United States Patent Office

2,695,249

Patented Nov. 23, 1954

2,695,249

PORCELAIN ENAMEL ARTICLE AND METHOD OF MAKING SAME

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No Drawing. Application April 5, 1950, Serial No. 154,188

2 Claims. (Cl. 117—70)

This invention relates as indicated to porcelain enameling and has more particular reference to an enameling procedure and articles produced therefrom characterized by the direct application to a ferrous surface of a finish coat porcelain enamel which is substantially free of all adherence promoting oxides and which enamel has higher surface gloss, more uniform color and higher acid and scratch resistance than any porcelain enamels heretofore used.

As indicated above, the prior art practice of insuring adequate adherence between porcelain enamel and steel has been to use adherence promoting oxides. These oxides are usually classified as the ground coat adherence promoting oxides such as nickel, cobalt and manganese and the finish coat adherence promoting oxides such as antimony and molybdenum. In applying a white or light colored finish coat porcelain enamel directly to a steel work piece the ground coat adherence promoting oxides can't be used since they are dark in color. The finish coat adherence promoting oxides such as antimony and molybdenum make enamels which are noted for their lack of opacity, acid resistance and weathering properties. Various methods, other than the use of adherence promoting oxides, have been used in an endeavor to improve the adherence of finish coat porcelain enamels to steel. One of such methods has been by the use of steels of special compositions. Another has been by the use of the so-called "nickel-flash" step by which an attempt is made to deposit a predetermined amount of nickel on the steel surface by galvanic action.

The use of special steels is undesirable for many reasons, the principal one being cost.

The use of the galvanic process is undesirable since that method leads to inconsistent results, in that the nickel deposits vary in character and amount from steel to steel or for that matter the nickel deposit will vary from one portion to the next on the same piece of steel.

As previously indicated besides the difficulty of obtaining proper adherence the direct application of a finish coat porcelain enamel to a steel surface is also faced with the problem of obtaining desirable surface characteristics of the fired enamel, uniform color and acid and scratch resistance.

In the art of porcelain enameling, the porcelain enamel frit is milled in water to a predetermined fineness in the presence of various electrolytes, opacifying agents and clay or clay-like materials. The clay or clay-like materials are added to providing suspending and binding properties to the milled porcelain enamel. Although suspending agents of type provide suspension properties their presence in ceramic slips, which are subsequently converted to vitreous coatings, have a great many undesirable properties. The presence of clays or the like in porcelain enamel finish coats markedly reduces gloss, changes the color, reduces the acid resistance, lowers scratch and abrasion resistance and increases the maturing temperature required to produce a satisfactory surface. Furthermore, in the art of porcelain enameling as now practiced, the application of ceramic materials, containing clay, to iron work pieces is accompanied by gas evolution attendant with the following reactions:

$$Fe+H_2O \leftrightharpoons FeO+H_2\uparrow$$

$$3FeO+H_2O \leftrightharpoons Fe_3O_4+H_2\uparrow$$

$$2Fe_3O_4+H_2O \leftrightharpoons 3Fe_2O_3+H_2\uparrow$$

The water for the above reaction is supplied by the clay.

Since clay is a hydrous material, during the step of firing the bisque coat onto the ferrous work piece the clay undergoes dehydration and liberates its water. The water thus liberated reacts with the ferrous work piece, as illustrated above, with the liberation of hydrogen. The liberated hydrogen in its attempt to escape forces its way through the melting porcelain enamel causing bubbles. It has been further ascertained and is well known to those skilled in the art of porcelain enameling, that the presence of clay affects the acid resistance of the fired porcelain enamel coating. The acid resistance of fired porcelain enamels is a direct function of the amount of clay used in the milling operation. In other words, the more clay that is used the lower the acid resistance of the fired porcelain enamel.

It is the principal object of our invention to provide a porcelain enamel article and a method of producing the same characterized by the direct application to ferrous work pieces of porcelain enamels which do not require the presence therein of any substantial amounts of adherence promoting oxides and the like.

It is a further object of our invention to provide porcelain enamel articles which are superior from the standpoint of surface characteristics, scratch resistance, gloss color and acid resistance to any which have been capable of production by any well known prior art methods.

Other objects of our invention will become apparent as the description proceeds.

To the accomplishment of the foregoing and related ends, said invention then comprises the features hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative, however, of but a few of the various ways in which the principle of the invention may be employed.

Broadly stated, this invention comprises the method of porcelain enameling wherein the surface of the ferrous article to be coated is first cleaned and roughened; a layer of nickel deposited thereon by the chemical reduction method and then there is applied thereto a finish coat porcelain enamel clay-free slip which does not require the presence of substantial amounts of adherence promoting oxides, said slip further characterized by the inclusion therein of surface active agents.

