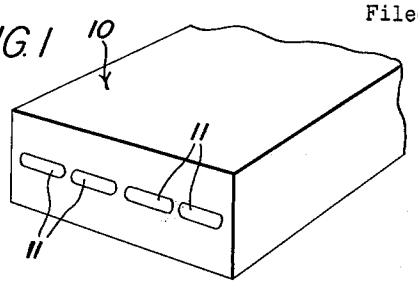
April 10, 1962 C. E. MAIER ETAL 3,029,155

ENAMEL-POWDER RESIST SYSTEMS

Filed Aug. 21, 1959

FIG. 1



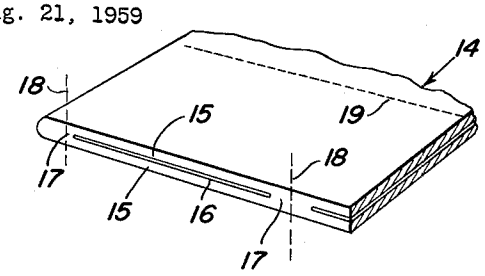
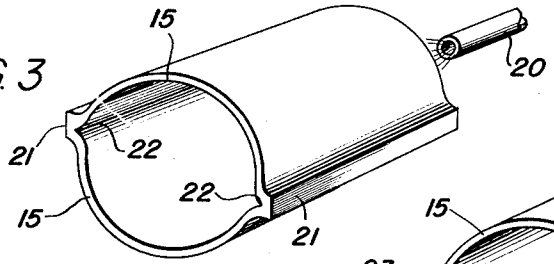


FIG. 2

FIG. 3



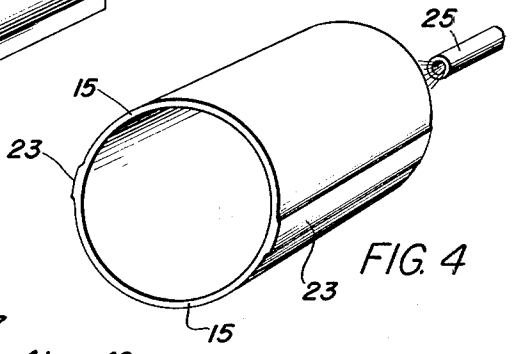


FIG. 4

FIG. 5

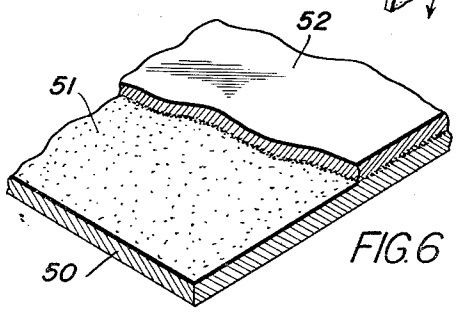


FIG. 6

INVENTORS

CURTIS E. MAIER

ROBERT M. BRICK

BY Mason, Porter, Dilks & Stewart,

ATTORNEYS

United States Patent Office 3,029,155 Patented Apr. 10, 1962

3,029,155

ENAMEL-POWDER RESIST SYSTEMS

Curtis E. Maier, Riverside, and Robert M. Brick, Hinsdale, Ill., assignors to Continental Can Company, Inc., New York, N.Y., a corporation of New York

Filed Aug. 21, 1959, Ser. No. 835,297
13 Claims. (Cl. 117—26)

This invention is concerned with the preparation of metal surfaces for receiving coatings of organic enamel, and more particularly relates to the preparation of the metal internal surfaces in the making of internally enameled containers.

It is known to make tubular bodies by rolling a billet having an internal longitudinal channel containing an anti-welding or resist material which is effective during the rolling to prevent the metal laminations present at the surface of the billet from sticking together in the strip being made. These laminations are connected, at the edges of the residue of the resist material, by integral metal connections. The strip is then opened or expanded to provide a tubular body which can be further operated upon for producing the container.

When such containers are to be employed for holding substances which can react with, or be acted upon by, the container metal, it is necessary to provide a protective internal coating. Thus, it is known to employ organic enamels of specific compositions to prevent action by acid fruits upon the container metal, to prevent a black discoloration of corn when canned, etc.

