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TECHNICAL NOTE 2865

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By Dwight G. Moore and Mary A. Mason

National Bureau of Standards

Washington

January 1953

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INVESTIGATION OF GASES EVOLVED DURING FIRING OF VITREOUS COATINGS ON STEEL

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SUMMARY

An investigation was made of the gases evolved during the firing of vitreous coatings. The scope of the investigation included: (1) Examination of gas evolution with a microscope while specimens were being fired, (2) examination of fired specimens for changes in bubble structure with firing time, (3) examination of changes in normal gas evolution when water-free enamels were used, (4) analysis with the mass spectrometer of gases trapped in the bubble structure after varying firing times, (5) determination of the source of carbon gases in the bubble structure using radio-active carbon (C^{14}) as a tracer, and (6) determination of the effect of various pretreatments of the clay used for suspending the coating slip on the resulting bubble structure of the fired specimens.

The results showed that the principal gases evolved during the firing were carbon monoxide, carbon dioxide, and hydrogen. The blistering that is often observed in the early stage of firing when vitreous coatings are applied to low-carbon steel was found to be caused by evolution of the carbon gases formed by the oxidation of the carbon in the steel. Evidence was obtained that the hydrogen formed from the reaction between the dissolved water in the coating and the hot iron base slowly diffuses into the coating as the firing continues. Some of the hydrogen also diffuses into the metal. On fast cooling this hydrogen is expelled causing bubbles to form in the coating at the interface. It was found that practically all of the bubble structure in a normally fired enamel is due to some impurity in the clay mill addition. The impurity is probably organic matter adsorbed on the clay particles.

INTRODUCTION

Gases are normally evolved when porcelain enamels are applied to low-carbon steel. The effects of the evolution sometimes are evidenced by blisters and pin holes on the fired ware but more often by changes in the bubble structure of the coating. In addition, such gases as hydrogen and carbon monoxide when evolved during firing are capable of producing

changes in the oxidation state of metallic oxides present in the coating layer and such changes could in turn affect the adherence.

Ceramic coatings for the high-temperature protection of metals and alloys may also be affected adversely by gas evolution. Such defects as blisters and pin holes are obviously undesirable in coatings of this type and a pronounced bubble structure could conceivably be deleterious in that the bubbles might permit diffusion of corrosive gases through the coating during service operation. As discussed in the appendix, some research has been done on the normal gas-forming reactions that occur during the firing of vitreous coatings on low-carbon steel. However, because it was believed that a more complete understanding of both the nature and the source of the gases evolved would ultimately lead to an improvement in the quality of high-temperature coatings, the study as herein reported was conducted as part of a broad program on ceramic coatings now under way at the National Bureau of Standards. This program is being conducted under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

The authors gratefully acknowledge the assistance of the Mass Spectrometry Section of the National Bureau of Standards, under the direction of Dr. F. L. Mohler, for performing the mass-spectrometer analyses and to Mr. Abraham Schwebel, of the Radioactivity Section, for making the counts on the samples containing radioactive carbon (C^{14}).

MATERIALS

Eight different metals or alloys were included in the investigation. These were obtained from commercial sources. Representative analyses are given in table 1.

Table 2 gives the mill batches for the E-1 and E-2 coatings. The frit used in these two ground-coat enamels was selected from an earlier study (reference 1) as being suitable for the preparation of a single-frit enamel ground coat. Frit 109-E in table 2 is the same as frit E described in reference 1. Frit 109-0 is also the same as 109-E except that the 109-0 contains no adherence oxides. Both the batch and computed oxide composition for frit 109-E are given in table 3.

EXPERIMENTAL PROCEDURES AND RESULTS

Observations with a Microscope of Coating Behavior during Firing

Two furnaces were designed and constructed for the observation under the microscope of the gassing behavior of coated specimens during firing.

Figure 1 is a schematic drawing of the gas-fired furnace while figure 2 is a photograph of the arrangement used for observations in an electrically heated muffle furnace.

A stereoscopic microscope was employed for all observations. A magnification of 150 was possible when specimens were heated by the oxygas flame while with the muffle furnace a magnification of only 25 was possible. With the muffle furnace, the specimen was positioned at a greater distance from the microscope objective because of the increased thickness of thermal insulation required. In the gas furnace only a small area of the specimen was heated to the firing temperature. In the muffle furnace the entire specimen was heated. In both cases the temperature of the specimen was obtained by a Chromel-Alumel thermocouple consisting of wires that were separately welded to the metal specimen. The wires were spot-welded 3/8 inch apart and the observations were made on the area encompassed by the wires.

Most of the early observations were made using coating E-1 which contained no cobalt, nickel, or manganese. This coating gave a clear glass and permitted observation, with good clarity, of the behavior of bubbles at and near the coating-metal interface.

Enough observations were made with the E-2 coating, however, to indicate that there was no significant difference in gas-evolution behavior between the two coatings, except for the fact that it became increasingly difficult to observe the interface with the cobalt-bearing coating E-2 as the firing continued at 1550° F.

Numerous observations made with both furnaces established a definite behavior pattern with respect to both coating appearance and bubble formation. This pattern can be conveniently broken down into the seven stages shown in table 4.

The present paper will be mostly concerned with primary boil (stage 4), the development of the cloudy layer with the cobalt-bearing coating (stage 5B), and the formation of the cooling bubbles (stage 6). In addition, some attention will be given to the effect of clay on the bubble structure of the fired enamel.

Investigation of Primary Boil

Primary boil occurs in the early stages of firing usually putting in an appearance on low-carbon steel specimens shortly after the ground-coat enamel fuses. In the primary-boil mechanism bubbles form in the enamel at the metal surface. They grow in size but, because of the high viscosity of the coating at the primary-boil temperature (approximately 1400° F), they do not immediately burst and seal over when they reach the

enamel surface. As the temperature increases the coating becomes more fluid and, by the time a temperature of 1550° F is reached (approximately 1 min later with 20-gage low-carbon steel), the primary-boil blisters have ordinarily disappeared. Primary boil is not normally troublesome in blue ground coats but with one-coat whites iron oxide may be carried to the surface by the boiling action causing a speckled discoloration on the finished ware. Primary boil does not reappear with a low-carbon steel if the specimen is subjected to a second firing.

Several experimental techniques were devised for studying the nature and the source of the gases causing primary boil. These included: (a) A study of the kinds of metal that show primary boil, (b) analyses of gases entrapped in the bubble structure, (c) tests for radioactivity of gases trapped in the primary boil blisters after applying a ground coat to a steel containing radioactive C^{14}, and (d) observations of primary boil on low-carbon steel using an enamel that had been vacuum-melted prior to application.

Metals and alloys showing primary boil.- The cobalt-bearing coating E-2 was applied at normal thickness to sandblasted specimens of the eight metals or alloys listed in table 1. Various firing times from 1 minute to 10 minutes at 1550° F were used. After firing, each specimen was examined visually and with the stereoscopic microscope for evidence of primary boil and for general bubble structure. Table 5 summarizes the results.

The only ferrous alloys to show any appreciable primary boil were the enameling iron and the cold-rolled steel. The titanium-bearing low-carbon steel showed a few scattered bubbles after $1\frac{1}{2}$ minutes of firing that might be construed as primary-boil blisters. There was no evidence of primary boil with stainless steel, copper, or Inconel. Monel metal and nickel, on the other hand, showed a type of blistering that might properly be called primary boil. The blister formation began during the early part of the firing treatment and gas evolution continued up to and including the maximum firing time of 10 minutes. It was difficult to apply a smooth, defect-free enamel to either of these metals because of the continued blister formation.

Analyses of gases entrapped in bubble structure of enamel.- The gases entrapped in the bubble structure of a ground-coat enamel after it has cooled to room temperature may be released by fracturing the enamel glass. Freeman and Meloche (reference 2) found that a sizeable quantity of gas could be collected from the bubble structure by flexing coated specimens under a suitable solution and then pulverizing the resulting flakes with a nickel-plated steel rod. In this investigation the E-2 enamel was applied to 150 ingot-iron specimens, 3 inches by $\frac{3}{4}$ inch by 0.037 inch, to give a thickness of 0.008 inch after a normal firing.

Of these specimens 50 were fired for 40 seconds at 1550° F (the primary-boil stage), a second 50 were fired for 2 minutes at 1550° F, and the remaining 50 for 6 minutes at 1550° F. After firing, the gases present in the bubbles of each lot were collected using the arrangement shown in figure 3. The specimens were first flexed by hand over the agate mortar while completely immersed in a salt-water and glycerin solution. The solution, which was identical with that used by Freeman and Meloche (reference 2), was prepared by blending equal parts by volume of glycerin and distilled water and then saturating the resulting mixture with sodium chloride. According to Freeman and Meloche, this solution has the lowest solubility for carbon dioxide and other gases of any practical confining liquid. Mercury would be impractical because the enamel flakes would float up into the sample tube and block the stopcock bore.

