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METHOD OF PRODUCING VITREOUS ENAMELLED METAL ARTICLES

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This invention relates to a method of producing vitreous enamelled metal products.

In the prior method of vitreous enamelling in general use today, the steel enamelling stock used is of a type having a rough surface and greater porosity than steels of like composition produced for other uses. The surface generally is a series of substantial peaks and depressions, providing what is generally referred to as a coarse or heavy "tooth."

The prior method of forming vitreous enamelling stock has may disadvantages, one of the most important being that, in the rolling, forming and fabricating operations the tooth of the metal is levelled off and reduced and the pores become filled with the lubricating oils, greases and compounds so that the overall porosity of the metal also is reduced.

As a result, the oils and greases must be removed from the metal and the metal pickled to restore the tooth and the porosity.

Furthermore, in the prior processes, the lubricants containing oils, greases, and fatty acids must be saponified and emulsified for removal. If not removed, they are detrimental to enamelling. In fact, if they remain long on the material, they etch and oxidize the surface to such an extent that the stock requires pickling and neutralizing to recondition it for enamelling.

Furthermore, the oils, greases and fatty acids have little body strength and cannot reinforce the tooth of the metal. Also, they penetrate deeply into the pores of the metal and, during rolling, drawing, and the like, become deeply entrapped so that they are difficult to remove even in strong alkaline baths. If not properly removed they carry over from the alkaline cleaning bath into the acid bath and congeal therein, forming stearates which are not removed during pickling and which render the stock surface unsatisfactory for enamelling by reducing the adhesion of the enamel. Most rejects in prior enamelling processes are due to these lubricants becoming entrapped in the metal prior to enamelling.

Vitreous enamel stock is received from the mill in clean condition. Starting with such clean, relatively porous and heavy toothed stock, the prior method of vitreous enamelling, or of forming articles for vitreous enamelling, comprises generally the following steps, in order: first, the clean stock is oiled and blanked out cold; next, it is coated with lubricating oil or greases and drawn or otherwise formed to shape and fabricated; then it is cleaned by boiling in a strong alkaline solution following which it is rinsed

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with water; after rinsing, it is subjected to a deep pickle step to restore the tooth of the metal which has been badly smashed down during the forming operations. After being deep pickled it is water rinsed and passed through a neutralizing bath, dried and then enamelled, the enamelling steps following the conventional procedure. As an example of the time cycle required, a given piece may be processed, beginning with the initial oiling for blanking and continuing through final drying preparatory to enamelling, in thirty-five minutes. Of this time, about thirty minutes is required for the deep pickling operation to restore the tooth which was damaged during forming.

In accordance with my invention the original tooth and porosity of the stock are preserved in substantially their original condition. My new process comprises coating clean vitreous enamel stock with a water soluble, self-adherent, dry, homogeneous, protective, lubricating and reinforcing coating so that the valleys between the so-called teeth of the stock are well filled and the teeth themselves coated over, blanking the coated stock, if blanking is required, in the absence of any additional lubricants, forming the stock in the condition in which it exists after blanking, or if blanking is not required, in the condition in which it exists after originally coating, washing off the stock with water, and then drying and vitreous enamelling the formed stock with the tooth thereof substantially in the shape in which it existed at the completion of the washing step.

If desired, in order to assure the optimum results and eliminate any troubles due to possible extraneous circumstances, such as slight contamination of the bath or stock from greases accidentally applied to the stock due to handling or by dripping from machinery, the stock, immediately after forming, may be washed in a mild aqueous alkaline cleaning solution instead of water as such a solution hastens the removal of the water soluble coating as well as tending to remove any slight incidental oil and grease. If the mild alkaline cleaning bath is used the stock should be cold rinsed in water promptly upon withdrawal therefrom.

The term "aqueous bath" as used in the claims is meant to include water alone as well as alkaline cleaning solutions and other aqueous cleaning solutions.

