United States Patent Office 2,872,352 Patented Feb. 3, 1959

2,872,352

METHOD OF PRODUCING ARTICLES FOR ENAMELLING

Frank R. Porter, Crown Point, and James W. Halley, Dune Acres, Ind., and James E. McFarland, Burnham, Ill., assignors to Inland Steel Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application June 11, 1953 Serial No. 361,082

3 Claims. (Cl. 117—130)

This invention relates to vitreous enamelware and to a novel method of producing the same, particularly by the use of a single cover coat.

In order to obtain acceptable adherence between an iron or steel article and a light colored enamel it has been customary in the enamel trade for many years to utilize a so-called ground coat which contains certain dark colored adherence-promoting oxides such as cobalt oxide, nickel oxide or manganese oxide. Since, such ground coats are dark in color, it has been necessary to employ one or more cover coats of light colored enamel over the ground coat in order to achieve an acceptable light colored enamel finish. Although the ground coat technique does not entirely solve the problem of eliminating surface defects in enameled articles, nevertheless, it is still used on a wide spread commercial scale in spite of the many efforts which have been devoted to the problem of eliminating the ground coat and providing a commercially acceptable single coat enameling procedure.

Obviously, the elimination of the ground coat in the production of light colored enameled articles would result in substantially lower costs of production both from the viewpoint of materials used and also by the elimination of one or more process steps. Moreover, it has been found that iron or steel articles having only a single coat of enamel are highly resistant to chipping and crazing of the enameled surface as compared with multi-coated articles having two or more enamel coats.

Various attempts have been made to improve the adherence of cover coat enamels to iron or steel articles without the use of a ground coat. For example, certain of the prior art workers have devised special compositions for the enamel frit or special process techniques in the preparation of the enamel slip which are said to improve adherence. Another widely used technique is the so-called nickel flash or nickel strike method by which a preliminary coating of nickel is deposited on the metal surface prior to the application of the enamel coat. Other workers in the art have advocated the provision of a substantial degree of surface roughness in the metal prior to enameling, the desired roughened surface being obtained by mechanical means or preferably by chemical pickling. Although many of these proposals may result in some degree of improvement in bond obtention, none of them has been sufficiently satisfactory in commercial practice to make possible the complete omission of dark colored adherence-promoting oxides from the enamel coat. Thus, to a large extent the industry has continued to employ the dark colored ground coat and one or more superimposed cover coats of light colored enamel.

Another approach to the problem has been by the use of enameling steels of special composition designed to eliminate surface defects and to improve the metal-enamel bond. Certain of these special steels have been highly successful to the extent that excellent single coat enamel adherence is obtained with a greatly reduced occurrence of surface defects and without the use of the conventional dark colored ground coat. However, wide scale use of

such special steels is often limited largely by reason of their obviously higher cost.

Although enameled articles are subject to many different types of surface defects which are associated with poor adherence or bond obtention, perhaps the most critical requirement for a satisfactory single coat enamel is freedom from fishscaling. Fishscaling is the expulsion, popping off or chipping off of small fishscale shaped pieces of the fired enamel coating and may occur during processing or some time after processing. According to the current theories, fishscaling is said to be caused by the release of hydrogen gas from the metal base upon cooling, the hydrogen presumably originating by the chemical reduction at enameling temperatures of water contained principally in the enamel frit. Generally speaking, fishscaling is associated with unsatisfactory enamel adherence so that the enamel coat is disrupted at various places under the excessive localized hydrogen gas pressure in the metal base. Consequently, the prerequisite of any acceptable single coat enameling technique is substantial freedom from fishscaling.

A primary object of our invention is to provide a relatively simple and inexpensive solution to the long existent problem of producing enameled articles having a satisfactory enamel bond with only a single cover coat of vitreous enamel thereby eliminating the necessity for a dark colored ground coat.

Another object of the invention is to provide a novel and inexpensive single coat enameling technique for use with light colored enamels.