It has been a practice to employ talc, mica, gypsum, graphite, and magnesia as resist materials during rolling, because they have been found to produce rolled strip which opens easily, that is, there are few or no adhesions between the laminations at the end of the rolling schedule. For specific employments, some of these resists have been found disadvantageous; for example, graphite is not desirable for use with steel or aluminum billet materials with a hot rolling as part of the schedule, because the graphite forms carbides with the steel, or presents electrochemical couples with aluminum or aluminum alloys.

It has been proposed to remove the resist residues, after opening the strip into tubular form. In practice, simple leaching is not satisfactory with the above resists, because the internal surfaces are not clean for satisfactory enamel adhesion, even after extensive washing with fluid jets under pressure. A further proposal is to employ an abrasive in the pressure fluid, for a mechanical removal of the resist particles. Such added operations are expensive, and add to the cost of preparation. When used in making container bodies on a competitive basis, with the further cost of drying before applying a lacquer or enamel, the expense removes the product from direct competition with containers formed by bending and soldering flat body blanks.

In practice, if residues of resist materials such as talc, graphite, mica, gypsum and magnesia are left on the internal surfaces, the adhesion of the enamel is very poor. When the resist is of glass particles, barytes, calcium silicate, or magnesium silicate, the adhesion is better but not commercially acceptable even after loose resist has been previously removed. Such materials undergo malleable deformation or flattening under pressure; and in general are not wetted by the organic enamel compositions employed as can lacquers, or exhibit a low bonding effect therewith.

It has been found that when solid refractory resist powders of alumina, titania, zirconia, silica, and tri-calcium phosphate are employed, all of which are harder on the Moh scale than aluminum, which is about 2.9, and which are highly resistant to malleable deformation or

flattening, and insoluble in organic enamel compositions, excellent enamel adhesion can be attained. Likewise, zinc oxides can be employed.

Therewith the resist material is selected for its response to the requirements of preventing welding during the rolling operation to form the strip; and its competence, while present in embedded form upon the internal surfaces, of accepting and establishing a good adhesive bond with the enamel. It is a characteristic of the organic enamel compositions that they readily wet such resist powders better than they wet the metals such as aluminum, steel, copper.

Therewith the microscopic roughening of the metal surface by the action of the resist greatly increases the exposure surface area for enamel adhesion, and the embedded particles provide a capillary structure into which the effectively wetting enamel composition enters, for a final anchoring together of the baked enamel, particles and metal. A notable effect is that, if grease, oxides or other contamination get onto the inner surface, the effect of the particles during rolling is to penetrate such films and provide a satisfactory bonding of the enamel to the metal even though such contaminations of themselves would normally inhibit the production of a satisfactory adherent enamel coating. Further, when zinc oxide is employed as the resist powder, and an oleoresin-containing enamel is employed, the baking causes an action by which the enamel coating has properties of the so-called "C" enamel types: and the application of enamels over surfaces having embedded alumina or silica particles resembles closely the effect of applying such enamels over anodized surfaces.

It is also known to provide metal and plastic surfaces with roughening by embedding hard particles therein during casting or by subsequent rolling, e.g., in making steps, floor plates, etc., where slippage of a user's shoes is to be prevented. Such embedded particles are purposefully large and spaced apart, to afford the desired traction, in comparison to the instant provision of microscopically fine roughening and capillary structure by which an organic enamel composition penetrates and fills the pores; and wherewith the microscopic roughening cannot engage with rubber and leather surfaces for the high frictional effect needed on floor plates and the like. Further, metal surfaces for lapping and like plates and disk have been prepared by embedding abrasive particles therein: but there also a spacing is necessary to provide clearance for the chips formed by the grinding, lapping or sawing operations therewith. In neither case is a microporous surface structure, with essentially smooth outer surface, either sought or attained which presents a major effective interface surface for an enamel.

The word "enamel" is used herein to designate an organic coating composition including a resin such as an oleoresin, a vinyl resin, an epoxy resin, or an ester resin to provide a continuous film after drying and baking; being applied in a volatile organic vehicle including a resin solvent. Other solid components can be present as fillers, pigments, driers, known in the art. The term is here synonymous with "lacquer."

The term "billet" is employed herein to designate a body of metal which can be rolled to a thinner section; and is inclusive of ingots, plates, bars, sheets and laminates which initially are thicker than the desired final gage and are reduced to such gage during the course of rolling. The term "sheet" is employed herein to designate a metal body of substantially uniform thickness, which may be a long strip or a short section, or may be the wall of a hollow tubular structure.