Another optional step following the cleaning in water, or in the aqueous cleaning bath, is to subject the sheet to a light pickle for superficially roughening the surface of the stock with-

out substantially affecting the shape of the tooth which latter, after the forming operation, is in substantially the condition it was in prior to forming. If the light pickle step is used, the stock is passed promptly thereafter through a neutralizing bath to eliminate from the stock any possible acids from the pickling bath. In fact, whether the light pickle step is used or not, the neutralizing step is desirable because it occasionally happens that there is some carryover of residual acids from the pickling steps performed at the steel mill in originally producing the vitreous enamelling stock.

As a comparative example of the time cycle required in my process, if it is assumed that the same piece heretofore mentioned in describing the time cycle of the prior process were processed in accordance with my invention, starting with the clean stock, coating, blanking, forming, washing with a mild aqueous alkaline cleaner, cold rinsing, light pickling, neutralizing and drying, the entire time required is about five minutes as compared to the thirty-five minutes required in the prior process, the light pickling step in my process requiring about one minute.

Thus I have found that by properly filling the valleys between the teeth and coating the teeth of the stock with an easily removed lubricating and reinforcing material which is water soluble and, when dried on the stock, produces a dry, solid, permanent, self-adherent, homogeneous, lubricating and protective film which has substantial body resistance to compression, the tooth of the metal can be laterally supported to an extent that it effectively resists the reduction and leveling off effect occasioned by the forming and fabricating operations so that, upon removal of the material after formation, the tooth and surface of the formed and fabricated stock are so nearly in their original condition that the stock is suitable without the heretofore required deep pickling step or other steps heretofore required for vitreous enamelling.

Further, I have found that by selecting such a material which also fills or seals the pores of the metal yet is easily removed without chemical action on the metal itself, the porosity of the metal, after forming and fabricating, can be maintained substantially in its original condition.

According to my present invention, the raw, coarse toothed, porous steel enamelling stock is coated with a homogeneous, completely water soluble material. This coating may be applied to the raw metal while it is in the condition in which it issues from the steel mill. However, if any oils, greases, rust proofing materials and the like have been placed on the material, at the mill or in subsequent handling prior to the coating step of the present invention, the metal is thoroughly cleaned so as to restore its surface as near to the original milled condition as possible.

A suitable coating composition for this process comprises lubricating and protective organic binder and water soluble alkaline earth metal borates, such composition being free from any inorganic barrier material.

The proportions of the ingredients of the dry mix composition for use in my process are as follows, the percentage given being by weight:

	Broad	Preferred
	Percent	*Percent*
a water soluble organic lubricating binder	10–33	20
water soluble alkali metal borates	90–67	80

The coating is applied by dissolving the composition in water in the ratio of about one pound of dry mix to one gallon of water and is applied to the stock by dipping or otherwise, followed by drying, and thereby forms on the stock a dry, homogeneous, self-adherent film which is both lubricating and protective.

One class of materials which may be used as the organic lubricating binders are water-soluble soaps, preferably having a melting point of at least about 36° C. upwardly and more particularly high titre soaps having a melting point of from between about 36 to 42° C. and up, specific examples being tallow soap, palm oil soap, stearic acid soap, cocoa butter soap, Borneo tallow soap, hydrogenated tallow soap, coaceric soap, Japanic soap, palmitic acid soap, stearin flux soap, multiple pressed tallow soap, hydrogenated palm oil soap, and multiple-pressed palm oil soap. It should be noted that each of the above soaps may be used individually or in admixture with one or more of the other soaps in any desired proportions, in so long as the amount of soap present is within the broad limits hereinbefore recited.

An additional class of materials are water-soluble aliphatic polyhydric alcohols having less than four hydroxy groups, fatty acid esters thereof or mixtures of either or both, and with a particular preference for those having a melting point of at least about 40° C., specific examples being polyethylene glycol, polyethylene glycol oleate, glyceryl stearate, propylene glycol sterate, di-glycol stearate, etc.

As hereinbefore indicated, mixtures of compounds in each class are contemplated for use in blending the ultimate compositoin. Moreover, it should be particularly stated that a mixture of the two aforementioned classes may be employed, such as, for example, a soap and a polyhydric alcohol, soap and an ester of the alcohol, a mixture of soaps and an alcohol or an ester or a mixture of the two. When employing such a mixture the soap preferably should be in the same or greater amount as the polyhydric alcohol.