It was estimated that over half of the total volume of gas collected was released during the flexing operation. The remaining gas was collected when the enamel flakes that settled into the agate mortar were pulverized with an agate pestle. The gases, on being released from the bubble structure of the enamel, rose up into the sample tube which is shown at the top of the inverted funnel in figure 3.

The volume of the sample tube was about 1.5 cubic centimeters. The volume of gases collected from a lot of 50 specimens, on the other hand, was only about 0.5 cubic centimeter. This meant that the sample tube still contained about 1 cubic centimeter of the water-glycerin solution after the collection was completed. Such a high contamination of the gas sample would be undesirable in the later analyses with the mass spectrometer. Contamination with helium would not interfere with the analysis and for this reason helium was introduced to displace the solution remaining in the sample tube.

Gases other than air, water vapor, and helium in the three samples are listed in table 6. These data show that carbon monoxide and carbon dioxide together constitute about 77 mole percent of the evolved gases at the primary-boil stage whereas after a 6-minute firing the carbon gases dropped to about 26 mole percent.

Tests with radioactive carbon.- A liquid carburizing bath was prepared in which a minor amount of the sodium cyanide present in the bath was added as the radioactive salt, that is, some of the carbon in the sodium cyanide was C^{14} rather than C^{12}. The batch composition of this bath is shown in table 7.

Fifty ingot-iron specimens, $2\frac{1}{2}$ inches by $\frac{1}{2}$ inch by 0.037 inch, were sandblasted and then immersed in the molten bath for 7 minutes at 1650° F. After a thorough rinsing in tap water, the specimens were next homogenized by heating for 4 hours at 1700° F in a purified helium atmosphere. The

carbon content after this latter treatment was only slightly higher than that of the original ingot iron. No appreciable surface decarburization was observed on etched sections after the homogenizing treatment. Also, radioactivity counts of the surface after machining off successive layers gave no evidence of surface decarburization.

After homogenizing, a thin layer of metal was filed off each specimen. Although the aforementioned evidence indicated the absence of any appreciable surface decarburization it was found that specimens which were only sandblasted before coating did not show so consistent a primary boil as those with a thin layer of metal removed from the surface. The specimens after filing and sandblasting were coated with enamel E-2 by firing to the primary-boil stage. After cooling, the coated specimens were flexed while immersed in the water-glycerin solution thus releasing the gases trapped in the primary-boil blisters. The released gases were collected in a sample tube and tested for radioactivity. A count of 7 disintegrations per second above background was obtained, thus proving that carbon in the steel is undergoing oxidation during primary boil.

Absence of primary boil on specimens with decarburized surfaces.- It was observed early in the investigation that primary boil did not occur on a low-carbon steel surface that had been previously decarburized for 3 hours in wet hydrogen at 1700° F. Even a relatively mild decarburization such as heating an ingot-iron specimen in air for 4 minutes at 1550° F and then lightly sandblasting off the resulting scale prior to application of the coating was found to reduce the amount of primary boil. Removal of the surface layer of such specimens after decarburization but prior to enameling gave a surface that again showed the normal number of primary-boil bubbles.

Primary boil on specimens coated with an enamel prepared with vacuum-melted frit.- Moore, Mason, and Harrison (reference 3) have shown, by a tracer technique, that water in the enamel is the principal source of defect-producing hydrogen during enameling operations, and, further, that by a prior vacuum melting of the frit a coating that is substantially free of water can be prepared. In the present study frit 109-E was first melted in vacuum following the procedure outlined in reference 3. The resulting frit was then dry-ground to pass through a 100-mesh sieve after which it was mixed with ethyl cellosolve to give a suspension suitable for spraying. A 2- by 2- by 0.037-inch specimen of ingot iron was cleansed by sandblasting and the 109-E suspension was applied at normal thickness. The specimen was fired in the furnace shown in figure 2. Primary boil in a normal amount was observed at stage 4 in the firing. If the primary boil resulted from hydrogen liberated by the reaction of the iron with the moisture present in the enamel coating, as suggested by Zapffe and Yarne (reference 4), then there should be less primary boil with the vacuum-melted enamel. The finding that there was the same amount indicates that primary boil is not associated with hydrogen evolution.

Primary boil of case-carburized specimens.- Several 2- by 2- by 0.037-inch ingot-iron specimens were case-carburized by immersion in the liquid carburizing bath (see table 7) for 7 minutes at 1650° F. This treatment gave a carburized case 0.0035 inch thick. The average carbon content of the case was 0.8 percent.

Enamel E-2 was applied and the firing behavior observed using the furnace shown in figure 2. Primary boil started at a specimen temperature of 1400° F but the blistering did not stop when the firing temperature was reached. It continued throughout the normal 5-minute firing period.

Probable cause of primary boil.- All of the aforementioned experiments indicated that primary boil is caused by an oxidation of the carbon in the steel, the evolution of the resulting carbon-oxide gases being responsible for the blistering.

Table 4 shows that primary boil began in these experiments when the temperature of the metal reached about 1400° F. At this stage of the firing, the enamel is in a molten condition but is not yet in contact with the metal. Figure 4 shows that the scale layer that formed on the iron prior to fusion of the enamel has not as yet been dissolved when the primary-boil blisters first appear. Thus, it appears that the oxygen necessary for oxidizing the carbon in the steel must come from the scale layer. Porter and Rosenthal (reference 5) stated in their study with cast iron that it appeared that gassing occurred only when free iron oxide was present at the iron surface. Pennington (reference 6), in his investigation of the thermodynamics of decarburization of steel by mill scale, determined that the evolution of carbon-oxygen gases (CO and CO_2) from a sealed box containing preoxidized steel specimens started suddenly at about 1300° F and continued quite satisfactorily at 1450° F. Thus, the probable cause of primary boil is believed to be as follows: During the heat-up period (before the enamel fuses) a scale layer forms on the steel. When a temperature of about 1300° F is reached, the enamel has melted and wet the scale layer but before it can dissolve the scale a reaction begins between the scale layer and the carbon in the underlying metal. This reaction produces CO and CO_2 to give the gas evolution known as primary boil. After the scale has been dissolved by the enamel, no appreciable reaction takes place and the primary boil stops. At this stage the outermost surface of a low-carbon steel is probably substantially free of carbon. With a high-carbon steel, on the other hand, there may still be sufficient carbon at the surface to cause a continued oxidation of carbon by the oxygen diffusing through the enamel layer. Therefore, with a high-carbon steel blistering might be expected to occur throughout the normal firing period. Actually this is the condition found with the specimens that had been case-carburized before coating.

As a confirmation of the theory, specimens of enameling iron were given a scaling treatment of 2 minutes at 1575° F which gave a scale layer

about 0.5 mil in thickness. Coating E-2 was applied directly over the scale and the firing was observed with the stereoscopic microscope. As anticipated by the theory, a large amount of primary boil resulted.

Cause of blistering with nickel and Monel.- The gases trapped in the bubble structure of Monel specimens after a normal firing at 1550° F were collected and analyzed with the mass spectrometer. The only gas other than air, water vapor, and helium in the sample was carbon dioxide. The mass-spectrometer analysis showed no trace of either carbon monoxide or hydrogen.

The Monel alloy normally contains 0.15 percent by weight of carbon. The finding that carbon dioxide was the only gas present in the bubble structure indicates that it is the oxidation of the carbon that causes the blistering difficulties with the Monel metal.

Nickel with 0.014 weight percent of carbon showed a blistering behavior almost identical to that of Monel (see table 5). It was found, however, that when a sheet of electrodeposited nickel was coated no blistering occurred. The electrodeposited nickel was formed by plating nickel to a thickness of 0.015 inch on a copper backing and then dissolving the copper by an acid treatment. Nickel formed in this way should be free of carbon. The finding that no blistering occurred on the carbon-free nickel, together with the mass-spectrometer analysis showing carbon dioxide to be the only gas present when the coating was applied to Monel, strongly indicates that the blistering with nickel and Monel (table 5) was caused by oxidation of the carbon present in their structures. When vacuum-melted frit that was substantially free of water was applied to these metals, the same blistering behavior was observed as with a normally smelted frit, thus again indicating that the blisters are not caused by hydrogen.

Investigation of Cloudy Layer

The presence of a cloudy or hazy layer in the enamel near the interface has been observed by numerous investigators (references 7 and 8). The layer increases in thickness with increased firing time until it reaches the surface of the enamel. When this stage of the firing is reached, the enamel loses its gloss and takes on a rust-colored appearance. The trade term for this condition is "burn-off."

