NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2695

MIGRATION OF COBALT DURING FIRING OF GROUND-COAT ENAMELS ON IRON

By William N. Harrison, Joseph C. Richmond,
Joseph W. Pitts, and Stanley G. Benner

National Bureau of Standards

Washington
June 1952

1J

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2695

MIGRATION OF COBALT DURING FIRING OF GROUND-COAT ENAMELS ON IRON

By William N. Harrison, Joseph C. Richmond,
Joseph W. Pitts, and Stanley G. Benner

SUMMARY

To determine experimentally what happens to the cobalt oxide in a porcelain-enamel ground coat during firing, a porcelain enamel containing a radioactive isotope of cobalt $\left(Co^{60}\right)$ smelted into the frit was prepared and applied to enameling-iron blanks. These specimens were fired under conditions which produced a normal porcelain enamel and underfired and overfired enamels. The enamel, metal, and interface layer between the enamel and metal were then removed separately, by chemical solution, and radioassays were made on the solutions and residues. Results of these radioassays lead to the following conclusions:

(1) A cobalt-bearing phase is formed at the enamel-metal interface

(2) The enamel layer is depleted in cobalt oxide near the interface

(3) The amount of cobalt in the deposit found at the interface varies directly with the severity of the firing treatment

(4) The deposit at the interface is metallic, rather than a silicate or oxide, but the amount of alloying, if any, has not been established

(5) The amount of deposit formed under normal firing conditions is extremely small - on the order of 0.01 micron thick when computed as a continuous layer of metallic cobalt

(6) No evidence was found to indicate that the metallic cobalt deposit penetrates into the enameling-iron base during firing

(7) The metallic cobalt-bearing phase penetrates into the enameling-iron base during prolonged heating at 1300° F

INTRODUCTION

The utility of a coating depends to a considerable extent upon its ability to adhere to the surface to which it is applied. When the adherence is destroyed, the coating flakes off, and the underlying surface is exposed.

Good adherence is particularly important for ceramic coatings in high-temperature service, because the service conditions usually tend to accentuate stresses between the coatings and the metal. Conventional porcelain-enamel ground coats are similar in many ways to high-temperature ceramic coatings but generally consist of a single glassy phase with no solids present. For this reason, they lend themselves more readily to studies of the mechanisms of adherence.

Cobalt oxide has been used to promote adherence of porcelain enamels to iron since the first commercial development of these coatings a half century or more ago. The early enamelers recognized the necessity for this material in the ground coat, even though they did not understand the mechanism by which it promotes adherence. If used alone, cobalt oxide is most effective in amounts of about 0.5 to 1.2 percent by weight of the enamel frit. Because of the high cost of cobalt oxide, however, it is usually supplemented with the less-expensive oxides of nickel and manganese, both of which appear to promote adherence in the presence of cobalt oxide, but neither of which is very effective by itself.

Conventional porcelain-enamel ground coats are complex alkali borosilicates, usually containing at least 8 and sometimes 10 or 12 components. Because of the similarity of the physical and chemical properties of iron, cobalt, and nickel, the identification and quantitative estimation of small amounts of one of these materials in the presence of the others in such a complex system are difficult by ordinary chemical and physical methods. The use of radioactive tracers greatly simplifies this problem, since the metal can be positively identified and the amount quantitatively estimated by this method in concentrations smaller by many orders of magnitude than is possible by any other method, including spectrography. A discussion of the properties of radioactive isotopes is given in appendix A.

A great deal of research has been done on the adherence of porcelain enamel to metal. As a result, a number of theories of adherence have been developed but no unanimity of opinion has thus far been obtained. A review of the literature dealing with these various theories of adherence is given in appendix B.

Practically all of the data reported in the literature dealing with the formation of metallic phases in the enamel or at the enamel-metal interface (a layer between enamel and metal) were obtained under conditions differing widely from those occurring in practice. Such expedients as use of a water-soluble borax glass, high concentrations of adherence oxides, or prolonged firing at temperatures above the normal firing range were employed to obtain amounts of the metallic phases large enough for study by the methods then available. Data obtained under such exaggerated conditions are always open to question.

A broad general investigation of the mechanism of adherence of porcelain enamels and ceramic coatings to metal was therefore undertaken at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics. The investigation reported herein was planned to obtain experimental evidence as to the behavior of cobalt in promoting adherence of porcelain enamel to iron by using very sensitive radioisotope techniques. A radioactive isotope of cobalt (Co^{60}), in the form of oxide, was obtained for this study from the Oak Ridge National Laboratory, Oak Ridge, Tennessee. The specific questions dealt with in the present investigation are: (1) Is metallic cobalt precipitated at the enamel-metal interface? (2) If metallic cobalt is precipitated at the enamel-metal interface, does it penetrate into the metal? and (3) Is there any type of segregation of cobalt oxide within the ground-coat enamel, or, on the contrary, is it uniformly distributed within the ground-coat layer?

EXPERIMENTAL PROCEDURE

Preparation of Specimens

A typical one-frit porcelain-enamel ground coat was prepared, having the composition indicated in table 1. A 2000-gram batch (melted weight) was weighed out and mixed dry in a ball mill for 1 hour, transferred to a 25-pound lard tin, and covered. The can was placed inside a dust-tight safety chamber, equipped with sealed-in rubber gloves, after which the chamber was closed. Approximately 0.15 gram of radioactive cobalt oxide, with total activity of about 3 millicuries, was added to the batch, and the can was closed and sealed with rubber tape. All of these operations were performed within the sealed chamber to prevent scattering of radioactive dust.

The can was removed from the safety chamber and revolved on ball-mill rolls for 1 hour to distribute the radioactive cobalt oxide throughout the batch. It was then replaced in the chamber, which was again sealed. The cover was removed, the batch was transferred to paper bags, about 200 to 250 grams to a bag, and each bag was sealed with cellophane tape. The bags were removed from the safety chamber, using long-handled tongs, and tested for radioactivity. All bags were found to have about the same amount of radioactivity, indicating that the radioactive cobalt oxide was well-distributed in the batch. The batch was smelted in an electric furnace, the top of which was enclosed in a hood attached to a suction fan. An alumina crucible was set in the furnace and heated to 2200° F overnight. This temperature was maintained in the furnace throughout the smelting operation. The batch was charged by dropping the paper bags one at a time through the hole in the top of the furnace into the crucible, the bags being handled only with long-handled tongs. This procedure eliminated dusting of the batch during smelting.

When the last charge had melted, 2 hours after the first charge, the batch was stirred with a platinum-coated stirring rod driven by a small electric motor by means of a flexible shaft. The furnace, with stirring rod in place, is shown in figure 1. The batch was stirred at 12 rpm until a sample indicated that all of the materials had been dissolved, a total time of 40 minutes. The molten glass was poured into water to produce frit I-109ER. The temperature of the outside of the crucible, as measured with an optical pyrometer just before pouring, was 2165° F.

A second frit, I-109E, of the same composition, in which none of the cobalt was radioactive, was smelted under identical conditions.

