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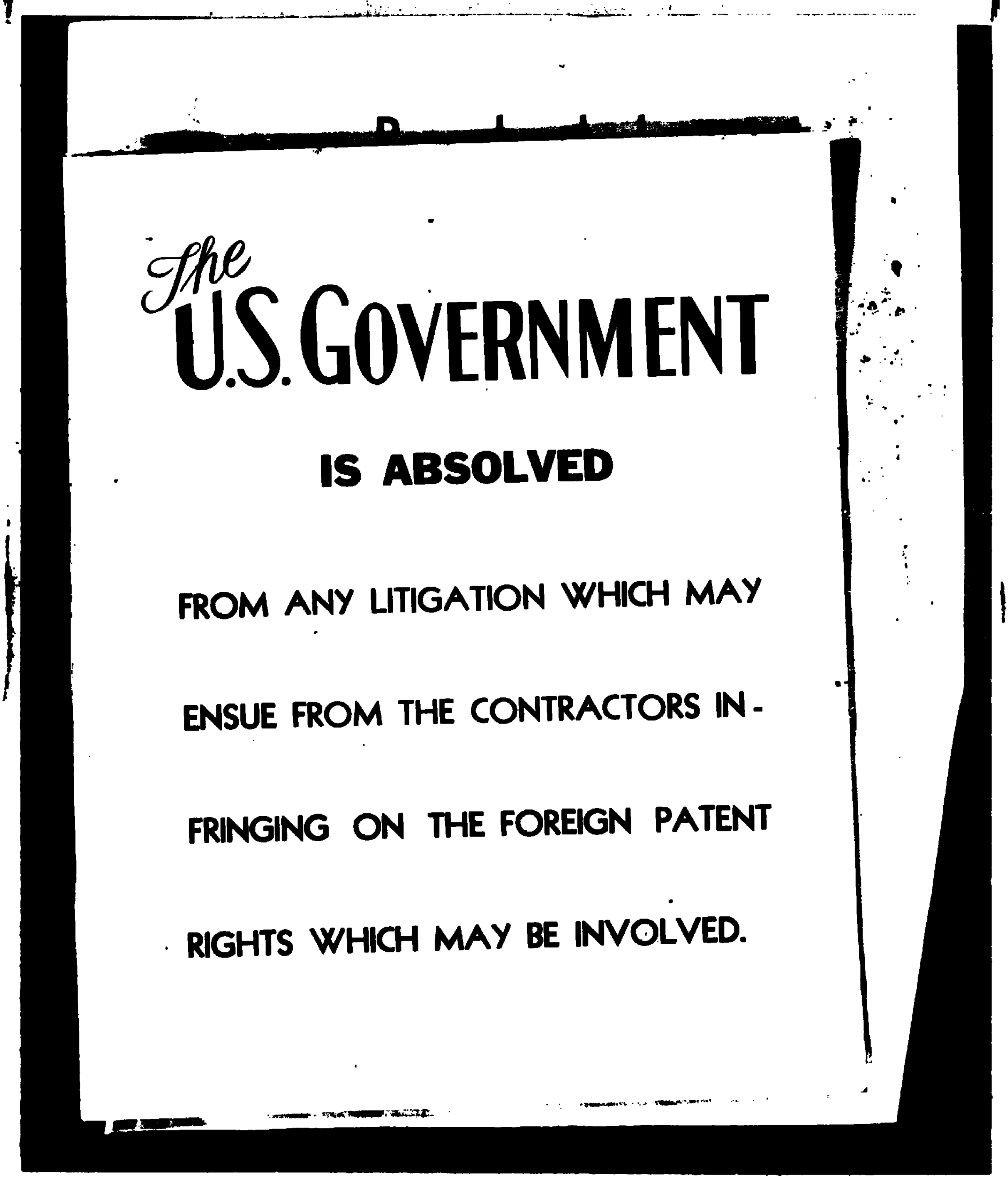

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AN EVALUATION OF THE METHOD AND A STUDY OF THE FACTORS INVOLVED IN USING FUSED CAUSTIC ALKALI FOR PREPARING METAL SURFACES FOR ENAMELING

BY

RAYMOND ALOIS SCHMIDT

B. S., Marquette University, 1929

M. S., Marquette University, 1940

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE IN CERAMIC ENGINEERING
IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF
ILLINOIS 1946

URBANA, ILLINOIS

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I. INTRODUCTION

A. Metal cleaning as a factor in porcelain enameling.

The quality of porcelain enameled surfaces depends upon many factors such as composition, the nature of the base metal, the method of application, firing temperature, and the duration of the firing period. Each of these factors could be further subdivided, but for the purposes of this investigation as reported herein, the factor of paramount importance is the nature of the base metal. This factor includes not only the chemical composition of the metal but also the character of the surface of such metal. In other words, the pretreatment given to metals must be specific and exact in order to bring about a set of surface conditions that will promote good quality porcelain enamel.

B. Standardized practices of the industry with respect to preparation of metal surfaces.

Porcelain enamel can be applied to such metals as sheet iron, cast iron, sheet steel, stainless steel, copper, aluminum and other metals or alloys. Percentage-wise, the largest amount of enameling is done on sheet steel.

For sheet iron and steel, the pretreatment of the metal consists essentially of three steps. The first step is concerned with the removal of oils and greases and is accomplished by using hot aqueous solutions of organic or inorganic detergents or emulsifying agents that attack the oil film and render it "soluble" to a degree, so that subsequent rinsing and agitation removes the oily film. After rinsing the next step consists of so-called acid pickle, for the purpose of removing oxidised iron scale. It usually is accomplished by immersion in aqueous solutions of either sulfuric or hydrochloric acid, at a temperature near 150°F for a period of five to fifteen minutes. This treatment is likewise subject to a rinsing operation in order to remove excess acid. The final step in the cleaning process is immersion in a hot alkali solution containing from 0.1% to 0.2% alkali as sodium oxide. This final step is for the purpose of neutralizing the effect of the acid pickle.

Sheet iron or steel may also be cleaned by annealing, scaling, or sandblasting.

Cast iron and stainless steel are usually prepared for enameling operations by blasting either with sand or steel grit.

C. Other special methods for cleaning sheet steel.

A search of trade literature today yields information on a good number of various special methods of preparing metals, either for subsequent porcelain enameling operations, electroplating, or any other industrial purpose. These special methods may or may not require the use of an electric current in order to make them efficient. This characteristic, namely the use of an electric current, affords a method of subdividing these special methods for consideration here, under the headings of "non-electrolytic" and "electrolytic" techniques.

1. Under "non-electrolytic" techniques there has developed the following:

   a. The so-called "hi-lo" pH degreaser[1], which utilizes two degreaser tanks, one consisting of an alkaline solution of low alkalinity (pH 7.5) and a second tank having a rather high (pH 11-12) degree of alkalinity. The reason for these two solutions is that the degreaser of low alkalinity is capable of removing the more difficult oxides of the drawing compounds present on the surface of the metal. After this task is completed, the ware to be cleaned progresses through the second tank of high alkalinity for the purpose of removing oil films and sludge. Next, the ware passes into a rinse; acid pickle and rinse; and finally into a neutraliser, just as in the case of the conventional acid pickle.

b. Heated metal plus a stream of oxygen gas[2]. This is a method which has been developed for making the cleaning operation a continuous one. It involves heating the metal strip or wire to a dull glow, below the annealing temperature, and while at this temperature direct a stream of oxygen over the surface of the metal in order to "burn" the oil-like residues and other contaminants which are removed by subsequent brushing or scraping.

c. Gas pickling[3], which is another method designed for continuous operations, consists of directing the metal strip or wire into a fired chamber where a mixture of methane gas and chlorine combine to form hydrogen chloride which attacks the metal surface removing undesirable oxides.

d. Fused salts and alkalies have recently come into the picture. The trade literature does not indicate specific uses for these various fused salt or alkali techniques. The fact that none are listed at the present time does not necessarily mean that uses will not be found for these techniques in the future. These fused alkalies and salts are as follows:

(1) Potassium chromate and potassium dichromate [4], covered by a German patent, is described as a method for treating metals of the iron group. No information exists as to what the bath of fused salts will do with respect to cleaning metals.

(2) Fused sodium hydroxide and fused sodium cyanide[5] are described in a patent issued to Dupont. These materials, as salt mixtures, are molten at 300-600°C and are used to

remove oxide scale from ferrous metal objects. A eutectic mixture of about 40% sodium cyanide and 60% sodium hydroxide is recommended for use. The melting point of the salt mixture may be adjusted by adding limited amounts of other salts such as carbonates or chlorides. The cleaning process may be applied to other metals, as for example, brass or copper or any other metal which will not react with the molten salt bath. According to the references, treating time of from one to thirty minutes usually suffices.

(3) Sodium hydroxide plus sodium hydride[6], is covered by a patent assignment to Dupont and is a method for cleaning ferrous and non-ferrous materials. In this process, sodium hydroxide is heated to 350-500°C and in this fused state metallic sodium and hydrogen are added. By this addition, sodium hydride becomes the active cleansing agent and it may vary from 1% to 20% with 2-5% preferred. Hydroxides other than sodium may be used. Approximately fifteen minutes is sufficient to bring about the desired cleaning action in this kind of solution.

(4) Sodium hydroxide plus sodium metal[7], again a Dupont patent, covers the use of molten sodium hydroxide to which sodium metal is added as reinforcement.

2. For "electrolytic" techniques, information is available on two distinct kinds. One kind consists of so-called anodic or cathodic cleaning in acid media (possibly 'reinforced' by the addition of salts) and the other consists of anodic or cathodic cleaning in fused salts or alkalies. Some of these are as follows:

a. Electrolytic cleaning of metals in acid media is discussed by

Hanley[8]. These methods involve the so-called anodic or cathodic processes. In the cathode process, the iron is made the cathode and an insoluble anode is used with either sulfuric or hydrochloric acid as the electrolyte. In operation, the acid is electrolyzed and the hydrogen released by this process is deposited on the ware. This hydrogen reduces the oxides of iron with the resultant formation of ferrous sulphate. In this process, only the oxides of iron are supposed to be attacked by the nascent hydrogen produced. The anode process, discussed by this same author, is very similar to the standardized acid pickling process. The ware to be cleaned is made the anode and the cleaning tank becomes the cathode. During electrolysis, the current at low voltage accelerates the pickling action due to the increased ionic activity. During the process, a thin layer of iron is dissolved with the evolution of hydrogen as in the chemical pickling process.

b. The Bullard Dunn[9] technique consists of descaling steel articles by making such articles cathodic in an electrolytic circuit using hot dilute sulfuric acid solution as the electrolyte. One gram of stannous sulfate is added for each liter of sulfuric acid solution. A current density of between 60 and 80 amperes is required for each square foot of metal surface treated. The voltage is low, 6 to 8 volts being sufficient. Wherever scale is removed from iron by this technique, a very thin layer of tin is deposited.

c. The Bullard Dunn technique has been slightly modified by Lewen[10] to the extent that the stannous sulfate is not added to the acid but instead there is added a small percentage of sodium chloride. This technique eliminates the possibility of tin deposition on iron but in its place there is probably deposited sodium ferrate.

d. Of the electrolytic techniques involving media other than acids a very recent development consists of using molten sodium nitrate or a mixture of sodium nitrate and potassium nitrate in an iron kettle. This process is covered by a patent assigned to American Steel and Wire Company[11] and involves the use of an electric current (d.c.) at a potential of 6 to 12 volts. The ware to be cleaned is made a part of the eletric circuit and lowered into the kettle. The immersion time is approximately 90 seconds. It is claimed that oxides on steel are converted to sodium peroxide which may be removed from the steel by a process of washing with water. The evolution of nitrogen oxides prevents sludge from adhering to the steel and the iron kettle.

e. Another method of the above type, of particular interest to the present work recorded here, is the so-called electrolysis in fused alkalies. This method was investigated by Evans of England and reported in Iron and Steel, June 1944[12]. The method is also described in a U.S. patent issued to Urlyn C. Tainton[13], in February 1945. Both of these methods involve the use of molten alkali, such as sodium or potassium hydroxide, in the range of 800°F. The ware to be cleaned is made a part of a low voltage direct current circuit and is lowered into the fused alkali for a short period of time. This particular technique is described in greater detail in subsequent pages of this report.

D. Reasons for the selection of the electrolytic fused alkali technique as a problem for investigation.

A review of the foregoing introductory material points to the fact that considerable effort is being extended in order to find other methods for the pretreatment of metal, which methods may be more suitable or practical than the traditional acid pickle technique now predominately used in the porcelain enameling industry.

Of the special methods that are enumerated in preceding paragraphs considerable work has been reported on electrolytic acid media techniques. All of these acid techniques still evolve hydrogen, and hydrogen in the porcelain enameling field is considered as being one of the causes of poor enamel adherence.

An analysis of the electrochemical reactions involved in the fused alkali or salt techniques, with or without electrolysis seems to hold some promise that the 'hydrogen-occluded-in-metal-problem' could be considerably diminished as a factor and further that such techniques, because they are relatively new, might possess something that would enhance the quality of porcelain enamel ware.

II. PREVIOUS INVESTIGATIONS ON THE ELECTROLYTIC FUSED ALKALI TECHNIQUE

A. Recent applications.

Current trade literature does not yield too much information on the application and success of the electrolytic fused alkali technique as a method for preparing metal for subsequent enameling. This fact is not too unreasonable however when it is considered that the first article by Evans[14] publicizing this technique appeared only as recent as 1944.

In this country, an electrolytic molten bath technique has had some measure of success in the field of metalurgy, plating-operations and metal cleaning as a result of the promotional work of the Kolene Corporation[15]. In fact "Steel" Magazine[16] of May 1945 carried an article which featured this technique and which claimed that this "New oxidizing-reducing process removes colloidal graphite, thus facilitating subsequent porcelain enameling of deep drawn sheet steel parts". This is the only reference that could be found to a porcelain enameling application by the electrolytic molten bath process.

B. The origin of the electrolytic fused alkali technique.

Evans, referred to above, reports that in 1936, a British patent (No. 442,859) was granted for a process for cleaning and descaling metal by electrolytic action in a bath of molten caustic soda. This method, as originally developed by the Bethelehem Steel Corporation, was successful for cleaning steel wire prior to electro-galvanizing. This combined process of cleaning and zinc plating became known as "bethenizing" and has been used extensively in Great Britain for the production of galvanised wire. The method has also been applied to the descaling of sheet steel, not as a preliminary to galvanizing but as a final treatment which confers a mild degree of resistance to rusting for an appreciable period, in contrast to the rapid rusting which follows pickling in acid. Going back to the original British patent, the details of the specifications in the patent mentions various chemicals for the bath, such as mixtures of sodium and potassium hydroxides, sodium nitrite and calcium chloride. According to Evans however, the only material used very widely in this technique was commercial caustic soda. Further, according to Evans, the operating conditions for the technique are said to be a temperature of 850°F (454.5°C), a current density of 100 amperes per square foot and an immersion time of 10-15 seconds. The metal to be cleaned was made the cathode and the iron pot or tank was made the anode.

C. Advantages of the electrolytic fused alkali process.

Quoting again from the Evans article, referred to above, the electrolytic fused alkali technique was reputed to have the following advantages:

1. "It produces a cleaner and more uniform surface than can be obtained by other methods, and consequently allows the production of better coatings, whether the steel is to be plated, tinned, enameled or otherwise treated.
2. The consumption of chemicals is small. (In the case of treating wire, as explained earlier, only 15 pounds of caustic soda is said to be consumed per ton of wire treated).
3. The process avoids the loss of weight which the steel undergoes in acid pickling. This may be an important factor when expensive alloys are involved.
4. The nature of the process precludes the possibility of embrittlement of the steel through absorption of hydrogen.
5. By the use of appropriate salts and proper temperatures the steel may be given heat treatment, such as annealing, tempering, etc., at the

same time as it is being cleaned.

6. The process completely clears metal surfaces from all organic material, so that no preliminary degreasing step is necessary.
7. The process can be used in place of sandblasting in nearly all cases; it is particularly effective as a preliminary to inspection to show defects in welds, castings, etc.
8. Steel cleaned by this process may be stored, transported, etc., without the rusting which occurs immediately after acid pickling. This makes it unnecessary to do the pickling immediately before the article is to be coated, permitting simplification of manufacturing plant flow sheets."

