coat and iron.
6. One or more factors other than roughness of interface also influence the adherence between a porcelain-enamel ground coat and iron.

NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C., *October 1, 1952.*

APPENDIX

REVIEW OF LITERATURE

Many writers have observed that the interface between enamel and metal is rough when adherence is good and smooth when adherence is poor, but for the most part adherence has been ascribed to some mechanism other than interfacial roughness. Tostmann (ref. 7) in 1909 postulated that adherence is due to a chemical action of the enamel on the iron. Part of the cobalt oxide is reduced to metal and forms a porous spongy alloy with the iron at the interface, which promotes adherence. However, he offers no experimental evidence for his theory.

Clawson (ref. 8) in 1929 studied adherence of ground coats containing normal amounts of adherence oxides, very small amounts of adherence oxides, and no adherence oxides. He made metallographic sections and prepared photomicrographs showing that there was a rough interface between enamel and metal when adherence was good and a smooth interface when adherence was poor. He ascribed adherence to the roughening of the metal and offered several theories as to the mechanism of the attack causing the roughening, but without experimental proof of any particular theory.

Staley (refs. 9 and 10) in 1934 proposed an electrolytic theory of adherence. According to this theory, all metals more noble than iron are precipitated from the molten enamel by galvanic ("electrolytic") action, and the plates adhere firmly to the iron. The precipitated metal protects the surface of the iron from attack by the molten enamel; hence, any surface roughness produced by pickling or sandblasting prior to enameling remains after the enamel has been fired. As the plating-out action continues, dendrites are formed, and the enamel is mechanically bonded to the base metal by the dendrite formation and by jagged projections and holes.

Dietzel (ref. 11) in 1935 described an investigation of enamel adherence in which he followed the development of bond by chemical methods and by microscopic examination of chips or flakes of enamel removed at various stages in the firing process. He concluded that the determinative reaction in the development of adherence was a galvanic attack on the iron by the enamel to give a roughened surface. The enamel then became mechanically anchored to the pitted surface.

Rosenberg (ref. 12) apparently considered adherence to be due entirely to mechanical forces. He states that the glass in its molten state has penetrated into the iron and is held there mechanically. According to his theory the glass itself acts as a reagent which reacts directly with the iron to produce cavities. The glass chemically reacts with the metal and takes the iron into solution. If this corrosion were regular, the bonding would not take place. The glass must therefore be an etching agent which produces a rough rather than a smooth interface to promote adherence. Rosenberg does not go into details in this paper as to the mechanism responsible for this selective attack on the metal, but was granted a patent in 1936 (ref. 13) based on a theory similar to that proposed by Dietzel.

Other writers, while noting the presence of a rough interface between enamel and metal when adherence is good, consider that adherence is due primarily to other causes. Howe's photomicrographs (ref. 14) show that roughness of interface is at least qualitatively correlated with adherence, but this correlation is largely overlooked in the text of his paper, and he ascribes adherence to another mechanism. Howe and Fellows (ref. 15), in describing tests made with manganese, cobalt, and nickel oxides, state that the iron interface was more irregular when cobalt was added, but there did not appear to be very much connection between this roughened condition and adherence. Kautz (ref. 16) states that there seems to be no relation between the degree of irregularity of the enamel-metal interface and the adherence after a normal firing. Rueckel and King (ref. 17), in contrast with other investigators, found that the interface became smoother with increasing cobalt content. Because of this observation, they concluded that adherence is not a function of the roughness of the contact line between enamel and metal. King (ref. 18) in another paper again states that roughness of surface and differential etching are not important factors in adherence.