A further object of the invention is to provide a novel method of pretreating iron or steel in order to prepare the same for enameling, said method being adapted to provide satisfactory single coat enamel adherence with a wide variety of irons or steels.

An additional object of the invention is to provide a novel enameled iron or steel article characterized by the presence of only a single light colored enamel cover coat which is substantially free of dark colored adherence-promoting oxides and having satisfactory adherence without fishscaling or other surface defects.

As hereinbefore briefly mentioned, some investigators in the porcelain enamel field have placed great stress on the importance of surface roughness in obtaining a satisfactory enamel bond and have recommended a severe crystallo-graphic etching of the metal surface prior to the application of the enamel. Thus, chemical pickling or etching baths containing sulfuric or nitric acid have been proposed for pretreating the metal, but in every case the sole desideratum has been a deeply etched surface characterized by a multiplicity of deep pits with sharp edged crests therebetween. Our experiments have shown that although on occasion there is some improvement in enamel adherence with increased surface roughness which can no doubt be attributed to better mechanical bonding and other effects associated with the increased surface area, yet there is no consistency in the results so obtained and the various etching and pickling methods heretofore advanced have not provided a satisfactory solution to the problem. We have found that something more than surface roughness per se is required in order to produce satisfactory enamel adherence in all cases.

Instead of surface roughness as a controlling factor, we have discovered that satisfactory enamel adherence depends upon the removal from the metal surface of a certain layer or skin of predetermined thickness and also upon the simultaneous deposition or redistribution on the metal surface of an adherence-promoting quantity of at least one of a selected group of metals above iron in the E. M. F. series. As hereinafter described in detail, we accomplish this result by subjecting the iron or steel base to pickling in an acid bath containing the adherence-

promoting metal in solution therein either as a bath addition, preferably as a salt of the acid comprising the pickling bath, or as dissolved from the iron or steel base during pickling. By means of a simple preliminary investigation, the critical amount of metal or surface skin which must be removed is readily determined beforehand for any given iron or steel and the pickling operation is then carried out to accomplish the removal of at least this quantity of metal. Concomitantly with the pickling operation, the selected adherence-promoting metal is deposited from the pickling bath onto the iron or steel surface in a quantity sufficient to effect satisfactory enamel adherence with a single white or light colored cover coat. As will hereinafter appear, the necessary quantity of the adherence-promoting metal varies somewhat with the acid used for pickling and also with the particular adherence-promoting metal being employed.

Our invention is predicated to a large extent on the experimental discovery of an important relationship heretofore unknown between enamel adherence and the phenomenon known in the art as "pickle lag." This phenomenon, which was first observed in the evaluation of tin-plate steels, is described by E. L. Koehler in Transactions of the ASM, volume 44 (1952), page 1076. Utilizing a rate of pickling test in 6 N hydrochloric acid at 194° F., it has been found that some steels will be attacked or pickled at substantially a constant rate throughout the test. However, many steels display an initial period in the early part of the test in which the steel is attacked at a considerably lower rate, the steel thereafter exhibiting a substantially linear final rate of pickling. The rate of pickling may be determined either by weight loss or by measurement of the hydrogen evolved. The initial period of low rate of pickling or increasing rate of weight loss during pickling is called the pickle lag period. The quantity of metal or surface skin which is removed during the pickle lag period, i. e. until the rate of weight loss becomes substantially constant, is designated as the pickle lag layer. Generally speaking, the depth of the pickle lag layer may be from about .0001 inch to about .001 inch, as calculated from the quantity of metal removed during pickle lag tests.

