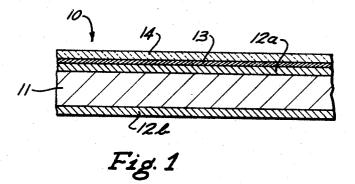
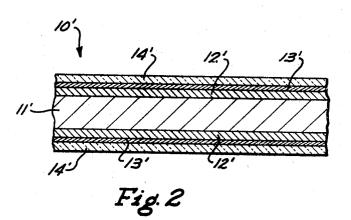
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D. S. HUBBELL ET AL 3,475,141 PORCELAIN-BNAMEL ON GALVANIZED STEELS BY MEANS OF AN ALUMINUM COAT Filed Dec. 7, 1966





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3,475,141 PORCELAIN-ENAMEL ON GALVANIZED STEELS BY MEANS OF AN ALUMINUM COAT Dean S. Hubbell and Robert E. Holmgren, Connersville, Ind., assignors to H. H. Robertson Company, Pitts-burgh, Pa., a corporation of Pennsylvania Filed Dec. 7, 1966, Ser. No. 599,949 Int. Cl. B23p 3/20; C23c 1/08; C23d 3/00 S Cl. 29-183 5 2 Claims U.S. Cl. 29-183.5

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### ABSTRACT OF THE DISCLOSURE

Porcelain enameled galvanized steel sheets and a method of preparing them. Galvanized steel is covered with a layer of aluminum or aluminum-rich alloy. A por- 15 celain enamel coating is fused to the covering layer.

This invention relates to porcelain enameled articles 20 such as building panels, having a galvanized steel core and to a method of making such articles.

#### PRIOR ART

The application of porcelain-enamel coatings to steel sheets has been practiced for many years. Such coatings are quite brittle and tend to shatter when subjected to impact. Any cracks or openings in the porcelain-enamel coating allow corrosion of the steel core to commence, the corrosion progressively undercuts the porcelain-enamel coating and destroys the bond between the coating and the steel sheet. To prevent the steel corrosion, one naturally considers a protective zinc or zinc-rich coating on the steel sheet as applied by the conventional galvanizing treatments.

However, heretofore it has not been possible to apply a porcelain-enamel coating to a galvanized steel sheet. The porcelain-enamel coating is essentially a fused coating formed from a bisque resulting from a spray-applied water suspension of glass frits, opacifiers, coloring oxides and other additives. Such water suspensions are called porcelain enamel slips. In order to fuse the bisque and create an adherent porcelain-enamel coating, it is necessary to heat the bisque-coated metal to a temperature above bisque melting point, i.e., about 900 to 1100° F. for low melting frits and about 1100 to 1600° F. for the high melting frits which are normally applied to steel sheets. At these temperatures which are required for fusing the porcelain enamel coating, the zinc film on the steel core will volatilize in the porcelain-enameling fur-50nace, since zinc has a substantial vapor pressure at tem-peratures of about 850° F. and higher. The zinc thus contaminates the porcelain-enamel coating and, more importantly, is removed from the steel core so that its protective action is no longer available. Where the zinc film 55 is fully alloyed with the steel of the sheet, the adverse volatilization does not occur. However, the porcelainenamel coating materials do not develop a suitable bond with the exposed zinc-steel alloys and for this reason the fully alloyed galvanized steel sheets are useless for por- 60 celain-enamel usage.

In summary there has been no successful commercial application of a porcelain-enamel coating to a galvanized steel sheet heretofore.

## THE PRESENT INVENTION

According to this invention a conventional galvanized steel sheet is coated with a thin film of aluminum or aluminum-rich alloy. The resulting aluminum coated galvanized steel sheet is thereafter coated with a porcelain-enamel composition having suitable bonding properties for the aluminum film. The porcelain-enamel coatings which

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are applied to aluminum sheets in general have a fusion temperature around 1000° F. which is less than the fusion temperature of porcelain-enamel coatings which are applied to steel sheets. The porcelain-enamel coatings achieve a reliable bond with the film of aluminum or aluminum-rich alloy. The aluminum or aluminum-rich alloy, in turn, is reliably bonded to the galvanized steel sheet. The resulting article exhibits the corrosion resistance of galvanized steel and has the long-life expectancy of a 10 porcelain-enameled article.

### OBJECTS

The principal object of this invention is to provide a porcelain-enameled galvanized steel article.

A further object is to provide a method of making a porcelain-enameled galvanized steel article.

These and other objects of the invention will be described in the following detailed description by reference to the accompanying drawings in which:

FIGURE 1 is a cross-sectional illustration of a porcelain-enameled galvanized steel article according to this invention; and

FIGURE 2 is a cross-sectional illustration of an alternative embodiment of the porcelain-enameled galvanized 25 steel article of this invention.

#### GALVANIZED STEEL

The galvanized steel sheets with which this invention is concerned have an essentially uniform steel thickness from about 28 gauge through about 12 gauge. These sheets of ordinary steel are protectively coated with a film of zinc metal or zince-rich alloys by the galvanizing processes which are well known in the metallurgical art. A typical galvanizing process involves the passage of a sheet of steel through a bath of the molten zinc-rich metal. The molten zinc-rich metal adheres to the steel surface in suitable thickness which can be regulated by directing blasts of air, blasts of steam or flame jets against the freshly coated metal while the zinc-rich coating remains molten. Various scrapers and roller devices also are known in the galvanizing arts to regulate the thickness of the protective zinc-rich coating. Occasionally the molten zinc is modified by the addition of tin, lead, aluminum, antimony, cadmium and other metallic ingredients for special purposes. The resulting galvanized steel is conventionally recoiled and delivered to the user in form of a coiled ribbon.