REFERENCES

1. Moore, D. G., Pitts, J. W., Richmond, J. C., and Harrison, W. N.: The Galvanic Corrosion Theory for Adherence of Porcelain-Enamel Ground Coats to Steel. NACA TN 2935, 1953.
2. Moore, Dwight G., Mason, Mary A., and Harrison, William N.: Relative Importance of Various Sources of Defect-Producing Hydrogen Introduced Into Steel During the Application of Porcelain Enamels. Jour. Am. Ceramic Soc., vol. 35, no. 2, Feb. 1, 1952, pp. 33–41. (Also available as NACA Rep. 1120.)
3. Harrison, W. N., Richmond, J. C., Pitts, J. W., and Benner, S. G.: A Radioisotope Study of Cobalt in Porcelain Enamel. Jour. Am. Ceramic Soc., vol. 35, no. 5, May 1952, pp. 113–120. (Also available as NACA TN 2695.)
4. Dietzel, A.: Molybdenum in Enamels. Emailwaren-Ind., vol. 18, nos. 13–14, 1941, pp. 30–31.
5. Housley, W. L., and King, R. M.: Mechanics of Enamel Adherence, XI Application of the Theory of Dendritic Adherence to the Development of White Ground Coats for Sheet Steel. Jour. Am. Ceramic Soc., vol. 18, no. 10, Oct. 1935, pp. 319–320.
6. Anon.: Test for Adherence of Porcelain Enamel to Sheet Metal, a Tentative Standard Test of the Porcelain Enamel Institute. Bull. T–17, Porcelain Enamel Inst. (Washington, D. C.), 1951.
7. Tostmann, C.: The Influence of Cobalt Oxide on the Properties of Ground Coat Enamels for Kitchenware. Keramische Rundschau, vol. 17, no. 2, 1909, p. 46.
8. Clawson, C. D.: A Study of Adherence of Ground Coats to Sheet Steel. Ceramic Ind., vol. 13, no. 2, Aug. 1929, pp. 164–166.
9. Staley, H. F.: Electrolytic Reactions in Vitreous Enamels and Their Relation to the Adherence of Enamels to Steel. Jour. Am. Ceramic Soc., vol. 17, no. 6, June 1934, pp. 163–167.
10. Staley, H. F.: Discussion of Lord Paper. Jour. Am. Ceramic Soc., vol. 20, no. 4, Apr. 1937, pp. 121–124.
11. Dietzel, A.: Adherence of Enamels to Sheet Iron. Sprechsaal Keramik, Glas und Email, vol. 68, no. 1, 1935, pp. 3–6; no. 2, 1935, pp. 20–23; no. 3, 1935, pp. 34–36; no. 4, 1935, pp. 53–56; no. 5, 1935, pp. 67–69; no. 6, 1935, pp. 84–85.
12. Rosenberg, J. E.: Outline of Interesting Enameling Problems. Products Finishing, vol. 1, no. 10, July 1937, pp. 5–12.
13. Rosenberg, J. E.: Production of Enamelware. U. S. Patent 2,043,559, June 9, 1936.
14. Howe, E. E.: Observations on the Adherence Phenomena of Sheet Iron Ground Coats. Better Enameling, vol. 9, no. 9, Sept. 1938, pp. 13–29.
15. Howe, E. E., and Fellows, R. L.: Effect of Manganese, Nickel and Cobalt Oxide Upon the Adherence and Reboiling Properties of a Ground-Coat Enamel. Jour. Am. Ceramic Soc., vol. 20, no. 10, Oct. 1937, pp. 319–324.
16. Kautz, K.: The Effect of Iron Surface Preparation Upon Enamel Adherence. Jour. Am. Ceramic Soc., vol. 20, no. 9, Sept. 1937, pp. 288–295.
17. Rueckel, W. C., and King, R. M.: Mechanics of Enamel Adherence, II Effect of Composition and Firing Atmosphere on the Adherence of Ground-Coat Enamels. Jour. Am. Ceramic Soc., vol. 14, no. 10, Oct. 1931, pp. 782–788.
18. King, R. M.: Sheet Steel Ground-Coat Enamels. Proc. Inst. Vitreous Enamelers, vol. 3, 1937, pp. 203–210; abstracted in Enamel Bibliography and Abstracts, Am. Ceramic Soc., Inc. (Columbus, Ohio), 1944, p. 150.

TABLE I.—BASIC COMPOSITION OF FRITS USED FOR PREPARING VARIOUS GROUND COATS

(a) Batch composition

Material	Parts by weight
Potash feldspar	30.82
Borax (hydrated)	44.25
Flint	30.50
Soda ash	9.16
Soda niter	5.15
Fluorspar	8.30
	128.18

(b) Computed oxide composition

Oxide	Percent by weight
SiO_2	51.0
B_2O_3	16.1
Al_2O_3	5.7
Na_2O	15.4
K_2O	3.5
CaF_2	8.3
	100.0

TABLE II.—MILL BATCH USED FOR PREPARING GROUND-COAT SLIPS

[Milling time, 4.2 hr; 50 ml water plus 3 drops saturated $Na_4P_2O_7$ added before removing slip from mill; fineness, 4 g on 200 mesh from 50 ml of slip]

Material	Weight, g
Frit	1,000
Enameler's clay	60
Borax	10
Water	425

TABLE III.—COATING IDENTIFICATION AND METALLIC OXIDES ADDED TO BASE FRIT BATCH

Coating designation	Oxide added	Parts by weight (a)
I–1	None	0
A	Co_3O_4	.01
B	Co_3O_4	.1
C	Co_3O_4	.2
D	Co_3O_4	.4
E	Co_3O_4	.8
F	Co_3O_4	1.6
G	Co_3O_4	3.2
H	Co_3O_4	6.4
J	Sb_2O_3	.8
K	As_2O_3	.8
L	CdO	.8
M	Cr_2O_3	.8
N	CuO	.8
O	MnO_2	.8
P	MoO_3	.8
Q	NiO	.8

a Added to quantity of raw batch required to make 100 parts of frit.