It will be observed from the foregoing broad statement of our invention that the method which comprises such invention for the production of articles which are likewise new, in that they have never been made heretofore, may be divided into three principal steps which for convenience in the further description of our invention will be treated in the order in which they are usually performed.

Cleaning and roughening the metal

The ferrous surface to which the enamel is to be eventually applied when practicing our invention needs to have two primary characteristics. First, it must be relatively clean, that is, free from all foreign materials such as dirt, grease and the usual coat of metallic oxide. Second, the surface must be reasonably rough for best adherence of the enamel. This preparation of the ferrous surface may be accomplished by chemical means or by mechanical means or by a combination of the two. If it is desirable to effect the preparation of the surface by chemical means, this can be accomplished conveniently by the use of pickling baths which leave a relatively rough surface. The pickling baths which are available for this purpose are, for example, those employing nitric acid and combinations of nitric acid with other acids and baths which are primarily sulphuric acid baths, but which also contain nitric acid or other oxidizing agents. This type of bath has two principal characteristics. First the bath is extremely vigorous in its action so that the required pickling time is relatively short and second, this type of bath produces a surface which may be identified, for convenience, as a deeply etched surface, in that it contains pits which are relatively deep with the crests between such pits relatively sharp. Because of this peculiar type of surface just described which is produced by pickling baths of the type just described they are preferred for use in our process since it has been found that adherence between

the enamel and the ferrous work piece is greatest when the steel surface is thus preliminarily prepared.

Instead of utilizing pickling baths of the type above described satisfactory results may be obtained by utilizing pickling baths in which the principal components are salts which are readily reduced in the presence of iron, for example, trivalent iron salts such as ferric chloride. Since the ferric chloride picking process wherein the effective components of the baths are continuously regenerated by the introduction of chlorine thereto are well known in the pickling art, it is believed unnecessary to further describe such process at this point.

If it is desired to use mechanical means for preparing the surface instead of the chemical means just described satisfactory results may be secured by a simple sand blasting operation which is effective to not only remove the foreign material, but also leave the sheet reasonably rough. It is within the contemplation of our invention to combine chemical and physical means for the preparation of the metal work piece and in this the sand blasting operation which is described may be preceded or followed by a second step and when the pickling step is last to be employed then it should be preferably of the type which will produce the deeply etched surface of the character previously described.

Nickel depositions

The "nickel flash" method previously referred to, i. e. the process for the deposition of nickel which depends upon galvanic action by the work piece and the bath has not been satisfactory for use in our process. It is believed that one reason why deposition of the nickel by galvanic action does not give satisfactory results is not only the inconsistency of that process and the variations in the deposits resulting therefrom, but also the nature or character of the nickel deposit resulting from such process. Since the very nature of the process is galvanic, this requires that there be a certain area of the steel surface always exposed to the action of the bath if the galvanic process is to proceed. The nickel layer thus laid down by the galvanic process is not what may be termed a uniform or substantially continuous layer of nickel. Instead it is a coating of nickel which is interrupted by areas wherein the base metal is exposed or only superficially coated.

It has been established that porcelain enamel deposited over a thick layer of pure nickel has very poor adherence to such nickel. It will be concluded therefore that for proper adherence by the enamel to the work piece there must be a certain amount of iron in combination or elemental form available in the bonded area. We have found that the iron thus available on a surface coated with nickel by the galvanic method is too great for best results and it is believed that this accounts for the poor bond which is secured between the base metal and the enamel if only the nickel formation is used and if there are not adherence-promoting oxide present in the enamel.

In order to provide a lower ratio of iron to nickel on the surface of the steel work piece and to bring such ratio into the range wherein greatest adherence between the enamel and the work piece is secured, it is essential that the nickel coating deposit be substantially uniform while at the same time permitting the occurrence of at least a minor amount in free or combined form of iron at the bond. The process of depositing nickel by means of an electrolytic bath will produce a substantially continuous layer of nickel but such process is unsatisfactory for a number of reasons. First it can be used successfully only on simple shapes such as flat sheets because if the article treated has any substantial contour deviating from a flat plane there will be sufficient variation in the thickness of the nickel deposited on the various areas of the article to produce best results. Since the nature of the nickel deposit, i. e. its thickness and character are quite critical, when the article is contoured the thickness of the coat on the high points, for example, will be sufficiently different from the thickness of the coat on the low points for example, so that if the coating on one place is adjusted to the narrower range for best results, the coating in the other area will be outside of such range. Thus the process of depositing the nickel electrolytically can be used satisfactorily only on flat surfaces such as unfabricated steel sheets and strips and even on such surfaces the character of the deposit laid down by the electrolytic method is sufficiently different from the character of the deposits laid down by a chemical reduction method that it is not possible to secure the high order of adherence with the electrolytic process as it is with the process wherein the nickel is laid down by chemical reduction.