The cloudy layer has never been observed by the authors in an enamel that is free of adherence oxides. Howe and Fellows (reference 7) observed that the cloudy layer was composed of very small particles that could be resolved at high magnification under dark-field illumination. Dietzel (reference 8) concluded that the particles were finely divided metallic cobalt formed by a reaction between cobalt oxide and the iron oxide

dissolved in the enamel near the interface. It has been observed by the present authors that a ground coat containing only cobalt oxide as an adherence promoter gives little if any cloudy layer, but when nickel oxide is present by itself or with the cobalt a very pronounced cloudy layer is observed.

In the present investigation frit 109-E was first melted in vacuum following the procedures outlined in reference 9. The resulting frit was dry-ground after which it was suspended in ethyl cellosolve and sprayed on an ingot-iron specimen. A second specimen was similarly prepared except that in this case the 109-E frit did not receive the vacuum-melting treatment. After a normal firing (4 min at 1550° F) the coated specimens were sectioned and examined with the metallurgical microscope. A distinct cloudy layer was present when the normal water-bearing coating was applied while with the vacuum-melted frit the cloudy layer was absent. It should be reemphasized that the only difference in these two enamels was that the one that showed no cloudy layer had been vacuum-melted prior to application.

From the above experiment (which was repeated several times) it was obvious that the formation of a cloudy layer is dependent on the presence of some constituent in the enamel that is mostly removed by the vacuum-melting treatment. The most likely constituent is believed to be the dissolved water in the frit. As was shown in a previous paper (reference 3) the dissolved water in the coating layer is capable of reacting with the hot iron base to give iron oxide and hydrogen. This earlier work showed that some of the hydrogen is taken up by the metal but did not prove that the metal was capable of absorbing all of it. The present observations indicate that part of the hydrogen formed from the iron-water reaction may slowly diffuse into the glass. The rate of diffusion is sufficiently slow to prevent bubble formation but the hydrogen would nevertheless be present in the glass structure. The presence of dissolved hydrogen in the glass would create strongly reducing conditions. Such oxides as iron oxide, cobalt oxide, and nickel oxide might be reduced to the metal thus giving the fine particles observed by Howe and Fellows (reference 7). The water formed from the reduction of the oxides would then be available for further reaction with the iron base.

Although the aforementioned explanation seems to agree with the observed phenomena, the mechanism cannot be accepted until the nature of the particles present in the layer can be determined. Identification of these particles was outside the scope of the present investigation.

Healy and Andrews (reference 10) also postulated that hydrogen from the water-iron reaction causes reduction of metallic oxides in the enamel. However, these authors further theorized that the reduced cobalt, in turn, becomes welded to the iron base and that therefore a glass-to-cobalt-to-iron triple adherence is present. That such an adherence

mechanism is probably not active is indicated by the observation that equally good adherence was obtained with the vacuum-melted enamel (where the system would be expected to have a low hydrogen content) as was obtained with an enamel containing the normal amount of dissolved water.

Investigation of Cooling Bubbles

It was observed while using the gas-fired furnace shown in figure 1 that gas bubbles rose from the interface during the cooling that followed a normal or hard firing. Both the E-1 and E-2 coating on ingot iron showed the cooling bubbles but it was found that the bubbles did not form if a short firing time was used (less than 5 min at 1550° F). When the specimen was fired at 1650° F for 5 minutes and the gas at the burner was suddenly turned off and the oxygen was left on, a great number of large bubbles formed. Under these conditions, the bubbles almost reached the coating surface. When the specimen was allowed to cool slowly by a gradual reduction of the amount of gas and oxygen supplied to the burner, the number and size of the bubbles decreased and, in some cases, no bubbles formed.

All of the ferrous metals, including the AISI Type 321 stainless steel, showed the formation of these cooling bubbles. With the stainless steel, however, the bubbles were smaller than with the low-carbon steels. There was little difference in the behavior of the ingot iron, the cold-rolled steel, and the titanium-bearing steel. Inconel behaved similarly to the stainless steel.

The formation of cooling bubbles could not be observed with the muffle furnace shown in figure 2 because a fast cooling rate could not be achieved without removing the specimen from the furnace. However, when the specimen was fired in this furnace until it was observed to be practically bubble-free and then removed to cool in air, bubbles could be seen at the interface under room-temperature examination that were not present at the firing temperature. Bubbles of this type, which are identified in table 5 as RB, were assumed to have formed during cooling. Such bubbles, however, were never so large or so numerous as those that were observed to form in the gas-fired furnace. When a vacuum-melted frit was used as an enamel none of these cooling bubbles formed.

The above experiments indicate that the cooling bubbles are caused by hydrogen expulsion from the metal as the specimen cools. During the firing the metal becomes saturated with hydrogen because of the reaction between the dissolved water in the enamel and the metal base. Both iron and nickel have much higher solubilities for hydrogen at elevated temperatures than at low temperatures and it is reasonable to believe that their alloys would follow the same pattern.

Figure 5 shows the temperature-solubility curve for ingot iron over the range of 1200° to 1700° F as plotted from the data of Sieverts, Zapf, and Moritz (reference 11). Point A represents the firing temperature of both the E-1 and E-2 coatings. If a specimen is fired at this temperature until the iron is saturated with hydrogen and subsequently cooled to a lower temperature, hydrogen will be expelled until the solubility limit at the lower temperature is attained. If the cooling is sufficiently rapid the hydrogen will be evolved from the metal at a rate faster than it can diffuse through the enamel layer and bubbles will form in the enamel at the interface. The temperature at which the hydrogen bubbles form will depend on the degree of saturation of the metal with hydrogen at the firing temperature, the slope of the hydrogen solubility-temperature curve, and the cooling rate. Although a review of the literature revealed no previous reference to cooling bubbles in the enameling of sheet steel, Porter and Rosenthal (reference 5) reported the formation of bubbles of this type on chilled cast iron, that is, iron in which the carbon at the surface is present as cementite (Fe_3C) rather than graphite. These authors stated that when a specimen of chilled cast iron was removed from the furnace after firing the cover coat it was free of blisters. As the specimens began to cool, blisters started to form and continued to form until the enamel set. The gas causing the blistering of this type was shown by these authors to be hydrogen.

In the present investigation it was believed that the formation of the cooling bubbles in the gas-fired furnace did not simulate commercial enameling because of the possible presence of moisture from the combustion of the oxygas flame. Although the surface of the specimen under observation was shielded from the flame, combustion gases may have diffused through cracks in the furnace setup causing the specimen to be fired in a moisture-laden atmosphere. Also, hydrogen may have formed from the moisture-iron reaction on the under side of the specimen, thus permitting a rapid saturation of the iron base with hydrogen. With another arrangement in which the firing atmosphere was free of moisture, the same pronounced formation of cooling bubbles might not be observed. From the data obtained, however, (see table 5) it appears likely that there is normally some hydrogen evolved from coated ferrous metals during the cooling that follows a normal firing.

Investigation of Effect of Pretreatment of Clay on Bubble Structure

The mechanisms of gas formation already discussed have all been dependent on a reaction between the base metal and the coating (or scale layer). Another important source of gas is from the coating itself and more particularly from the clay mill addition.

In most enameling operations clay is added to suspend the enamel slip and also to give a suitable consistency for spraying or dipping.

According to Higgins (reference 12) a further requirement of a clay used for ground-coat enamels is that it promotes the right kind of bubble structure during firing. Higgins found that only those clays that produced a good bubble structure had good resistance to fishscaling.

Two clays were used in the present study. One was a Florida plastic kaolin and the other a German clay that was widely used in the enameling industry prior to World War II, that is, German Valendar. The E-2 enamel was prepared and applied to ingot-iron specimens using these two clays, (a) as-received and (b) heat-treated for 20 hours at 1000° F in an air atmosphere. An additional enamel was also prepared using Florida kaolin that had been rehydrated after the heat treatment at 1000° F. The rehydration was accomplished by autoclaving for 300 hours at 406° F (250 lb/sq in.). This treatment successfully restored the chemically combined water in the kaolinite molecule (see reference 3).