Practice of the invention is shown in the accompanying drawing, illustrating the production of a laminate expand-

able strip having internal surfaces prepared by the instant process, and in which:

FIGURE 1 is a perspective view of a billet for rolling to form an expandable metal strip;

FIGURE 2 is a perspective view, on a greatly enlarged scale, of a part of a rolled strip;

FIGURE 3 is a perspective view of a container tube, made by opening a blank prepared from the strip of FIGURE 2;

FIGURE 4 is a like perspective view of the reworked tube, with application of an enamel to the internal surfaces;

FIGURE 5 is a perspective view, showing a further form of practice, for the production of sheet material having enamel coating on a surface thereof;

FIGURE 6 is a perspective view, on a greatly enlarged scale, showing a portion of an enameled article, with a part of the enamel coating absent to show the article surface.

In FIGURE 1, the aluminum or aluminum alloy billet 10 may be prepared by casting or other operations as set out in the Valyi et al. Patent 2,375,334. It has a plurality of internal longitudinal channels of predetermined size and arrangement, each filled with a core material 11 which is effective during the rolling operation to resist welding of the metal laminations to one another, and selected from the refractory powders which are chemically inert relative to the metal around the channels and have a Mohs hardness at least equal to that of the aluminum, that is, being of a hardness value 2.5 or above on the Mohs scale or Knoop values of better than about 400; of which the group of alumina, titania, zirconia, silica, tri-calcium phosphate, and zinc oxide has been found satisfactory. Such inorganic refractory powders can be described as hard and brittle and highly resistant to malleable deformation or flattening under pressure, as compared to the ductility and malleability of the aluminum, noting the technical difficulty of comparing the hardness of a brittle substance with that of a ductile material. The powder must be hard enough to indent the metal: and materials of Mohs hardness values over 5 are preferred with aluminum.

The refractory powder is present as particles which may have sizes of 60 mesh down to a micron; and preferably have sharp edges and corners. With friable particles of granular calcined alumina, in agglomerated form, e.g., of 100 mesh or larger, fracturing occurs during the rolling. It is preferred to have the particle sizes, at the completion of rolling, below 600 mesh, and preferably in the range of one to 15 microns. Each particle is preferably of a form, during the rolling, in which its several dimensions are of the same order: that is, needle-like particles are avoided.

Such a billet 10 for making expandable laminate stock may have a thickness of 8 to 12 inches, and a width of 30 to 60 inches, and be 10 to 14 feet long. The channels may be 0.250 inch thick and 4.00 inches wide, four such channels being shown in the drawings, spaced 0.250 inch apart, and located midway between the top and bottom surfaces of the billet.

The billet is then heated for homogenizing, and subjected to a schedule of hot and cold rolling operations to reduce it to a strip 14, FIGURE 2, having a thickness of say 0.025 inch, with each channel region now having metal laminations 15 about 0.012 inch thick at the top and bottom surfaces, and a residue 16 usually less than 0.001 inch thick of the resist material present between these laminations. The laminations are connected at the edges of the resist residue by solid and integral metal connections 17. The number of residue layers is determined by the number of cores in the billet 10. Such a strip can be called "multi-wide" because there are several laminate regions extending longitudinally, and spaced transversely by the metal connections 17. The strip can then be severed into narrower strips, each having a laminate region with integral edge connections, along longitudinal surfaces normal to the upper and lower faces of the strip, as represented by the dotted lines 18, and severed transversely, as represented by the line 19; whereby individual blanks are produced.

Such a blank can then be opened by bending the metal laminations 15 apart, FIGURE 3, to provide a tubular body. When the billet has been rolled to such low thickness of the residual resist layer and microscopic size of the individual particles, it is not necessary to remove loose powder before enameling: when organic enamel solution is sprayed on such a surface, the solution penetrates easily through the loose and embedded powder and around each particle thereof, down to the composite metal-resist interface, and the particles become bound during the baking. It is permissible, if desired, to remove loose particles: e.g., by dry mechanical operations of tapping and employment of an air blast from the nozzle 20, essentially all of the loose resist powder can be removed. The opened blank has externally projecting fins 21 formed by the portions of the integral metal connections 17 which were parts of the individual blank, with reentrant angles 22 at the positions of the edges of the resist residues. In practice, it is preferred to reduce the projections, as by external hammering, wherewith the reentrant angles essentially disappear, and the resulting tubular body has essentially smooth internal and external surfaces, usually with elevations 23 of minor width at the former locations of the fins.