These frits were milled according to normal practice, using the mill batch shown in table 2, to produce enamel I-2R, containing radioactive cobalt, and enamel I-2, without radioactive cobalt.

Fifty-six 4- by 4-inch specimens of 18-gage enameling iron were cleaned by sandblasting and coated with enamel I-2 by dipping, to produce an enamel of fired thickness of 0.005 ± 0.001 inch. These specimens were fired separately under a wide range of conditions, varying from 2 minutes at 1450° F to 10 minutes at 1750° F. The specimens were then deformed in the hydraulic press as specified in the Porcelain Enamel Institute tentative standard adherence test (reference 1) and graded visually for adherence. On the basis of this visual rating, the following firing conditions were selected for use in this study:

Firing condition	Time (min)	Temperature (°F)
Underfired	4	1450
Normally fired	4	1575
Overfired	6	1750

The conditions for underfiring and overfiring were selected to represent the extremes of commercial practice, which result in unsatisfactory wear.

Additional 4- by 4-inch specimens of 18-gage enameling iron were cleaned by sandblasting and then coated with enamels I-2 or I-2R. In each case the enamel was applied at the weight required to give a fired thickness of 0.005 ± 0.001 inch. Seven specimens coated with each enamel were fired under each of the above firing conditions and then tested for adherence by the Porcelain Enamel Institute test (reference 1). The results are shown in table 3 and indicate that the two enamels have the same good adherence when fired under normal conditions. When both enamels were either underfired or overfired, the enamel containing radioactive cobalt oxide had slightly better adherence.

Deposition of Cobalt on Iron

In the exploratory work with the radioactive cobalt-bearing enamel, several 2- by 2-inch specimens were coated and fired to give an overfired enamel. The enamel was removed from one specimen by sandblasting, and the metal blank was found to be moderately radioactive. Similar results were obtained when the enamel was removed from a second specimen by de-enameling with molten sodium hydroxide. This material melts at 605° F and is used at a temperature not over 700° F. Under these conditions the enamel is readily dissolved, and the oxide layer at the interface is partially dissolved, but the metallic iron and cobalt are not affected.

To obtain quantitative data, the radioactive cobalt-bearing enamel was applied to six enameling-iron specimens $1\frac{1}{4}$ inches square. Duplicate specimens were fired under conditions to give underfired, normally fired, and overfired coatings. Each of these specimens was de-enameled with molten sodium hydroxide, rinsed in hot water, and dried; then its radioactivity was determined.

The radioactivity determination was made with an end-window Geiger-Müller tube attached to a decade scaler. This process will hereafter be referred to as counting. All specimens were counted using identical geometry unless otherwise indicated. The radioactivity is expressed as counts per minute.

Figure 2(a) is a photomicrograph of a metallographic section of an overfired specimen treated as described above. Figure 2(b) is an autoradiograph of the same section. The dark areas in the autoradiograph indicate the presence of radioactivity at the surface of the metal.

After counting, the oxide layer on the surface of each of the six specimens was removed by solution in a 10-percent aqueous solution of ammonium citrate, 65 hours of treatment with constant agitation being used. The ammonium-citrate solution was prepared by dissolving 10 grams of ammonium citrate in 90 milliliters of water. This reagent dissolves the oxides of iron and cobalt at room temperature but does not dissolve the enamel. Both metallic iron and metallic cobalt are slightly soluble in this reagent but much less so than the oxides. After this treatment the specimens were rinsed in hot water, blotted dry with laboratory tissue, and again counted. Results are shown in table 4.

A normally fired ground coat containing radioactive cobalt was dissolved from the enameling-iron base by treatment with molten sodium hydroxide. The radioactivity of the metal blank was then determined by counting, and a value of 1182 counts per minute was obtained. The blank was then treated with ammonium-citrate solution to remove the tightly adherent film of iron oxide, rubbed with a damp rag to remove any loose particles of cobalt metal, and again counted. The new value was 207 counts per minute. This large decrease in radioactivity can only be accounted for by removal of radioactive metallic cobalt present in, or under, the film of iron oxide, since any cobalt present as oxide would presumably have been dissolved in the enamel glass and hence would have been removed by the molten caustic.

The ground coat used in this investigation reaches normal maturity when fired 4 minutes at 1575° F. Some diffusion of cobalt into the iron would be expected at temperatures even lower than this if sufficient time were allowed. However, a specimen fired for 6 minutes at 1750° F (photomicrograph shown in fig. 3(a)) gave practically no indication of diffusion of cobalt into the base metal, as can be seen in the autoradiograph in figure 3(b).

To determine the effect of prolonged heat treatment, a specimen which had been coated with the radioactive cobalt-bearing ground coat and fired to give an enamel of normal maturity was heated in air at 1300° F for 270 hours. The enamel was removed by treatment with molten caustic and the radioactivity of the enamel-free iron surface was determined by counting. A count of 1075 per minute was obtained. After treatment with ammonium-citrate solution and rubbing, the count dropped to 951, a relatively small decrease. An overfired specimen was subjected to the same heat treatment (photomicrograph shown in fig. 4(a)) and an autoradiograph of this specimen (fig. 4(b)) indicates that there has been appreciable diffusion of the cobalt into the iron base metal.

Distribution of Cobalt in Fired Enamel

Several enameling-iron specimens were coated with the radioactive cobalt-bearing enamel, using the three firing conditions as before. Portions 1/2 inch square were cut from each specimen, and the enamel on one side and most of the metal were removed by grinding. The remainder of the metal was then removed by treatment in an iodine and potassium-iodide solution. The iodine and potassium-iodide solution was prepared by dissolving 20 grams of potassium iodide in 90 milliliters of water and then dissolving 20 grams of iodine in the resulting solution. This reagent dissolves metallic iron and cobalt at room temperature but does not dissolve the enamel. The oxides of iron and cobalt are very slightly soluble in this solution, but for these purposes they can be considered insoluble. The iodine and potassium-iodide solution was tested after removal of the iron base and found to be radioactive in each case. Counts were made on each side of each of the chips of enamel. The iron oxide at the enamel-metal interface was then removed by solution in ammonium citrate, and the chips were again counted on each side. The ammonium-citrate solution was tested after removal of the oxide layer and was found to be very slightly radioactive after this treatment. Results are shown in table 5.

The counts before and after removal of the iron oxide are not comparable because different geometry factors apply. However, identical geometry factors do apply to the measurements on opposite sides of each chip, either before or after removal of the oxide, so these measurements can be directly compared. The difference in counts between the opposite sides of any one chip, expressed as a percentage of the count on the outerface side, is independent of the geometry and can be used in comparing different chips.

Before removal of the oxide, each chip was placed on an aluminum plate, without cover, for counting. With this arrangement, the chip could be placed close to the window of the counter tube, and a relatively high geometry factor was achieved.