D. An evaluation of the claims and a statement of the objectives of the present work.

A review of the above claims points to the fact that the electrolytic fused alkali technique possesses the possibility of improving some of the standard practices with respect to the pretreatment of metals for porcelain enameling. The main object of the present investigation was to find the most favorable conditions of temperature, time and current density for carrying out the process. Having established such factors it was deemed advisable to coat the metal treated by this technique with a suitable porcelain enamel and to fire such enamel to maturity. Samples of enamels obtained in this manner would be compared with samples of enamel obtained by using the same enamel coatings on metal pretreated by the standard acid pickle process. The efficiencies or suitableness of the electrolytic fused alkali technique would be determined by an appraisal of the enamel surfaces and subjecting such surfaces to usual tests for adherence.

Inasmuch as the Kolene Corporation, Detroit, Michigan, furnished a supply of their metal cleaning materials for any investigational work that might be undertaken, it was decided to use these materials along with and in comparison with the fused alkali technique wherever it was deemed practicable to do so. The chemicals supplied by the Kolene Corporation were found to give an alkaline reaction to phenolpthalein and methyl orange test solutions and therefore, because of such alkaline character and the fact that high temperature and electrolysis is necessary for these materials to do their work, they were considered as alkali substances and included in this investigation.

III. EXPERIMENTAL PROCEDURE AND DATA

A. Apparatus used in the reported series of investigations.

Figure I, page 13, represents a schematic drawing of the apparatus and accessories used in conducting the series of investigations reported herein. The apparatus is a cabinet into which there is built equipment for performing three related tasks, which tasks could very well serve as zones for considering the experimental setup. From a zone of point of view the apparatus consists of as follows:

1. Heating or melting zone. (Figure I, page 13)

The melting pot (item 3) is constructed of forged steel approximately 1/4 inch in thickness. The pot dimensions are six inches in diameter and seven inches in depth. A convenient apron surrounds the pot at its top periphery.

This pot is encircled by means of a shielded electric heating unit which is connected to a 220 volt alternating current line and the circuit is controlled by means of a four stage stove switch (high, medium, low and off). The switch is portrayed as item 2.

When the pot is charged with caustic alkali, it requires approximately 1000 grams of material. This quantity of material will require a heating time of one hour with full current in order to bring it to a molten or fused state at a temperature of 800°F. Temperature recordings are made by means of a Leeds-Northrup potentiometer and the millivolt readings obtained in this manner are converted to temperature readings in degrees. The manual switch allows the temperature to be controlled to within plus or minus ten degrees Fahrenheit if a careful job is done in watching the heating rate.

2. Low voltage direct current supply. (Figure 1, page 13)

The electrolysis that occurs within the pot is accomplished by

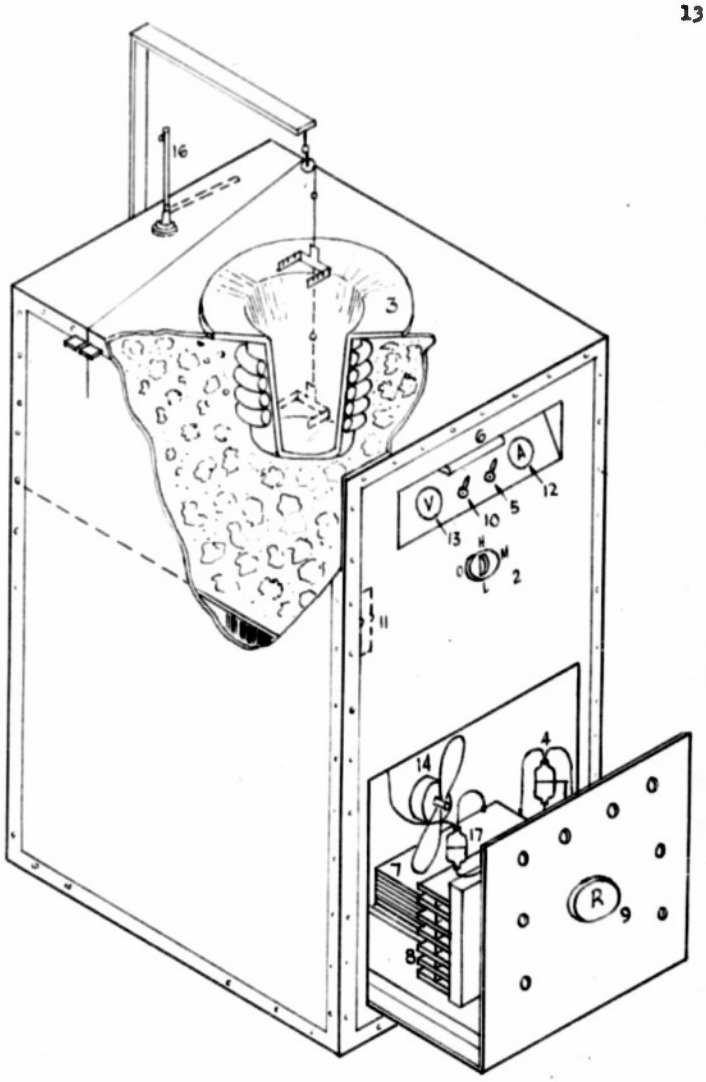


FIGURE 1.
SCHEMATIC DRAWING OF APPARATUS USED FOR PREPARING METAL SURFACES IN FUSED CAUSTIC ALKALI.

means of a low voltage direct current supply obtained by rectification of 110 volts alternating current, all the equipment for which is within the lower sliding cabinet.

The 110 volts, alternating current, is tapped off the three wire circuit through a disconnect plug (item 4), and led into a transformer (item 7). The stepped down voltage is rectified by means of a copper oxide rectifier (item 8). The direct current voltage is controlled by means of a variable rheostat (item 9), and the entire current ends in another disconnect plug (item 17).

The rectification circuit is made complete by means of a toggle switch (item 5), which on closing, lights an incandescent lamp (item 6), over the instrument panel and it also causes a small electric fan (item 14), to operate in order to cool the copper oxide rectifier.

3. The electrolytic circuit. (Figure I, page 13)

From the disconnect plug (item 17), the low voltage circuit continues to a double pole double throw toggle switch (item 10), mounted on the instrument panel. One side of the circuit is lead through a shunt (item 11), across which there is connected a center zero ammeter (item 18), calibrated in amperes 0-25 for 'reduction' in one direction and 0-25 for 'oxidation' in the other direction. A voltmeter (item 13), is connected across this low voltage line. One end of the direct current circuit is grounded to the melting pot at position (item 15), and the other side of the circuit terminates at a binding post (item 16), which is fitted up with a movable arm. This movable arm permits a flexible wire cord to be clipped onto the metal bracket-like holder. This bracket holder is insulated from a cable which is directed through a pulley supported on a framework over and in-line with the melting pot. The cable allows the bracket to be raised or lowered into the molten alkali. The work or metal under test is placed in the notches of the bracket in such a manner that the test plates are held in a vertical position and such plates are exactly the same distance away from each other.

4. Wiring diagram of the experimental setup.

Figure 2, page 16, portrays diagrammatically, the wiring connections for the entire physical setup. Each component carries a numerical designation which corresponds to the position of the equipment in the schematic drawing of Figure 1, page 13.

B. Materials used.

1. Cleaners.

The fused alkalies used in the series of investigations reported in this work were three in number as follows:

a. Caustic alkali commercial grade, which is referred to as alkali "A" in the report of tests which follows herein. The composition of the commercial grade, alkali "A" is as follows:

Sodium Hydroxide	98.10%
Sodium Carbonate	0.50%
Inert Ingredients	1.40%

b. Proprietary cleaner, labelled Kolene No. 1, was obtained from Kolene Corporation, Detroit, Michigan. This material is referred to as alkali "B" in the report of test procedures and results. Nothing is known about the composition of the material except that it is received for use in steel drums and in the form of chips or flakes similar to commercial flake caustic alkali and that it hydrolyses in water to give an alkaline reaction.

c. Proprietary cleaner, designated Kolene No. 4, obtained again from the Kolene Corporation, is received in the form of a solid mass in steel drums. A faint blue coloration permeates the solid structure.

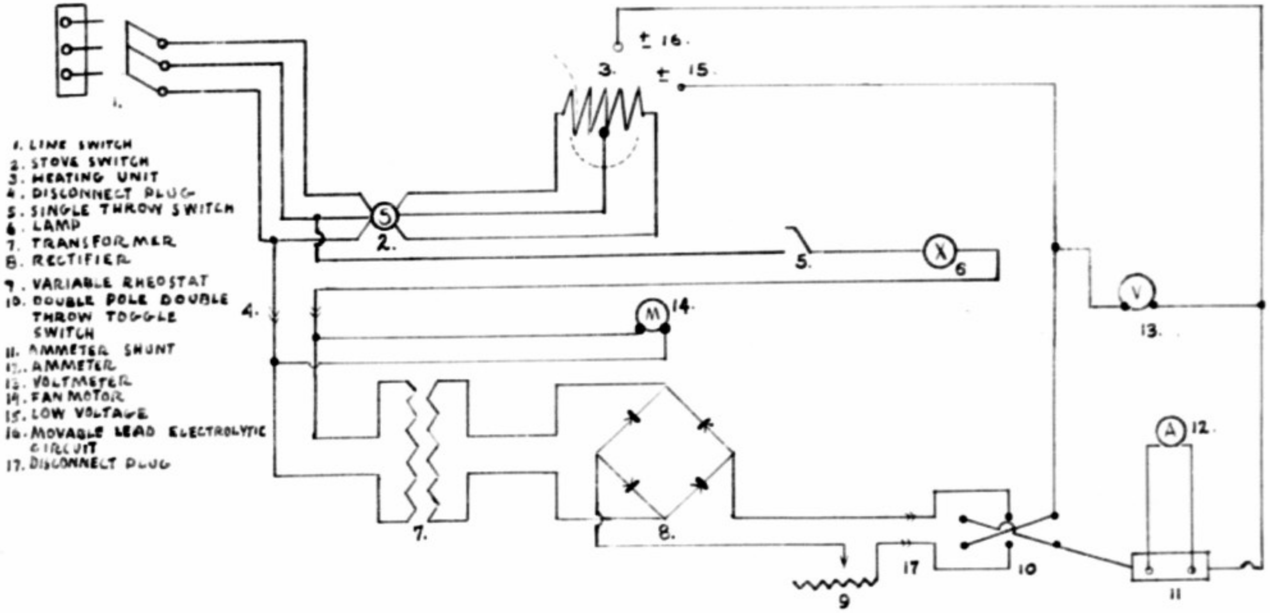


FIG. 2

WIRING DIAGRAM OF EXPERIMENTAL
APPARATUS AS SKETCHED IN FIG. 1.

This material is designated as alkali "C" in this report for the reason that it imparts a pink coloration to phenolpthalein.

2. Metals.

The metals used in the series of investigations consisted of standard sheet steel enameling stock of 22 gauge. The test plates were cut from a standard size sheet into 2 inch by 4 inch size test plates. The stainless steel used, is known as number "302" stainless, and it likewise was used in the form of 2 inch by 4 inch test plates.

3. Acid Pickling.

Whenever it was necessary to turn out test plates of sheet steel for an acid pickle control, the materials used and procedure followed for such pickling was identical to that prescribed for this technique in Andrews and Cook[17], "Enamel Laboratory Manual" Table 7, page 21 therein.

4. Enamels.

In the series of investigations conducted on the various metal test plates, the efficiency or the pretreatment given to such metal plates was based primarily on the behavior of porcelain enamels applied to the plates. Two types of enamels were used. The sheet steel plates were covered with a cobalt ground coat and some of the plates were covered with an antimony-free single white cover coat. The single white cover coat was also applied to the stainless steel specimens used in the investigation.

The cobalt ground coat used had the following composition:

Frit Batch		Mill Batch	
Feldspar	31.00	7.00%	Clay
Borax	37.00	0.75%	Borax
Quartz	17.00	45.00%	Water
Soda Ash	6.00		
Soda Nitre	4.00		
Fluorspar	3.00		

Frit Batch (continued)

Cobalt Oxide	0.50	Fineness 8-9 grams on
Nichel Oxide	0.50	200 mesh.
Manganese Dioxide	1.00	Fire 1550°F for 3 minutes

The sheet steel white cover enamel, antimony free, had the following composition:

100	lb.	No. 1300 Chicago Vit Frit	
7	lb.	Clay	
1 1/2%		Opax 21-H	Fineness 3-4 grams on
1/8%		Sodium nitrate	200 mesh.
38%		Water	Fire 1500°F for 3 minutes

C. Adherence Testing.

All tests for the adherence of enamels were conducted using the apparatus described in Andrews[18] "Enamels" page 352, by which the test plate receives an impact from a falling weight which weight is directed onto the plate by means of a pair of upright guide rods. The degree of enamel adherence was determined by comparison with a set of standards which was agreed upon in advance as being satisfactory for enamel adherence performance.

D. General Information on Experimental Methods:

1. The electrolytic effect.

The experimental apparatus, as described in Section III, A, afforded an opportunity to investigate the relative merit of various alkali substances as a means for cleaning, descaling and surface conditioning metals such as sheet steel and stainless sheet.

This was accomplished by first placing a quantity of alkali material in the iron pot of the apparatus. The heating element was turned on and after a one hour heating period, the alkali was in a fused or molten state. As was explained earlier, the temperature of the fused alkali was determined by means of a Leeds-Northrup potentiometer. Two temperature ranges were employed, one at 600°F ± 10°F and 800°F ± or 10°F.

By means of a movable overhead bracket, test pieces of metal were lowered into the fused alkali. The bracket holder formed one side of the low voltage direct current supply. The electric circuit for electrolysis was controlled by means of toggle switch which permitted a change of polarity within the fused alkali.

The resultant electrolytic effect allowed the following chemical reactions to occur:

a. The electrolysis of caustic soda (assuming that the fused alkali was essentially sodium hydroxide) to produce sodium metal;

b. The reduction of iron oxide at the cathode by sodium;

c. The reformation of sodium hydroxide.

The preceding series of effects can be produced at will at either the anode or the cathode within the electrolytic cell by simply controlling the direction of current flow. Thus two cycles are possible, which, for the purpose of this investigation are called 'reduction cycle' and 'oxidation cycle'.

The 'reduction' cycle consists in making the ware to be cleaned, the cathode in the process. This is practically accomplished, by means of the experimental apparatus used, by simply placing the metal test plate between the notches of the metal bracket support. The bracket is made the cathode by flipping the toggle switch on the instrument panel board of the apparatus. The metal then as cathode is 'reduced' by reason of the sodium ions of the electrolytic solution attacking the oxygen of the oxides of iron that exist as scale or rust on the metal and which are considered undesirable. The result of such reduction treatment is to cause violent action to take place on the surface of the metal. Such action can be observed as a gaseous stream occurring on the faces of the metal and the upper edge of the metal which is practically visible during the process. When the test specimen is removed for examination, after rinsing with live steam, the piece of metal is free of iron scale or rust and has a decided metallic grey color similar to the color of sheet iron which is cleaned by the acid pickling technique.

The 'oxidation' cycle consists in establishing electric polarity so that the metal bracket, which contains the ware, is made the anode. When this is done, the piece of sheet iron is oxidised by the hydroxyl ions and oxygen ions of the electrolytic solution and as a result one or more oxides or hydroxides of iron are formed which imparts a dark discoloration to the piece of iron. The degree of discoloration or or oxide formation is function of time, temperature and current density. In other words, any shade of color, from gray, brown, red, blue or black, or combinations of these colors in colorful mosaics can be effected by simply controlling the variables as enumerated in the preceding sentence.

2. A consideration of variables that would influence laboratory procedures.

An examination of what has been reported so far would indicate that many factors and variables and specific behavior of the apparatus would have to be taken into account in establishing a sequence of investigational operations. In their order, these experimental considerations might be listed here as follows:

a. The operating character of the laboratory apparatus.

b. The performance of the separate alkali substances under different conditions of temperature, electric polarity, voltage and current density.

c. The effect of sheet iron and steel in the various alkali substance while being treated on an oxidation or a reduction cycle.

d. The effect of time, temperature, voltage, current density, oxidation or reduction treatment, and method of cleaning for sheet iron and stainless steel and how such surface treatment influences the quality of porcelain enameled surfaces.

e. The effect of enamel composition, firing range, and duration of firing time on metal which has received a specific surface treatment.

Accordingly, a series of experimental investigations were setup in schedule form and are reported in Section E which follows herewith.

E. Sequence of experimental procedures.

1. Preliminary investigations designed to determine the operating character of the experimental apparatus.

a. Charging the apparatus with caustic alkali.