The zinc-rich coating (1) may be partially alloyed with the steel sheet at the interface of the two materials; (2) may be fully alloyed with the steel coating; or (3) may be essentially non-alloyed, but instead, merely adherent to the steel sheet. The conventional galvanized sheeting contains from about 0.17 to 2.5 ounces of zincrich coating material per square foot of the steel sheet (including both sides of the sheet).

Zinc-rich coatings also can be applied to steel sheets by vapor deposition processes which are carried out under conditions tending to minimize alloying of the zinc with the steel sheets. A preferred zinc-rich coating on the steel sheet constituting about 150-1000 micro-inches thickness (average). Where both sides of the steel sheet is coated with the zinc, the total zinc thickness thus is preferably from 300 to 2000 micro-inches.

## ALUMINUM COATING

After the galvanized steel sheeting is obtained, a thin film of aluminum metal or aluminum rich alloy is applied over at least one surface of the sheet. Preferably the aluminum coating is applied by vapor deposition processes to a thickness of about 25 to 100 micro-inches. Thus where both surfaces are coated with the aluminum or aluminum-rich alloys, the metal thickness ranges from about

50 to about 200 micro-inches. The aluminum or aluminum-rich alloy is firmly bonded to the galvanized steel sheet by the vapor deposition technique. It may be desirable to apply the aluminum coating to only one surface of the galvanized steel sheet, i.e., that surface which will subsequently be coated with porcelain-enamel. Conventional vapor deposition techniques provide a convenient means for applying aluminum coating to one side of the galvanized sheet. See, for example, U.S. Patent 2,996,037.

# PORCELAIN ENAMEL COATING

Porcelain enamel coatings suitable for application to aluminum or aluminum-rich alloys are described in U.S. Patents 2,544,139, 2,642,364 and 2,932,584. In general these are prepared from relatively low melting frits (lower melting than those normally associated with porcelainenameling of steel). Such coatings can be adhered to the aluminum surface in about three to ten minutes exposure in a porcelain-enameling oven maintained at temperatures of about 900 to 1100° F.

# EXAMPLE 1

A 24-gauge steel sheet was obtained with an essentially non-alloyed zinc-rich coating on one surface having an average thickness of 100 micro-inches. The zinc-rich coat-25ing was applied by vapor deposition. Exteriorly of the zinc coating was an aluminum alloy coating having a thickness of about 50 micro-inches. A commercial blue-color porcelain-enamel slip, as described in U.S. Patent 2,932,584, was spray coated on the aluminum coated surface. The sheet was passed through a commercial porcelain-enameling oven which was maintained at a temperature of 1000°  $F.\pm 50^{\circ}$  F. The residence time in the oven was about five minutes. The article was removed from the oven and aircooled. The resulting enamel coating was about two mils in thickness. The coating was visually attractive and appeared to be tightly adherent to the metal substrate. There was no detectable evidence of zinc volatilization in porcelain-enamel coating or in the porcelain-enameling oven.

#### **EXAMPLE 2**

A 24-gauge sheet of steel was coated with an essentially non-alloyed zinc-rich coating on one surface having an average thickness of 100 micro-inches. The zincrich coating was applied by vapor deposition. A film of aluminum alloy, 5 micro-inches thick, was applied exteriorly over the zinc coating. The same blue-color porcelain-enamel slip described in Example 1 was sprayed over the aluminum coating. The article was passed through the commercial porcelain-enameling oven maintained at a temperature of  $1000^{\circ}$  F. $\pm 50^{\circ}$  F. in about five minutes and thereafter allowed to air cool. The porcelain-enamel coating was about two mils thickness. The 4

coating was visually attractive and was tightly adhered to the metal substrate. There was evidence of some zinc volatilization in the porcelain enamel coating or in the porcelain enameling oven, indicating that the thin aluminum coating was not capable of suppressing zinc volatilization.

Referring to FIGURE 1, there is illustrated a porcelainenameled galvanized steel sheet 10 according to this invention. The article includes a steel sheet core 11 having a thickness of about 28-gauge to about 12-gauge. The steel is coated with a zinc-rich protective coating 12. One surface 12*a* of the sheet is covered with an aluminum-rich coating 13 which in turn is coated with a porcelain-enamel decorative coating 14. In a typical service as a build-15 ing construction sheet, for example, the porcelain-enamel surface 14 will be exposed to the external weather whereas the zinc-rich surface 12*b* will be sheltered from the weather. The steel core 11 remains protected against corrosion.

In FIGURE 2, the aluminum-rich coating 13' extends as an envelope over the entire galvanized steel sheet 11' and over its zinc-rich coating 12'. The porcelain-enamel coating 14' may be applied over both surfaces (as shown) or over only one surface. Typically the proposed exposed surface will be coated with a desired color porcelainenamel and the proposed unexposed surface will be undecorated, although a paint coat may be applied.

- I claim:
- 1. As an article of manufacture:
- a galvanized steel sheet;
- a coating of aluminum or aluminum-rich alloy applied over at least one surface of the said sheet;
- a porcelain-enamel coating applied over the said coating of aluminum or aluminum-rich alloy.

2. The article of claim 1 wherein the said galvanized steel sheet has a steel core with a thickness of 28-gauge to 12-gauge and a

- zinc-rich coating from 150 to 1000 micro-inches thick; and
- 40 the said coating is from 25 to 100 micro-inches thick.

#### **References Cited**

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HYLAND BIZOT, Primary Examiner

U.S. Cl. X.R. 29—195