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PROCESS FOR COATING METAL SURFACES

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This invention relates to a process of coating metallic surfaces, particularly iron and steel surfaces, with a vitreous and fused enamel coating effectively bonded thereto by the use of materials or bonding agents which act to control the amount or degree of thermal oxidation, the invention being particularly applicable to medium firing enamels fusing in the range of approximately 1260° F. to 1460° F. To that end the invention primarily has in view a new bond-dip solution of special formula introduced into the pickle line for the metal plate.

In the enamelling art it has been customary to increase the adherence of wet process enamels to steel by immersing the steel in an aqueous solution of nickel sulphate or, variously, nickel ammonium sulphate, buffered and controlled as to hydrogen-ion concentration by the further addition of ammonium carbonate and boric acid. Processes are known in the art whereby various other dipping solutions, such as cobalt chloride and or ammonium molybdate have been employed to accomplish a similar purpose. However, all such dips require elaborate control and are expensive, due to either the rapid exhaustion of the metal in solution or the build up of iron salts carried into the baths on the surface of the ferrous metal.

With the new bond-dip of the present application, control has been virtually eliminated, the operating range has been increased and the resultant adherence improved. Blistering, boiling or black specking and other surface defects are eliminated.

It has been determined that ferrous metal immersed in a bath composed of antimony trichloride, arsenic trichloride and stannous chloride, in solution in 18° Baumé hydrochloric acid, will bond to porcelain enamel films. In the above bath the arsenic trichloride acts catalytically as a depolarizing agent to free the surface of the metal from hydrogen bubbles caused by the action of the muriatic acid on the iron, thus permitting the deposition by hydrogen overvoltage of both antimony and arsenic on the metallic surface, and as an inhibition to lessen such attack. It is necessary that the iron salts present in such a bath be maintained in a ferrous state, and a reducing agent such as stannous chloride is added periodically to reduce the ferric iron formed on or carried over on the metallic surface.

To meet the objections above specified the present invention specifically contemplates employment, for a bond-dip bath or solution, chlorides of antimony, arsenic and tin in a strongly acid solution which deposits the metallic film on the immersed ferrous surface and controls the bond of the glass to the ferrous metal surface by controlling the oxidation of the same, the said bath or solution being of such a nature that a thin, strongly adhering film of antimony and arsenic is electrochemically deposited on the ferrous metal surface immersed in the same.

While the advantages of the special bond-dip solution of the present invention are quite numerous over the usual and conventional cobalt and/or nickel dips, among the more particular advantages of the present invention are:

1. Little or no control except as to concentration is required.
2. No rinse tank required between the pickle tank and the bond-dip tank.
3. More uniform and tightly adhering bonding film is produced on ware that is tightly packed in a pickling basket.
4. Due to the high acid reserve in this type bonding solution little or no change occurs which affects the film formed and therefore the type bond produced.

In carrying forward the invention the new bond-dip solution is preferably made up according to the following formula and procedure, to wit:

First, a solution of antimony trichloride is made up by dissolving commercial antimony tetraoxide in cold 18° Baumé muriatic acid in the proportion of 0.6 lb. of commercial antimony tetraoxide to each gallon of 18° Baumé muriatic acid. To that solution is next added arsenic trioxide in the ratio of one part of arsenic trioxide by weight for each 1000 parts by eight of antimony tetraoxide employed, thereby converting such arsenic trioxide into trichloride. This resultant solution will then have a yellow or amber color and then a solution of stannous chloride in strong muriatic acid is added in a sufficient amount to turn the said prepared solution colorless or pale green. This prepared bond-dip solution is now ready for use according to the procedure described as follows:

1. Metal sheet first cleaned in a boiling alkali cleaner for 15 to 20 minutes to remove grease, oil and dirt.
2. Rinsed in a running hot or cold flowing water rinse from 1 to 5 minutes.
3. Pickled in a 6–10% (by weight) sulfuric acid bath for 15 to 45 minutes at 140° F. to 160° F.
4. Introduced in the above described bond-dip solution.
5. Rinsing for from 1 to 5 minutes in a cold flowing water rinse.
6. Neutralizing in a bath containing ¼ to 1 ounce per gallon of a mixture of 10 to 90% borax and 90 to 10% soda ash at 140° to 180° F. for 2 to 8 minutes.

Referring to the action involved in steps 3 and 4 above noted, the action of sulfuric acid in step

3 tends to produce ferrous salts on the surface of the metal together with some ferric salts formed from scale and formed in the acid pickle bath on standing idle, and appreciable amounts of these salts are carried over into the bond dip tank where ferric salts are objectionable. This condition is corrected by adding the reducing agent employed, namely stannous or bivalent tin chloride. Also, it will be noted that the effect of the arsenic trioxide is to depolarize the surface of the metal to permit the antimony to flash on by overvoltage.

An example of a glass or frit which can be used with the above bonding method is as follows:

	Parts by weight
Feldspar	20.9
Borax	40.2
Silica	22.9
Soda ash	5.1
Sodium nitrate	4.8
Fluorspar	6.1

This material is mixed, smelted, fritted and dried in the usual manner, and to produce a light grey coating the mill additions of the above will be as follows:

	Parts by weight
Frit	100
Clay	7
Opacifier	3
Illmenite	5/8
Black oxide iron	1/8
Borax	3/4
Water	40

This material is ground or milled to a fineness of 0–25% residue on a 200 mesh screen, preferably 4–8% residue, and the metal as previously processed in the bond-dip solution is then coated with this milled slip by spraying, dipping or slushing. Finally the coated piece is dried and fired at from 1260° to 1460° F.

In the method described the temperature employed for firing the coated metal is much lower than that employed in the conventional sheet metal enamel processes, thereby permitting the invention to be carried out in connection with lighter gauge metal sheets than heretofore possible. Accordingly, the coated metal is fired in an oxidizing atmosphere above the fusing point of the glass or enamel but at the same time below the critical point of the steel. The glasses selected for use with the bonding materials herein referred to mature at relatively medium temperatures—from 1260° F. to 1460° F., all of which can be bonded to the metal surface by the use of the appropriate antimony-arsenic salts or compounds.

I claim:

1. In the process of enamel-coating ferrous metals the new step of applying to the sheet a bond-coat containing an acid solution of antimony trichloride and arsenic trichloride, and stannous chloride.

2. In the process of enamel-coating ferrous metals including the new step of subjecting the sheet to a bond-dip bath containing a muriatic acid solution of antimony trichloride, arsenic trichloride, and stannous chloride.

3. A bond-dip solution for processes of enamel-coating ferrous metals composed of antimony trichloride and arsenic trichloride dissolved in muriatic acid, and a reducing agent consisting of an acid solution of stannous chloride.

4. A process of preparing a bonding compound for use in enamel-coating processes which consists in first dissolving antimony tetraoxide in muriatic acid to convert the said tetraoxide into antimony trichloride, then adding to that solution a quantity of arsenic trioxide thereby converting the latter into the trichloride of arsenic and finally adding to the resultant solution an acid solution of stannous chloride.

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