The internal surfaces appear smooth and matte visually and, upon microscopic inspection, particles of the resist material are found embedded therein. When the resist has been fine aluminum oxide powder, in a billet of aluminum or aluminum alloy, the effect resembles that of having provided an internally anodized hollow body insofar as enamel adhesion is concerned. The thickness of the residual resist layer has an effect upon the exposed surface of the baked enamel film. For example, when 5 milligrams per square inch of the usual enamel compositions are applied with the minimum thickness of silica resist for easy openability, a matte appearance is present. When 8 to 10 milligrams per square inch are sprayed, a bright smooth surface is present. In each case, there is excellent adhesion.

An enamel coating can now be applied to the internal surfaces, as by spraying from a nozzle 25, and baking. In practice, it has been found that the adhesion of phenolic enamels, oleoresinous enamels, modified vinyl-oleoresinous enamels, and epoxy enamels was all greater upon the resist-surfaced bodies than upon the usual rolled and degreased aluminum sheets. The oxygen-spinach test, commonly employed to determine process enamel adhesion in cans, showed the exceptional adhesion values thus attained. Titania, zirconia, silica, and tri-calcium phosphate likewise showed high adhesion values with the same enamels. Zinc oxide showed high adhesion values with phenolic, oleoresinous and epoxy enamels; but not with vinyl enamels, noting that it can act as a curing accelerator for vinyl enamel compositions and thereby can produce local over-curing effects.

When an insufficient thickness of resist is present at the end of the rolling schedule, local sticking by welding has been noted. However, in some cases, even doubling the thickness of the original cores 11 was not sufficient to prevent the local sticking. Further, when too much resist is present in the rolled strip, the internal surfaces demand an excessive amount of enamel, to avoid the presence of "dry" or dull spots: for example, when the retained resist powder after removal of loose particles presents too thick a layer at the internal surface, when an enamel of the normal coating weight of 5 to 7 milligrams per square inch is absorbed within this layer so that the effect of the excess powder particles at part of the exposed surface is that of destroying the gloss when such is desired. It will be understood

that when high fluid pressures can be employed for opening the laminate regions, as practiced in making refrigerator coils or evaporators, such adhesions are separated without major difficulty: but when it is desirable to make bodies with thinner walls, and to initiate the opening by suction cups or like low-tension devices, such adhesions cause troubles in economics. It has been found that the difficulty can be resolved by employing a hot rolling schedule of reduction down to about four times the final thickness, wherewith the core or resist residue is still a layer having a thickness of many powder grain diameters and no welding occurs; and then conducting a cold rolling schedule with the strip passing around the rolls or through staggered rolls, so that there is mechanical tension and bending during the progress of the cold rolling; with movement of the metal laminations relative to one another to maintain powder distribution and to break minor adhesions which may start to form.

In the practice according to FIGURE 5, the billet 30 is prepared with a single resist-containing longitudinal channel or discontinuity 31 containing the hard powder particles, with metal layers 32, 33 above and below it, and with these metal layers integrally connected at the margins 34 of the billet. Such a billet may be prepared as an ingot or roll-bonded structure, and may be subjected to a schedule of hot and cold rolling, including the action of a final pair of rolls 35, 36 so that the billet is essentially a laminated plate as it comes to these rolls and leaves them as a laminate strip 37 in which the resist residue 38 is very thin, e.g., less than 0.001 inch, and the individual laminations 39, 40 are of the thickness intended for the sheet stock. During the rolling, the presence of the integral margin connections 34 prevents penetration of dirt, rolling lubricant, and other material into the discontinuity between the laminations, and prevents loss of the resist material.

After leaving the rolls 35, 36, the edges of the strip 37 are trimmed by severance along the lines 41 which are spaced from the edges of the strip so that severance occurs through the resist residue, and the marginal strips 42 are removed. The portion of the laminate strip is then separated into the upper and lower bands or sheets 44, 45 of metal stock, each having a surface with embedded resist particles, as shown by the stippling on band 45. To indicate continuity of rolling and coating, the band 44 is shown as passing over a coating roller 46 which takes up enamel 47 from the trough 48 and delivers the same onto the resist-embedded lower surface of the band 44. The coated band then passes through an oven 49 shown by dash lines, in which the enamel is baked to its cured form. Like treatment is given to the band 45.