In charging the working pot of the apparatus with caustic alkali two separate methods were followed. The first method consisted of pouring into the pot a 1500 gram portion of caustic alkali in one operation. The other method consisted of first filling the pot with a 500 gram portion of caustic alkali and then making additions of 500 gram portions until a total of 1500 grams was in the pot. Of the two methods the latter method proved to be the more satisfactory for the reason that it afforded a chance for the heat of the solution to assist melting the solid alkali.

b. Determination of average heating time.

On the average, it required usually one and one-half hours at full heating capacity to melt a fresh batch of flake caustic alkali and to have such material reach a temperature of 750°F. In the case of reheating the solid mass of caustic alkali, the heating time needs to be increased to two hours in order to reach the same temperature. Both heating rates required the full current as afforded by the "high" position on the four-point stove regulating switch. The molten caustic can be kept in a molten condition by covering the pot area with a piece of transite insulating board and maintaining the heating element on the "low" position of the heat control switch. The design of the pot is such that on heating the molten alkali the internal expansion simply raises the level of the caustic alkali without any damage to the pot or without any sudden explusion of the alkali due to the accumulated heating effect.

c. Excessive vapors.

No noticeable amount of vapor occurs until the fused alkali is in the temperature range of 700°F to 800°F. At that temperature there is a certain amount of obnoxious vapors coming off especially in the case of the proprietary compound alkali "C" as used in this work. Ventilation of the working area is necessary while conducting experiments.

d. Method of holding the ware during cleaning.

At the outset of this investigational work it was decided that the method as reported by Evans, which employed bus bars and bolted straps to hold the ware, would not be followed for the reason that it was thought to be more desirable to reproduce the production line setup as used in electroplating where the ware is suspended from an electrode into the solution.

The first method used consisted of simply suspending the ware into the pot by means of a spring clip to which there was fastened a copper wire leading to the side arm connector of the 10 volt current supply system. This method was not satisfactory for the reason that excessive heating caused the zinc plating of the spring clip to drain over the ware. The spring clip also became covered with alkali making it difficult to remove the ware when such ware was removed from the pot. Using the spring clip method also resulted in clip marks appearing as a stain on the test plates.

The foregoing method was set aside in favor of a piece of apparatus which consisted of a pair of hooks made of steel wire and formed in such a manner that a test plate could be laid across the two 'fingers' of the hook-like arrangement. This method permitted the test plates to rest in a flat position with respect to the solution. The two hooks were made fast to a piece of iron designed for its weight and its ability to serve as a junction for the two steel hooks. This method was a little more satisfactory than the spring clip. It still had the disadvantage of permitting only one test piece to be cleaned at one time and further it permitted the outside of the test plate to be stained by reason of the burning effect of electrolysis.

Because the two steel fingers would not adequately support the work during electrolysis, (as was made evident by the staining that occurred on the underside of the test plates), a new method of supporting the work was devised which consisted of a metal bracket support as indicated in Figure 1, page 13. This bracket holder was very satisfactory for several reasons. One important reason that it was satisfactory is that it eliminated the staining. Another reason is that it tripled the number of plates that could be treated at one time and finally it was satisfactory because the test plates were in a vertical position with respect to the electrolytic solution which permitted a certain amount of drainage during the electrolytic process.

e. Rinsing operation.

After each electrolytic or cleansing cycle, the test plates, upon removal from the cleaning solution, were coated with alkali, loose scale and sponge iron or iron oxide dust. At first these test plates were transferred from the working pot by means of a pair of forceps and then cleaned by immediately plunging the coated ware into cold water as recommended by Evans. This method was not satisfactory for the reason that violent spattering occurred and the caustic alkali and loose scale was not entirely removed by this process.

The foregoing method of rinsing was slightly improved by immersing the test plate first into a tank of nearly boiling water followed by vigorous rinsing in another tank of boiling water. Even this method did not entirely reduce the spattering effect and occasionally the ware was not cleaned as well as it should be, due to either insufficient rinsing time or rinsing in the water which had built up a degree of alkalinity due to excessive use.

The method that proved most satisfactory for rinsing consisted of simply removing the ware by means of the forceps and allowing such ware to cool slightly in air. The length of time necessary for cooling was determined by observing the slight solidification of alkali on the surface of the metal. As soon as the alkali took on a noticeable 'set' the test plate was held under a jet of live steam. The test plate was turned as necessary during this steam treatment in order to remove all scale and sludge. In using live steam, care must be taken so as not to use steam which has been contaminated with oil as might be the case where high pressure steam was first used in power plant work and then the low pressure steam made available for cleaning. Steam, contaminated with oil, leaves a residue on the steel plates which interferes with subsequent good enameling practice.

f. Storage of test plates.

All test plates, after cleaning and rinsing in live steam, were transferred to a large dessicator. The dessicator had been previously filled with the necessary amount of anhydrous calcium chloride which served as the drying agent.

g. Removal of oil films.

Pieces of sheet iron were given a light coating of lard oil prior to their being immersed in the fused caustic alkali. Only a few seconds were necessary to decompose and remove this oil film. The heat of reaction was sufficient to "burn" off the oil with attendant vapors exuding from the pot. No electric current was necessary. Rinsing these test plates resulted in pieces of metal that were clean or free of oil to a degree that no wetting of surface occurred when such plates were immersed in clean hot water.

h. Removal of scale of oxides of iron.

Fused caustic alkali, without current, is not effective in removing deep seated iron oxide scale. In fact, not even superficial scale is removed by this technique.

When test plates with iron oxide areas on it's surface were immersed in hot alkali, on an "oxidation" cycle and for a period of two minutes, such treatment failed to remove the oxide layer.

In order to remove iron oxide from sheet steel, it was necessary that the test plates be subjected to a "reduction" treatment and that the temperature of the alkali be at least 700°F and the time of treatment at least two minutes.

i. Effect of high temperature and oxidizing conditions on sheet steel.

Test plates were treated by means of a reduction cycle and such test plates were then raised from the solution until the lower half only remained in the electrolytic solution. With the electrolytic circuit off, the upper portions of such test plates were "blued" by simply being held immediately above the hot caustic alkali level, thus giving an indication as to the amount of heat and the temperature at which the bath operates.

This blueing effect could only be removed by re-immersing the plate in the electrolytic solution and having it take on another reduction treatment. In other words, the heat of the alkali solution was transferred to the air-exposed portion of the test plate and the oxidation or "blueing" occurred under these conditions. This points to the fact that the ware must be completely immersed for electrolytic treatment and after such treatment it must be completely removed from contact with the solution or else this blueing will occur.

j. Effect of stainless steel on the fused alkali solution.

It was found that if a pot of alkali which had been used for cleaning and surface treating sheet iron or steel was also used for cleaning or preparing stainless steel, then such alkali would be contaminated by the chromium or nickel of the stainless steel so that subsequent sheet iron metal cleaning in that pot was inefficient. The degree of inefficiency was in proportion to the amount of contamination by the chromium and nickel in the form of hydroxides of these metals. The hydroxides of chromium and nickel imparted a flocculent precipitate to the fused alkali bath. This condition required that the alkali bath be used exclusively for either sheet steel or stainless but not both.

k. Hazards of fused alkali.

Fused caustic alkali is certainly not mild mannered material. Aside from the fuming that occurs while metal is being electrolyzed, there are several conditions that need to be watched carefully while the process is in operation. The first caution is the matter of spattering. Water can never come in contact with the hot solution because this will cause spattering to occur. Next, electrical contacts must be solid because any electric arc caused by a loose connection (as in the case of the flexible lead to the jig holding the ware in place) will cause a slight explosion at the surface of the alkali due to the escaping hydrogen formed during electrolysis.

Prior to cleaning with live steam, the danger of spattering did exist when test plates were removed from the hot alkali and immediately plunged into cold or hot water. This danger was eliminated by using live steam but with this improvement, a new hazard was introduced which involved obnoxious fumes given off during the rinsing process. It was necessary to afford proper ventilation while performing this operation.

2. Loss and Gain-in-weight studies of sheet steel in fused alkali.

a. Method.

Two by four inch samples of 22 and 20 gauge standard sheet steel stock were used in the tests. Ordinary commercial grade of sodium hydroxide alkali "A" was used as the alkali medium. The alkali was heated to a temperature of 800°F and maintained at that temperature to within ± 0.1 millivolt as determined by a Leeds-Northrup potentiometer.

Samples of sheet steel were previously air dried and their weight before treatment accurately determined by means of a sensitive chainomatic analytical balance. Each piece of sheet steel was stamped by means of a metal die in order to assign an identification number to each piece.

The samples were immersed in the fused alkali by means of a bracket holder which holder constituted one end of the low voltage direct current supply. The bracket holder was of such construction that permitted loading with either one, two or three 2"x4" plates for each immersion treatment.

The fused alkali was contained within the cylindrical pot. On lowering samples of the sheet steel into the caustic material, a preferential arrangement with respect to current density effective on each plate of sheet steel is immediately set up due to the circular design of the pot. This factor immediately required that the loss or gain in weight studies take into account this preferred position. In order to keep this factor constant, the test plates were always set up in the pot in the same relative position as in the original arrangement for the first immersion treatment of the series.

Further, since the metal bracket holder held samples of the metal parallel to each other, it was necessary to conduct investigations with single, double and triple samples at a time because the current density effective on each plate is a function of current flow in parallel circuits. The single plate had the entire line voltage and current acting across its faces, while the two sheets of iron in parallel had the line voltage but only one half the line current effective on each of the two faces of the two test pieces. This reduction in effective current on the test pieces was one of the factors deemed desirable to investigate in this particular study.

A time schedule of successive treatments was decided upon in advance. This schedule was arbitrarily set at intervals of one-half minute, two-minute, four four-minute treatments and one final ten-minute immersion period.

The test plate or plates were immediately withdrawn from the fused alkali and allowed to cool to the point where as explained before, the adhering hydroxide film took a final "set" as a solid. The piece or pieces then were very carefully rinsed using a jet of live steam. After rinsing, each test piece was placed in an air oven for a ten minute period (140°F) and 40° R.H.

Loss or gain in weight was determined by means of an analytical balance.

Two series of investigations were conducted. One series could be termed an 'oxidation' series when the sheet steel became the anode and after electrolysis, the surface of the iron was colored with oxide films. The other series consisted of a 'reduction' treatment where the sheet iron became the cathode and after electrolysis such plates were 'reduced' to a clear metallic color free of black or colored oxides.

The oxidation series consisted of plates numbered as follows:

Plate #5	single
Plates #6 & #7	double
Plates #8, #9 & #10	triple

The reduction series consisted of plates numbered as follows:

Plate #11	single
Plates #12 & #13	double
Plates #14, #15 & #16	triple

In addition to the above two series, separate test plates were immersed for a thirty minute period each on a straight 'no-current' cycle (Plate #17), straight oxidation (Plate #18) and straight reduction (Plate #19).

b. Data.

The data sheet for the changes in weight of the separate test plates for the oxidation series are as reported in Table 1, page 31 and Table 7, page 38. The specific gain or loss in weight values for the oxidation series at short time intervals appears in Table 2, page 32 and is set forth in cumulative gain or loss in weight as reflected in Table 3, page 33.

The numerical data for the oxidation studies is portrayed graphically (see Graphs Nos. 1, 2 and 3, pages 34, 35 and 35a).

The data sheet for the changes in weight of the separate test plates for the reduction series are as reported in Table 4, page 36 and Table 7, page 38. The specific gain or loss in weight values for the reduction series at short time intervals appears in Table 5, page 37 and is set forth in cumulative gain or loss in weight as reflected in Table 6, page 38.

The numerical data for the reduction studies is portrayed graphically in Graphs Nos. 4, 5 and 6, pages 39, 40 and 40a.

TABLE 1

OXIDATION OF SHEET STEEL
IN
FUSED ALKALI

Temperature of Alkali = 800°F
Effective Voltage = 4 Volts DC
Effective Amperage = 14 Amperes
Unit of Weight = Grams

Time (Minutes)	SAMPLE NUMBER					
	#5	#6 and	#7	#8,	#9 and	#10
Original Weight or Zero Time	38.8945	38.9236	38.8264	39.1083	38.9720	38.4732
0.5	".8950	".9250	".8276	".1096	".9736	".4753
1.5	".8950	".9244	".8273	".1088	".9720	".4737
2.0	".8989	".9287	".8291	".1091	".9771	".4773
4.0	".8993	".9285	".8308	".1117	".9821	".4787
4.0	".9020	".9316	".8351	".1202	".9905	".4809
4.0	".9070	".9293	".8335	".1137	".9830	".4779
4.0	".9000	".9248	".8311	".1040	".9818	".4767
10.0	".8978	".9232	".8320	".1060	".9790	".4740

TABLE 2

GAIN OR LOSS IN WEIGHT*
AS REFLECTED IN TABLE 1

Time (Minutes)	SAMPLE NUMBER					
	#5	#6 and #7		#8,	#9 and #10	
0.5	+.0005	+.0014	+.0012	+.0013	+.0016	+.0021
1.5	.0000	-.0006	-.0003	-.0008	-.0016	-.0016
2.0	+.0039	+.0043	+.0028	+.0003	+.0051	+.0036
4.0	+.0004	-.0002	+.0017	+.0026	+.0050	+.0014
4.0	+.0027	+.0031	+.0031	+.0085	+.0084	+.0022
4.0	+.0050	-.0023	-.0016	-.0065	-.0075	-.0030
4.0	-.0070	-.0045	-.0024	-.0047	-.0012	-.0012
10.0	-.0022	-.0016	+.0009	-.0030	-.0028	-.0027

TOTALS

30	+.0033	-.0004	+.0056	-.0023	-.0070	+.0008

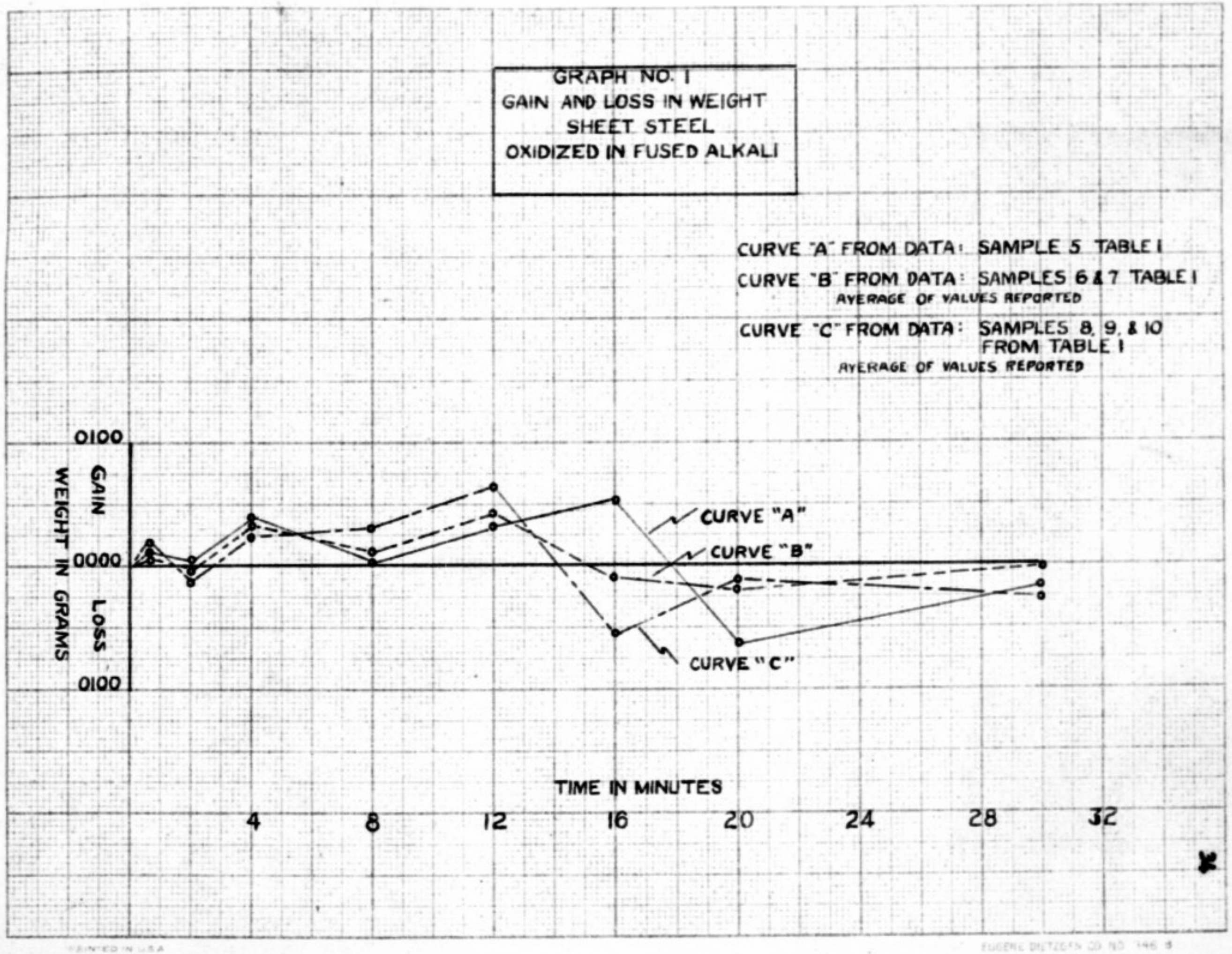
* Gains = +
Loss = -
Unit of Weight = grams