As reported by Koehler, another method of evaluating pickle lag involves measuring the negative corroding potential of the test sample in 6 N hydrochloric acid at 194° F. against a reference electrode such as a saturated calomel half cell. It has been found that the negative pickle or corroding potential for any given metal eventually approaches a constant value regardless of the pickling rate and that the length of time required to attain a leveling out of the pickle potential curve is an excellent measure of pickle lag. By determining the weight loss in the test specimen during the pickle potential test, the quantity of the pickle lag layer can also be calculated, i. e. the quantity of metal removed until a constant corroding potential is reached. For purposes of our invention either the pickle potential method or the direct rate of weight loss method may be utilized, but in most cases the pickle potential method will be found to give better results.

Although the phenomenon is not entirely understood, there is evidence that the existence of pickle lag is associated with a thin layer of metal at the surface containing grain boundary oxides.

As a result of extensive experimental investigations we have found a highly significant correlation between pickle lag and enamel adherence for many different irons or steels. In brief, we have found that in order to obtain satisfactory enamel adherence it is necessary to remove from the iron or steel base an amount of metal at least equivalent to the pickle lag layer for the particular metal involved. The pickling or etching treatments heretofore proposed have not been adequate because their objective has been merely to roughen or etch the metal surface without regard for the quantity of metal removed. There is substantial variation in the depth of the pickle lag layer for different heats or lots of iron or steel, but by means of the pickle lag tests heretofore described it is a comparatively simple matter to estimate the depth or amount of the pickle lag layer and thereby predict the quantity of metal which must be removed by pickling in order to obtain satisfactory enamel adherence. The phenomenon and the test methods in general are fully presented in the literature and will be familiar to those skilled in the art.

Although removal of the pickle lag layer is essential for the realization of satisfactory enamel adherence, we have also discovered that this factor alone is not sufficient to insure good adherence. In addition, the pickled metal surface must also be provided with or have deposited thereon a certain minor but effective quantity of at least one of a selected group of metals which occur above iron in the E. M. F. series. The metals which we have found to be most effective for our purpose are copper, platinum, palladium, iridium, rhodium, and gold. Copper is the preferred metal for several reasons. Obviously, copper is the least expensive of the foregoing metals but in addition copper is frequently found in enameling irons and steels in substantial amounts. This is particularly true today when relatively large quantities of scrap metal are employed in the open hearth steel-making process. The open hearth process does not result in the removal of copper and consequently the charging of copper-containing scrap metal to the open hearth process eventually results in a substantial accumulation of copper in the open hearth steel product.

It is essential that the adherence-promoting metal, i. e. copper, platinum, palladium, iridium, rhodium or gold, be deposited or redistributed on the iron or steel surface during the pickling process. This can be accomplished most conveniently by adding to or having present in the pickle bath a sufficient quantity of the metal ion to obtain the desired minimum deposit by galvanic action or displacement. Preferably, the metal is added to the pickle bath as the salt of the acid of the bath, e. g. copper sulfate in the case of a sulfuric acid pickle bath, copper chloride in the case of a hydrochloric acid bath, etc. The minimum quantity of adherence-promoting metal which is required to obtain satsifactory enamel adherence will vary somewhat with the pickling acid and also with the metal being added. For example, when copper is the adherence-promoting metal being employed a minimum deposit of about 5 mg./sq. ft. is necessary in the case of sulfuric acid pickling while a minimum deposit of about 10 mg./sq. ft. is reguired when a hydrochloric acid pickle bath is used. Our experiments have shown that in the case of sulfuric acid the minimum copper deposit will usually be obtained if the acid bath contains at least from about .04 to about .06 gram per liter of copper sulfate, and in the case of hydrochloric acid pickling the bath should contain at least about .3 gram per liter of cuprous chloride in order to insure the desired minimum deposit of copper. Of course, it will be understood that the foregoing minimum deposits of copper are expressed in terms of milligrams per square foot of apparent surface area, i. e. surface area as calculated from external dimensions, and does not take into account any effect of surface roughness.