When flat steel sheets are prepared by the electrolytic process and they are then subsequently formed into the various shapes required by the enameling industry, such forming, especially if it is accomplished with any burnishing, grinding or welding steps will either sufficiently disrupt the layer of deposited nickel or destroy it entirely so that the resultant work piece is defective because of unsatisfactory adherence in the area where these operations have been performed.

Accordingly our invention comprises the coating of the work piece with nickel which is deposited thereon from a bath wherein the nickel is generated by chemical reduction.

As previously indicated, the amount of nickel deposited is critical for best results. There is one feature, however, which has an influence on the amount of nickel which will produce optimum results and that is the roughness characteristic of the steel sheet. It will be found that as the roughness or etched characteristics of the sheet vary the amount of nickel to be deposited will vary also. As indicated above, preferred results are secured when the surface preparation of the work leaves it in a deeply etched condition. On this type of surface the amount of nickel to be deposited for best results will be found to lie between 0.100 and 0.200 gram of nickel per square foot of surface area. A coating of approximately 0.150 to 0.1750 gram of nickel per square foot of surface area will generally be the preferred range with best results secured in the neighborhood of about 0.1625 gram of nickel per square foot of surface area. The baths which may be used for the chemical reduction of nickel and its deposition onto the work are described in the literature. These baths may be either alkaline or acid. The alkaline baths are described in Journal of Research—National Bureau of Standards, July 1946. A typical example of an alkaline bath which may be used in carrying out our invention is as follows:

	G./liter
Nickel chloride	30
Sodium hypophosphite	10
Ammonium chloride	50
Sodium citrate	100

Ammonium hydroxide to a pH of 8 to 10.

The alkaline baths have one drawback in that they are, under certain circumstances, inconvenient and uneconomical because at elevated temperatures there is a rapid loss of ammonium and the bath gives off copious fumes. The acid type baths which may be used in this step of my process are described in the Journal of Research—National Bureau of Standards, November 1947. A representative example of an acid bath is as follows:

	G./liter
Nickel chloride	30
Sodium hypophosphite	10
Sodium acetate	10

pH 4 to 6.

Since the acid baths generally operate with a very low loss of constituents by vaporization this type of bath is somewhat more controllable than the alkaline type baths described above.

In carrying out the nickel deposition step the previously treated sheet, as prepared by step 1, of our improved process, is immersed in the bath for a length of time on the order of about one minute at about 70° C., i. e., for a period of time depending on temperature and other conditions such as the condition of this bath in order to lay down a deposit of nickel within the range specified above. After the work is removed from the nickel bath it is washed, preferably in warm water, preparatory to receiving the application of enamel which occurs in the third step of our process. The application of the enamel comprises the third step of our process and should be performed within a reasonable time after the completion of the nickel deposition. It should be noted that the surface of the nickel will not change substantially from the condition in which it was immediately after the nickel was laid down.

Enamel step

It has long been recognized by those skilled in the art of porcelain enameling that a material and method of suspending ground porcelain enamel frit without the use of clay is extremely desirable. We have found that by adding small amounts of a cationic surface active agent instead of clay we can provide a porcelain enamel which when fired onto a ferrous work piece will have none of the aforementioned undesirable properties. We have also found that if the porcelain enamel slip, containing a cationic surface active agent, sets up too much or becomes too thick for spraying, anionic surface active agents can be used to cause the slip to become thinner or less viscous. Thus we have provided a material and method for simply and economically controlling the "set" of a porcelain enamel slip.

In the preferred embodiment of the present invention we use water soluble surface active agents. We have found that by using the water soluble type we can more readily control the "set" or loss of "set" of the porcelain enamel slips. However, it is to be noted that the water insoluble types can be used. In combination with the surface active agents we can use any of the well known mill additions such as potassium chloride, potassium carbonate, sodium nitrite, etc. to eliminate "tearing" of the fired piece and sodium aluminate, potassium fluoride, etc. to obtain desired hardness of the bisque coat.

The following table gives a partial list of cationic surface active agents which we have found to be particularly useful in the present invention:

I

Trade Name	Chemical Composition
Emcol 888	Alkyl-aryl pyridinium chloride.
Triton K-60	Alkyl dimethyl benzyl ammonium chloride.
Alro Quaternary O	High molecular weight imidazolinium chloride.
Alkaterge C	Substituted oxazoline.