Figure 6 shows the resulting bubble structure after a 4-minute firing at 1575° F for the coatings prepared with Florida kaolin. The results were substantially the same for the German Valendar clay except that in this case there was no specimen available to represent the rehydrated clay. It is apparent from figure 6 that the clay mill addition is largely responsible for the bubble structure observed in a normally fired enamel. Further, the results show that there is some bubble-forming constituent present in the raw clay that is removed by the heat treatment at 1000° F. That this constituent cannot be the chemically combined water is evident by comparing figure 6(c) with 6(a). If the bubble formation is related to the chemically combined water, both enamels should show approximately the same bubble structure. Because there is much less bubble structure in the enamel prepared from the rehydrated clay, the bubble structure of a normally fired enamel must therefore be associated with impurities that are present in the raw clay. These impurities could be adsorbed carbonaceous material, possibly tannin in some form, or the impurities could be carbonates of calcium and magnesium. A typical analysis of the Florida plastic kaolin shows 0.20 weight percent of magnesium oxide (MgO) and 0.15 weight percent of calcium oxide (CaO). Higgins (reference 12) was able to duplicate the type of bubble structure obtained with enameling clays by adding small amounts of methylene blue at the mill. Because of these results he concluded that the bubble structure imparted by enameling clays is apparently due to their organic-material content.

In an attempt to determine the stage in the firing process that the bubbles are formed from the impurities in the clay, 40 specimens of 3- by 3- by 0.037-inch ingot iron were cleaned by sandblast. The E-2 enamel floated with raw Florida kaolin was adjusted to a dipping consistency so as to give a dry thickness of 0.007 inch after which 20 of the specimens were dipped and dried. The dry thickness of each specimen was determined with a micrometer both before and after coating. Nine

specimens of the twenty were selected that showed a dry coating thickness of 0.007 ± 0.0002 inch and each of these was fired for a different time ranging from 1/2 to 30 minutes. The thickness was redetermined after firing and the change in thickness with firing time at 1550° F was determined. The same procedure was used for coating the second 20 specimens except that in this case the E-2 enamel was prepared from the Florida kaolin that had been heated to 1000° F and then rehydrated.

Figure 7 shows the resulting curves. In each case the thickness of coating is directly related to the percentage of bubbles in the enamel inasmuch as both enamels are of substantially the same composition. The curve for the E-2 enamel with the raw clay shows that the bubbles are formed by an oxidation of impurities in the clay early in the firing period after which they slowly fine out. The normal firing time for the E-2 enamel at 1550° F is 5 to 6 minutes. At this stage, the enamel with the raw clay shows a greater number of bubbles (less decrease in thickness) than does the enamel with the treated clay. This is in keeping with the photomicrographs of figure 6.

Figure 7 shows that the bubbles formed from air trapped in the enamel layer during fusion and from primary boil rapidly fine out of the enamel that is floated with rehydrated clay. After only 2 minutes of firing the bubble structure has reached a minimum and there is no further change with longer times of firing.

One observation of interest is that both the treated and untreated clay show primary boil, which is indicated by the abrupt change of slope of the curves between 1/2- and 1-minute firing times. Thus it follows that the gases causing primary boil do not originate from the same source as the gases responsible for the bubble structure when a raw clay is used.

DISCUSSION OF RESULTS

The various experiments concerned with primary boil all tended to show that the gases causing the phenomenon with low-carbon steels are carbon monoxide and carbon dioxide and further that the source of the gas is the oxidation of the carbon in the steel. The titanium-bearing steel, on the other hand, also contains carbon but it does not show significant primary boil. A possible explanation for this difference in behavior is that the carbon in the titanium-bearing structure is in a less reactive form (TiC). In the case of low-carbon steels some of the carbon is present as cementite (Fe_3C) and it is possible that the exposed particles of cementite at the surface are the determining factors in primary boil. In this connection, McGohan (reference 13) also believed,

after metallographic examinations, that primary boil is caused by a reaction between iron carbide at the surface and the oxide layer that forms before the enamel softens. The resulting bubbles of carbon monoxide grow in size until they reach the surface. When they break, a fresh supply of oxygen comes in contact with the iron carbide to form more carbon monoxide. According to McGohan, this process will continue until all of the carbide is consumed, or until the enamel is "fired-off."

An incidental observation in the present investigation was that only those low-carbon steel specimens that showed primary boil showed fishscaling tendencies. It has been demonstrated that fishscaling is caused by hydrogen evolving from the steel after the specimen has cooled (references 3, 12, and 14). Primary boil, on the other hand, is caused by oxidation of carbon. Thus it would appear that carbon in the steel may be responsible for hydrogen retention. In this connection, Bardenheuer and Thanheiser (reference 15) showed that the ease of diffusion of hydrogen through steel at or near room temperature is affected by the carbon content, the higher the carbon the slower the rate of diffusion. These same authors found that the condition of the carbon affects the diffusion rate. In the titanium-bearing steel, the carbon is probably present in a form where it does not interfere with the movement of hydrogen through the metal. With ordinary low-carbon steels or ingot iron, on the other hand, it can be postulated that the carbon is present in a form that gives a tight structure with respect to hydrogen, that is, a structure through which the hydrogen does not diffuse readily. Thus, when a coated specimen of this type is cooled rapidly after a normal firing, a considerable amount of hydrogen could be trapped in the metal because it is unable to diffuse out at a high enough rate to achieve equilibrium with the metal. Therefore, after such a specimen cools to room temperature it might be supersaturated with respect to hydrogen. The subsequent slow diffusion of hydrogen to the surface of the metal could then cause the type of coating defect known as fishscales.

The finding that the cloudy layer is absent when a vacuum-melted enamel is used is important for two reasons. First, it tends to indicate that there is a reaction between the dissolved water in the coating and the steel base during firing, a mechanism that was postulated from the results of an early study (reference 3). Second, the finding is of interest in the development of a theory of adherence in that it tends to show that a considerable variation in the amount of hydrogen in the enamel-iron system has no effect on the resulting adherence.

The observation that bubbles form at the interface as a specimen cools after a normal firing is important in again showing that hydrogen is introduced into the steel during the firing operation.

The significance of the experiments with clay is in demonstrating that it is not the evolution of the chemically combined water in the

kaolinite molecule that causes most of the bubble structure in the coating layer but rather some impurity present in the raw clay. There is believed to be a practical significance to the finding that there was practically no bubble structure generated when using a clay that had been heated in air for 20 hours followed by autoclaving to restore the chemically combined water. A clay so treated yielded a slip that had suspension and flow characteristics similar to those of one prepared from the as-received clay. Thus, it appears possible to prepare a clay that will work well in a slip from the suspension standpoint and yet yield a coating that is practically bubble-free. A dense, bubble-free coating would be desirable both for ceramic coatings for alloys and for cover-coat enamels where high resistance to gouging and scratching was a required characteristic.

The data listed in table 6 are of considerable interest other than as additional confirming evidence that primary boil is caused by oxidation of carbon in the steel. These data indicate that the gas retained in a ground-coat enamel changes in composition with increased firing, the percentage of hydrogen increasing substantially at the expense of the carbon gases.

Table 6 shows that after a normal firing time, the collected gas sample consisted of 60.5 percent hydrogen (by volume) and 39.5 percent of the two carbon gases. Figures 6 and 7, on the other hand, imply that nearly all of the gas that forms bubbles in a normally fired ground-coat enamel is produced by some impurity in the clay. The burning out of this impurity would be expected to contribute carbon gases but little, if any, hydrogen. Figure 7 indicates that the impurity produces gassing for a short period in the early stages of firing after which the gas evolution ceases and the occluded gas bubbles slowly fine out of the enamel. During this fining period, the quantity of hydrogen produced by the reaction between the dissolved water in the frit and the hot metal base is increasing. Most of the hydrogen thus formed is taken up by the metal base. When the specimen is later cooled, a part of this hydrogen is evolved at the interface to form cooling bubbles. When room temperature is reached, the pressure in these cooling bubbles may have increased to several atmospheres by a continued slow diffusion of hydrogen from the steel, whereas the pressure in the larger and more numerous carbon gas bubbles would be considerably below atmospheric because they are formed in the glass at 1550° F and then cooled to room temperature. Therefore, even though most of the bubbles noted in a normally fired enamel may be due to carbon gases originating from the clay impurity, these bubbles of carbon monoxide and carbon dioxide,[1] because of their reduced pressure,

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[1]It is possible that the bubbles formed from the clay impurity might also contain some hydrogen. This hydrogen could have diffused through the enamel structure and into the bubbles both during firing and during the cooling process.

might contribute less gas to the collected sample than the pressurized bubbles of hydrogen at the interface.

CONCLUSIONS

The following conclusions appear justified as a result of various experiments and observations made in a study of the gases evolved when a ground-coat enamel is applied to low-carbon steel:

1. Primary boil is caused by carbon gases evolved from a reaction between the carbon present in the steel and the scale layer that forms during the early stage of firing, that is, before the coating fuses.

2. The formation of the so-called cloudy layer near the coating-metal interface on cobalt-bearing ground coats is dependent on appreciable amounts of dissolved water being present in the enamel glass. If the coating is vacuum-melted prior to application no cloudy layer forms.