Many of the chips cracked during removal of the iron oxide. To minimize loss, each chip was mounted before treatment on cellulose tape, the outerface of the chip being next to the tape. This tape could not be removed after the treatment without further damage to the chip. A mount for counting was prepared by stretching a piece of cellulose tape across a 1-inch-diameter hole in a thin aluminum sheet. The chip was then mounted on this tape, with the innerface of the chip next to the tape. The chip was thus covered on each side with one layer of cellulose tape. One layer of this tape reduces the count on a specimen containing radioactive cobalt by about 40 percent because of absorption. The chip, mounted in this way, was placed at a somewhat greater distance from the window of the counter tube than was the loose chip before removal of the iron oxide. Both of these effects reduced the geometry factor, so a lower net count resulted after removal of the iron oxide.

The area of each chip was measured by photographing the chip at about 7-diameter enlargement and measuring the area on the photomicrograph with a planimeter. All counts in table 5 are corrected to counts per square inch of enamel.

DISCUSSION OF RESULTS

The results reported in table 4 indicate that there was a cobalt-bearing phase present at the enamel-metal interface, which was not removed by the molten-sodium-hydroxide treatment and which was only partially removed by the ammonium-citrate treatment. The presence of this radioactive layer accounts for the results shown in figure 2(b). Since contact with the radioactive cobalt-bearing enamel could not induce radioactivity in the surface of the iron, it follows that the deposit left after removal of the enamel by molten caustic must contain cobalt. The data in table 5 indicate that this deposit was removed from the chips of enamel along with the metallic iron during the iodine and potassium-iodide treatment and that the cobalt therefore was in the metallic form.

The counts on the two sides of the chips from which the metal base had been removed, given in table 5, indicate that the enamel was depleted in cobalt content near the enamel-metal interface during firing, resulting in a concentration gradient within the enamel layer.

The data on the radioactivity of the de-enameled specimens (table 4) indicate that the amount of the cobalt-bearing deposit increases with the severity of the firing treatment. The data on the radioactivity of the iodine and potassium-iodide solution with which the metal base was dissolved (table 5) also indicate an increase in the amount of cobalt at the enamel-metal interface with an increase in severity of firing. The data in table 5 giving the difference in counts obtained on the two sides of each chip also indicate that the depletion of cobalt oxide from the interface side of the enamel increased with the severity of the firing treatment.

Unfortunately, radioassay techniques do not give direct evidence of the nature of the cobalt-bearing deposit, since the radioactive decay process is not affected by the chemical or physical form of the radioactive isotope. The case for the metallic nature of the cobalt deposit therefore rests upon the fact that the deposit is removed with the iron base metal during the iodine and potassium-iodide treatment (producing a radioactive solution) but is not completely removed by 65 hours of treatment with ammonium citrate. The experiments performed so far do not indicate whether the cobalt is present as cobalt metal or as an alloy with iron, nickel, or both.

The amount of metallic cobalt deposited at the enamel-metal interface is extremely small. Assuming the ground coat to be applied at 20 grams per square foot (about 0.004 in. thick) on one side, the total amount of cobalt oxide present is 20 × 0.006 = 0.12 gram per square foot, which is equal to about 0.1 milligram of cobalt metal per square centimeter. Since cobalt metal has a specific gravity of 8.9, this would produce a continuous layer of cobalt only 0.11 micron thick if all of the cobalt was deposited at the interface.

The amount of cobalt removed with the iron by the iodine and potassium-iodide treatment can be computed by use of the following equation:

$$X = \frac{C/G}{A \times 3.7 \times 10^7}$$

where

X amount of cobalt removed, grams per square inch

C count on solution, counts per second per square inch of enamel (1664 per min or 27.7 per sec, from table 5)

G geometry factor for measuring conditions used

A activity of cobalt present in enamel, millicuries[1] per gram of cobalt metal (about 0.35 millicurie for cobalt used)

The geometry factor is the ratio of counts recorded to the number of disintegrations and is determined by such factors as the solid angle subtended by the window of the counter tube from the center of the specimen, expressed as a decimal fraction of the surface of a sphere of the same radius, the counting efficiency of the tube for the radiations involved, a back-reflection factor, and absorption of the tube window, air, and any other material between the sample and tube. This geometry factor has not been accurately evaluated but is 0.04 ± 0.02 for the conditions used for counts on dried residues from solutions.

---

[1] A millicurie of any substance is defined as that quantity of material undergoing 3.7×10^7 disintegrations per sec.

Substituting these values in the formula,

$$X = \frac{27.7/0.04}{0.35 \times 3.7 \times 10^{7}}$$

$$= 534.7 \times 10^{-7} \text{ gram/sq in.}$$

which is equivalent to 82.8×10^{-7} gram per square centimeter.

Dividing by the density of cobalt, 8.9 grams per cubic centimeter,

$$\frac{82.8 \times 10^{-7}}{8.9} = 9.3 \times 10^{-7} \text{ cm}$$

or 0.0093 micron, approximately 0.01 micron, the thickness of the layer of cobalt if it is present as a continuous layer of metallic cobalt. It is not surprising that such a layer has not been found by microscopic examination since its thickness is much less than the resolving power of the best light microscope. Even if it is deposited in dendritic form, its minute quantity explains why the photomicrographs of cobalt dendrites shown in the literature were not obtained under normal conditions but only with large increases in the cobalt content of the enamel and the time held at high temperature, beyond the range of enameling practice.

Figure 3 and the results reported in the section "Deposition of Cobalt on Iron" do not indicate that there is any significant penetration of metallic cobalt into the base metal during firing. If there was such penetration, it would be impossible to remove the deposit by scrubbing with a wet cloth, as was done. The findings that the deposited cobalt does not diffuse into the base metal during a normal firing and that most of it is not firmly attached to the steel indicate that the cobalt deposit, as such, probably does not contribute in a major way to the adherence. If for some reason the coating should adhere better to cobalt than to iron, no large improvement in adherence would be noted unless the cobalt showed a strong gripping action to the iron. Because this gripping does not develop during a normal firing, the cobalt must play some other role in the development of adherence.

CONCLUSIONS

Previous investigators postulated that cobalt oxide was reduced to the metal at the enamel-metal interface by the electrolytic action of the hot iron base during firing of a cobalt-bearing ground coat. Experimental evidence to verify this reaction, however, could only be obtained under exaggerated conditions, markedly different from those encountered in practice, because the amount of metallic deposit was too small to be identified or even found by the techniques then available.

By use of very sensitive radioisotope techniques, a cobalt-bearing metallic phase has been shown to be deposited at the enamel-metal interface when a normal cobalt-bearing ground coat is normally fired on iron. In addition, considerable information about this deposit has been obtained. The findings may be summarized as follows:

1. When a cobalt-bearing procelain-enamel ground coat is applied to enameling iron and fired, a cobalt-bearing phase is formed at the enamel-metal interface.

2. When a cobalt-bearing porcelain-enamel ground coat is applied to enameling iron and fired, the enamel layer is depleted in cobalt oxide near the interface.

3. The amount of the deposit formed at the enamel-metal interface varies directly with the severity of the firing treatment.