TABLE 3

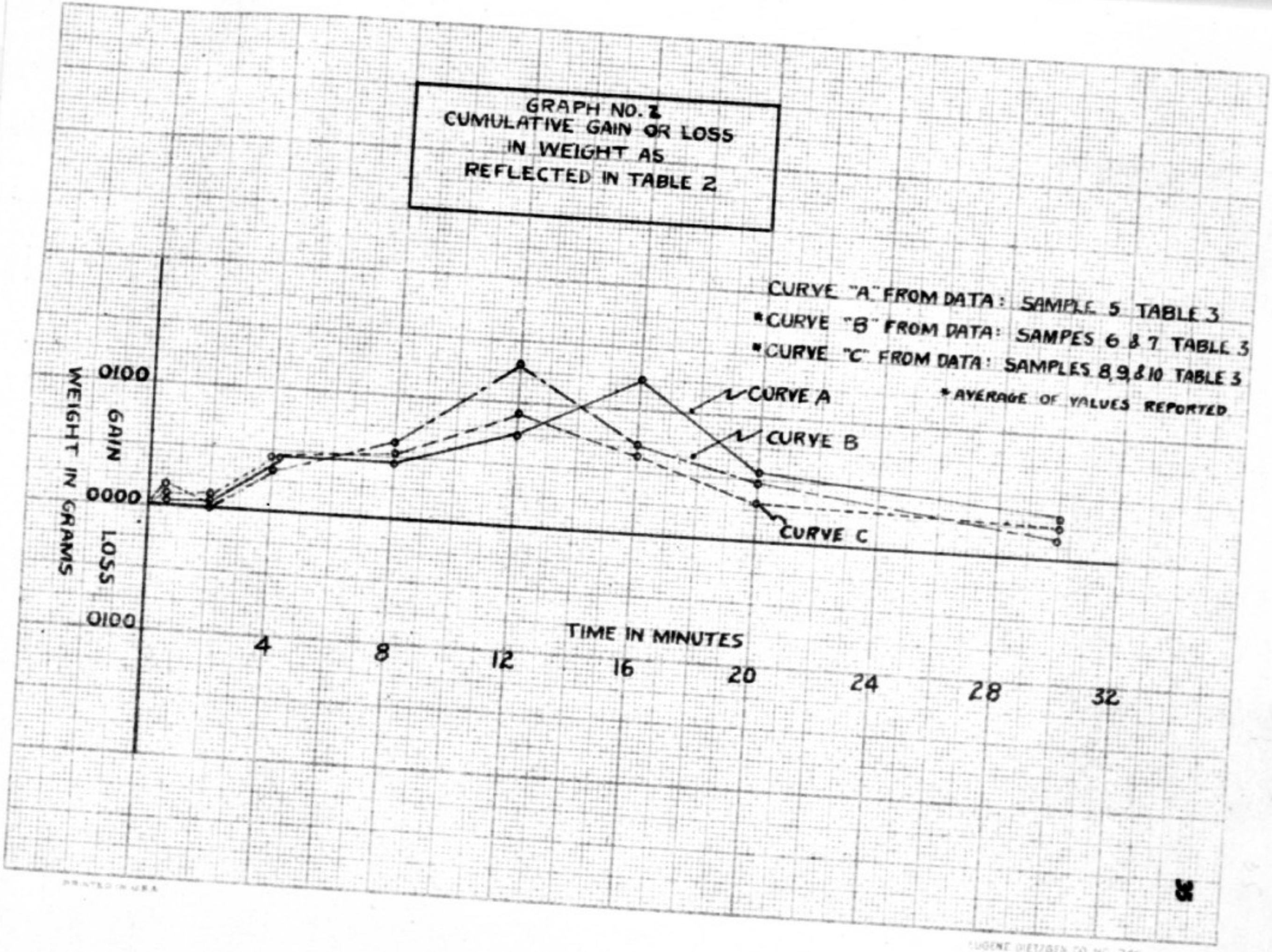
CUMULATIVE GAIN OR LOSS IN WEIGHT*
AS REFLECTED IN TABLE 2

Time (Minutes)	SAMPLE NUMBER						Average
	#5	#6 and #7		#8,	#9 and #10		
0.5	.0005	.0014	.0012	.0013	.0016	.0021	.0013
2.0	.0005	.0008	.0009	.0005	.0000	.0005	.0006
4.0	.0044	.0051	.0037	.0008	.0051	.0041	.0039
8.0	.0048	.0049	.0054	.0034	.0101	.0055	.0057
12.0	.0075	.0080	.0097	.0119	.0185	.0077	.0105
16.0	.0125	.0057	.0071	.0054	.0110	.0047	.0077
20.0	.0055	.0012	.0047	.0007	.0098	.0035	.0062
30.0	+.0033	.0004	+.0056	-.0023	+.0070	+.0008	.0023

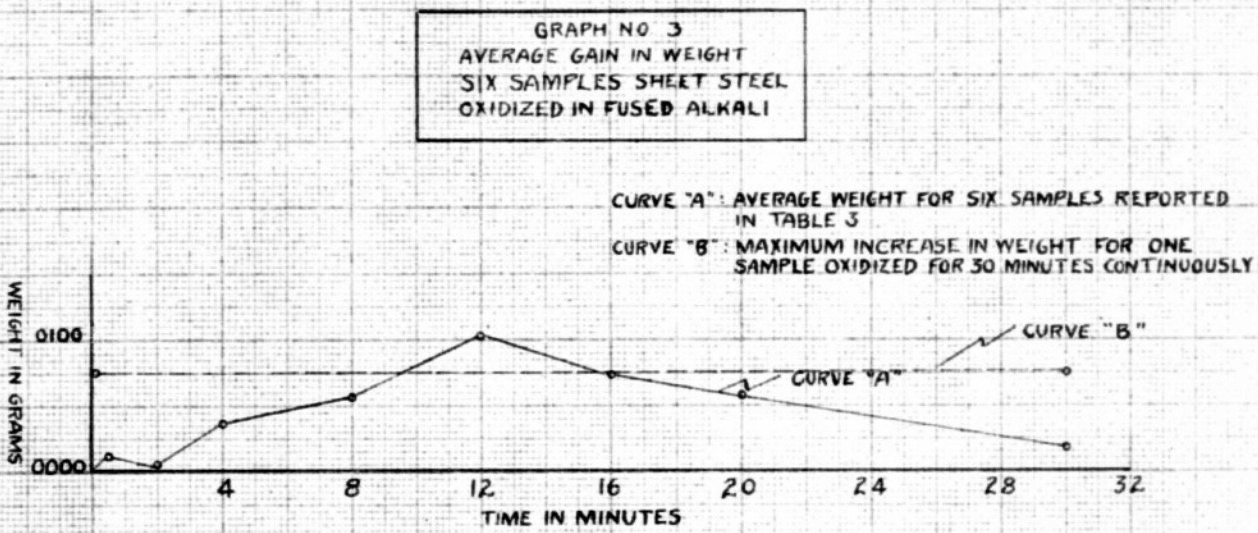
* Gain = +
Loss = -
Unit of Weight = grams



GRAPH NO. 1
GAIN AND LOSS IN WEIGHT
SHEET STEEL
OXIDIZED IN FUSED ALKALI



GRAPH NO. 2
CUMULATIVE GAIN OR LOSS
IN WEIGHT AS
REFLECTED IN TABLE 2



GRAPH NO 3
AVERAGE GAIN IN WEIGHT
SIX SAMPLES SHEET STEEL
OXIDIZED IN FUSED ALKALI

CURVE "A": AVERAGE WEIGHT FOR SIX SAMPLES REPORTED IN TABLE 3

CURVE "B": MAXIMUM INCREASE IN WEIGHT FOR ONE SAMPLE OXIDIZED FOR 30 MINUTES CONTINUOUSLY

TABLE 4

REDUCTION OF SHEET STEEL
IN
FUSED ALKALI

Temperature of Alkali = 800°F
Effective Voltage = 4 Volts DC
Effective Amperage = 14 Amperes
Unit of Weight = grams

Time (Minutes)	#11	#12 and	#13	#14,	#15 and	#16
Original Weight or Zero Time	31.7144	31.6600	31.6776	31.7570	31.6600	31.6505
0.5	".7150	".6622	".6787	".7651	".6600	".6487
1.5	".7060	".6586	".6758	".7580	".6568	".6486
2.0	".7080	".6616	".6788	".7576	".6631	".6514
4.0	".7110	".6660	".6845	".7605	".6629	".6550
4.0	".6894	".6599	".6720	".7500	".6511	".6450
4.0	".6642	".6361	".6605	".7554	".6505	".6471
4.0	".6435	".6364	".6574	".7430	".6478	".6410
10.0	".6139	".6047	".6350	".7380	".6400	".6310

TABLE 5

GAIN OR LOSS IN WEIGHT*
AS REFLECTED IN TABLE 4

Time (Minutes)	SAMPLE NUMBER					
	#11	#12 and	#13	#14,	#15 and	#16
0.5	+.0006	+.0022	+.0011	+.0081	.0000	-.0018
1.5	-.0090	-.0036	-.0029	-.0071	-.0032	-.0001
2.0	+.0020	+.0030	+.0030	-.0004	+.0063	+.0028
4.0	+.0030	+.0046	+.0057	+.0029	-.0002	+.0036
4.0	-.0211	-.0101	-.0125	-.0105	-.0118	-.0100
4.0	-.0257	-.0198	-.0115	+.0054	-.0006	+.0021
4.0	-.0207	-.0027	-.0031	-.0124	-.0027	-.0061
10.0	-.0296	-.0287	-.0224	-.0050	-.0078	-.0100
TOTALS						
30	-.1005	-.0453	-.0426	-.0190	-.0200	-.0195

* Gains = +
Loss = -
Unit of Weight = grams

TABLE 6

CUMULATIVE GAIN OR LOSS IN WEIGHT*
AS REFLECTED IN TABLE 5

Time (Minutes)	SAMPLE NUMBER						
	#11	#12 and	#13	#14	#15	#16	Average
0.5	+.0006	+.0022	+.0011	+.0081	.0000	-.0018	+.0017
2.0	-.0084	-.0014	-.0018	+.0010	-.0032	-.0019	-.0043
4.0	-.0064	+.0016	+.0012	+.0006	+.0031	+.0009	+.0028
8.0	-.0034	+.0062	+.0069	+.0035	+.0029	+.0045	+.0033
12.0	-.0245	-.0034	-.0056	-.0070	-.0089	-.0055	-.0126
16.0	-.0502	-.0237	-.0171	-.0006	-.0095	-.0034	-.0083
20.0	-.0709	-.0264	-.0202	-.0140	-.0122	-.0093	-.0066
30.0	-.1005	-.0451	-.0426	-.0190	-.0200	-.0195	-.0411

* Gain = +
Loss = -
Unit of Weight = grams

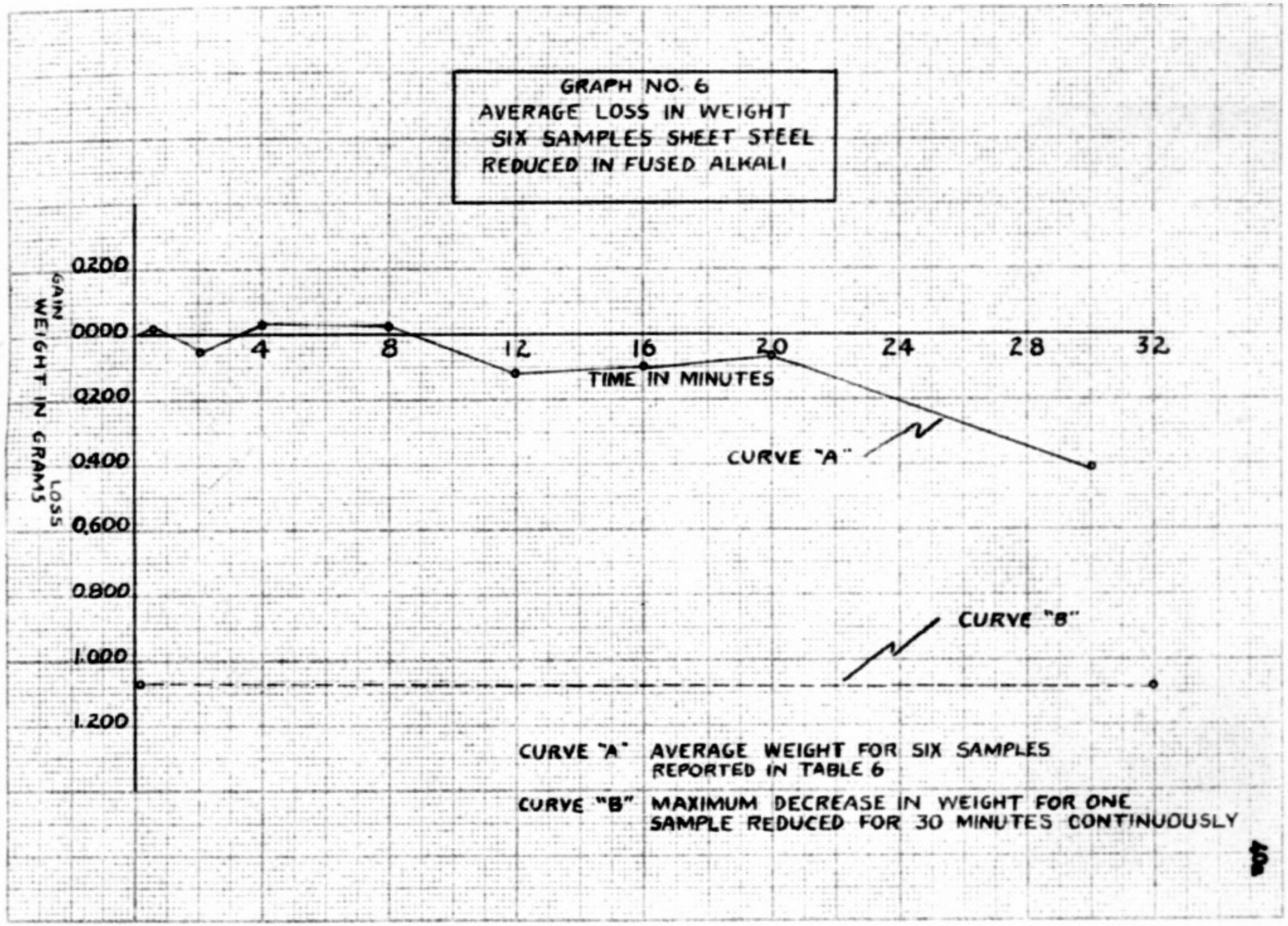
TABLE 7

GAIN OR LOSS IN WEIGHT OF SHEET STEEL IN FUSED ALKALI

(Thirty Minute Period)

SAMPLE NO.	TREATMENT	VOLTS	AMPS	ORIGINAL WEIGHT	FINAL WEIGHT	DIFFERENCE*
17	No current	-	-	31.3708	31.3384	-.0324
18	Oxidation	4	14	31.6843	31.6768	-.0075
19	Reduction	4	12	31.1820	30.0762	-.1058