3. Gas is evolved from low-carbon steel in the form of bubbles at the interface when a coated specimen is rapidly cooled after a normal firing. Indications are that the gas responsible for these cooling bubbles is hydrogen.

4. A considerable proportion of the bubble structure in a normally fired enamel is due to some impurity in the clay mill addition. The impurity is probably organic matter adsorbed on the clay particles.

National Bureau of Standards
Washington, D. C., June 15, 1952

APPENDIX

PREVIOUS WORK

A review of the literature indicates a surprising lack of investigations of the normal gas-forming reactions that occur during the firing of vitreous coatings on steel.[2] Most of the earlier work appears to have been concerned with such low-temperature gas-evolution defects as fishscaling[3] and reboiling[4] (references 12, 14, 16, and 17). Very little mention is made of primary boil[5] in the literature, yet this phenomenon can be troublesome in enameling operations especially when white coats are being applied directly to steel.

More study has apparently been directed to the cause of gas formation when enamels are applied to cast iron, possibly because of the greater blistering difficulties encountered in cast-iron enameling. Krynitsky and Harrison (reference 18), for example, determined in 1930 that the gases causing blistering in cast iron were carbon monoxide and carbon dioxide. They also found that the condition of the surface of the casting affected its blistering tendency, a microchill layer at the surface of a gray cast iron being especially undesirable from the standpoint of blister formation. Porter and Rosenthal (reference 5) have confirmed that the major cause of gassing in dry-process enameling of gray cast iron is the evolution of "carbon oxide" gases. On the other hand Zapffe (reference 19), after a study of wet-process enamels, states that hydrogen is apparently the only systematic cause of the blister type of defects in wet-process enamel on cast iron up to the highest usual firing temperatures, 870° C. Zappfe and co-workers (references 4 and 14) also infer that practically all blistering and boiling phenomena of enamels on steel are caused by hydrogen evolution, the carbon gases (CO and CO_2) playing only a minor part in the observed behavior.

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[2]There have been numerous investigations of the formation of isolated blisters on production parts caused by contamination of either the steel or the enamel. Such defects are abnormal, however, and do not logically constitute a part of a study of the gases evolved during the normal firing of vitreous coatings on steel.

[3]Fishscaling is a localized fracture of coating glass caused by excessive gas pressure at or near the coating-metal interface.

[4]Reboiling is the blistering at about 1050° F of a vitreous coating on low-carbon steel when it is reheated after the first firing.

[5]Primary boil is the rapid bubbling of the enamel layer during the early stages of firing. It does not reappear during a second firing.

Gases entrapped in the bubble structure of enamels on low-carbon steel after cooling to room temperature have been analyzed by Freeman and Meloche (reference 2). Besides nitrogen and oxygen, which probably originated from entrapped air, these authors found carbon monoxide, carbon dioxide, hydrogen, and an unidentified hydrocarbon to be present in the bubbles in significant amounts after a normal firing. Lucian and Kautz (reference 9) analyzed by spectrographic methods the gases evolved from enameling iron and from ground-coat enamel when samples of these two materials were heated separately in vacuo. Their method is obviously not applicable to the determination of gases evolved during the firing of enamel on iron.

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TABLE I.- REPRESENTATIVE COMPOSITIONS OF EIGHT METALS OR ALLOYS

Metal or alloy	Parts by weight of -										
	C	Cr	P	Si	S	Mn	Ti	Cb	Ni	Cu	Fe
Ingot iron[1]	0.012	----	0.005	----	0.025	0.017	---	----	----	---	99+
Cold-rolled steel[2]	0.084	----	0.008	----	0.036	-----	---	----	----	---	----
Titanium-bearing steel[3]	0.09	----	0.040	----	0.050	0.50	0.2 to 0.5	----	----	---	99+
AISI Type 347 stainless steel[1]	0.08	18.0	-----	----	-----	----	---	0.80	10.5	---	70.6
Copper[4]	-----	----	-----	----	-----	----	---	----	----	99+	----
Inconel[5]	0.08	14.0	-----	0.25	0.008	0.25	---	----	78.5	0.2	6.5
Monel[5]	0.15	----	-----	0.1	0.01	1.0	---	----	67	30	1.4
Nickel[2]	0.014	----	-----	----	-----	----	---	----	99+	---	----

[1]Analyses from "Metals Handbook," Am. Soc. Metals (Cleveland), 1948, pp. 424 and 554.

[2]Analysis by Analytical Chemistry Section of NBS.

[3]Nominal analysis listed by Inland Steel Co. in advertising literature published in 1949.

[4]Commercial grade of deoxidized copper.

[5]Information from Bulls. T-7 and T-5, Development and Res. Div., The International Nickel Co., Inc., revised April 1946 and Oct. 1946, respectively.

TABLE 2.- MILL BATCHES AND MILLING DATA FOR COATINGS E-1 AND E-2

[Fineness, 6 to 8 percent on 200-mesh sieve; application thickness, 4 to 6 mils]

Ingredient	Parts by weight in –	
	Coating E-1	Coating E-2
Frit 109-0	1000	----
Frit 109-E	----	1000
Florida kaolin	60	60
Borax	10	10
Water	425	425

TABLE 3.- BATCH AND COMPUTED OXIDE COMPOSITIONS OF FRIT 109-E[a]

Batch composition		Computed oxide composition	
Material	Parts by weight	Oxide	Percent by weight
Potash feldspar	29.68	SiO_2	50.21
Borax	43.66	Al_2O_3	5.49
Flint (silica)	30.35	B_2O_3	15.97
Sodium carbonate	7.46	Na_2O	14.58
Sodium nitrate	5.99	K_2O	3.79
Potassium nitrate	1.01	CaF_2	7.66
Fluorspar	7.66	MnO_2	1.00
Manganese dioxide	1.00	CoO	.60
Nickel oxide	.70	NiO	.70
Cobalt oxide	.60		
	128.11		100.00

[a]Composition of frit 109-O same as that of 109-E except that it contains no MnO_2, CoO, or NiO.

TABLE 4.- PATTERN OF GAS EVOLUTION FROM A GROUND-COAT ENAMEL ON INGOT IRON AND LOW-CARBON STEELS

Firing stage	Time interval (min)	Temperature interval (°F)	Coating appearance at 25X
1	0 to 1/2	Room temperature to 1150	No change in coating
2	1/2 to 3/4	1150 to 1300	Fine network of cracks in bisque
3	3/4 to 1	1300 to 1400	Fusion, cracks healing, small entrapped bubbles present
4	1 to $2\frac{1}{2}$	1400 to 1550	Primary-boil blisters,[a] many small bubbles
5A	$2\frac{1}{2}$ to 5	1545 to 1555	Bubbles increasing in size and slowly fining out of coating
[b]5B	$2\frac{1}{2}$ to 5	1545 to 1555	Same as 5A except cloudiness developing at interface
[c]6	5 to $5\frac{1}{4}$	1350 to 1300	Bubbles forming at interface
[c]7	$5\frac{1}{4}$ to 7	1300 to room temperature	No further change

[a]Primary-boil blisters do not appear on titanium-stabilized steel nor are they always visible on low-carbon steel unless application thicknesses that are normal or above normal are used (4 mils or greater fired thickness).

[b]Applies to cobalt-bearing E-2 coating only.

[c]Observed most readily in tests with a gas-fired furnace where fast cooling rates are easily attained.

TABLE 5.- TYPE OF BUBBLES PRESENT IN A COBALT-BEARING GROUND COAT AFTER FIRING FOR VARYING TIMES AT 1550° F ON EIGHT DIFFERENT METALS OR ALLOYS

Base metal	Metal thickness (in.)	Type of bubbles in ground coat after indicated firing time (min) at 1550° F of - (1)								
		1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	4	6	8	10
Ingot iron	0.037	P_m,b	B,b	B,b	B,b	B,b	RB,B,b	RB,B	RB,B	RB,B
Cold-rolled steel	0.025	P_p,b	B,b	B,b	B,b	B,b	RB,B,b	RB,B	RB,B	RB,B
Titanium-bearing steel	0.049	S	P_t,b	B,b	B,b	B,b	RB,B,b	RB,B	RB,B	RB,B
AISI Type 347 Stainless steel	0.050	S	C,b	O,B,b	O,B,b	B,b	B,b	RB,B	RB,B	RB,B
Copper	0.019	C,b	O,B,b	B,b	B,b	B,b	B,b	RB,[2]B	RB[2]	RB[2]
Inconel	0.041	S	b	B,b	B,b	B,b	B,b	RB,B	RB,B	RB,B
Monel	0.067	S	C,b	O,P_m,b	P_p,B,b	P_p,B,b	P_p,b	P_p	P_p	P_p
Nickel	0.032	C,b	-----	-----	-----	-----	P_p,B	-----	P_p,B	----

[1]Letter designations: P, primary-boil blisters; B, large bubbles; b, small bubbles; RB, bubbles that appear to be lined with reduced metal at or near interface; C, coating crawled; O, coating orange-peeled; S, coating sintered. Modifying subscripts: t, trace; m, moderate; p, pronounced.