4. The deposit at the interface is metallic, rather than a silicate or oxide, but its degree of alloying, if any, has not been established.

5. The amount of metallic deposit formed under normal firing conditions is extremely small - on the order of 0.01 micron when computed as a continuous layer of metallic cobalt.

6. There is no evidence to indicate that the metallic cobalt-bearing deposit penetrates into the enameling-iron base during firing.

7. The metallic cobalt-bearing phase penetrates into the enameling-iron base during prolonged heating at 1300° F.

National Bureau of Standards
Washington, D. C., October 1, 1951

APPENDIX A

PROPERTIES OF RADIOACTIVE ISOTOPES

A radioactive isotope is identical to the normal stable element in all chemical properties and most physical properties. The electronic structures are identical - they have the same number and configuration of planetary electrons - which accounts for the chemical properties and those physical properties associated with the size of the atom or ion, such as atomic volume, compressibility, and so forth. The radioactive isotope has a different nuclear structure from that of the normal stable element and hence a different mass number and atomic weight. This difference in atomic weights results in a slight difference in those physical properties associated with mass, such as specific gravity.

A radioactive isotope can be positively identified and the amount quantitatively determined by radioassay procedures in concentrations smaller by many orders of magnitude than is possible by any chemical method, including spectrography. There is no interference from other materials present, provided only one radioactive isotope is used at a time.

The nucleus of a radioactive isotope is unstable. It will spontaneously disintegrate, giving off one or more high-speed particles and eventually forming a new, more stable nucleus of lower free energy. This process is called radioactive decay, or radioactivity.

Radioactive decay is statistical in nature. A single radioactive atom may decay at any time, regardless of its decay constant or half life - there is no basis for predicting when this will occur. With a large number of atoms, each particular radioactive isotope has a characteristic decay constant λ defined by the equation:

$$N = N_o e^{-\lambda t} \tag{1}$$

where

N number of atoms present at time t

N_o original number of atoms

The radioactive decay constant λ has the unit of reciprocal time, usually second^{-1}, and is not convenient to use. By substituting $N = 1/2N_o$

and solving for t, a more convenient constant, $t_{1/2}$, is obtained as follows:

$$t_{1/2} = \frac{0.693}{\lambda} \tag{2}$$

The $t_{1/2}$ defined by equation (2) is called the half life and is expressed in conventional time units. It is the time required for half of the original atoms to decay.

The rate of radioactive decay is an independent property of a radioactive isotope and cannot be altered by the chemical or physical form of the atoms which are decaying.

Several different types of high-speed particles are given off during the radioactive-decay process. The type of particle or particles and their energy or velocity are characteristic of the particular isotope involved. Any radioactive isotope can be identified by its half life and the type and energy of the particles given off during its decay.

The energy of a radioactive particle is expressed in terms of million electron volts, abbreviated Mev. The electron volt is defined as the kinetic energy imparted to an electron in passing through a potential rise of 1 volt. It is equal to 1.601×10^{-12} erg. Because of the small size of the electron volt, the usual unit is a million electron volts.

The radioactive isotope Co^{60} used in this investigation has a half life of 5.3 years and emits one 0.31-Mev beta particle and two gamma rays of 1.17- and 1.33-Mev energies per disintegration, forming stable Ni^{60}.

Beta and gamma rays are similar in that they both affect a photographic plate, cause fluorescence, and ionize any material through which they pass. They travel in straight lines and hence obey the inverse-square law.

A beta ray consists of electrons traveling at a velocity less than that of light. These electrons have a spectrum of energies - that is, there will be some electrons with every energy value between zero and a maximum value. This maximum value is spoken of as the "E value" (sometimes E max.) or energy of the particular beta ray involved. Beta rays have low penetrating power but high ionizing power as compared with gamma rays. The maximum range of the beta particles from Co^{60} is

0.8 millimeter of water. They can be completely stopped by any material weighing more than 80 milligrams per square centimeter. The total ionizing power of a beta particle is proportional to its initial velocity, but the amount of ionization per unit of path length varies inversely with the square of the velocity.

Gamma rays are electromagnetic radiations, which travel with the speed of light. The photons have no rest mass, and the energy is an inverse function of the wavelength. They are identical to X-rays, except that in general they have higher energies and shorter wavelengths. Gamma rays are monoenergetic; that is, all of the particles making up a gamma ray have the same energy or wavelength. Gamma rays are not completely stopped by any thickness of material but obey a law defined by the following equation:

$$I = I_o e^{-\mu T} \tag{3}$$

I	intensity of beam after passing through absorber of thickness T
I_o	initial intensity of beam
μ	linear absorption coefficient
T	thickness of absorber

The linear absorption coefficient μ is dependent upon the energy of the gamma ray and the atomic number of the absorber and is expressed in reciprocal thickness units. The linear absorption coefficients for lead for the 1.17- and 1.33-Mev gamma rays of cobalt 60 are about 0.70 and 0.60 per centimeter, respectively. For each absorber and each gamma-ray energy, there is a thickness of absorber called a half thickness, which will reduce the intensity of the gamma ray by one-half. These values for lead for the two gamma rays of Co^{60} are 0.40 and 0.44 inch, respectively.

APPENDIX B

REVIEW OF LITERATURE

There has been a great deal of research on the adherence of porcelain enamel to metal, and many papers have been written on the subject. According to reference 2, a recent survey of the literature cites more than 325 references, of which a substantial number relate directly to adherence. There is no unanimity of opinion as to the mechanism or mechanisms responsible for adherence, but the various theories of adherence can be conveniently classed under six headings as follows:

(1) Mechanical gripping

(2) Dendrite

(3) Electrolytic

(4) Oxide layer

(5) Chemical bond

(6) Hydrogen (nonadherence)

The mechanical-gripping theory as advanced by Clawson (reference 3) and others is based on the observation that there is a rough interface between enamel and metal when adherence is good, while the interface is relatively smooth when adherence is poor. The enamel is said to corrode the iron selectively during firing, giving an uneven and undercut surface which serves to attach the enamel layer firmly to the iron by a mechanical gripping action. Clawson states that cobalt oxide promotes a dissolving or fluxing action of the enamel, producing a spongy surface on the iron to which the enamel readily adheres.

The dendrite theory advanced by King (reference 4) is based on the observation that when the enamel adheres to the iron, metal dendrites are present. These dendrites are said to be responsible for the marked adherence of cobalt- and nickel-oxide enamels to iron. The dendrites were identified as alpha iron by Schwartzwalder and King (reference 5). The dendrites are said to overcome the strains set up by differential expansion, permitting the inherent attractive forces between enamel and metal to act, thus producing adherence. King (reference 6) ascribes the formation of these dendrites to the simultaneous oxidation and reduction of a ferrous-oxide (FeO) phase, forming iron (Fe) and ferroso-ferric oxide (Fe_3O_4).

