

A MULTI-LAYER COMPOSITE STRUCTURE

This invention relates to a multi-layer composite structure, and in particular, to a composite structure having a layer bonded to the substrate of the composite structure to impart resistance to delamination when subjected to impact and/or thermal shock.

Many attempts have been made by industry to make a multi-layer composite structure including a substrate of appreciable strength and stiffness, wherein the layers are resistant to delamination when subjected to high impact or when subjected to thermal shock. When subjected to high impact from either side of the structure, one of the layers, the finish layer, may deform, crack, craze, or chip, and another layer may delaminate from the substrate. Delamination may also occur when the composite structure is subjected to thermal shock.

According to a first aspect of the present invention, there is provided a thermal-shock resistant composite structure comprising:

a metal substrate having a ceramic enamel layer on at least one side thereof;

the ceramic enamel layer having bonded thereto by means of a silane coupler a layer of plastics to form a reinforced laminate;

the plastics layer having a thickness of at least 1/8 in. (3.175 mm) and having a density between about 20 lbs. per cu. ft. and about 125 lbs. per cu. ft. (320 and 2000 kg m⁻³) whereby the composite structure is resistant to delamination when subjected to a sudden temperature change of at least about 180 degrees Fahrenheit (100 degrees Centigrade).

According to a second aspect of the present invention, there is provided a high-impact resistant

delamination when subjected to thermal shock.

In a further embodiment of the invention, an enamelled-steel composite structure has a reinforced-plastics layer chemically bonded to one side.

5 A relatively inexpensive method for bonding a resin layer to an enamelled-steel plumbing fixture is also provided.

The invention may be put into practice in many ways, but certain specific embodiments will now be
10 described, by way of example, with reference to the drawings, in which;-

Fig.1 is a top plan view of an enamelled-steel bathtub constructed in accordance with the invention;

Fig.2 is an elevational view of one end of the
15 bathtub of Fig.1;

Fig.3 is a top plan view of an enamelled-steel washbasin constructed in accordance with the invention;

Fig.4 is an elevational view of the washbasin
of Fig.3;

20 Fig.5 is a top plan view of an enamelled-steel shower tray constructed in accordance with the invention;

Fig.6 is an elevational view of the shower
tray of

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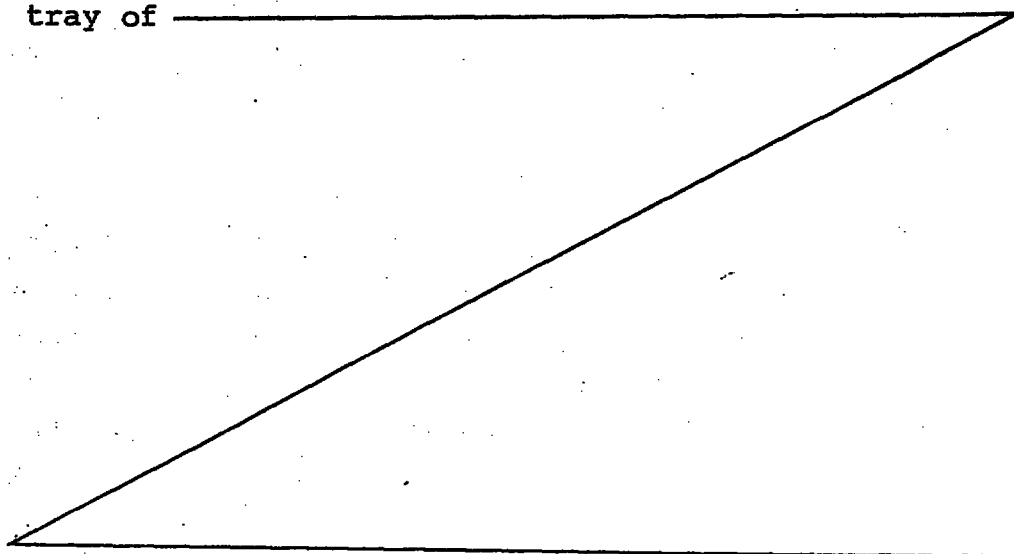


Fig.5;

Fig.7 is an isometric view of an enamelled-steel panel constructed in accordance with the invention; and

Fig.8 is a greatly enlarged sectional view taken from within the broken line circles of Figs.2,4,6 and 7 which illustrates the composite structure of the invention.

In Figures 1 to 7, enamelled-steel plumbing fixtures and an enamelled-steel wall panel such as is used for bathtub surrounds or shower stalls, are constructed in accordance with the present invention. The bathtub 10, washbasin 12, shower tray 14, and wall panel 16, are all formed having the composite structure 20 shown in Figure 8.

Composite structure 20 includes a substrate 22 of steel to which enamel layers 24, 26 are bonded on either side. In accordance with general practice in the manufacture of enamelled-steel plumbing fixtures, the enamel layers 24, 26 have a thickness in the range of about 1/64 to 1/32 of an inch (0.39 to 0.79 mm). The enamel consists of inorganic oxides with a high concentration of silicon dioxide, ^{i.e. a ceramic enamel} forming a glassy layer when fused to the steel substrate 22.