[2]Reduced material on inside of bubble cavity has a different appearance than that obtained with ferrous alloys.

TABLE 6.- RELATIVE AMOUNTS OF CARBON DIOXIDE, CARBON MONOXIDE, AND HYDROGEN IN ENAMEL BUBBLE STRUCTURE AFTER FIRING COATING E-2 ON 0.020-INCH-THICK INGOT IRON FOR VARIOUS TIMES AT 1550° F

Firing time at 1550° F (min)	Firing condition	Relative amount[1] (mole percent) of -		
		CO_2	CO	H_2
2/3	Primary-boil stage	16.7	60.0	23.3
2	Normal fire	6.2	33.3	60.5
6	Hard fire	2.9	22.8	74.3

[1]Computed from mass-spectrometer analyses.

TABLE 7.- BATCH COMPOSITION OF CARBURIZING BATH

Ingredient	Parts by weight
Sodium cyanide[1]	22
Barium chloride	22
Sodium chloride	25
Sodium carbonate	30
Potassium cyanate	1

[1]One millicurie of radioactive C^{14} represented by about 0.02 gram of radioactive NaCN was added per each 100 grams of batch.

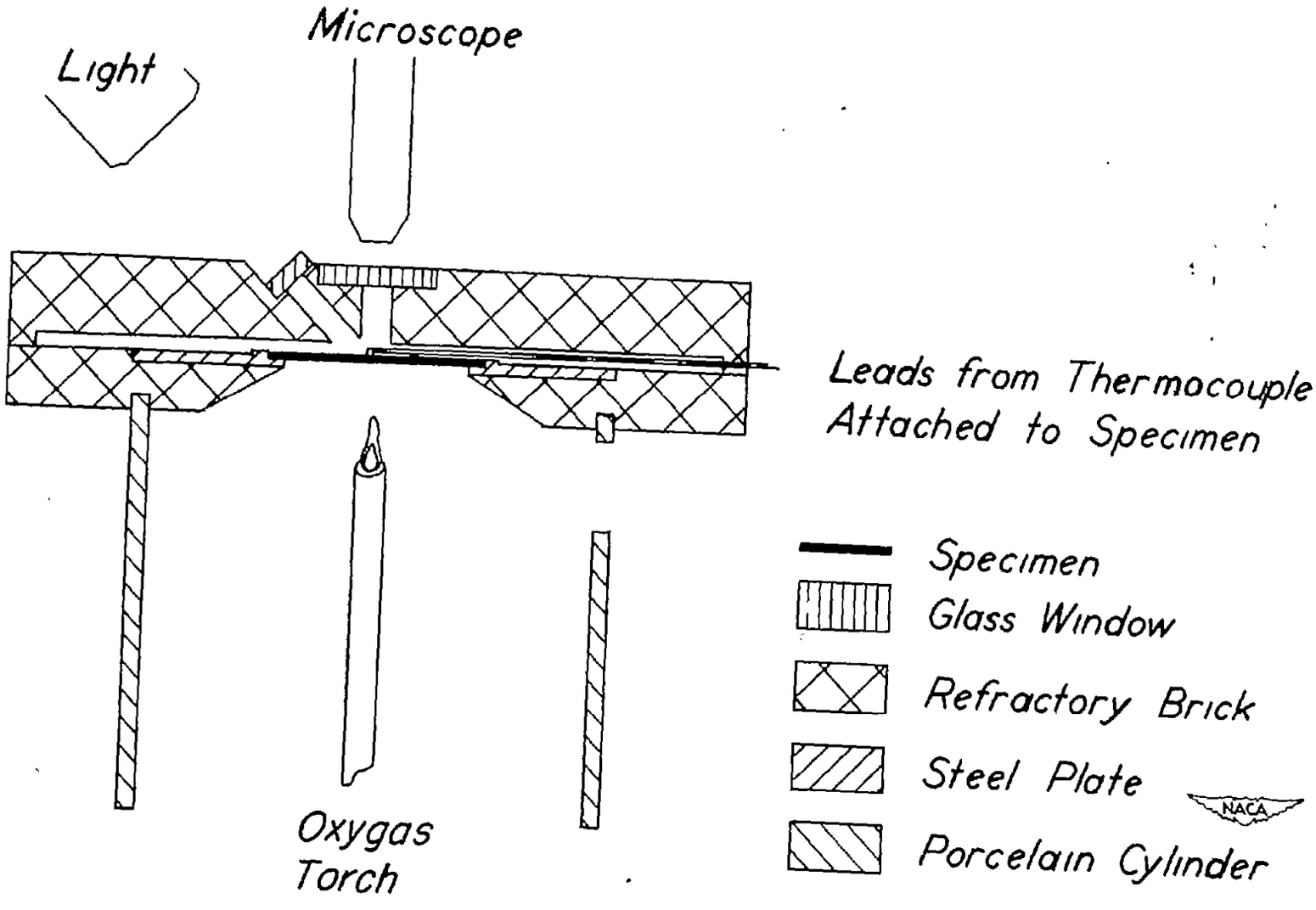


Figure 1.- Schematic drawing of gas-fired furnace.

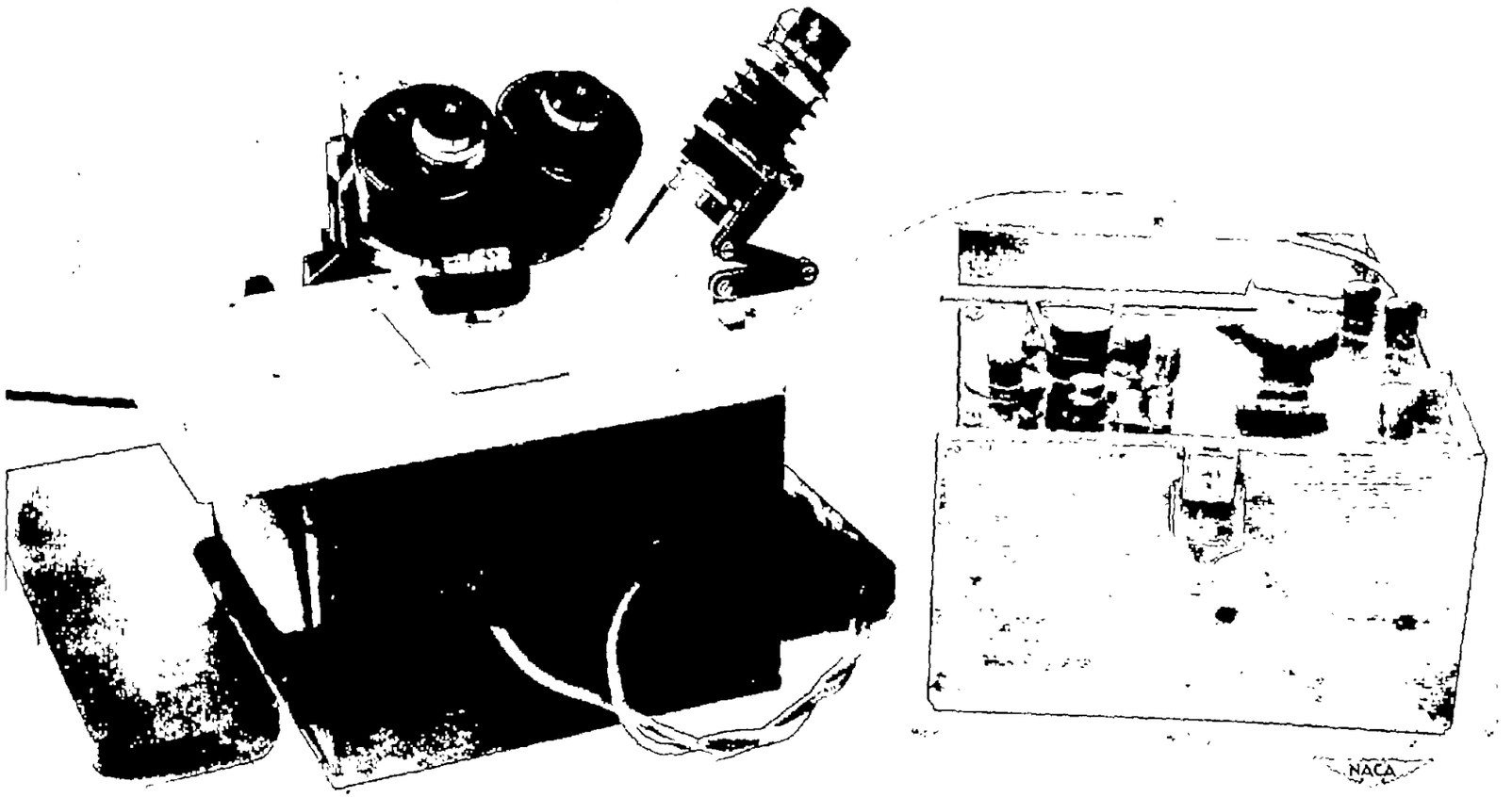


Figure 2.- Electric muffle furnace with microscope and light source in position for observing gas evolution from specimen during a normal firing operation.