In each form of practice, the product is as shown on greatly enlarged scale in FIGURE 6. The rolled metal stock 50 has its surface 51 coated over the entire area with embedded particles of resist material so that visually a continuous surface is present, but microscopically a porous condition is present. The enamel coating 52 has a continuous outer or exposed surface, and extends around the resist particles down to the metal so that it is tightly keyed and adherent thereto.

The procedure permits obtaining the exceptional adhesion characteristics for the enamel because the internal surfaces are protected and thus cleaner from oils, etc., as compared with normal rolled metal surfaces, noting that rolling lubricants are required and traces remain unless expensive and thorough electrolytic cleaning operations are performed. The metal surface is rougher on a microscopic scale, with a greater contact area between enamel and metal, with much of the area in shear rather than in tension during peeling, as the microscopic local areas of surface are not parallel to the general or macroscopic surface, but inclined at varied angles relative to it. With many combinations of enamels and metals, the adhesion of the enamel per unit area of the interface of contact is less than the cohesion within the enamel for a like sectional area and hence, under stress, the cleavage is at the interface and peeling occurs: with the present procedure, the effective area of the interface is increased per unit of nominal surface area. The preferred resist materials have surface tension characteristics, relative to enamel solvents and resins, which permit the enamels as applied and their solid deposits to exhibit wetting effects to the individual powder particles; so that the enamel is pulled by capillarity between adjacent particles of resist until the enamel reaches the true metal surface and fills all pores present, with the resist particles becoming in effect pigment particles within the enamel. Particles of the resist become embedded in the metal surface during rolling and, when subsequently wetted by the enamel, give a mechanical "tooth" effect in assisting the adhesion of the enamel: noting that such behavior is based not only on chemical factors but also on physical, crystallographic, elastic, plastic and like properties of the several intercontacting materials. In practice with talc, gypsum, magnesia and like soft resist materials, they are found to give flat plate-like particles which lie parallel to the surface without bonding or keying into the same by forces corresponding to those of desirable enamel adhesion, and their shaping and positions tend to resist the penetration of the enamel to the metal, and they resist wetting by the normal enamel vehicles such as ketones, hydrocarbons and esters. Magnesium oxide further has the difficulty, with oleoresinous enamels, or oil-modified vinyl or epoxyl enamels, that there is reaction with the fatty acid radicals present, so that fatty acid soaps of low adhesion are formed at the resist interface, and enamel adhesion is destroyed for containers which are packed with aqueous products.

The procedure leads to the preparation of an article, either a hollow body or a sheet, which has a metal base with the particles embedded therein and providing a microporous surface, having an enamel coating tightly adherent thereto with parts of the coating extending in the microporous structure and with a continuous outer surface.

It will be understood that the illustrative embodiments described are not restrictive, and that the invention can be practiced in other forms within the scope of the appended claims.

What is claimed is:

1. The method of preparing a metal article having an enamel coating thereon, which comprises the steps of applying an inorganic powder to a surface of a metal billet, the powder being harder than the billet metal and having a particle size not exceeding 60 mesh, rolling the powder and billet for reducing the billet to the desired thickness for the article and thereby effecting embedding and adhesion of powder particles into the metal surface, portions of said particles being exposed at the surface of the rolled article, and applying an organic enamel composition to the said article surface.

2. The method of preparing a metal article having an enamel coating thereon, which comprises the steps of applying an inorganic powder to a surface of a metal billet, said powder being friable and having a particle size not exceeding 60 mesh, the powder being composed of a substance harder than the billet metal, rolling the powder and billet for reducing the billet to the desired thickness for the article and thereby effecting extension of the surface area in contact with the powder and thereby effecting embedding and adhesion of powder particles into the metal surface and breakage of the particles into particles of 1 to 15 microns size with portions of the particles being exposed at the surface of the rolled sheet, and applying an organic enamel composition to said embedded surface at a coating weight of 2 to 15 milligrams per square inch.

3. The method of preparing a metal article having an enamel-coated surface, which comprises preparing a malleable metal billet thicker than the predetermined thickness of the article, applying to the surface of the billet

at which enamel coating is to be performed a layer of loose powder particles of an essentially non-malleable material having a hardness greater than that of the billet metal providing said surface and having a particle size not exceeding 60 mesh, rolling the billet and powder to elongate the same and establish the said predetermined thickness thereof and therewith causing particles of said hard material to become embedded in the surface during the elongation thereof, and applying an enamel to the said particle-embedded surface.

4. The method as in claim 3, in which the particles are of brittle material, and are fractured to smaller sizes during the rolling.