The alkali metal borates employed in combination with the organic lubricating binder include borax, lithium borate, and potassium borate. Borax is the preferred material due to its ready availability and low cost and also, in certain methods of application, the other borates tend to disburse the organic binder and if the coated metal stock stands for any considerable period of time it tends to become tacky.

In some instances, it will be found beneficial to combine with the aforesaid composition a minor amount of an organic hydrophillic colloidal material such as, for example, cornstarch, potato starch, wheat starch, etc. Under such circumstances, the colloidal material will be present in an amount from between about 1% to 8%, the lubricating binder about 15 to 25%, and the borate about 67 to 84%.

After forming, the article is washed in water in any conventional washing machine and then dried. It will be found that the water soluble coating is completely removed from the valleys between the projections or teeth of the metal and from the pores by the water cleaning operation, and that neither the tooth nor porosity has been adversely affected substantially by the cold forming and fabrication operations. Accordingly, without any further steps, the dried article is then enamelled in the usual manner of enamel-

ling flat raw enamel stock having its original heavily toothed and porous surface.

It must be understood, however, that if there is to be an appreciable time delay between the step of water washing and enamelling, it is desirable to protect the surface of the article temporarily from rust and foreign matter. For this purpose, a protective film compatible with the enamel material or frits is used. Such a film may be sodium carbonate, borax, lithium borate, or a combination thereof, or sodium cyanide, or nickel salts.

The borate, and particularly borax, whether from the original coating used during forming or from a subsequent step, such as rust proofing, is highly beneficial in limited quantity to the subsequent enamelling operation as it acts as a flux for the enamelling material. Therefore, extreme care in washing after forming is not essential.

Thus, in accordance with the present process, the cavities or valleys between the teeth or projections of the material are filled with a substance having sufficient body to reinforce the teeth and prevent their reduction and distortion during rolling, drawing and the like; the pores are filled and prevented from clogging with material which is difficult to remove; the material which operates in this manner is readily applied and is as easily removed and any slight amount left on the article is beneficial in the enamelling operation.

It has been found that the present method, in addition to being applicable with various steels and alloy stocks of heavy tooth and high porosity such as commonly used for vitreous enamelled articles, is applicable to ordinary carbon steels. Its applicability to ordinary carbon steel results from two factors. First, the pickling steps of prior methods, when applied to ordinary carbon steels, bring the carbon of the steel to the surface and render the surface unsuitable for enamelling. Furthermore, the tooth and porosity of the original ordinary carbon steel is limited and is further reduced during drawing and fabricating in accordance with prior practices. Since the pickling step is eliminated and the mechanical reduction of the tooth is prevented by the present method, ordinary carbon steels can be enamelled in accordance herewith. This is particularly true of ordinary carbon steels which have been "dull rolled."

Indirect advantages result from the practice of the above process, in that the number of rejects is reduced from a relatively high percentage of processed pieces to a negligible amount, the die life is increased indefinitely, and the down time for die touch-up, repair, jamming and the like is eliminated.

Having described the composition to be employed in my new process it therefore becomes convenient to list a few illustrative examples of such compositions, the percentages given being by weight:

Example 1

	Parts
Tallow soap	15
Borax	85

Example 2

Palm oil soap	18
Borax	82

Example 3

Tallow soap	24
Borax	76

Example 4

	Parts
Tallow soap	10
Palm oil soap	6
Borax	84

Example 5

Palm oil soap	20
Borax	80

Example 6

Polyethylene glycol	15
Borax	85

Example 7

Polyethylene glycol	22
Borax	78

Example 8

Polyethylene glycol Polyethylene glycol oleate	20
Borax	80

Example 9

Polyethylene glycol oleate	7
Lithium borate	93

Example 10

Polyethylene glycol	28
Potassium borate	72

Example 11

Glyceryl monostearate Polyethylene glycol oleate	12
Potassium borate	88

Example 12

Propylene glycol stearate	30
Lithium borate	70

Example 13

Diglycol stearate	18
Borax	82

Example 14

Propylene glycol stearate do Glycol stearate	20
Lithium borate	80

Example 15

Polyethylene glycol stearate Propylene glycol stearate	15
Borax	85

Example 16

Tallow soap	5
Polyethylene glycol	10
Borax	85

Example 17

Palm oil soap	10
Polyethylene glycol	12
Borax	78

Example 18

Tallow soap Palm oil soap	10
Polyethylene glycol Polyethylene glycol oleate	10
Lithium borate	80

Example 19

Cocoa butter soap	30
Polyethylene glycol oleate	5
Lithium borate	65

Example 20

	Parts
Stearic acid soap	5
Polyethylene glycol	30
Potassium borate	65

Example 21

	Parts
Borneo tallow soap	20
Glyceryl monostearate Polyethylene glycol oleate	5
Potassium borate Borax	75

Example 22

	Parts
Hydrogenated tallow soap	7
Propylene glycol stearate	25
Lithium borate	70

Example 23

	Parts
Coaceric Japanic	10
Diglycol stearate Propylene glycol stearate	8
Lithium borate Borax	82

Example 24

	Parts
Palmitic acid soap	15
Diglycol stearate	5
Borax	80

Example 25

	Parts
Stearin flux soap	20
Borax	80

Example 26

	Parts
Hydrogenated tallow soap	35
Borax	65

Example 27

	Parts
Hydrogenated palm oil soap	10
Lithium borate	90

Example 28

	Parts
"Triple-pressed" tallow soap Hydrogenated palm oil soap	30
Potassium borate	70

Example 29

	Parts
Cocoa butter soap	18
Potassium borate	82

Example 30

	Parts
Stearin flux soap	15
Lithium borate	85

Example 31

	Parts
Coaceric soap	25
Borax	75

Example 32

	Parts
Japanic soap	22
Potassium borate Borax	78

Example 33

	Parts
Borneo tallow soap	20
Borax Lithium borate	80

Example 34

	Parts
Stearate acid soap	28
Borax	72

Example 35

	Parts
Stearin flux soap Stearic acid soap	15
Borax Lithium borate	85

Example 36

	Parts
Borneo tallow soap "Triple-pressed" palm oil soap	20
Borax	80

Example 37

	Parts
Stearin flux soap	17
Borax	80
Sulphonated castor oil	3

Example 38

	Parts
Hydrogenated tallow soap	22
Borax Lithium borate	73
Liquid glycol Sodium lauryl sulphate	5

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.

This application is a continuation-in-part of my copending application, Serial No. 690,833, filed August 15, 1946 and now abandoned.

I therefore particularly point out and distinctly claim as my invention:

1. The method of producing vitreous enamelled metal articles comprising coating heavy tooth porous metal stock to a thickness sufficient to coat the peaks of the teeth of the stock and substantially fill the valleys between the teeth with a water-soluble, homogeneous, self-adherent and tenacious dry lubricating and protective reinforcing coating having sufficient body resistance to compression to reinforce and prevent substantial deformation of the teeth of the stock during cold pressure forming thereof between two metallic dies, cold pressure forming the coated stock into the desired shape between two metallic dies in the absence of any additional lubricants, washing off in an aqueous bath at least a major portion of the coating material remaining after the shaping operation, drying the shaped stock, whereby the teeth and porosity of the stock are preserved, and subsequently, in the absence of any pickling operation sufficient to cause substantial change in the shape of the teeth of the stock, vitreous enamelling the shaped stock directly on the formed surface while its tooth and porosity are substantially in the condition in which they existed at the completion of the washing step.

2. The method according to claim 1 characterized in that said composition comprises essentially organic lubricating and binding material and a larger portion of inorganic glass forming and water liberating material.

3. The method according to claim 2 characterized in that said organic lubricating and binding material is soap and the inorganic glass forming and water liberating material is borax.