Temperature of Fused Alkali - 800°F
* Loss = +
Gain = -
Unit of Weight = grams

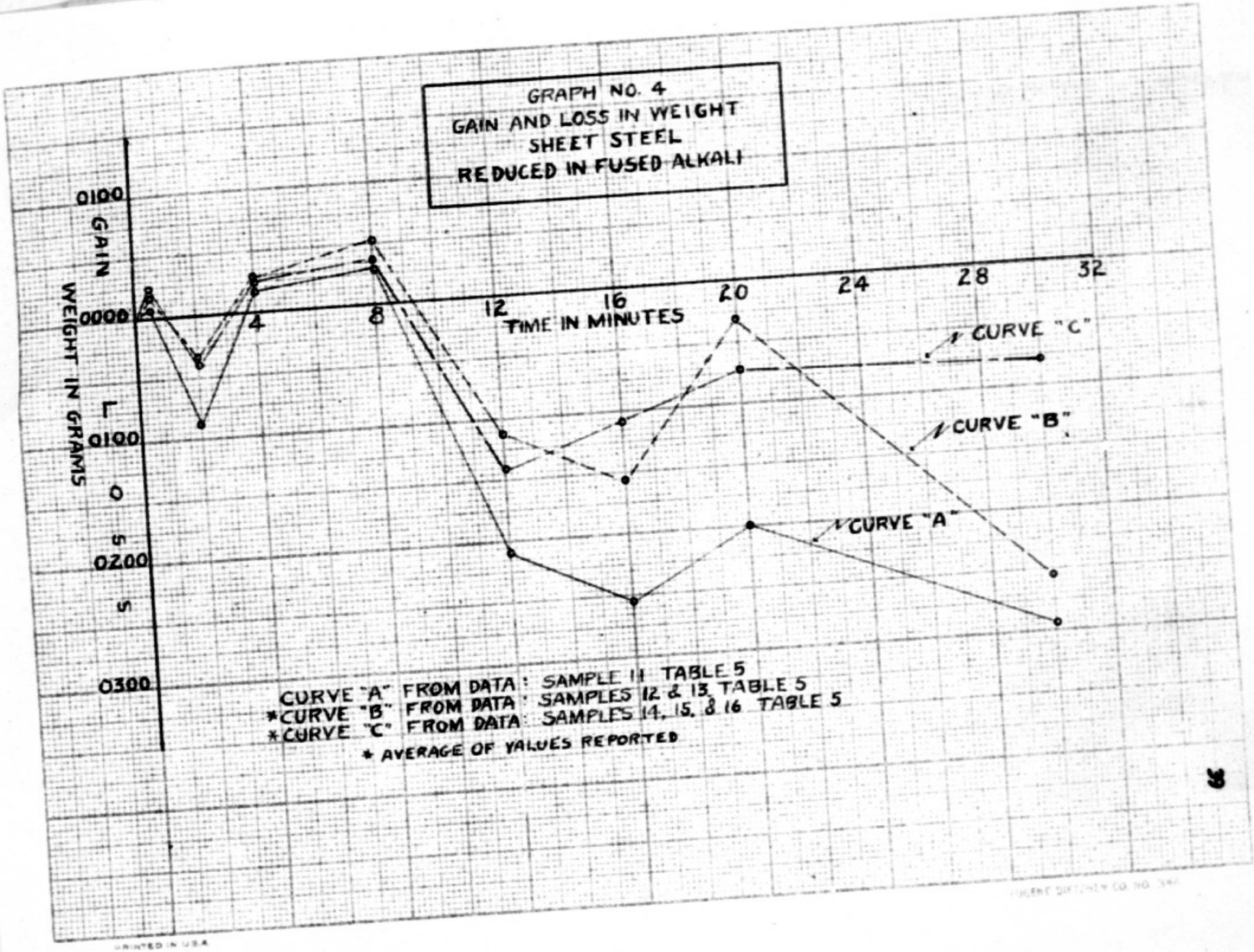


GRAPH NO. 6
AVERAGE LOSS IN WEIGHT
SIX SAMPLES SHEET STEEL
REDUCED IN FUSED ALKALI

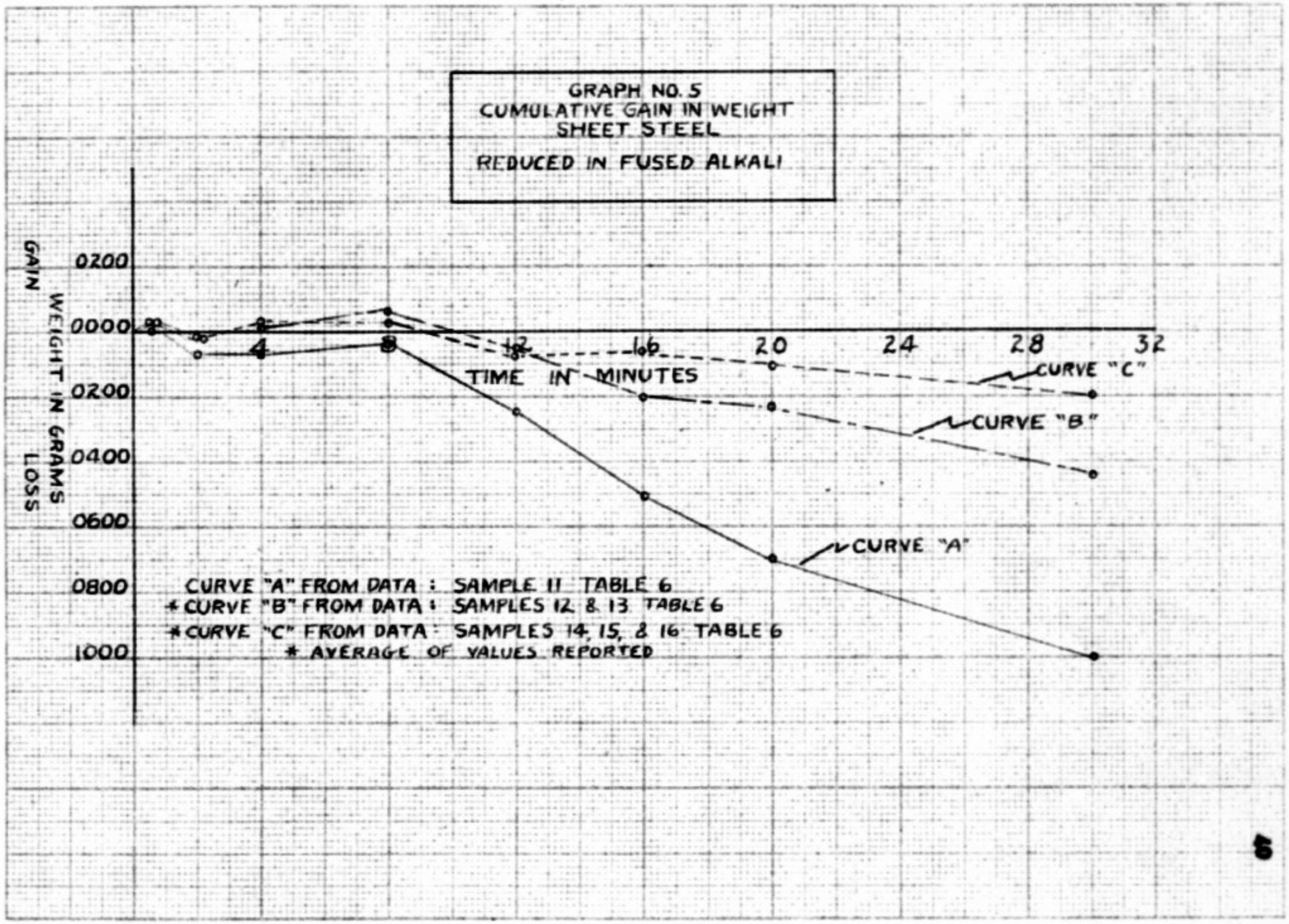
CURVE "A" AVERAGE WEIGHT FOR SIX SAMPLES REPORTED IN TABLE 6

CURVE "B" MAXIMUM DECREASE IN WEIGHT FOR ONE SAMPLE REDUCED FOR 30 MINUTES CONTINUOUSLY

GRAPH NO. 4
GAIN AND LOSS IN WEIGHT
SHEET STEEL
REDUCED IN FUSED ALKALI



CURVE "A" FROM DATA : SAMPLE 11 TABLE 5
*CURVE "B" FROM DATA : SAMPLES 12 & 13 TABLE 5
*CURVE "C" FROM DATA : SAMPLES 14, 15, & 16 TABLE 5
* AVERAGE OF VALUES REPORTED


GRAPH NO. 5
CUMULATIVE GAIN IN WEIGHT
SHEET STEEL

REDUCED IN FUSED ALKALI

CURVE "A" FROM DATA : SAMPLE 11 TABLE 6
* CURVE "B" FROM DATA : SAMPLES 12 & 13 TABLE 6
* CURVE "C" FROM DATA : SAMPLES 14, 15, & 16 TABLE 6
* AVERAGE OF VALUES REPORTED

3. A study of the surfaces of metals which were prepared for enameling by treatment in fused alkali.

a. Method.

The preceding loss and gain-in-weight study gives evidence of the fact that a time period of from two to four minutes in fused alkali was the critical time of immersion insofar as special conditioning of the metal surfaces is concerned. Accordingly, it was decided to set up a series of metals and using a specific treating time, the effect of the alkali on such metal surfaces could be observed. Previous investigational work pointed to the fact that a temperature of 800°F was most favorable to the operation of the equipment and that this temperature produced the greatest number of consistent samples with a given alkali. It was decided therefore, that 800°F would be the temperature to use in this particular investigation.

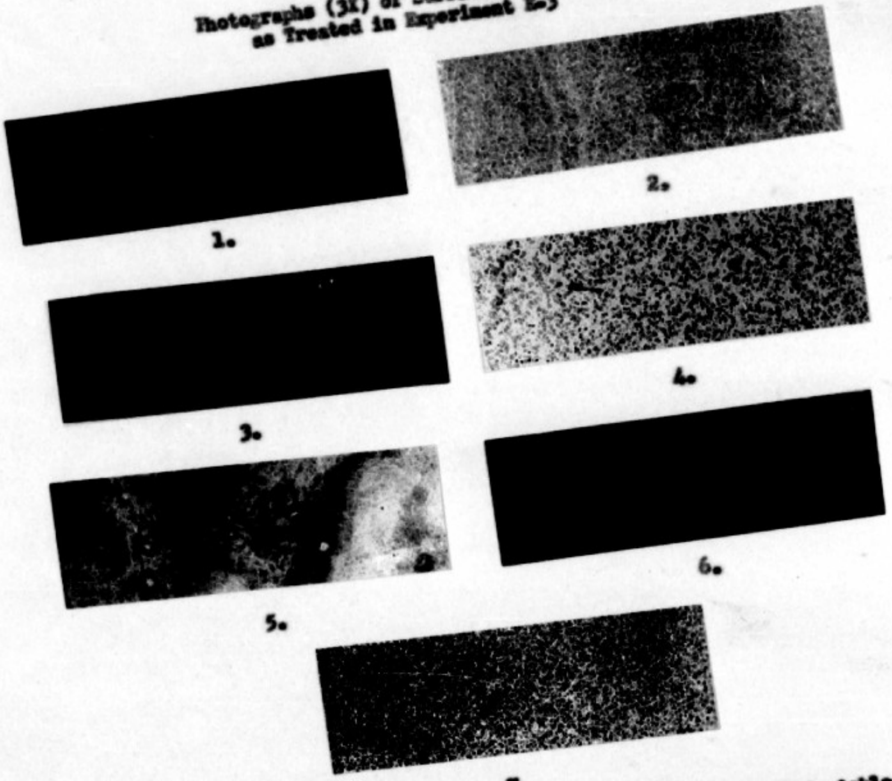
Samples of sheet steel and stainless steel were immersed in commercial alkali "A". The test pieces were either oxidized, reduced or simply immersed in the alkali with the electrolytic circuit closed. When the plates were electrolysed, the effective voltage used was four volts with a current density of fourteen amperes. As a control for appearance, a piece of sheet steel was acid pickled and a piece of stainless steel was sandblasted. Rinsing and drying was in accordance with the best practice as reported earlier in this report.

b. Results.

After the electrolytic alkali treatment or after plain immersion in fused alkali each test plate yielded a surface which was very specific in its appearance. Figure 3, page 42 contains photographs

FIGURE 3

Photographs (3X) of Surfaces of Metal as Treated in Experiment E-3



1. 2. 3. 4. 5. 6. 7.

1. Sheet steel, oxidized.
2. Sheet steel, reduced.
3. Sheet steel, no-current.
4. Sheet steel, acid pickle.
5. Stainless steel, reduced.
6. Stainless steel, no-current.
7. Stainless steel, sandblasted.

of the surfaces of the various test plates. Each photograph is a section of the metal plate magnified several diameters. Oblique lighting was used to emphasize the detail. From these photographs it can be seen that the oxidized sheet steel (No. 1) possesses a decided 'oxidic' character which is uniformly a reddish brown to black colored film on all plates that received this particular treatment. All kinds of color can be obtained depending upon the length of exposure, kind of alkali and temperature.

The reduced sheet steel (No. 2), after electrolytic treatment, was free of the oil and the few rust spots that covered its surface originally. The final color of this test plate was a metallic gray color very similar to that obtained by the acid pickling technique (No. 4).

Immersing sheet steel in fused alkali for a two minute period at 800°F without electrolysis results in a test plate No. 3 that has an appearance similar to that of a test plate which received a reducing treatment in fused alkali. The color is slightly different however, tending to a gray rather than a silvery metallic appearance.

Stainless steel test plates, on a reduction cycle (No. 5), take on a straw yellow color which color is not too pronounced. On plain immersion (No. 6), stainless steel is discolored to a feeble brown color. The fused alkali removes the shiny silvery appearance of clean commercial stainless steel.

Inasmuch as proprietary compound alkali "B" was especially recommended by the supplier as being very suitable for cleaning without using an electric current, it was decided to run a few sheet steel test plates in this material and compare the results with those test plates obtained by immersion in alkali "A" under the same conditions of time and temperature.

To make the foregoing study rather complete, two and four minute immersion periods were decided upon. The results of plain immersion of sheet steel plates in alkali "A" and "B" is reflected by means of photographs that appear in Figure 4, page 45. A visual examination points to the fact that there is not very much of a difference between the two alkalies as to their effect on the surface and color of the metal. All test plates possessed the usual metallic gray color characteristic of acid pickling.

At this point it was decided that a procedure be established for investigating the relative merit of various electrolytic treatments using alkali "A" and alkali "C". The series of treatments that was finally selected consisted of oxidation; reduction; no-current; oxidation-reduction; reduction-oxidation; and finally reduction-oxidation-reduction. Two minute periods were allowed for each of these treatments. In other words, the oxidation-reduction treatment required a total of four minutes (two minutes oxidizing and two minutes reduction) while the reduction-oxidation-reduction treatment required six minutes.

Figure 5, page 46 shows the results of the various cyclic treatments. These enlarged photographs illustrate the specific character of the surface of the sheet steel plates with each treatment. Again on visual examination, the differences in appearance are too small to indicate greater or lesser merit of one alkali over the other or the merit of one electrolytic treatment over another. In Figure 5 just referred to, the letter "O" represents oxidation while "R" represents reduction. "N-C" indicates that no current was used during the immersion period or in other words a 'non-electrolytic' process.

FIGURE 4

Photographs (3X) of Surfaces of Metal
as Treated in Experiment E-3
Showing Effect of Alkali and Immersion Time

SHEET STEEL - 800°F

ALKALI "A"

ALKALI "C"

2 - Minutes

1.

3.

4 - Minutes

2.

4.

FIGURE 5

Photographs (3X) of Surfaces of Metals
as Treated in Experiment E-3
Showing the Effect of Alkali and Cyclic-treatment

SHEET STEEL - 800°F

ALKALI "A"

ALKALI "B"

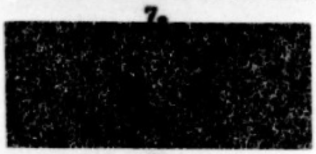

1.

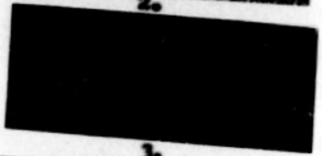
O.


7.

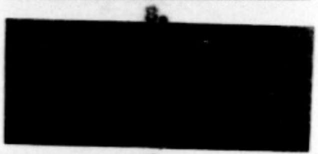

2.

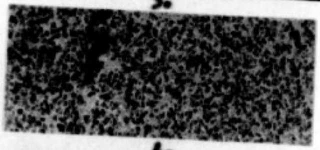
R.


8.

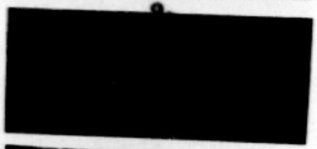

3.

N.C.


9.


4.

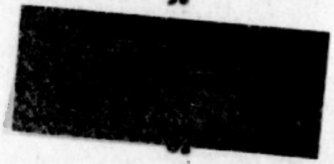
OR



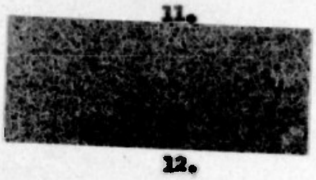

5.