As hereinbefore mentioned, if the iron or steel base already contains a substantial amount of copper, it is possible to omit the deliberate addition of a copper salt to the initial pickling bath. In such case, sufficient copper is presumably dissolved in the bath during the pickling reactions and redeposited in more uniform distribution on the pickled metal surface. This is particularly true in the case of sulfuric acid pickling, but even in this case it will generally be desirable to add some copper sulfate to the original pickle bath so that the necessary copper

deposit will be insured even if the copper content of the metal being pickled should change.

The provision of the adherence-promoting metal on the iron or steel surface must be effected during or concomitantly with the pickling action in order to obtain the full benefits of our invention. Our experiments have shown, for example, that electrodeposition of the required amount of copper on iron or steel which has been previously pickled to remove the pickle lag layer does not result in satisfactory single coat enamel adherence.

We do not have a complete explanation of our discoveries in enamel adherence, but our investigations have definitely shown that sufficient pickling to remove at least the pickle lag layer from the surface of the metal and the concomitant deposition of a certain minimum amount of copper, platinum, palladium, iridium, rhodium or gold are both essential to the realization of a satisfactory enamel bond with a single cover cost of light colored enamel which is substantially free of the usual dark colored adherence-promoting oxides. Although we do not wish to be bound by our present theories, it is our hypothesis that removal of the pickle lag layer is necessary to provide a "clean" metal surface upon which the adherence-promoting metal may be chemisorbed and then perhaps catalyze the reactions which take place in the formation of a strong metal-enamel bond. According to the classification by Linus Pauling in his work "The Nature of the Chemical Bond," all of the adherence-promoting metals hereinbefore named (as well as iron) fit into a particular group having rather definite characteristics. In the first place, all of these metals are above iron in the E. M. F. series so that they will readily deposit on iron. Secondly, they all have a cubic closest-packed lattice or crystal structure with a coordination number of 12. Finally, the smallest interatomic distances or shortest distances between neighbors in the crystal structures of these metals are less than 3.000 A.

With respect to the pickling operation, the usual mineral acids may be employed such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid and the like. The pickling conditions are chosen and correlated, as will be well understood by those skilled in the art, to obtain at least the desired minimum extent of pickling so that removal of the pickle lag layer is insured. Sulfuric acid is the preferred pickling reagent and will generally be used at a concentration of from about 5% to about 20% by weight, a temperature of from about 150° F. to about 200° F., and with a pickling time of from about 5 to about 60 minutes. Hydrochloric acid being somewhat more active can be generally used at a 1:1 dilution (6 N) with a much shorter time at the same temperature level. In the case of nitric acid, generally shorter times will suffice. For example, in many cases a pickling time on the order of one minute or so at room temperature will be satisfactory.

One of the outstanding advantages of our invention is the fact that the technique produces good results with a wide variety of enameling irons and steels. Typical analyses of metals which have been used with marked success in our invention are as follows:

TABLE I

	C (wt. percent)	Mn (wt. percent)	P (wt. percent)	S (wt. percent)	Cu (wt. percent)
Enameling Iron	.035	.07	.007	.029	.08
Mild Steel	.08	.35	.007	.030	.08
Rephosphorized Enameling Iron	.035	.07	.060	.029	.08

We prefer to employ rimmed steels and rephosphorized irons in particular since the latter pickle more rapidly and have better sag resistance during enameling.

Following the pickling operation as described above during which the adherence-promoting metal is also deposited on the metal surface, we have found that it is also desirable to employ the conventional nickel strike or nickel flash technique which is well understood in the art and which produces a nickel deposit on the pickled metal surface which ranges preferably from about .1 gram to about .2 gram/sq. ft. The nickel strike procedure further improves enamel adherence or bond obtention and in many cases permits the use of a somewhat lower firing temperature for the enamel cover coat.