4. The method of producing vitreous enamel metal stock articles comprising coating heavy tooth metal stock to a thickness sufficient to coat the peaks of the teeth of the stock and substantially fill the valleys between the teeth with a water-soluble, homogeneous, dry, lubricating and

protecting coating comprising the following ingredients by weight:

	Per cent
Water-soluble organic lubricating binder	about 10–33
Water-soluble alkali metal borate	do 90–67

cold pressure shaping the coated stock to the form desired between two metallic dies in the absence of any additional lubricant, washing off in an aqueous bath at least a substantial portion of the coating material remaining after the shaping operation, drying the shaped stock, whereby the teeth and porosity of the stock are preserved, and subsequently, in the absence of any pickling operation sufficient to cause substantial change in the shape of the teeth of the stock, vitreous enamelling the shaped stock while its surface is in substantially the condition in which it existed at the completion of the washing step.

5. A method in accordance with claim 4 wherein in the washing operation after the coated stock has been shaped, a portion of the lubricating and protective coating is permitted to remain on the shaped article to function as a flux during the vitreous enamelling operation.

6. A method in accordance with claim 4 wherein the lubricating and protective coating comprises the following ingredients by weight:

	Per cent
Water-soluble soap	about 10–33
Water-soluble borate	do 90–67

7. A method in accordance with claim 4 wherein the organic lubricating binder is a water-soluble soap having a titre of at least about 36° C.

8. A method in accordance with claim 4 wherein the organic lubricating binder is tallow soap.

9. A method in accordance with claim 4 wherein the organic lubricating binder is palm oil soap.

10. A method in accordance with claim 4 wherein the lubricating and protecting coating comprises the following by weight:

	Per cent
Water-soluble soap	about 10–33
Borax	do 90–67

11. A method in accordance with claim 4 wherein the lubricating and protecting coating comprises:

	Per cent
Starch	1–8
Water-soluble soap	15–25
Borax	67–84

12. The method of producing vitreous enamelled articles comprising coating heavy tooth porous vitreous enamel metal stock to a thickness sufficient to coat the peaks of the teeth of the stock and substantially fill the valleys between the teeth with a water-soluble, homogeneous, self-adherent and tenacious dry lubricating and protective reinforcing coating of organic lubricant and binder comprising essentially at least one from the group consisting of water-soluble soap, water-soluble aliphatic polyhydric alcohols having less than four hydroxy groups, fatty acid esters of said alcohols, and any mixtures of any of the foregoing, and a larger portion of inorganic water-soluble glass forming and water liberating material, cold pressure forming the stock into the desired shape between two metallic dies in the absence of any additional lubricants, washing off in an aqueous bath at least a major portion of the coating material remaining after the shaping operation, drying the shaped stock, whereby the teeth and porosity of the stock are preserved in condition for vitreous enamelling, and subsequently, in the absence of any pickling operation sufficient to cause substantial change in the shape of the teeth of the stock, vitreous enamelling the shaped stock directly on the formed surface while its teeth and porosity are substantially in the condition in which they existed at the completion of the washing operation.

13. The method according to claim 12 characterized in that the stock is subjected to a light pickling operation operative to superficially roughen the surface of the stock without substantially affecting the shape of the teeth, as they existed after the forming operation, prior to vitreous enamelling.

14. The method of producing articles to be vitreous enamelled from heavy toothed porous vitreous enamel stock comprising coating heavy toothed porous vitreous enamel stock to a thickness sufficient to coat the peaks of the teeth of the stock and substantially fill the valleys between the teeth with a water soluble, homogeneous, self-adherent and tenacious dry lubricating and protective coating having sufficient body resistance to compression to reinforce and prevent substantial deformation of the teeth of the stock during cold pressure forming thereof between two metallic dies, cold pressure forming the coated stock into the desired shape between two metallic dies in the absence of any additional lubricants, washing off in an aqueous bath at least a major portion of the coating material remaining after the shaping operation and then drying the stock, whereby the tooth and porosity of the stock are preserved and subsequent pickling for restoring the teeth is unnecessary.

ROLAND A. WHITBECK.

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