RO


11.


6.

ROR


12.

4. A study of the firing range of cobalt ground-coated sheet steel samples prepared for enameling using fused alkali "A" and electrolytic treatment.

a. Method

From the preceding experiment it was evident that mere visual examination of the test plates after treatment in alkali would not be sufficient to determine either the efficiency of the alkali or the treatment during immersion. At this point it became apparent that the satisfactory character of the metal surface treatment would rest with how well such treatment contributed to the quality and adherence of an enamel which was fired onto its surface. Thus it was decided that the merit of a particular surface treatment would be determined by measuring enameling characteristics. Before this could be accomplished it would be necessary to establish the firing characteristics of an enamel on such specially prepared metal surfaces.

Accordingly a cobalt ground coat enamel was selected and made ready for application to test plates that had been given electrolytic or non-electrolytic treatment in fused alkali "A". Three treatment procedures were selected for the test plates to be enameled. These treatments consisted of oxidation-reduction; reduction-oxidation and acid pickle as a control. The time of treatment for each treating cycle was two minutes. The temperature of the bath was 800°F. Electrolysis was conducted with an effective voltage of four volts and fourteen amperes across the plates. The plates were run through the electrolysis apparatus three at one time. Acid pickling was accomplished using the standard acid pickling technique. All plates were dipped in the cobalt ground coat enamel to the same dry weight basis, namely forty grams per square foot of sheet metal stock.

A firing range from 1400°F to 1750°F with 50 degree intervals was set up. A firing schedule of three and five minutes was employed. Two plates were fired for three minutes at a specified temperature and one plate was fired for five minutes at the same temperature. One test plate for the three minute firing treatment and the one plate for the five minute period was subjected to an adherence test by means of a falling weight device previously described.

b. Data and Results.

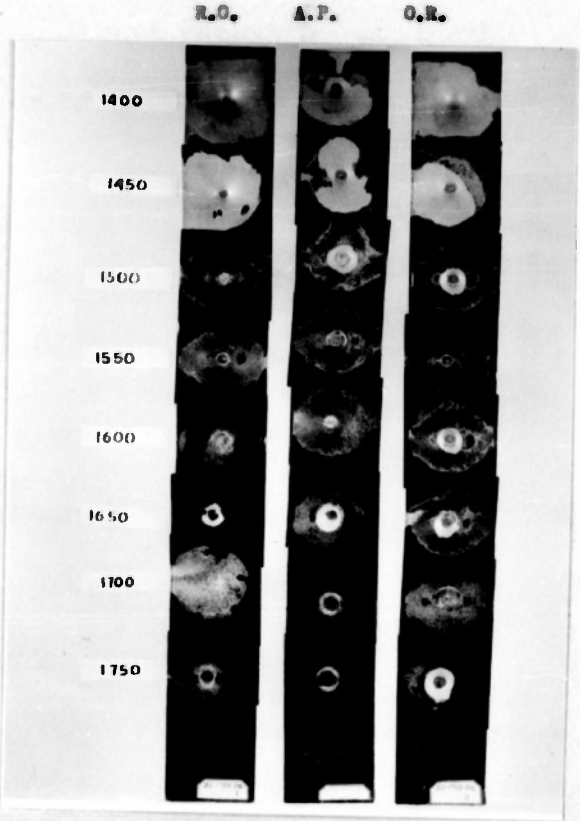
The results of firing these test plates are recorded in the photograph of Figure 6, page 49. It was found that the five minute firing period did not appreciably shift the firing zone and it was therefore concluded that a photograph of the 'five-minute' series was not of sufficient importance to be included in this report.

The 'oxidised-reduced' samples of metal afforded the larger number of better quality enameled surfaces and did have better adherence than did the 'reduced-oxidised' series. There was very little to choose between the 'oxidised-reduced' and the acid pickled samples.

The experiment did furnish evidence that in subsequent investigations cobalt ground coat enamel of the formulation used this investigation could be fired at 1550°F and for three minutes. With this enamel and its firing conditions known, any sheet steel samples submitted to later alkali treatment can be evaluated in terms of how effective is the treatment they receive.

FIGURE 6

Photographs Illustrating Firing Range of
Cobalt Ground Coats on Sheet Steel



5. A comparison of the acid pickling technique as a means of preparing sheet steel for enameling with cobalt ground coats as against metal preparation by means of fused alkali without electrolysis.

a. Method.

The preceding experiment (E-4) was concerned primarily with enamel surfaces obtained on metal which had been prepared for enameling by electrolytic treatment in fused alkali. This method eliminated for a moment the possible value of cleaning and preparing metal for enameling using fused alkali but without electrolysis. Accordingly this particular investigation was decided upon to determine the value of fused alkali without electrolysis compared to acid pickling technique.

Alkali "A" and alkali "B" were used in the test. The pieces of sheet iron were immersed for two minute and four minute periods. The temperature of the alkali was 800°F.

After careful rinsing and drying, such plates were dipped in cobalt ground coat enamel (in the same manner as the previous experiment) and then dried and fired. Sheet steel samples that had been acid pickled were used as controls for evaluating this method. Such acid pickled sheets were enameled and fired in the same manner as alkali treated sheet steel samples.

The firing temperature was 1550°F and for a firing time of three minutes.

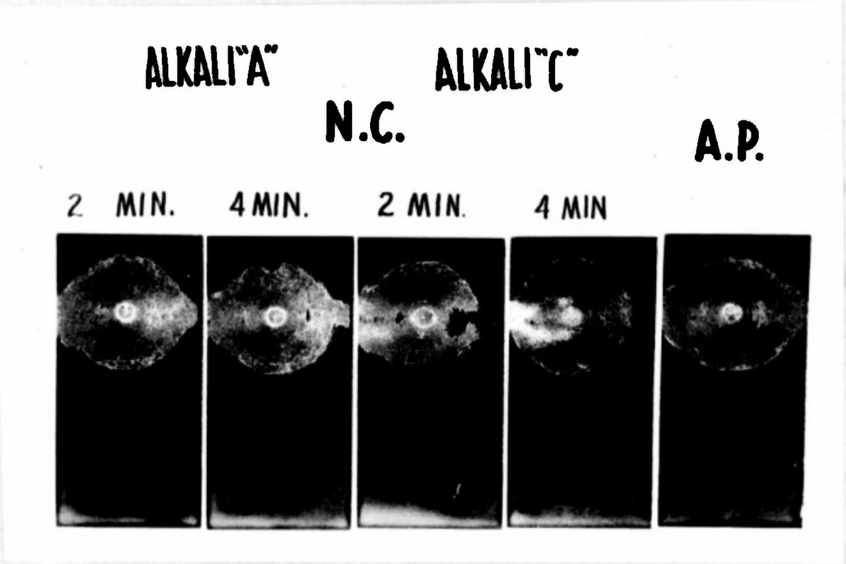
The samples were tested for adherence by the falling weight method.

b. Data and Results.

Figure 7, page 51 illustrates the kind of adherence obtained by following the procedure described in "a" above. It can be ob-

FIGURE 7

Photographs Illustrating Effect of Alkali and Immersion Time in Firing Cobalt Ground Coats on Sheet Steel



served that all test plates show equal good quality and good adherence. It might be concluded erroneously then at this point that electrolysis is superfluous in the treatment of sheet steel for subsequent enameling operations.

Before this conclusion is arrived at, may the caution be offered at this point that the sheet steel samples used happened to be particularly free of iron oxide scale and other inclusions and, as was pointed out earlier, the fused alkali alone is not efficient in removing scale and other similar contaminants.

6. A comparison of the relative value of alkali "A" with proprietary alkali "C" for preparing sheet metal for enameling with a cobalt ground coat.

a. Method.

All experimental work up to this point has indicated that the electrolytic technique held forth the best promise for doing the most adequate job of preparing sheet steel for subsequent porcelain enameling. Accordingly since two alkali substances were on hand to do this particular task, it was decided to set up the same series of electrolytic treatments as used in experiment E-3 and recorded in Figure 5. The usual 'non-current' and acid pickle controls were likewise included. The treating time was two and four minutes for each of the cycles and the temperature of the alkali bath was held at 800°F. The effective voltage was four volts and the current density fourteen amperes. A total of fifty-six test plates were dipped in the cobalt ground coat used in all the previous investigations. All enameled plates were fired at 1550°F for a three minute firing period. All samples were carefully marked as to the particular kind of treatment that the basic metal received. The finished enameled plates were tested for adherence using the standard falling weight method.

b. Data and Results.

Figure 8, page 54, reflects typical samples from each of the test series. The samples are arranged under alkali "A" and alkali "C" with a further subarrangement to cover the two minute and four minute cycle treatment. An examination of the results of the adherence tests shows that there is very little to choose in the way of one cleaning or surface preparing technique over the other. The adherence test certainly does show however that the four minute cyclic treatment is no better than the two minute treatment and is therefore a possible waste of electric energy and time. The test results further indicate that alkali "C" gives no better performance than does alkali "A", when the factor of adherence is used as the sole measure of quality.

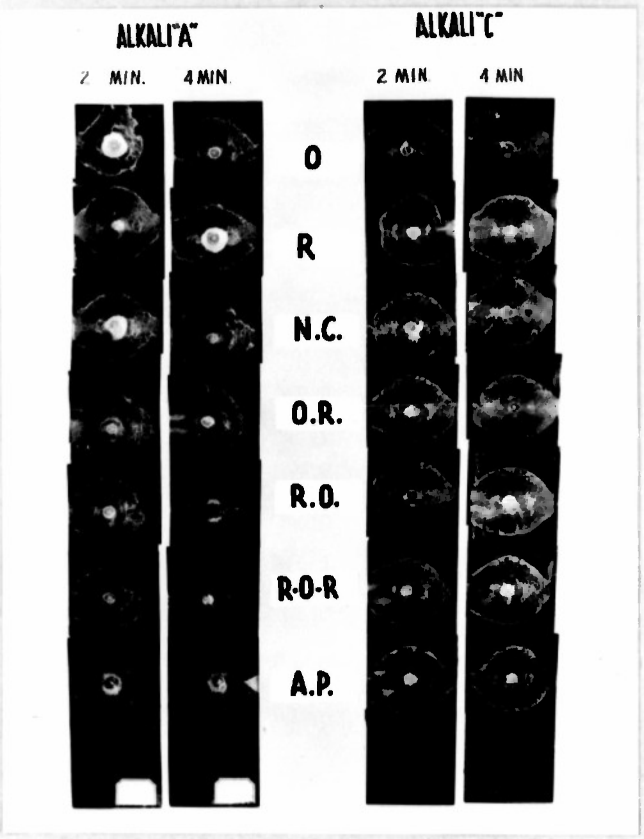
7. Study of oxidation and reduction treatment in alkali "C" and the effect of cobalt ground coat on such sheets.

a. Method.

The preceding experiment, E-6, covered a total of seven special treatments given to sheet steel while using two different alkalies and two time periods for treatment. The results were not too conclusive in favor of any special technique or in favor of a particular alkali. However, since considerable outside commercial interest exists in favor of alkali "C" as a proprietary material, it was deemed advisable to more thoroughly investigate the value of alkali "C" as a cleaning medium. Accordingly a series of sheet samples was subjected to oxidation treatment on a two minute cycle and another series was given a four minute oxidizing treatment. Also a number of sheet steel samples were reduced by electrolytic immersion in

FIGURE 8

Photographs Illustrating the Effect of Alkali,
Immersion Time and Cyclic Treatment on
Firing Cobalt Ground Coats on Sheet Steel



fused alkali "C" for a two minute and a four minute period.

The foregoing procedure was decided upon so that after enameling and firing the resultant adherence test might indicate something of importance as to which specialized electrolytic treatment to use or whether or not alkali "C" was superior in some way to ordinary commercial alkali designated as alkali "A" in the series of investigations reported herein.

b. Data and Results.

The results of the adherence test and the general appearance of the enameled test plates obtained as a result of the treatment described in the foregoing paragraphs is shown in Figure 9, page 55. An examination of the test plates that appear in this figure indicates that the adherence and enameled quality are no better than that obtained from acid pickle samples or any other of the fused alkali treated test plates.

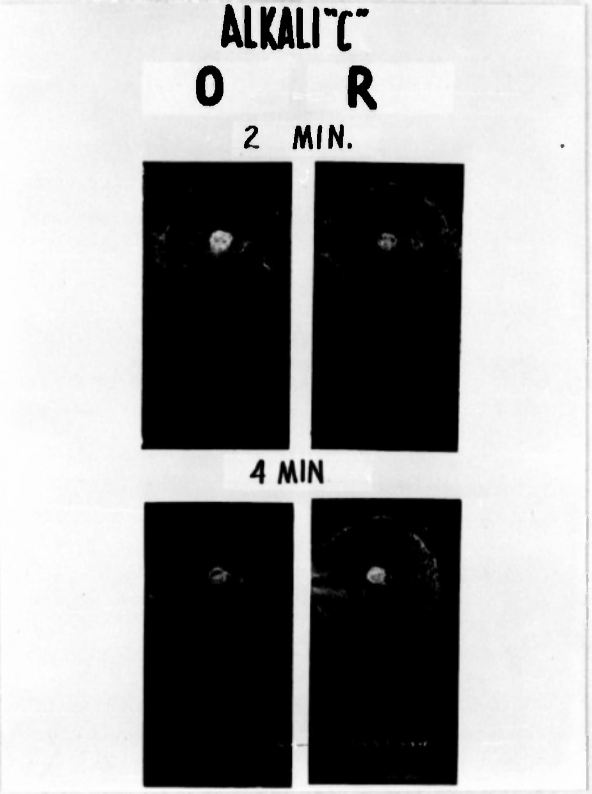
8. The effect of electrolytic versus non-electrolytic treatment of sheet steel in alkali "A" using single cover coat enamel.

a. Method.

The cobalt ground coats were not too successful as a means for reflecting and evaluating the results of various electrolytic treatments and other special treatments given sheet iron samples subsequently enameled. Inasmuch as the trend in the industry today is in the direction of single white cover coat enamels it was thought that if a satisfactory enamel of this type were compounded and applied to sheet metal subjected to the electrolytic fused alkali technique that it might be a way of indicating the relative merit of such treatment in a more satisfactory manner. This line of reasoning suggested that sheet metal be prepared for enameling by using electrolytic

FIGURE 9

Photographs Illustrating Effect of Time and Cyclic Treatment in Alkali "C" in Firing Cobbalt Ground Coats on Sheet Steel



cycles of two and four minute oxidizing and reducing periods in a given fused alkali and compared with the surface treatment obtained by simple immersion in fused alkali without an electrolytic treatment. Again, acid pickled sheets were run as a control.

b. Data and Results.

Figure 10, page 57, shows the results of the degree of adherence and the quality of enameled surfaces of the alkali series test plates obtained in this particular experiment. It can be noted that all plates that had been subjected to either the electrolytic or non-electrolytic alkali technique produced plates that gave very poor adherence and poor appearing enameled surfaces. The acid pickle samples were improved noticeably.

9. The effect of cobalt salt additions to fused alkali.

a. Method.

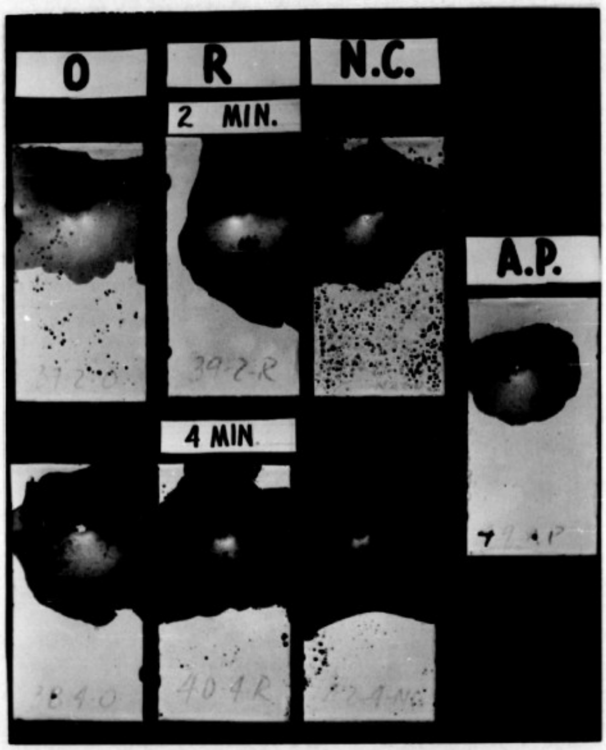
The preceding experiment indicated that the fused alkali technique was not too successful for preparing sheet metal samples for subsequent enameling with a single cover coat white enamel. Such enamels simply would not adhere due possibly to the absence of cobalt.