5. The method as in claim 3, in which loose particles are removed prior to the application of the enamel.

6. The method as in claim 3, in which the article is a sheet, and the prepared billet has a thickness about four times the predetermined final thickness, and in which the particles and billet are cold-rolled to said predetermined thickness.

7. The method of preparing an internally enameled metal tube, which comprises preparing a billet having a longitudinal internal channel filled with a powdered resist having a hardness greater than that of the billet metal providing such channel, the resist powder having a particle size not exceeding 60 mesh, rolling the billet to provide a strip having metal laminations separated by the residue of said resist and wherewith particles of the resist become embedded in the internal surfaces of the laminations, the laminations being integrally connected by metal at the edges of the resist residue, moving the laminations apart to form a tube, and applying an organic enamel to the internal surfaces of metal and embedded resist.

8. The method as in claim 7, in which loose resist material is removed from the interior of the tube before enamel is applied.

9. The method of preparing an internally enameled tubular body, which comprises preparing a billet having a longitudinal internal channel filled with a powdered brittle resist material having a hardness greater than that of the billet metal providing such channel, said resist material being essentially non-malleable under pressure and having a particle size not exceeding 60 mesh, rolling the billet to provide a strip having metal laminations separated by the elongated residue of the resist material and to embed particles of the resist material in the internal surfaces of the laminations, the laminations being integrally connected by metal at the edges of the resist residue, continuing the rolling in the cold until the laminations are of predetermined thicknesses and moving the strip around roll surfaces to cause the laminations to move relative to one another, thereafter moving the laminations apart to form a tube, and applying an enamel to the internal surfaces of metal and embedded resist.

10. The method of preparing an internally enameled metal tube, which comprises preparing a metal billet having a longitudinal internal channel with particles of an inorganic powdery resist therein having a hardness greater than that of the billet metal providing such channel, said particles being not over 60 mesh in size and being friable when pressed together during rolling, wherewith during the rolling parts of individual particles are caused to become embedded in and adherent to the metal while other parts of the embedded particles project from the internal metal surface and provide a capillary coating thereon, said rolling being effective to produce a strip having metal laminations separated by a layer of said resist with the laminations connected at their edges by integrating metal, bending the laminations apart to form a tube, and applying an organic enamel composition capable of wetting the resist material to the internal surfaces of the tube.

11. The method of preparing metal sheets having enamel coating thereon, which comprises preparing a metal billet having an internal longitudinal channel containing an inorganic powdery material which is harder than the billet metal with the powder having a particle size not exceeding 60 mesh, rolling the billet with the powder therein wherewith the billet metal is extended to produce a laminate strip having the laminations separated by the extended residue of the powder and thereby effecting embedding and adhesion of powder particles into the channel surfaces with portions of the embedded particles being exposed beyond the channel surfaces, terminating the rolling when the strip has a thickness dimension from the powder residue to the adjacent strip surface equal to that of the metal sheet base to be produced, the billet and strip having integral marginal metal portions enclosing the powder during rolling, severing marginal portions from the rolled strip along longitudinal lines intersecting the powder residues, separating the remaining portion of a strip between said severance lines and along the powder residue to provide a metal sheet having powder particles embedded therein, and applying an organic enamel composition to the said particle-embedded surface of said metal sheet.

12. An article of manufacture comprising an integral tubular metal body having embedded in its internal surface particles of a powdery refractory material essentially covering the said surface with parts of embedded particles projecting from the metal surface, said powder having a particle size not exceeding 60 mesh and being of a material harder than the material of said metal body, and a baked organic enamel coating covering the metal and particles and present between the particles and providing a continuous exposed surface.

13. An article comprising a rolled metal surface having embedded therein microscopic particles of an essentially non-malleable material harder than the said metal and providing a microscopically porous structure adherent to the metal and wettable by a baked organic enamel composition, and an enamel occupying the pores and providing a continuous exposed surface.

References Cited in the file of this patent

UNITED STATES PATENTS

254,199	Cosgrove	Feb. 28, 1882
377,317	Marshall	Jan. 31, 1888
1,536,524	Pfersdorff	May 5, 1925
2,158,461	Koehring	May 16, 1939
2,187,086	Koehring	Jan. 16, 1940
2,354,113	Gould	July 18, 1944
2,375,334	Valyi et al.	May 8, 1945
2,906,006	Neel	Sept. 29, 1959