TABLE IV.—ADHERENCE, ANCHOR POINTS PER CENTIMETER, AND INTERFACE RATIO FOR COATINGS WITH VARIOUS COBALT CONTENTS

Coating designation	Cobalt content, percent	Adherence index	Error (a)	Anchor points, no./cm	Error (a)	Interface ratio	Error (a)
Applied to pickled metal							
I–1	0	5.68	3.25	63	43	1.11	0.020
A	.01	2.64	1.52	8	11	1.07	.012
B	.1	4.90	1.86	228	68	1.24	.032
C	.2	7.60	2.75	304	79	1.27	.032
D	.4	62.8	6.00	583	126	1.41	.060
E	.8	93.9	1.86	729	115	1.48	.071
F	1.6	91.6	2.09	898	134	1.59	.061
G	3.2	74.4	4.09	839	118	1.53	.061
H	6.4	65.3	2.89	1,012	135	1.68	.074
Applied to sandblasted metal							
I–1	0	1.80	1.06	173	49	1.25	0.033
A	.01	5.62	2.00	319	83	1.24	.047
B	.1	14.7	4.05	323	80	1.31	.059
C	.2	42.4	10.27	945	128	1.69	.095
D	.4	58.6	6.30	1,028	126	1.62	.095
E	.8	90.7	2.67	1,052	175	1.85	.132
F	1.6	84.8	4.06	1,347	156	1.92	.139
G	3.2	84.3	2.52	1,701	208	1.90	.091
H	6.4	77.6	2.91	1,233	148	1.71	.105
Applied to polished metal							
E	0.8	90.5	4.80	823	145	1.36	0.051
H	6.4	61.7	4.33	933	139	1.52	.064

a 95-percent confidence error for average value reported in preceding column.

TABLE V.—ADHERENCE INDEX, ANCHOR POINTS PER CENTIMETER, AND INTERFACE RATIO FOR COATINGS CONTAINING 0.8 PERCENT OF VARIOUS METALLIC OXIDES

Coating designation	Metal-oxide addition	Adherence index	Error (a)	Anchor points, no./cm	Error (a)	Interface ratio	Error (a)
Applied to pickled metal							
E	Co_3O_4	93.9	1.86	729	115	1.48	0.071
J	Sb_2O_3	62.5	8.27	603	117	1.43	.061
K	As_2O_3	3.33	1.14	91	50	1.13	.051
L	CdO	2.78	.76	87	63	1.14	.035
M	Cr_2O_3	.89	.32	16	19	1.07	.013
N	CuO	2.90	2.14	106	54	1.18	.039
O	MnO_2	1.80	1.50	35	31	1.08	.018
P	MoO_3	1.89	1.14	8	11	1.09	.012
Q	NiO	76.3	6.82	556	126	1.36	.053
Applied to sandblasted metal							
E	Co_3O_4	90.7	2.67	729	115	1.48	0.071
J	Sb_2O_3	14.3	3.04	528	87	1.44	.070
K	As_2O_3	15.2	3.95	520	106	1.53	.100
L	CdO	18.6	2.48	394	79	1.46	.112
M	Cr_2O_3	7.9	1.61	567	124	1.48	.110
N	CuO	7.0	1.60	693	110	1.64	.119
O	MnO_2	4.2	3.95	378	87	1.40	.083
P	MoO_3	7.7	3.41	614	101	1.60	.111
Q	NiO	41.7	11.35	772	95	1.67	.100

a 95-percent confidence error for average value reported in preceding column.

TABLE VI.—ADHERENCE INDEX, ANCHOR POINTS PER CENTIMETER, AND INTERFACE RATIO FOR ENAMEL E (0.8 PERCENT COBALT) FIRED VARIOUS TIMES AT 1,550° F

Firing time, min	Adherence index	Error (a)	Anchor points, no./cm	Error (a)	Interface ratio	Error (a)
Applied to pickled metal						
2	40.2	28.4	657	109	1.37	0.036
4	97.5	2.21	717	123	1.44	.051
6	96.9	2.28	740	110	1.50	.039
8	92.1	2.93	732	99	1.48	.040
12	88.3	3.50	744	103	1.46	.053
18	84.2	4.48	763	107	1.50	.047
Applied to sandblasted metal						
2	48.7	11.2	787	122	1.64	0.091
4	91.1	3.0	1,091	122	1.91	.105
6	91.3	3.2	886	135	1.66	.096
8	89.7	3.4	953	124	1.73	.082
12	85.3	4.6	847	131	1.67	.079
18	78.4	3.1	870	154	1.63	.090

a 95-percent confidence error for average value reported in preceding column.

TABLE VII.—CORRELATIONS BETWEEN ADHERENCE AND ROUGHNESS OF INTERFACE

Specimens			Correlation coefficients	
			Adherence against—	
Variable	Metal preparation	Number	Anchor points/cm	Interface ratio
All	All	48	0.786	0.662
Cobalt content	Pickled	9	.904	.873
	Sandblasted	9	.926	.964
Metal-oxide content	Pickled	9	.986	.961
	Sandblasted	9	.844	.816
Time of firing	Pickled	6	.806	.816
	Sandblasted	6	.663	.457

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