At the present time, throughout the enamel industry, considerable work is being done in the way of cobalt and nickel flashing sheet iron in order to promote enamel adherence. These special cobalt and nickel flashing techniques in the industry today are extra operations in the usual surface treatment of such metals. The flashing is accomplished in special baths and may or may not employ electro-plating techniques for applying the films of cobalt or nickel metal. None of the techniques for doing this work employ temperatures beyond 150°F.

Chemical literature is completely barren of any information on

FIGURE 10

Photographs Illustrating the Effect of Time and Cyclic Treatment in Firing White Cover Coats on Sheet Steel



cobalt flashing or nickel flashing in fused caustic alkali in the temperature range of 800°F. Accordingly it was decided to try to dissolve or to disperse anhydrous cobalt chloride in fused caustic alkali and to lower a sheet metal test plate into this mixture at a temperature of 800°F and to attempt to deposit cobalt in some form on the surfaces of the metal.

Two series of plates were prepared. One series consisted of a two-minute immersion treatment on a reduction cycle in fused alkali "C". Just prior to the removal of the test plates, each was given a thirty second oxidation treatment, then rinsed, dried and enameled with single white cover coat enamel.

The other series was given a two minute oxidation and a two minute reduction treatment in fused alkali "C" to which there had been added 30 grams of cobalt chloride. Again, just prior to the removal of the plate, a thirty second oxidation treatment. During this oxidation, cobalt was deposited on the test plate as was made evident by the blue discoloration characteristic of cobalt oxide. The above method was good for treating as many as eight samples in this manner. During the preparation of the ninth test plate, on the oxidation cycle, the voltage and amperage did not remain steady due to local electrolysis on the surface of the sheet metal plate.

The eight samples prepared by this special technique were carefully rinsed with live steam and air dried in an air oven. These cobalt oxidized coated metal samples were dipped in the single white cover coat enamel used in the preceding experiment and were fired at a temperature of 1450°F for a three minute period and finally given the usual enamel adherence test.

b. Data and Results.

Figure 11, page 60, shows two typical samples of sheet metal, one from each series, enameled with the single cover coat white enamel as explained above. The specimen on the left is a piece of sheet metal treated on the reduction cycle in fused alkali that did not have any cobalt chloride salt present during electrolysis. The sample on the right is one that had cobalt chloride on its surface prior to dipping in the cover coat enamel. An examination of the two specimens indicates that the cobalt free sample fractures in long splinters that readily flake away from the metal base. The other test plate indicates fractures that are very small and needle like and are somewhat more difficult to remove from the base metal. The standard enamel adherence tester does not show any marked degree in the difference of adherence.

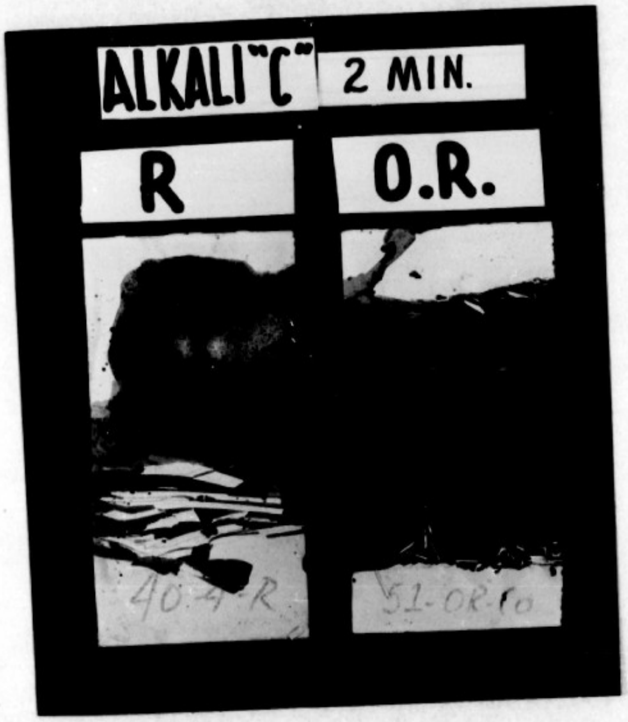
Although the experimental evidence is not too conclusive, the belief exists that the adherence of the white cover coat enamel was slightly improved by the addition of cobalt during the electrolytic treatment in fused alkali.

An examination of the individual flakes of enamel that can be peeled away from the test plates shows two distinctive oxidic surfaces at the interface. In the case of the cobalt free sample, the flake is gray to brown in appearance and is without a decided luster, whereas the flake from the cobalt treated experiment is blue-black in color and has a kind of glossy appearance. Samples of the enamel flakes were subjected to X-ray analysis and the results of such X-ray treatment is reported in section X-12 of this report.

10. A study of the value of the fused alkali technique in preparing stainless steel samples for enameling.

FIGURE 11

Photographs Illustrating the Effect of Cobalt Salt Additions to Fused Alkali for Preparing Sheet Steel for Enameling with Single Cover Coat Enamel.



a. Method.

Standard industrial practice for preparing stainless steel for enameling consists of sandblasting and annealing the stainless steel. The fused alkali technique has been found successful in preparing metal for tinning and babbiting and it was therefore decided that this method should be investigated in order to determine if it might prove as satisfactory as sandblasting for preparing stainless steel for enameling.

Accordingly stainless steel samples were immersed in fused alkali and subjected to electrolytic treatment to the same number and kinds of treatment as given to sheet steel samples reported in experiment E-6.

The fused alkali bath, consisting of alkali "A" was maintained at 800°F and each electrolytic or immersion treatment was of four minutes duration. Also the effective voltage was four volts and a current density of 14-15 amperes per test plate was employed.

For purposes of comparison, stainless steel samples were annealed and sandblasted; annealed and acid pickled; and acid pickled.

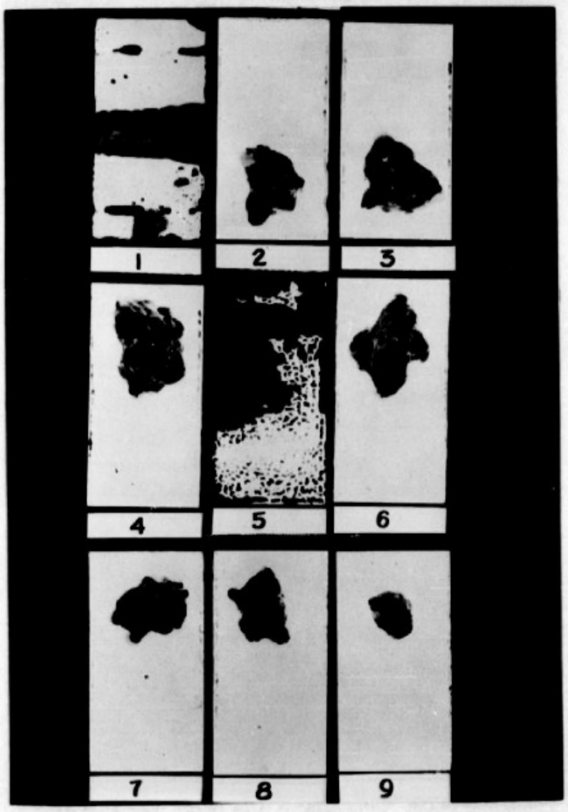
All stainless steel samples were marked and sprayed with the white cover coat enamel used on the sheet steel samples reported in preceding experiments. The enamel samples were fired at 1450°F for three minutes and subjected to the falling weight apparatus for test-adherence.

b. Data and Results.

Figure 12, page 62, shows the results of adherence tests and the appearance of the enamel surfaces. The test plates are arranged in the order of numbers 1 to 9 inclusive. Notes on each photograph are as follows:

FIGURE 12

Photographs Illustrating the Effect of Surface Treatment of Stainless Steel in Fused Alkali



Specimen	Treatment	Quality of Enamel Surface	Adherence
No. 1	Oxidized	poor	poor
No. 2	Reduced	fair	fair
No. 3	No-current	fair	fair
No. 4	Oxidized and reduced	fair	fair
No. 5	Reduced and oxidized	very bad	very bad
No. 6	Reduced, oxidized and reduced	fair	fair
No. 7	Annealed and sandblasted	fair	fair
No. 8	Annealed and pickled	fair	fair
No. 9	Acid pickled	fair	fair

The foregoing points definitely to the fact that oxidized surfaces on stainless steel do not lend themselves to satisfactory enameling. The 'reduce, oxidize and reduce again' treatment is unnecessary when compared to simple reduction. Simple reduction appears as good as annealing, sandblasting, pickling or any combination of these latter methods. The 'no-current' cycle appears to be as good as the reduction cycle.

11. A study of the use of fused alkali without electrolysis as a means of preparing stainless steel for enameling.

a. Method.

The foregoing experiment (E-10) indicated that fused alkali, without the electrolytic effect, appeared satisfactory for preparing stainless steel for subsequent enameling with one cover coat white enamel.

Inasmuch as there was available a commercial alkali, alkali "B", specifically recommended for its cleaning ability without the use of electric current, it was decided to investigate this material and compare it with the results of caustic alkali "A" used in the previous experiment. Further, since the investigations of the preceding experiment (E-10) was carried out on the basis of four minute treating cycles, it was decided to investigate the value of two minute cycles.

Accordingly, two series of alkali runs without electrolysis were made on stainless steel specimens. The alkalies used were "A" and "B". The temperature of the alkali was again 800°F and the time cycles two and four minutes.

The separate stainless steel plates were sprayed with the cover coat enamel, then dried, fired and tested as in experiment E-6.

b. Data and Results.

Figure 13, page 65, shows four enameled plates obtained by this experiment. The enameled surfaces of all four pieces could be adjudged fair to good. The adherence was distinctive to the extent that the two minute samples displayed a lower degree of adherence than did the four minute samples. All in all alkali "B" did not perform to any more superior degree than did alkali "A".

12. X-Ray Investigations.

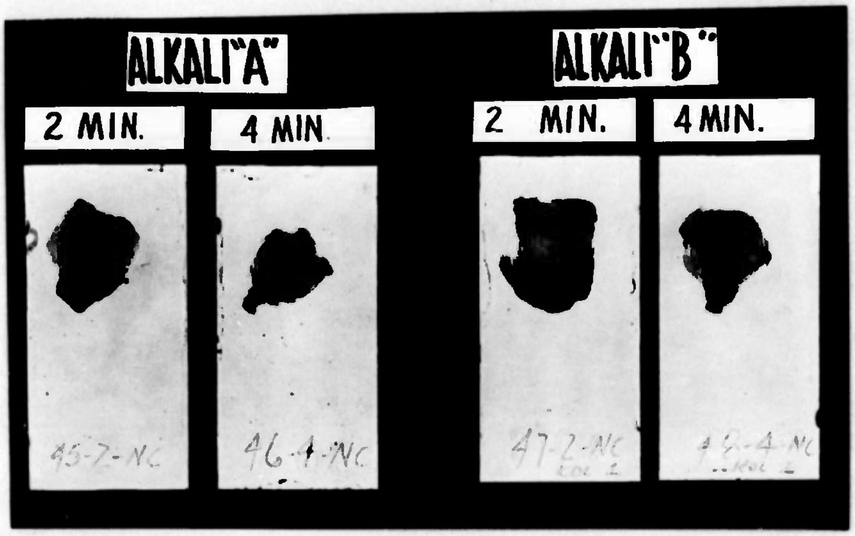
a. Method.

In performing the series of experimental procedure reported in this work it developed that two areas were of particular interest that warranted further investigation by use of X-Ray techniques. One of these areas involved sheet steel and what happened to the surfaces of the steel when it was subjected to treatment in fused alkali by the oxidation and reduction electrolytic techniques.

The other area involved determining by X-Rays what may have

FIGURE 13

Photographs Illustrating the Effect of Time
in Fused Alkalies for Preparing Stainless
Steel for Enameling with Single Cover
Coat Enamel



happened when cobalt chloride was deposited by electrolysis on an oxidation cycle in fused alkali and how such deposition may have influenced the degree of adherence of a single white cover coat enamel that was fired on the piece of metal prepared in this manner.

For the X-Ray investigational work, a cobalt tube at 30 KV and 10 milliamperes was used. The specimens were mounted within the camera at an angle so that the incident X-Ray beam grazed the sample. The incident ray was directed through a pinhole system with a limiting diameter of .025 inches. An iron oxide filter was mounted on the collimator in order to have monochromatic X-Rays. Exposure time was four and one-half hours duration.

b. Diffraction Patterns.

A total of six X-Ray pictures were taken. These pictures are as follows:

Figure 14, "A", page 67, shows a diffraction pattern of sheet steel that had received an oxidized treatment in fused alkali.

Figure 14 "B", is a diffraction pattern for sheet steel reduced in fused alkali. The fewer number of lines due to iron oxide can be noticed in this picture.

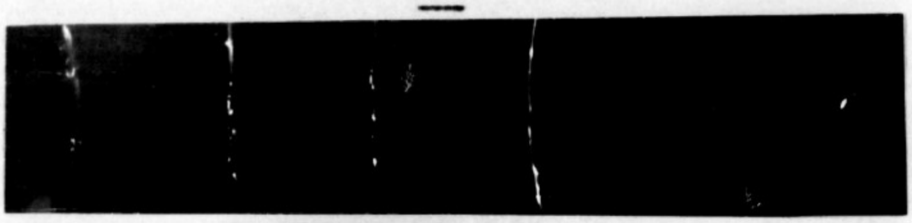
Figure 14 "C", is a diffraction pattern for sheet steel which received an acid pickle treatment. The number of lines are the same as for the reduced sheet in "B" above. There is a decided shift however of the lines in this picture over the lines visible in "B".

Figure 15, page 69, contains a series of diffraction patterns for the enamel flake and its surfaces. The preparation of the enamel and its surfaces is as explained in experiment E-9.

FIGURE 14

Diffraction Patterns of Sheet Steel

Surface-Conditioned by Several Methods



A. Oxidized in Fused Alkali.

B. Reduced in Fused Alkali.

C. Acid Pickled.

Figure 15 "A", is a diffraction pattern for the topside of the white cover coat enamel which was removed from the sheet steel samples as a flake.

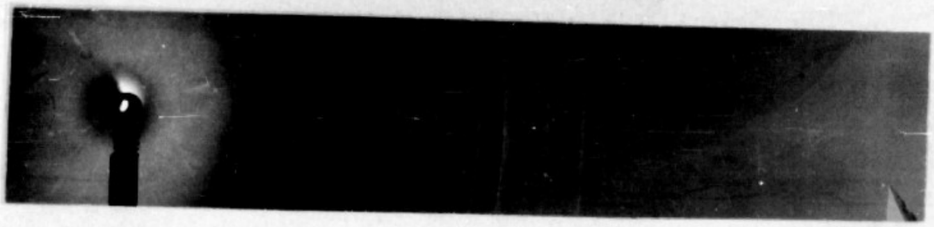
Figure 15 "B", is a pattern of the underside of the enamel flake removed from sheet steel which had been prepared for enameling by a reducing treatment in fused alkali.

Figure 15 "C", is a pattern of the underside of the enamel flake removed from sheet steel which had been oxidized-reduced in fused alkali to which cobalt oxide had been added.

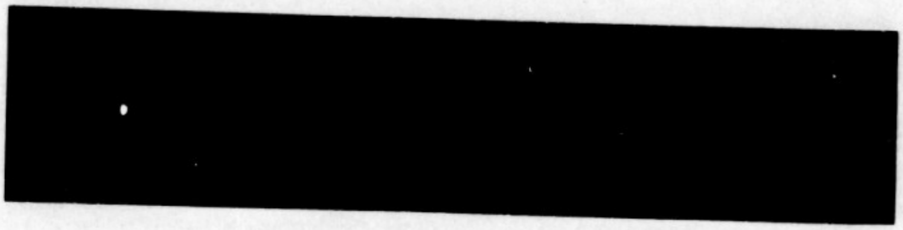
The iron oxide lines of Figure 15 "B" are absent from Figure 15 "C". In addition there is a shift of the lines in Figure 15 "C" compared to Figure 15 "A", thus indicating that the small addition of cobalt chloride had some effect on conditioning the surface of the sheet steel.