To recapitulate, our invention involves three essential steps in the pretreatment of the iron or steel base prior to the application of the vitreous enamel cover coat: (1) pickling the base to a sufficient extent to insure the removal of an amount of metal at least equivalent to the pickle lag layer, (2) depositing from the bath or providing on the metal surface concomitantly with said pickling an adherence-promoting metal, which may be copper, platinum, palladium, iridium, rhodium or gold, in a sufficient quantity to provide satisfactory enamel adherence with a cover coat enamel which is substantially free of the usual dark colored adherence-promoting oxides, and (3) coating the pickled metal surface with a nickel strike or nickel flash deposit. Following the foregoing steps, the iron or steel base may be enameled by the application of a cover coat enamel which is then fired in the usual manner. For the reasons already described, excellent enamel adherence will be obtained with only a single white or light colored cover coat which is substantially free of dark colored adherence-promoting oxides. Inasmuch as our invention does not rely on the presence of special dark colored adherence-promoting oxides or other dark colored components in the enamel coating to obtain satisfactory adherence, it will be understood that the invention may be practiced with a wide variety of light colored enamel compositions which are well known in the art.

In order to illustrate some of the features of the invention, but not by way of limitation, the following specific examples are presented.

Example I

Early in our investigations it was discovered that for most irons or steels it was possible to obtain good enamel adherence provided the iron or steel base was pickled to a sufficient extent with sulfuric acid. However, with hydrochloric acid as the pickling reagent, considerable difficulty was encountered in realizing satisfactory adherence. Further investigation and spectrographic analyses of both the pickled metal and the used pickle liquor led to the conclusion that the presence of copper on the pickled metal surface was responsible for the good adherence obtained with sulfuric acid pickling. It was found that the sulfuric acid solution would not remove copper from the metal to any substantial extent. Instead, the copper contained originally in the iron or steel was apparently redistributed upon the pickled metal surface and resulted in a uniformly satisfactory bond on all areas of the specimens. Hydrochloric acid, on the other hand, tended to dissolve out or extract the copper originally contained in the iron or steel. These conclusions were verified by extensive tests in which cuprous chloride additions to the hydrochloric acid baths were found to result in good enamel adherence.

The experimental data presented in Table II will illustrate the foregoing statements. In each case the tests were conducted with 1:1 or 6 N hydrochloric acid as the pickling bath and the test specimens were from a mill normalized enameling iron having the following composition on a weight percent basis: .035% C, .07% Mn, .007% P, .029% S, .08% Cu.

Preliminary investigation of the test specimens showed that this particular enameling iron had a pickle lag layer of approximately 3.4 grams per sq. ft. The test speci-

mens were subjected to pickling under the conditions indicated and with varying amounts of cuprous chloride added to the pickle bath. Following the pickling operation, the specimens were subjected to a nickel strike treatment by dipping in a bath containing 35 grams of $NiSO_4.6H_2O$ in 1000 cc. of water (pH of 3.5) for 10 minutes at 170° F. A white cover coat enamel was applied to the nickeled specimens by spraying and then firing for approximately 5 minutes at about 1500° F.

The enamel frit had the following composition on a weight per cent basis:

	Percent
SiO_2	42.8
B_2O_3	15.8
Na_2O	10.5
K_2O	3.7
TiO_2	19.6
Al_2O_3	1.5
LiO_2	0.6
MgO	0.9
P_2O_5	2.8
F	1.8
	100.0

The enamel slip was prepared by milling the following in the indicated proportions:

	Grams
Frit	3400
Clay	84.5
Sodium nitrite	4.25
Sodium aluminate	8.5
Bentonite	17.0
Potassium carbonate	8.5
Gum tragacanth	2.1
Water	1300

After milling to a fineness of about 2 gms. on a 200 mesh screen, the following mill additions were made:

	Grams
Sodium nitrite	2.1
Urea	12.7

The enamel specimens were tested for adherence by the well known impact test and the results evaluated by visual observation.