Staley (reference 7) advanced the electrolytic theory. According to this theory, all the metals between iron and copper in the electromotive-force series of metals, if dissolved in glasses, are plated out of solution, when the glasses are fired as sheet-iron ground coats, by the electrolytic action of the iron base.

Of these plates cobalt, nickel, and antimony promote adhesion because according to Staley: (1) They adhere to iron; (2) the coefficient of thermal expansion is intermediate between the coefficients of iron and the enamel; (3) the enamel glass is mechanically bonded to the metal plate by dendrites, aided by jagged projections and holes; and (4) the metal plates are insoluble in the molten enamel, hence any structure favorable to adherence once formed remains.

Dietzel (reference 8) goes into somewhat more detail about the mechanism by which electrolytic deposition of cobalt and nickel promotes adherence. Cobalt oxide and nickel oxide are reduced by iron to the elements cobalt and nickel. Because of the precipitation of these metals on the iron, local currents appear which produce a strong selective corrosion of the iron surface at high temperature. The enamel goes into the cavities formed in this process and adheres by mechanical gripping.

The oxide-layer theory was first advanced by Cooke (reference 9). He states that the oxidation of the iron during firing is a vital step in successful enameling. The oxide is continuously dissolved in the enamel, forming a transition layer of varying composition. Kautz (reference 10) reported a layer of FeO approximately 0.00003 inch thick at the enamel-metal interface, to which he attributes the adherence of the enamel glass to the iron. Cobalt oxide was said to increase the solubility of ferric oxide in the enamel and to act as an oxygen carrier. This was in direct opposition to Vielhaber (reference 11) who said that cobalt oxide partially saturates the glass, thus reducing its iron-oxide dissolving power. In a later paper Kautz (reference 12) identified the iron oxide layer as consisting of essentially FeO with smaller amounts of Fe_3O_4 and Fe.

The chemical-bond or solution-bond theory was advanced by Howe (reference 13). He states that the adherence of sheet-iron ground coat to enameling iron is due to an oxidation of the iron with subsequent solution or chemical union bond. The function of cobalt oxide is said to be to increase the solubility in the enamel of the initial oxide and to act as an oxygen carrier, thus keeping a balance between the phases which tend to go out of equilibrium. Douglas and Zander (reference 14) elaborated on this theory somewhat by ascribing adherence to the sharing of oxygen bonds between the enamel and iron, following solution of the initial oxide layer. They state that oxidizing conditions must be continuously maintained at the enamel-iron interface to obtain adherence, and that cobalt acts as an oxidizing agent in the enamel to maintain the layer of shared oxygen at the interface.

The hydrogen theory of adherence or, more precisely, the theory of the cause of nonadherence advanced by Deringer (reference 15) is based on the assumption that porcelain enamel has inherent adherence for iron, just as it has for copper, whether or not cobalt oxide is present in the glass, and the difference between adherence to copper and to iron is caused by some property associated with iron that is not associated with copper. This difference in behavior is thought to be caused by the hydrogen gas in the iron. Nascent hydrogen readily diffuses through iron, even at room temperature, but not through copper. The hydrogen evolved during the firing of enamel on sheet iron acts as a barrier between the base metal and the enamel and blankets the metal surface to prevent the glass from wetting it. The presence of iron oxide at the interface indicates that the hydrogen (the obstacle to adherence) has been removed by oxidation to form water, which dissolves in the enamel glass. This oxide layer must be of the proper thickness - either too much or too little gives poor adherence. The function of cobalt oxide is to act as an oxygen carrier in maintaining the delicate balance required to give the amount of iron oxide at the interface necessary to oxidize the hydrogen.

From the foregoing it can be seen that cobalt oxide may promote adherence by (1) acting as an oxygen carrier, as proposed by Kautz, Howe, Douglas and Zander, and Deringer; (2) increasing the solubility of iron oxide in the enamel, as proposed by Clawson, Kautz, and Howe; (3) promoting the formation of alpha-iron dendrites, as proposed by King, or (4) being plated out on the iron as cobalt metal, as proposed by Staley and Dietzel.

REFERENCES

1. Anon.: Test for Adherence of Porcelain Enamel to Sheet Metal, a Tentative Standard Test of the Porcelain Enamel Institute. Porcelain Enamel Inst. (Washington, D. C.), 1951.

2. O'Bannon, L. S.: Hypothesis of Adherence of Porcelain Enamels to Metal - A Treatise of Published Works. Abstract, Bull. Am. Ceramic Soc., vol. 30, no. 3, March 1951, p. 93.

3. Clawson, C. D.: A Study of Adherence of Ground Coats to Sheet Steel. Ceramic Ind., vol. 13, no. 2, Aug. 1929, pp. 164-166.

4. King, R. M.: Mechanics of Enamel Adherence. VIII, Part B - Studies in Firing Enamels under Reduced Pressure. Jour. Am. Ceramic Soc., vol. 16, no. 5, May 1933, pp. 233-238.

5. Schwartzwalder, Karl, and King, R. M.: Mechanics of Enamel Adherence. VI - A Petrographic, Metallographic and X-Ray Study of Enamel-Metal Contact Zones. Jour. Am. Ceramic Soc., vol. 15, no. 9, Sept. 1932, pp. 483-486.

6. King, R. M.: Mechanics of Enamel Adherence. XIII - A Review of the Theoretical Explanations for the Formation of Metal Particles in "Cobalt" Ground Coats and Some Pertinent Experiments. Jour. Am. Ceramic Soc., vol. 20, no. 2, Feb. 1937, pp. 53-55.

7. 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.

8. Dietzel, A.: Adherence in Sheet-Iron Enamelware. Sprechsaal für 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. Abstract, Ceramic Abstracts, 1944, p. 67.

9. Cooke, R. D.: The Effect of Furnace Atmosphere on the Firing of Enamel. Jour. Am. Ceramic Soc., vol. 7, no. 4, April 1924, pp. 277-281.

10. Kautz, Karl: Further Data on Enamel Adherence. Jour. Am. Ceramic Soc., vol. 19, no. 4, April 1936, pp. 93-108.

11. Vielhaber, L.: Behavior of Metal Oxides in Ground Coats on Sheet Steel. Keramische Rundschau, vol. 33, 1925, pp. 53-55. Abstract, Ceramic Ind., vol. 4, no. 5, May 1925, p. 371.

12. Kautz, Karl: Oxide Film between Fired Ground-Coat Enamels and Iron. Jour. Am. Ceramic Soc., vol. 22, no. 8, Aug. 1939, pp. 247-255.

13. Howe, E. E.: Observations on the Adherence Phenomena of Sheet Iron Ground Coats. Better Enameling, vol. 9, no. 9, 1938, pp. 13-29.

14. Douglas, G. S., and Zander, J. M.: X-Ray Diffraction Study of the Oxidation Characteristics of Nickel-Pickled Sheet Iron as Related to Enamel Adherence. Jour. Am. Ceramic Soc., vol. 34, no. 2, Feb. 1951, pp. 52-59.