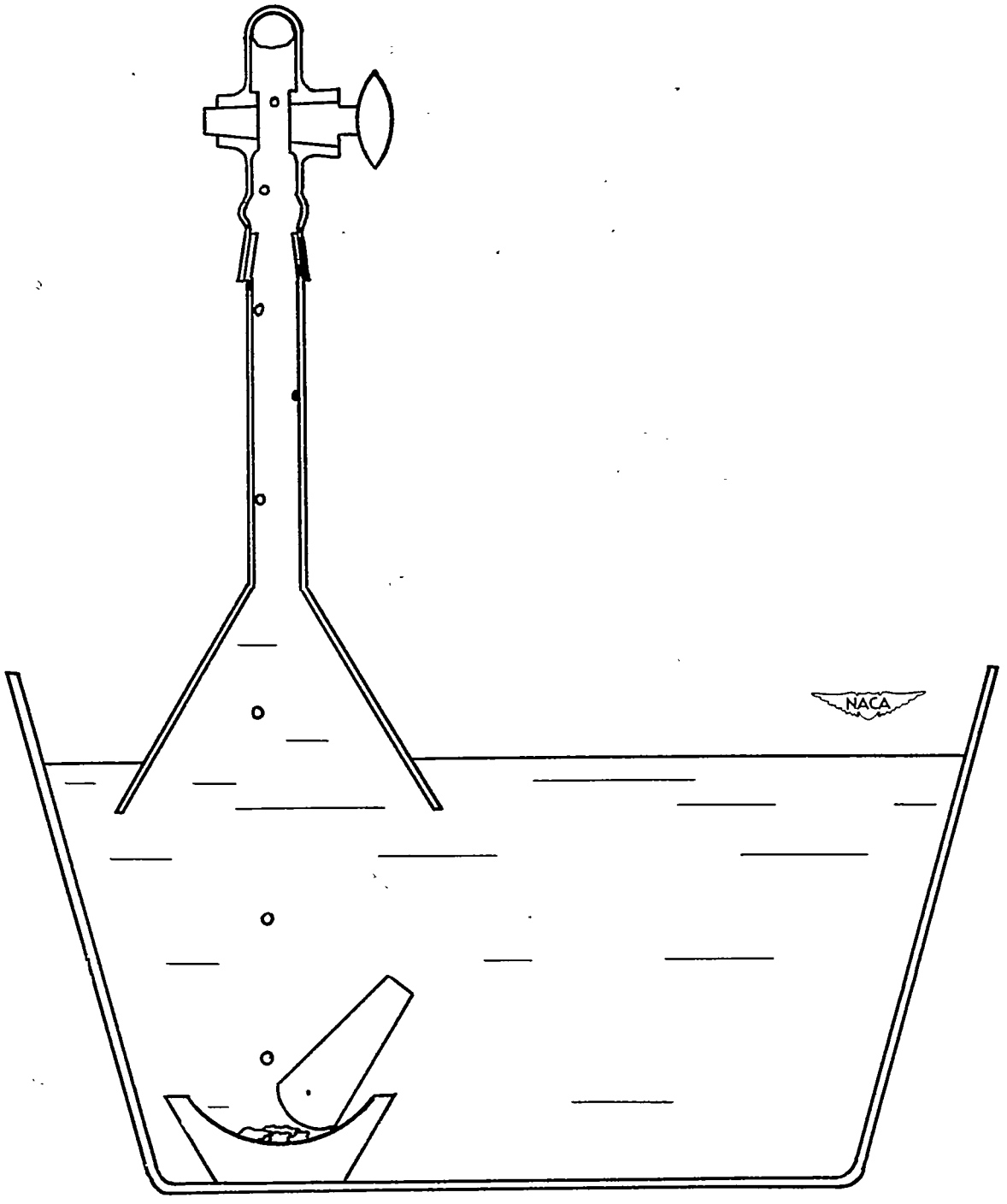


Figure 3.- Schematic drawing of equipment used for collecting gases entrapped in bubble structure of vitreous coatings after application to a metal base.

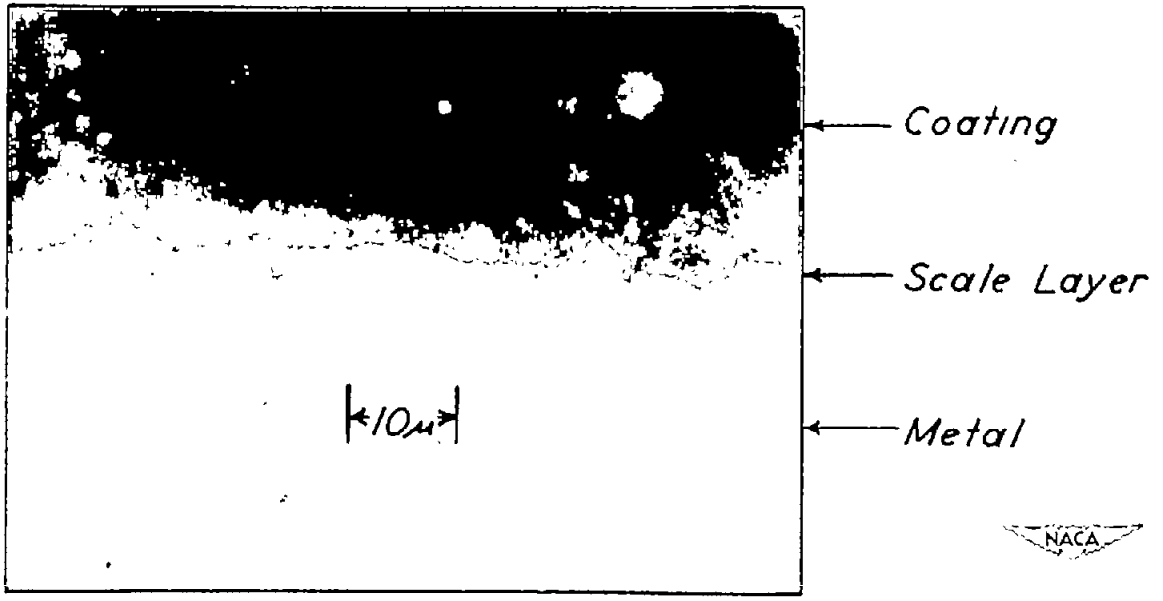


Figure 4.- Photomicrograph (X1000, unetched) of coating-iron interface at the primary-boil stage of firing. Note oxide layer at interface.