FIGURE 15

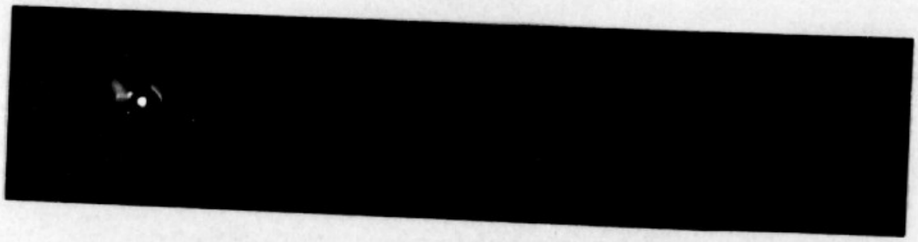
Diffraction Patterns of Enamel Flakes



A. Top-side of White Cover Coat Enamel.



B. Under-side of White Cover Coat Enamel Flake Removed from Sheet Steel Reduced in Plain Fused Alkali.



C. Under-side of White Cover Coat Enamel Flake Removed from Sheet Steel Oxidized-Reduced in Fused Alkali in which Cobalt Chloride was Dispersed.

IV. SUMMARY AND INTERPRETATION OF RESULTS

A. Interpretation of the detailed findings of the twelve experimental methods reported in this work.

A review of section III of this report indicates that a rather wide field of experimental procedures was followed in order to determine the merit of the fused alkali technique as against the standard acid pickling method for preparing metal surfaces for subsequent porcelain enameling. Before any final conclusions are drawn it was deemed desirable to briefly summarize and interpret the detailed findings of each of the experiments performed.

Experiment No. 1, page 21, was designed to acquire experience with the experimental apparatus and to record the operating character and limitations of the equipment. The fused alkali technique requires a consideration of certain details that in standard acid pickling processes are not of too much importance. It was found that the fused alkali technique is sensitive to temperature changes, effective voltage and current density. Also, considerable care must be given to the necessary rinsing operations after the work has been subjected to treatment in this medium. The fused alkali technique, since it is a high temperature operation, involves a certain number of hazards that demand respect in order to make the process safe for normal operations.

Experiment No. 2, page 27, entitled "Loss and Gain-in-Weight Studies" was set up as the foundation work for the entire series of investigational procedures. At the outset of work on this problem, the impression existed that the fused alkali technique, because of the high temperature and the corrosive nature of the material, would cause a rapid breakdown of metal. A review of the data and results of the loss and gain-in-weight studies reported in this experiment indicates that the loss in weight is negligible after immersion for a thirty minute period in corrosive fused alkali at 800°F even with electrolysis taking place in order to assist decomposition. Too, before any work was done on investigating this problem, it was thought that continued exposure to fused alkali on an oxidation cycle would cause a continuing increase in the degree of oxidation that a metal would encounter under these conditions. This impression was likewise found untrue because examination of the data points to the fact that while oxidation does take place in the initial period of exposure, that on long treatment, the gain due to oxidation tends to level off and become constant. This fact might be interpreted to mean that the metal builds up a degree of passivity and this having occurred limits the further effect of the fused alkali and electrolysis.

In both the oxidizing and the reduction treatments there is a point in time at which the greatest effect due to either of these processes takes place. In the case of oxidation, this critical time period is in the range of twelve minutes exposure to the electrolytic action in fused alkali. In the case of the reduction process, this time interval is some where between eight and sixteen minutes of exposure.

Examination of Graph No. 2, page 35, indicates that the rate of oxidation is a function of the effective voltage and current density acting on that plate. A single plate in the fused alkali bath is acted upon to a greater extent than is a pair of plates in parallel to each other in the same bath. This fact is exactly as expected when the laws of electrochemistry are taken into account in affording an explanation.

An examination of the reducing effect as revealed in Graph No. 4, page 39, likewise points to the fact that voltage and current acting upon the exposed ware determines the degree of loss in weight that a piece of metal will encounter during this treatment.

Most of the successful work that was accomplished during the entire investigation was based on samples of metal that had been oxidised or reduced for a periof of time not to exceed two minutes. In other words, two minute exposure to the action of fused alkali is sufficient to cause surface reactions to take place on the metal which will specifically influence the behavior of such metal in an enameling operation.

Experiment No. 3, page 41, was concerned with the appearance and character of sheet steel and stainless steel that had been exposed to treatment by the fused alkali. A summary of the results of the investigations on this problem would indicate that the surface of a metal can be built up to any condition that is considered desirable. In other words, the action of fused alkali during an electrolytic or non-electrolytic cycle, can be controlled so as to produce a piece of metal with a surface condition 'tailor-made' for any subsequent enameling operation.

The most difficult problem in this entire investigation was the absence of a measuring stick for the evaluation of metal surfaces for use in subsequent enameling. A review of enameling literature indicates that the surface of the metal is of paramount importance (aside from enamel composition) but no information of the conclusive type exists to indicate specifically what the metal surface should be like for successful enameling.

Without this conclusive information then on what metal surfaces should be like, the investigational work reported herein was obliged to be guided by the trial and error method in order to determine whether or not oxidizing, reduction, combinations of these, or just plain immersion in fused alkali would be as good or superior to the standard metal preparation techniques of the industry.

Experiment No. 4, page 47, was included early in this investigation for the reason that the proof of which metallic surface was most desirable would have to be determined by how well it would enamel. Since this then became the measuring stick, it was necessary that enameling practices be standardized so that later experimental procedures would yield results that were uniform with respect to the enameling factor.

The fused alkali technique, as indicated earlier, can produce metal plates that can be oxidized or reduced to any degree deemed desirable. This factor required that the performance of a darkened oxidized plate be checked against the gray metallic appearing reduced plate in order to determine whether the presence or absence of oxides influences the quality, the degree of adherence, and the firing range of an enamel designed as a standard.

An examination of the results of this particular experiment indicates that for cobalt ground coat enamels it does not seem to make very much difference whether sheet metal is oxidized or reduced. This experiment also furnished a slight amount of evidence that for a large number of samples, on the average, a greater degree of adherence could be expected from those metal plates that had received the 'reduction' treatment in fused alkali.

The foregoing statement may be true for the reason that when reduced plates are considered, the possibility of loose iron oxide scale is removed as a factor causing poor quality or ware of low adherence. The likehood exists that when a large number of pieces of metal are subjected to an oxidizing treatment in fused alkali, some of these pieces will not be entirely freed of iron oxide scale. Therefore, percentage-wise, redused plates will show a better record of performance toward cobalt ground coats than will oxidized plates. In other words, the oxide layer theory in explanation of enamel adherence is neither proved nor disproved at this point.

Experiment No. 5, page 50, was designed for the purpose of determining whether or not it would be necessary to add the factor of electrolysis in order to make the fused alkali technique satisfactory. Accordingly the acid pickling technique was compared with the fused alkali technique without electrolysis. As it developed there was very little in the way of a difference between the two techniques. This last statement is made with the caution that the fused alkali technique without an electric current is good only when the sheet steel is not excessively covered with iron oxide scale prior to immersion in fused alkali. If too badly corroded, it requires reduction treatment in fused alkali to be as good as acid pickled sheets.

The experiment considered alkalies "A" and "B" for the reason that alkali "B" was furnished with a statement by the supplier of the material that it was particularly adaptable for cleaning metal. The results of the experiment indicated that the performance of alkali "A" and alkali "B" were on a par when their enameling quality is used as a measure of cleaning efficiency.

Experiment No. 6, page 52, was devised for the purpose of determining the relative efficiency of alkali "A" with alkali "C" for preparing sheet metal for enameling. An examination of the results of the tested enameled plates points to the fact that the two materials are equally suitable for preparing sheet steel for enameling with cobalt ground coat enamels.

During the cleaning and surface preparing operations of sheet steel in alkali "C" it was observed that the action was slightly more vigorous than the action in alkali "A". This activity was made evident by the greater degree of fuming that occurred while alkali "C" was in operation. This additional fuming did not result in any apparent change or appearance of the metal when examined individually or measured by increased performance during enameling.

Experiment No. 7, page 53, logically followed experiment No. 6 for the reason that alkali "C" apparently was doing a more vigorous job of preparing the surface of sheet steel in some manner. In order to ascertain with certainty that something special was going on while using alkali "C" it was decided to run a series of oxidation treatments and another series of reduction treatments using this material on sheet iron. Having these surface treated test plates, each was dipped in a cobalt ground coat enamel and fired to maturity. A set of test plates of sheet steel that had been conditioned by the acid pickle technique were used as controls. Both the fired acid pickle plates and the alkali treated plates were examined for quality and each was subjected to an adherence test. The overall performance of both sets was exactly the same. In other words, the performance of the alkali "C" treated plates was no better than those plates treated by alkali "A" in the preceding experiment. With another kind of enamel or possibly a deviation from the standard firing conditions, the alkali "C" treated plates might have indicated something different than what is reported here.

Experiment 8, page 54, is probably the most disappointing of the entire series, for the reason that caustic alkali on the oxidation cycle should impart the right number and kind of oxides that would promote enamel adherence if the oxides of iron are a factor in determining enamel adherence. Accordingly oxidation and reduction in fused alkali were the methods employed to prepare sheet steel for enameling with a single white cover coat enamel. In addition plates were immersed in fused alkali without electrolysis. These enameled pieces were fired to maturity and compared with acid pickled sheets likewise enameled and fired. The results were very disappointing. The enamel adherence was very poor for all samples regardless of surface preparation.

Experiment 9, page 56. This experiment was devised for the purpose of determining whether or not the poor performance of the fused alkali technique as demonstrated in the preceding experiment could be improved.

It is well known that cobalt plating and nickel flashing does promote enamel adherence. The cobalt and nickel flashing or plating is accomplished at relatively low temperatures and in a bath specifically designed to do the job. Chemical literature failed to indicate where cobalt salts had ever been used in molten caustic for the purpose of electro-depositing cobalt on metals. The opportunity existed for giving this notion its first trial and accordingly a small amount of anhydrous cobalt chloride was added to the molten caustic alkali and mechanically stirred so as to effect possible solution and dispersion. The results of the experiment shows promise that cobalt can be flashed on metal at high temperatures and in the presence of caustic alkali. It is admitted that the technique as employed in this particular experiment is highly inefficient but further research and investigation might contribute greatly to improve the efficiency of the process.

Experiment No. 10, page 59. This experiment gave the best results for the amount of work done in investigating the merit of the fused alkali technique for preparing metal surfaces for enameling. Unfortunately all factors that influence the behavior of metals that are prepared for enameling were not investigated as thoroughly for stainless steel as was done for sheet steel. The results of the experiment indicate however that the fused alkali technique does as good a job of preparing stainless steel for enameling as does standard sandblasting and annealing. The most important observation from the experiment is that the specific fused alkali treatment should be one of reduction in the alkali rather than oxidation. Oxidized surfaces on stainless steel did not fire out very well at all.

Experiment No. 11, page 63. Inasmuch as the preceding experiment pointed to the fact that the fused alkali technique (except electrolytic oxidation) was satisfactory for preparing stainless steel for enameling, it was in order to determine whether or not the electrolytic cycle in fused alkali was absolutely necessary. Accordingly plain immersion treatments were conducted with the time of immersion as the factors for variation. The results of the experiment indicate that plain immersion is as satisfactory as the electrolytic treatment in fused alkali. The optimum time of immersion in this particular application was found to be four minutes. It was found that the shorter period of immersion (two minutes) resulted in pieces of enameled stainless steel that did not have as good adherence as those which had received the four minute treatment.

B. General Summary.

1. Sheet steel and cobalt ground coatings.

A review of the work done points to the fact that sheet steel can be coated with a cobalt ground coat and fired to a satisfactory enameled surface when such sheet steel is prepared for enameling by using the fused alkali technique. The enameled surfaces of sheet steel prepared in this manner are the same as sheet steel enameled samples that were prepared for enameling by the acid pickling process. The fused alkali technique is not superior in any respect over the acid pickling technique for preparing sheet metal for enameling with a cobalt ground coat. This conclusion is arrived at by considering only the factor of enameling adherence and the general appearance of the enameled surface. The fused alkali technique does not broaden the firing range for a particular cobalt ground coat.

a. The electrolytic versus non-electrolytic treatment of sheet steel in fused alkali.

Based on the laboratory work performed there is no essential difference between the electrolytic and the non-electrolytic treatment of sheet steel in fused alkali when these methods are employed for preparing metal for enameling with cobalt ground coats. The one slight general exception from this observation might be the fact that the electrolytic treatment may be superior to the non-electrolytic treatment in the case of sheet metal stock which has encountered a rather high degree of rust. In this particular instance then, electrolytic treatment on the 'reduced' cycle should give a better prepared metal sheet than would simple immersion in fused alkali for the same period of time.

b. The kind of alkali.

Three kinds of alkali substances were used in the various investigations reported in the experimental procedures. No really marked differences in performance could be assigned to anyone of the three alkali substances. All three alkalies performed equally well on either electrolytic or non-electrolytic cycles during treatment of sheet metal in the fused alkali. Alkali "C" did appear to react with a slightly more vigorous action than did alkali "A" at the same temperature and cyclic treatment.

2. Sheet steel and white cover coat enamels.

The fused alkali technique was not helpful in improving the quality and adherence of single cover coat white enamels. Based on the results of the adherence tests and the quality of the enameled surfaces, sheet metal prepared in fused alkali did not fire out any better with this type of enamel than did sheets prepared by the acid pickling technique. In fact, the acid pickled sheets were slightly better.

a. The electrolytic versus non-electrolytic treatment in fused alkali.

Just as in the case of sheet metal with cobalt ground coat by these special techniques no apparent difference was discernible between these two techniques applied to metal fired with a single cover coat white enamel.

b. Kind of alkali.

The kind of alkali likewise did not make very much difference in the way sheet metal behaved towards the fired enamel after treatment in these alkali substances.

3. Stainless steel.

Stainless steel prepared for enameling by use of the fused alkali technique responded more sensitively to the alkali cleaning process than did the sheet steel. Based on the number of test pieces fired, the fused alkali technique appears as satisfactory as sandblasting as a method for the preparation of stainless steel for enameling.

a. Electrolytic versus non-electrolytic treatment in fused alkali.

These two techniques were found satisfactory for preparing stainless steel for enameling, with the exception of electrolysis on the oxidation cycle in the fused alkali.

b. Kind of alkali.

The kind of alkali used for surface conditioning stainless steel does not seem to make very much difference.

C. General statement regarding the practicability of cobalt additions to fused alkali.

This particular phase of the investigational work was found most interesting. As was explained earlier in this work, for this particular experiment the amount of improved enamel adherence was small. Nevertheless, it is believed that the slight increase was produced by the presence of the light film of cobalt oxide that was deposited on the surface of the sheet metal.

It is believed that this is the first time cobalt salts were ever deposited by electrochemical means on a piece of metal in the presence of a fused alkali. The laws of electrochemistry may have been violated in this instance (as was indicated by the electrolytic breakdown) but for the number of plates obtained the experiment was considered successful. By the judicious selection of chemical substances it may be possible to cobalt-flash in fused alkali under controlled conditions for any length of time.

V. CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions.

The overall conclusion that could be fairly stated as a result of all the foregoing experimental work is that the fused alkali technique is as satisfactory in the laboratory as the acid pickling technique for the preparation of sheet steel for enameling provided that due consideration is given to the matter of the additional hazards brought about by the use of this high temperature technique. The fused alkali technique it is believed can and may be substituted for the standardized acid pickling process in industry today in certain applications but only after a consideration of the economics involved in the problem and after pilot plant operations have been successfully proven. It is true that the fused alkali technique requires only a few minutes for the complete cleaning cycle as against forty-five or more minutes which is the minimum time than an acid pickling operation with all of its various operations can be brought to completion. This factor in itself should make the process attractive to industry.

It can be further concluded, based on findings in the laboratory, that the fused alkali technique is as satisfactory as the sandblasting technique for preparing stainless steel for subsequent enameling. This conclusion is likewise made without any regard for the factor of safety or of the economics involved in the process.

B. Recommendations.

It is recommended that further work should be done on investigating other alkali substances and fused salts. Such materials as potassium or lithium hydroxide would probably be considerably more effective than sodium hydroxide as materials for preparing the surfaces of metals for enameling. Early in this work, mention was made of the material sodium hydride which likewise is a substance that possesses great possibilities.

The foregoing recommendation, it is realized would require high temperature operations. However, another recommendation is in order that would take the work out of the high temperature field and bring it down into the range of present acid pickling techniques. The material, tetra methyl ammonium hydroxide is available from chemical supply houses and it has a melting point of 110°C. The material is costly at the present time but its corrosive action in the fused state is said to be as severe as is molten caustic alkali. It may be very worth while to investigate the use of this organic alkali as a material for preparing metal surfaces for enameling.

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