TABLE II

Metal Added to Pickle Bath	Concentration		Pickling Conditions		Metal Removed by Pickling (g./sq. ft.)	Metal Deposited from Pickle Bath (g./sq. ft.)	Enamel Adherence
	g./l. of Cu_2Cl_2	g. atoms/l. of Cu	Time (min.)	Temp. (° F.)			
None			10	173	17.0		Poor.
None			5	173	12.7		Do.
Cu_2Cl_2	.06	.0003			6.8	.008	Do.
Cu_2Cl_2	.125	.0006	12	170	6.2	.008	Do.
Cu_2Cl_2	.18	.001	15	170	3.9	.012	Fair to good.
Cu_2Cl_2	.25	.0012	21	170	4.4	.028	Fair.
Cu_2Cl_2	.30	.0014	7	170	2.4	.035	Fair to good.
Cu_2Cl_2	.33	.0017	17	170	4.3	.054	Excellent.
Cu_2Cl_2	.67	.0034	23	170	6.8		Do.

From the first two tests in the above table it will be readily apparent that even though substantially more than the pickle lag layer was removed by pickling, the enamel adherence was poor because of the absence of the required deposit of copper. The remaining tests with increasing amounts of copper in the pickle bath demonstrate that a minimum of about 10 mg. of copper per sq. ft. of metal surface had to be deposited on the metal before consistently good enamel adherence was obtained. Thus, both the critical extent of pickling and the deposition of a certain minimum amount of copper were necessary for best results.

Example II

In Table III below experimental results are shown to demonstrate that platinum, palladium, iradium, rhodium and gold will also result in excellent enamel adherence provided the pickle lag layer is also removed. These tests were conducted in generally the same manner as in Example I with test specimens of an enameling iron having substantially the same analysis as in Example I and a pickle lag layer of about 5.0 gm./sq. ft.

TABLE III

Compound Added to Pickle Bath	Concentration		Pickling Conditions		Metal Removed by Pickling, g./ft.²	Metal Deposited from Pickle Bath g./ft.²	Enamel Adherence
	g./l. of Compound	g. atoms of metal/l.	Time (min.)	Temp. (° F.)			
$PtCl_2$	.798	.003	1¾	123	9.4	.033	Poor to Fair.
$PtCl_2$	.798	.003	3	123	22.7	.095	Excellent.
None	None	None	16	170	25.0	None	Very Poor.
$PdCl_2$	.642	.003	½	170	14.1	.041	Excellent.
None	None	None	12	170	15.0	None	Very Poor.
$RhCl_3$	.627	.003	½	170	10.6	.040	Excellent.
None	None	None	9	170	11.0	None	Very Poor.
$AuCl_3.HCl.3H_2O$	.625	.0014	18	170	23.0	.063	Good.
None	None	None	16	170	25.0	None	Very Poor.
$IrCl_4$	1.0	.003	5	170	4.7	.057	Good.
None	None	None	6	170	5.0	None	Very Poor.

With the foregoing metals, it will be noted that the rate of pickling was substantially higher so that the required degree of pickling to remove at least the pickle lag layer was accomplished in much shorter periods of time. With respect to the platinum tests, it has also been found that poor enamel adherence was obtained when the extent of pickling was insufficient to remove the pickle lag layer.

Example III

The following data in Table IV were obtained using a 6 weight percent sulfuric acid (approximately 1 N) pickle bath and a mill normalized enameling iron substantially the same as described in Example I:

TABLE IV

Compound Added to Pickle Bath	Concentration		Pickling Conditions		Metal Removed by pickling (g./sq. ft.)	Metal Deposited from Pickle Bath (g./sq. ft.)	Enamel Adherence
	g./l. of Compound	g. atoms of metal/l.	Time (min.)	Temp. (° F.)			
None			10	176	3.7	.004	Excellent.
None			40	175	10.2	.010	Do.
$CuSo_4.5H_2O$	.04	.0004	30	170	4.9	.035	Good.
$CuSo_4.5H_2O$	.08	.0008	22	170	3.0	.100	Excellent.
$CuSo_4.5H_2O$	.18	.0018	30	170	6.7	.185	Good to Excellent.