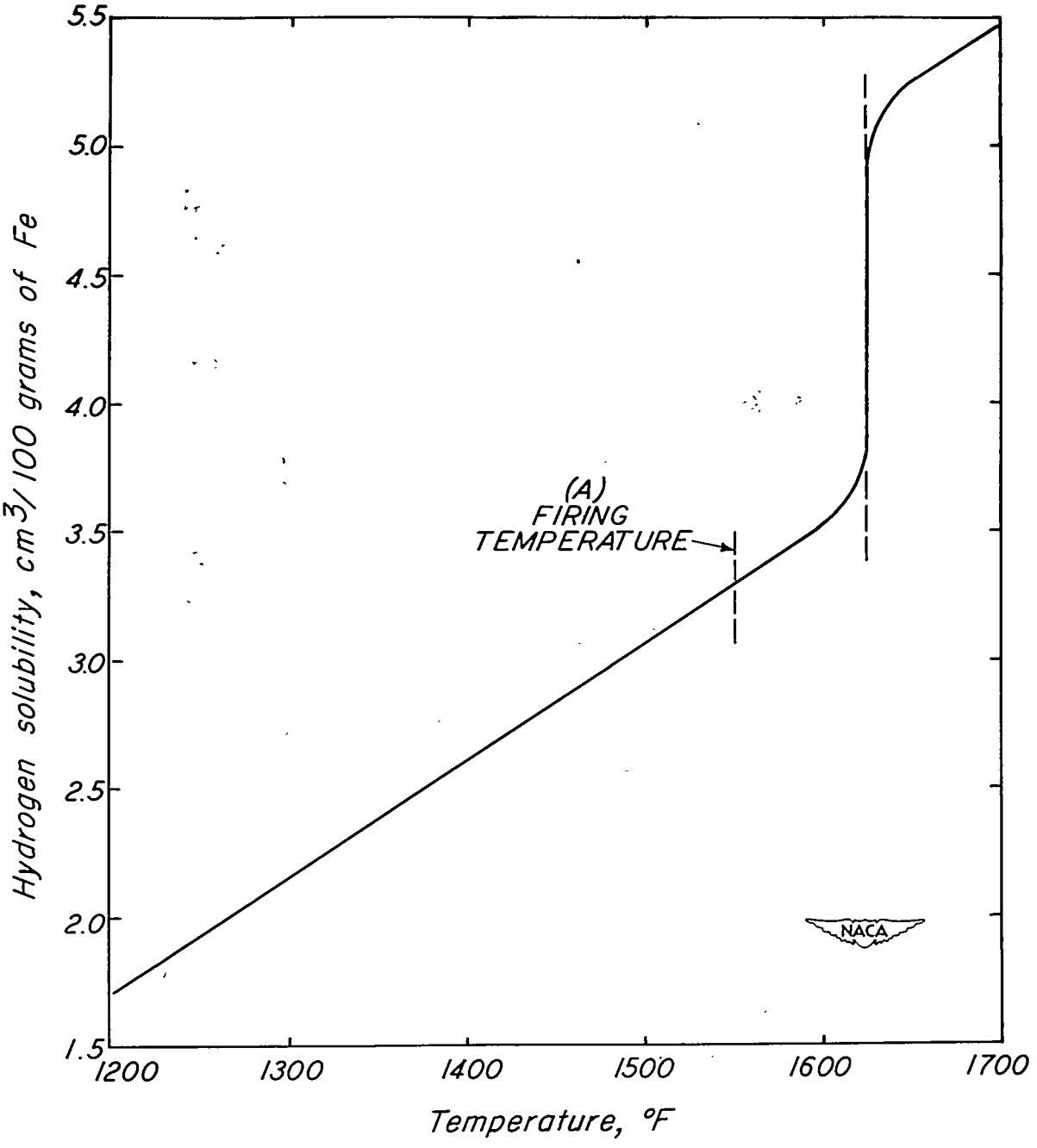
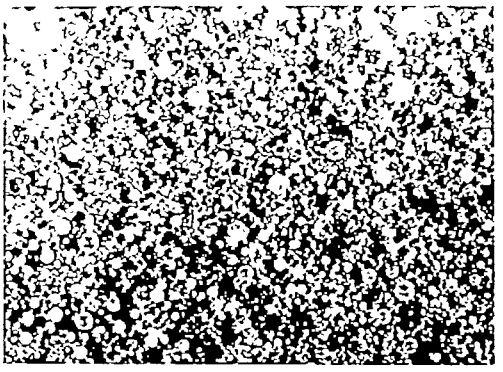
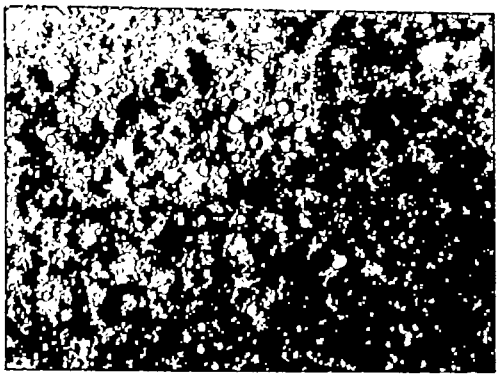


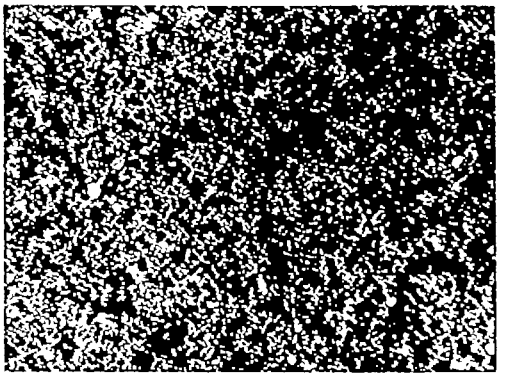
Figure 5.- Portion of solubility-temperature curve for hydrogen in ingot iron.



(a) Untreated clay.



(b) Clay heated 20 hours at 1000° F.



(c) Clay heated 20 hours at 1000° F followed by autoclaving for 300 hours at 406° F.

Figure 6.- Photomicrographs (X26, oblique illumination) of surface of coated ingot-iron specimens after normal firing. Coating in (a), (b), and (c) was identical except for treatment of Florida kaolin mill addition used for suspending the slip.

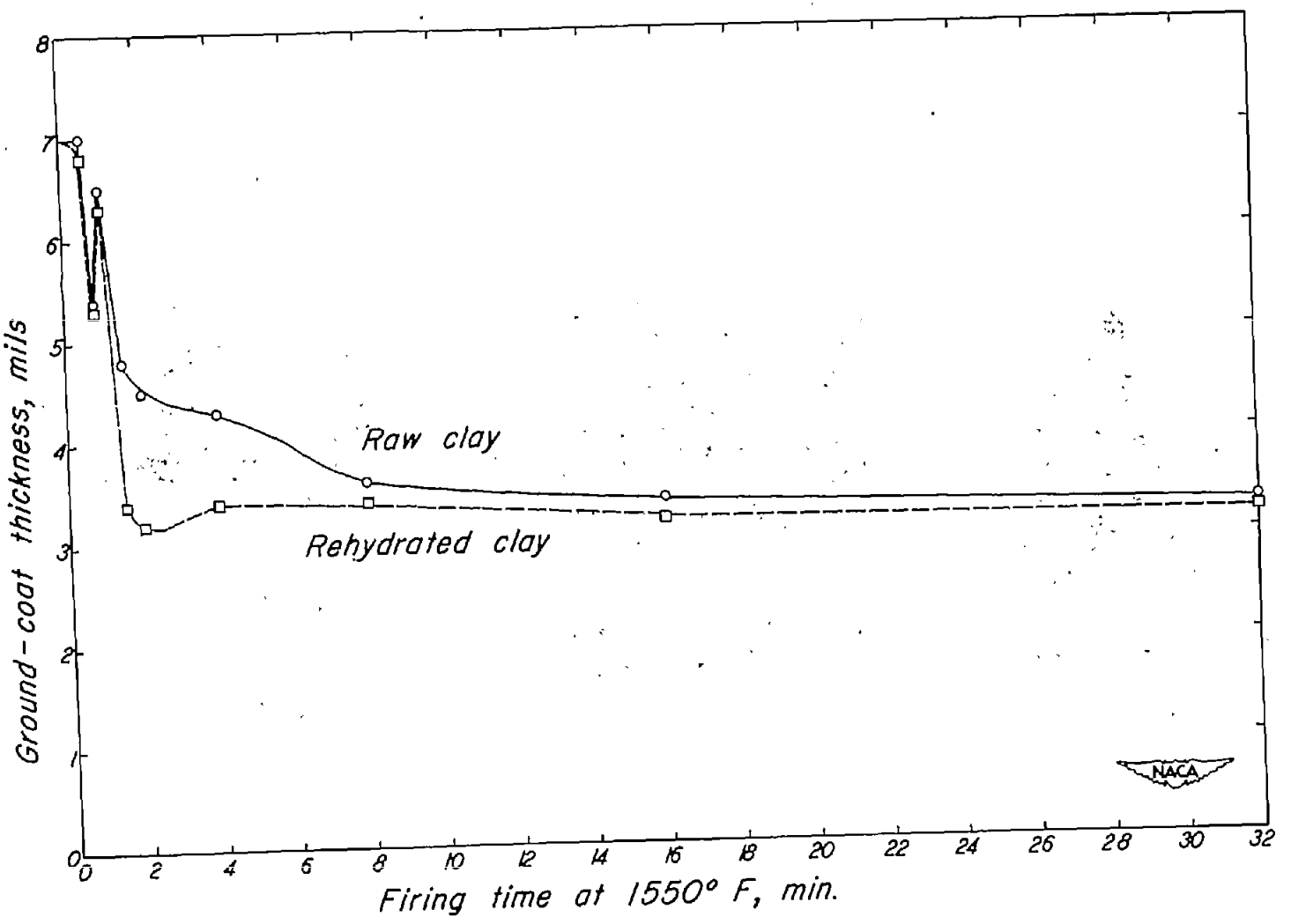


Figure 7.- Change in coating thickness with time of firing for two ground coats that were the same except for treatment of clay used as mill addition.

NACA-Langley - 1-22-53 - 1000