15. Deringer, W. A.: Relation of Hydrogen to Adherence of Sheet Steel Enamels. Jour. Am. Ceramic Soc., vol. 26, no. 5, May 1943, pp. 151-162.

TABLE 1.- COMPOSITION OF FRIT I-109E[1]

(a) Batch composition.

Material	Parts by weight
Oxford crystal feldspar	29.68
Borax	43.66
Soda niter	5.99
Flint	30.35
Saltpetre	1.01
Fluorspar	7.66
Soda ash	7.46
Manganese dioxide	1.00
Cobalt oxide	.60
Nickel oxide	.70
	128.11

(b) Computed oxide composition.

Oxide	Percent by weight
SiO_2	50.21
Al_2O_3	5.49
B_2O_3	15.97
Na_2O	14.58
K_2O	3.79
CaF_2	7.66
MnO_2	1.00
CoO	.60
NiO	.70
	100.00

[1] Frit I-109E identical to I-109ER except that latter contained 3 millicuries (0.15g) of irradiated cobalt oxide per 2000-gram batch (0.0075 percent by weight) in addition to ingredients shown here.

TABLE 2.- MILL BATCH OF COATINGS I-2 AND I-2R

[Milling time, 4.2 hr; fineness, 4 grams on 200 mesh from 50 ml of slip]

Material (1)	Weight (grams)
Frit	1000
"X" clay	60
Borax	10
Water	425

[1] Before removal from mill, 50 grams water and 3 drops saturated $Na_4P_2O_7 \cdot 10H_2O$ were added.

TABLE 3.- RESULTS OF ADHERENCE TESTS ON COATINGS I-2 AND I-2R

Coating (1)	Firing conditions (2)	Adherence index (percent) (3)	95-percent confidence error (percent)
I-2	U	64.2	±9.6
I-2R	U	75.5	±5.0
I-2	N	93.1	±2.3
I-2R	N	92.1	±1.7
I-2	O	76.5	±2.6
I-2R	O	83.4	±2.2

[1] I-2, normal cobalt-bearing ground coat; I-2R, radioactive cobalt-bearing ground coat.

[2] U, underfired, 4 min at 1450° F; N, normally fired, 4 min at 1575° F; O, overfired, 6 min at 1750° F.

[3] Average value for seven specimens when tested by the Porcelain Enamel Institute's test (reference 1). By this test, adherence index of 0 would indicate no adherence and index of 100, excellent adherence. Any value below 50 has usually been considered unsatisfactory.

TABLE 4.- COUNTS ON METAL SPECIMENS ENAMELED WITH RADIOACTIVE COBALT-BEARING ENAMEL, THEN DE-ENAMELED

Specimen	Firing treatment (1)	Counts per minute	
		After de-enameling	After removal of oxide
1	U	1464	180
2	U	1681	189
3	N	8324	1788
4	N	8231	2345
5	O	8377	2759
6	O	9494	2685

[1] U, underfired, 4 min at 1450° F; N, normally fired, 4 min at 1575° F; O, overfired, 6 min at 1750° F.

TABLE 5.- COUNTS ON RADIOACTIVE ENAMEL CHIPS AND IODINE AND POTASSIUM-IODIDE SOLUTION AFTER REMOVAL OF METAL BASE

Specimen	Firing condition (1)	Counts on radioactive enamel chips and I-KI solution						
		After iron removal			I-KI solution (counts/min/sq in.) (2)	After oxide removal		
		Innerface (counts/min/sq in.)	Outerface (counts/min/sq in.)	Difference (percent)		Innerface (counts/min/sq in.)	Outerface (counts/min/sq in.)	Difference (percent)
1	U	15,755	18,484	14.8	----	4090	4813	15.1
2	U	16,474	19,659	14.8	----	3205	3549	10.8
Average		------	------	14.8	1344	----	----	12.4
3	N	14,211	18,246	22.2	----	2594	3429	24.3
4	N	14,641	18,141	19.3	----	2484	3193	22.2
Average		------	------	20.8	1664	----	----	23.2
5	O	9,339	14,100	33.8	----	1917	1926	(3)
6	O	8,737	13,106	33.3	----	1818	2581	29.6
Average		------	------	33.6	2784	----	----	29.6

[1] U, underfired, 4 min at 1450° F; N, normally fired, 4 min at 1575° F; O, overfired, 6 min at 1750° F.

[2] To remove metal from two $1\frac{1}{4}$-in.-square specimens of each type, 200 ml of solution was used. A 2-ml aliquot of this solution was evaporated to dryness, and a count was made on the residue. This count was corrected for volume and area to obtain value in table.

[3] Chips shattered during ammonium-citrate treatment. Results are questionable and are not included in average.