Good enamel adherence was obtained even without the addition of copper sulfate to the bath, but this was found to be explained by the fact that the original enameling iron contained an appreciable quantity of copper which was not removed by the sulfuric acid pickle bath but merely redistributed on the pickled metal surface. The addition of extra amounts of copper sulfate to the bath resulted in more uniform adherence throughout all areas of the test specimens. Accordingly, in the actual practice of our invention we prefer to employ copper sulfate as a bath addition to the sulfuric acid pickle liquor in order to realize this added benefit even in the case where the metal being pickled already contains effective amounts of copper. In addition, by so fortifying the sulfuric acid pickle bath with added copper sulfate, the same bath may be employed for all irons or steels regardless of their initial copper content.

It will be seen from the foregoing that our invention provides a highly simple and economical means of eliminating the use of dark colored enamel ground coats in the manufacture of enameled steel articles. The enameler ordinarily subjects the iron or steel base to a pickling operation for the removal of rust prior to the enameling step, and consequently the principles of our invention can be readily introduced without the necessity of special processing equipment. Also, an important advantage of the invention is that it is applicable to a wide variety of enameling irons and steels thereby greatly simplifying the problem in the enameling shop of obtaining satisfactory single coat enamel adherence regardless of the source of supply of the iron or steel base.

We claim:

1. A method of treating enameling iron or steel of the type exhibiting pickle lag to prepare the same for single coat vitreous enameling, said method comprising the steps of preliminarily determining the amount of the pickle lag layer of the metal, pickling the metal in an aqueous bath of mineral acid to remove from the surface of the metal an amount of metal at least equivalent to the predetermined pickle lag layer, said bath containing an adherence-promoting metal above iron in the E. M. F. series and selected from the group consisting of copper, platinum, palladium, iridium, rhodium, and gold, and depositing said adherence-promoting metal from the bath onto the surface of the pickled metal concomitantly with said pickling and in an amount sufficient to produce satisfactory enamel adherence with a cover coat of vitreous enamel which is substantially free of dark colored adherence-promoting oxides.

2. A method of treating enameling iron or steel of the type exhibiting pickle lag to prepare the same for single coat vitreous enameling, said method comprising the steps of preliminarily determining the amount of the pickle lag layer of the metal, pickling the metal in a copper-containing sulfuric acid pickling bath to remove from the surface of the metal an amount of metal at least equivalent to the predetermined pickle lag layer, and depositing copper from said bath onto the metal surface concomitantly with said pickling, the quantity of copper so deposited being not less than about 5 mg. per square foot whereby to produce satisfactory enamel adherence with a cover coat of vitreous enamel which is substantially free of dark colored adherence-promoting oxides.

3. A method of treating enameling iron or steel of the type exhibiting pickle lag to prepare the same for single coat vitreous enameling, said method comprising the steps of preliminarily determining the amount of the pickle lag layer of the metal, pickling the metal in a copper-containing hydrochloric acid pickling bath to remove from the surface of the metal an amount of metal at least equivalent to the predetermined pickle lag layer, and depositing copper from said bath onto the metal surface concomitantly with said pickling, the quantity of copper so deposited being at least about 10 mg. per square foot whereby to produce satisfactory enamel adherence with a cover coat of vitreous enamel which is substantially free of dark colored adherence-promoting oxides.

References Cited in the file of this patent

UNITED STATES PATENTS

1,946,766	Shonkwiler et al.	Feb. 13, 1934
2,377,321	Brown	June 5, 1945
2,469,123	Martin	May 3, 1949
2,495,762	Porter	Jan. 31, 1950
2,495,835	Comstock	Jan. 31, 1950
2,570,299	Zademach	Oct. 9, 1951
2,581,310	Swco	Jan. 1, 1952
2,733,999	Rodman	Feb. 7, 1956

OTHER REFERENCES

Hansen: A Manual of Porcelain Enameling, The Enamelist Publishing Co. (1937), p. 312.