Table II gives a partial list of anionic surface active agents which are useful in thinning an enamel slip with too high a set.

II

Trade Name	Chemical Composition
Ultrawet 30 E	Alky aryl sulfonate.
Nopco 1067	Sulfonated alkylated aromatic.
Michelene DLC	Alkyl aryl sulfonate and alkyl amido alcohol.

While in the preferred embodiment of our invention we use cationic surface active agents of the type shown above, we have found that a volatile organo halogenosilane such as methyl chloro-silane can also be used as an agent to cause particles of milled frit from settling. Porcelain enamel frit is ground dry in a conventional ball mill in a moisture laden atmosphere containing a small percentage of methyl chloro-silane. Under the condition of grinding, the frit particles are reduced to the desired size and at the same time acquire a surface condition which renders them water repellant. The frit thus milled is then mixed with water by agitation to a suspension having the desired properties for application to metal by any of the accepted application techniques. The suspension so prepared shows little or no tendency for the suspended frit particles to settle out over extended periods of time. If a condition arises wherein it is necessary to lower the "set" of the suspended frit in water the anionic surface active agents, used in the preferred embodiment of our invention can be used.

We have found that only a small amount of cationic surface active agent is necessary to give excellent suspension of the ground frit in water. It is to be understood that the amount of surface active agent used is based on the active ingredients, since the surface active agents contain water or other inert ingredients. In other words, if it is necessary to use 0.39% of alkyl dimethyl-benzyl ammonium chloride to get proper "set" it would be necessary to actually add 1.56% of the Triton K-60

in order to get 0.39% of active ingredients in the enamel slip. We have successfully used 3% cationic surface active agent (based on the active portion of the cationic surface active agent). However, from an economic standpoint we prefer using from 0.001% to about 0.5% of the surface active agent since this range gives adequate suspending properties and any amount over 0.5% is superfluous.

The enamel which may be used in this step may be any conventional finish coat enamel and need not contain any substantial amount of adherence-promoting oxides. An example of such an enamel is as follows:

	Pounds
Dehydrated borax	159
Feldspar	143
Sodium nitrate	363
Cryolite	195
Zinc oxide	96
Boric acid	345
Powdered quartz	1205
Titanium dioxide	294

As a striking example of the unexpected results which can be secured by the use of our process, a sample of ordinary cold rolled steel, which up to the time of our invention was considered to be practically unusable for direct finsh coat application, was pickled at room temperature in a nitric acid bath comprising one volume of nitric acid to four volumes of water; pickling time one minute. The sheet was then rinsed in warm water and immersed in the chemical acid reduction nickel bath, the analysis of which was given above, at a temperature of 70° C. for one minute. The sheet was then rinsed again in warm water and dried. By chemical analysis the sheet was found to carry a coating of .163 gram of nickel per square foot of surface area.

The prepared sheet was then sprayed with a finish coat porcelain enamel, of the type shown above. The enamel prior to being sprayed on the prepared sheet was milled in the following manner:

	Parts by weight
Frit	100.0
KCl	0.5
$NaAlO_2$	0.75
Emcol 888	0.032
Water	46.0

This slip was then sprayed on the above prepared sheet at a weight of about 20–30 grams (dry components) per square foot and fired at about 1520° F. for about 3½ minutes.

The finished fired sheet had an extremely smooth texture, no surface pits or copperheads, superior gloss-metal adherence and excellent acid and scratch resistance.

The process comprising our invention may be used to advantage, for example, in enameling shops and when used makes possible the fabricating of the desired work pieces from untreated cold rolled steel which is one of the lowest cost forms of sheet steel available today.

Other modes of applying the principle of the invention may be employed change being made as regards the details described, provided the features stated in any of the following claims or the equivalent of such be employed.

We, therefore, particularly point out and distinctly claim as our invention:

1. In the method of porcelain enameling a cleaned and roughened steel work piece surface having deep sharp edged pits therein, the steps comprising immersing said roughened work piece in an aqueous solution of a nickel salt and depositing from about 0.1 to about 0.2 gram per square foot of nickel thereon by the hypophosphite reduction process, wherein there is no ion exchange between the work piece and said solution, applying thereto a finish coat porcelain enamel clay-free hydrous slip said porcelain enamel being substantially free of adherence promoting oxides, said slip further characterized by the inclusion therein of from about 0.001% to about 3.0% per 100 parts of frit of a synthetic organic cationic surface active agent and finally firing said porcelain enamel onto said work piece.

2. The method of claim 1 wherein said porcelain enamel is a titanium dioxide opacified finish coat porcelain enamel.

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