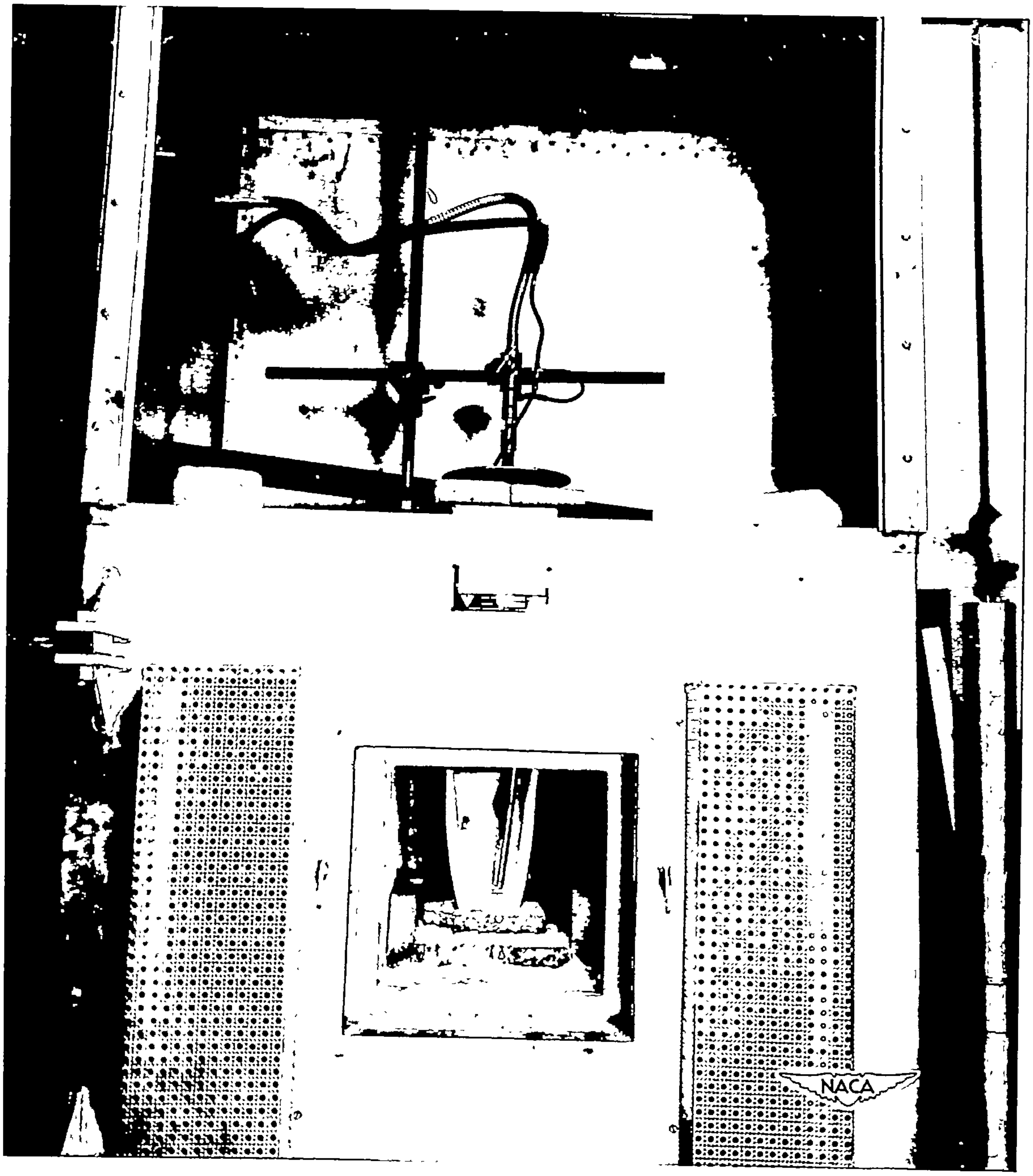
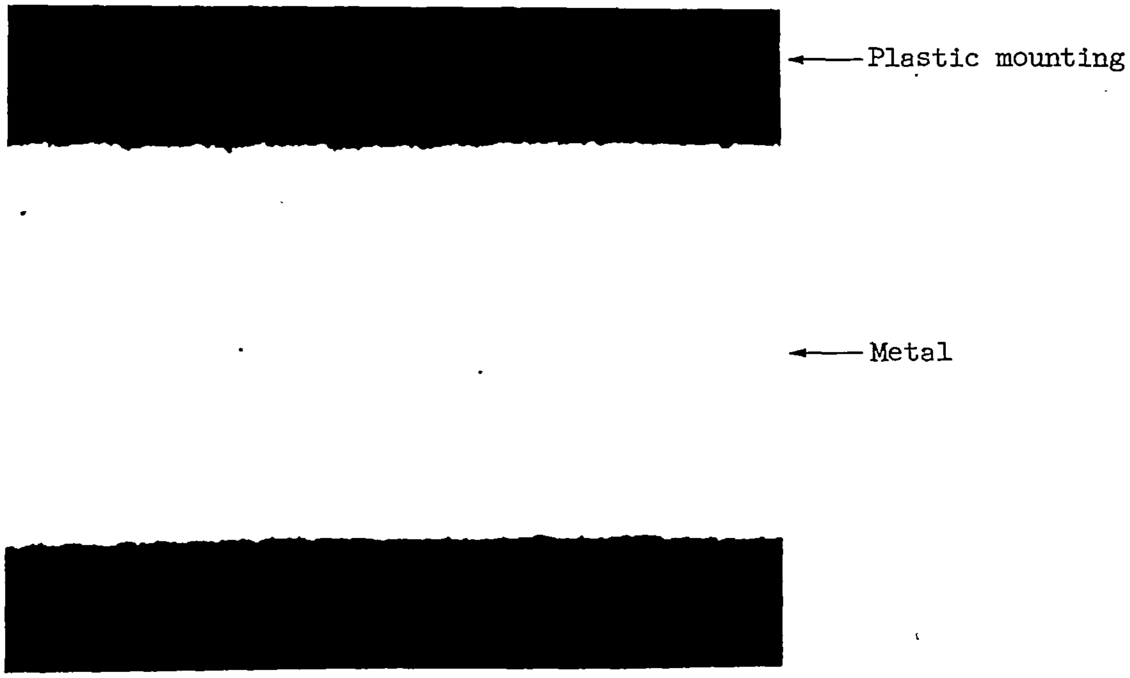
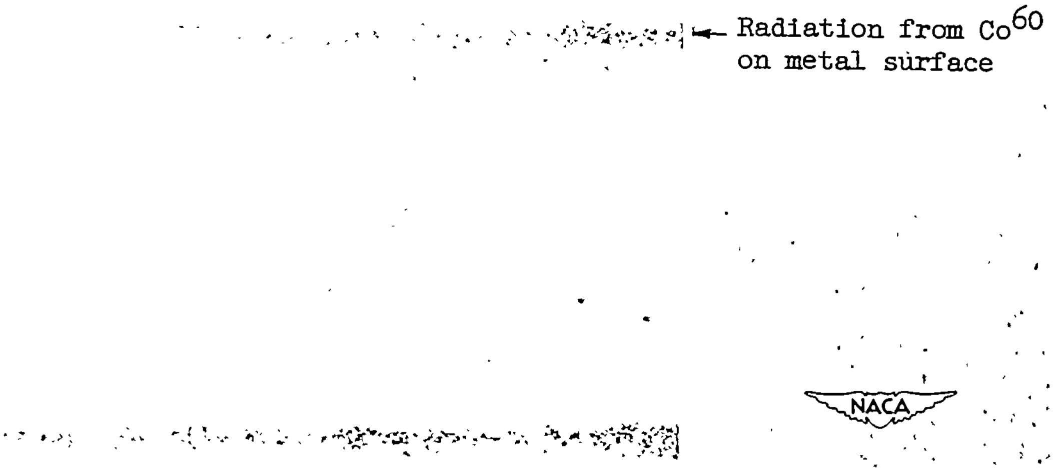


Figure 1.- Photograph of furnace used for melting frits used in this study, with stirring rod in place. A broken crucible was placed in furnace to show position of stirring rod.

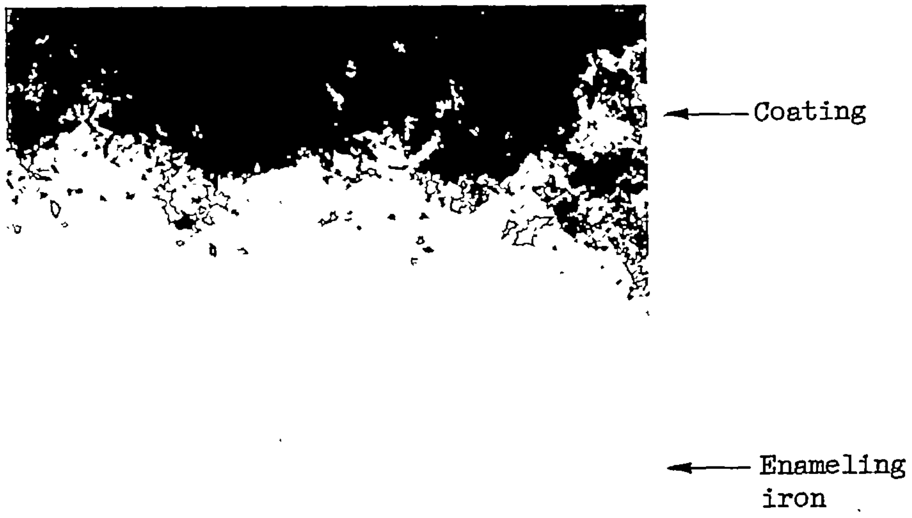


(a) Photomicrograph (specimen unetched). Note rough surface of metal.

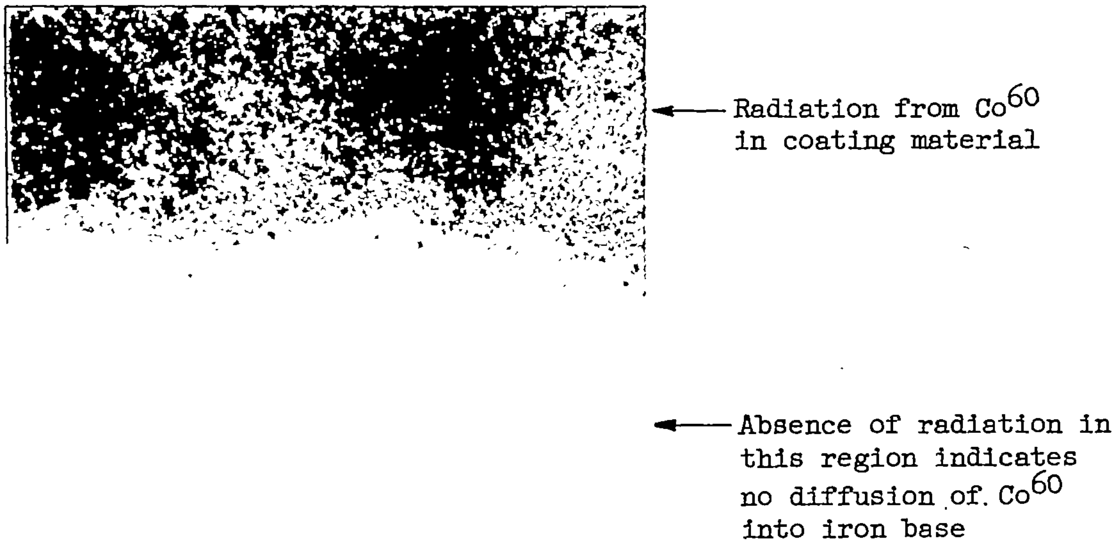


(b) Autoradiograph. Because of scattering of radiations, resolution is poor and a broad diffuse line is produced.

Figure 2.- Photomicrograph and autoradiograph (same field, both X50) of metallographic section of enameling-iron specimen coated with radioactive cobalt-bearing enamel, overfired, and enamel removed with molten caustic.

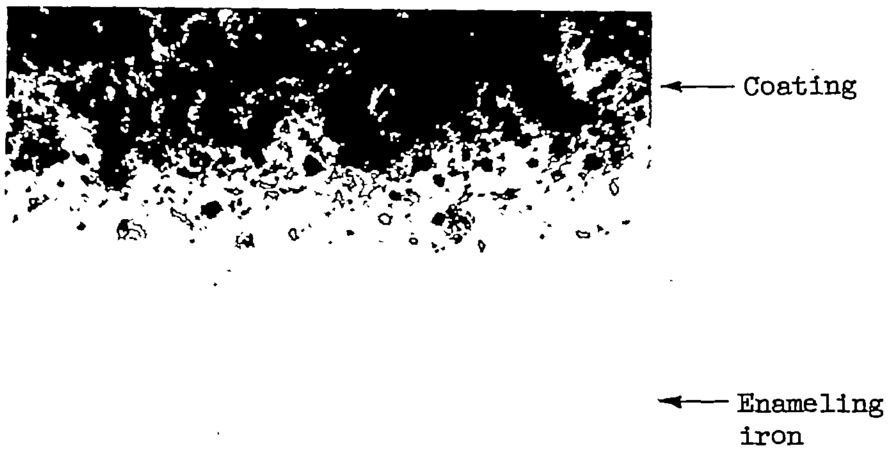


(a) Photomicrograph.

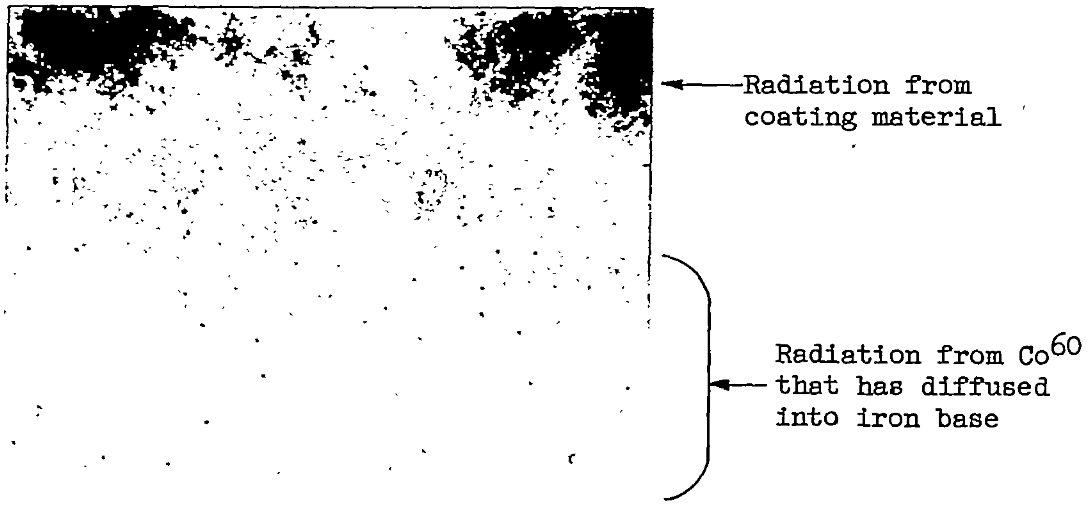


(b) Autoradiograph.

Figure 3.- Photomicrograph and autoradiograph (same field, both X45) of specimen of enameling iron that had been coated with ground-coat enamel containing radioactive Co^{60} (as cobalt oxide) by firing for 6 minutes at 1750° F. Specimen was sectioned at small angle (approximately 3°) to coating-iron interface. Autoradiograph shows little or no penetration of Co^{60} into iron by this firing treatment.



(a) Photomicrograph.



(b) Autoradiograph.

Figure 4.- Photomicrograph and autoradiograph (same field, both X45) of specimen of enameling iron that had been coated with ground-coat enamel containing radioactive Co^{60} (as cobalt oxide), overfired, and then heated for 270 hours at 1300° F in air. Specimen was sectioned at small angle to coating-iron interface. Penetration of Co^{60} into iron base is demonstrated by (b).

NACA-Langley - 6-19-52 - 1000