After the plumbing fixture or wall panel has been enamelled, a plastics layer 28 is bonded to the enamel layer 26. The plastics material may be applied for example, by spray-up, hand lay-up, reactive or resin injection or insert moulding, or such moulding with reinforcement, or resin-transfer moulding (RIM, RRIM, or RTM). The thickness of plastics layer 28 may vary. For example, in the bathtub shown in Figure 2, the side walls may have a thickness of plastics material as little as 1/8 inch (3.175 mm) and the base or sump as little as 1/4 inch (6.35 mm). Such thicknesses are adequate to provide an effective amount of plastics on the bathtub 10

so that it is resistant to chipping, cracking, crazing, deformation and delamination when subjected to impact forces of energy levels to which an unreinforced product would not be resistant. Also, the plastics layer resists delamination when subjected to thermal shock.

Various resins may be used in practising the present invention, for example : unsaturated polyester containing vinyl monomer, epoxy, polyurethane, isocyanurate, nylon and others. The resin may be either foamed or unfoamed, with or without a filler such as glass fibres and/or aluminium trihydrate when bonded to an enamelled-steel structure. When using unsaturated polyester resin containing a vinyl monomer, the bonding materials or couplers found suitable are the silane coupling agents such as a vinyl silane, for example 3[2(vinyl benzylamino) ethylaminol propyltrimethoxy silane.

The resin can be filled to provide reinforcement by any suitable material, for example: glass spheres, fibres and weaves; ceramic spheres and fibres; boron; carbon fibres; graphite; wollastonite; an aromatic polyamide fibre, made, for example, by Dupont Co.

The enamelled-steel fixture is incorporated into the composite structure by means of insert-moulding techniques. The resin mixture is introduced into the mould to provide a packing factor of from about 20% to 100%. The packing factor is the ratio of the volume of resin mixture to the volume of the mould.

A typical resin mixture is formulated of the following compounds and materials:

	<u>Parts</u>
Unsaturated Polyester Resin Containing Vinyl Monomer (Pioneer 236) R.T.M.	100
Aluminium Trihydrate	100
1/4" (6.35mm) Chopped Fibreglass (OCF 832-FC)	5

Cumene Hydroperoxide	0.5
Dimethylethanolamine	3.5
Polymethylene Polyphenylisocyanate	10
(Upjohn Papi 901)	
Silicone Surfactant (Dow Corning 193)	0.3
Pigment	0.5
Water	0.25

In practising the invention, it is preferred that the RIM or RRIM process be employed although other means for applying the resin, whether it is foamed or unfoamed, may be used. For example, an enamelled-steel plumbing fixture such as a bathtub is placed in a mould in which a resin, such as an unsaturated polyester containing a vinyl monomer, with or without a filler, a reinforcement, a surfactant, a catalyst, a blowing agent and a vinyl silane coupler which can be part of the mixture or can be applied to the fixture as a primer, are mixed under high pressure, injected into the mould, and allowed to cure. The mould cycle is at least 1 minute for particulate composite structures or about 3 minutes for a bathtub.

The enamelled-steel bathtub is removed from the mould. The resulting plastics-backed bathtub has bonded thereto a resin foam layer of an unsaturated polyester-polyurethane copolymer which is resistant to delamination when subjected either to high impact forces or thermal shock. Further, the finished enamel surface is resistant to chipping, cracking, or crazing when subjected to direct impact forces and resists deformation and pop-off of the finish layer when subjected to reverse forces such as are encountered during installation or shipping.

The physical properties and characteristics of the plastics-backed enamelled-steel composite structure are equal to or better than most of the physical properties

or characteristics of existing state-of-the-art sanitaryware products. The improved product performance is exemplified by the impact test results shown in the following tables. The testing procedure followed is that of American National Standard Z 124.1-1980 4.3 Impact Loads except that the test area has a 3" (76.2 mm) unsupported diameter.

Table I shows the impact that is required to cause damage to the finished surface when the impact is applied to the finished surface of the sanitaryware and is the type of damage that may result after its installation. Table II shows the results of the reverse-impact test, that is, when the load is applied to the plastics-backed surface of the sanitaryware and is the type of damage caused by handling, trucking, and installation.

TABLE I

Direct Impact

<u>Sanitaryware</u>	Impact to cause Damage (1) to <u>finished surface</u> (ft-lbf) (Joules)	
Fibreglass-Reinforced Polyester/ Gel Coat	1.50	2.03
Fibreglass-Reinforced Polyester/ Acrylic	2.00 ⁽²⁾	2.71
Enamelled Steel	1.25	1.69
Enamelled Cast Iron	1.75	2.37
Plastics-Backed Enamelled Steel of the Present Invention	2.50	3.39

TABLE II

Indirect Impact

<u>Sanitaryware</u>	<u>Impact to cause damage (1) to finished surface</u> (ft-lbf) (Joules)	
Fibreglass-Reinforced Polyester/ Gel Coat	1.0	1.36
Fibreglass-Reinforced Polyester/ Acrylic	2.5	3.39
Enamelled Steel	1 - 2	1.36-2.71
Enamelled Cast Iron	1 - 2	1.36-2.71
Plastics-backed Enamelled Steel of the Present Invention	5	6.78

(1) Damage is defined as a craze, dent or material delamination of the finished surface layer.

5 (2) Incipient structural damage with surface cracking observed at an impact energy level of 4.0 ft-lbf (5.42 Joules).

10 Another physical property of the plastics-backed enamelled-steel structure of the present invention is its ability to resist thermal shock. A product such as a wall panel is subjected to temperatures of approximately 180°F (82°C), and thereafter the panel is removed from the temperature source and placed in a temperature environment of 0°F (-18°C) or below, for example, a
15 freezer. The sudden change in temperature through 180 degrees Fahrenheit (100 degrees Centigrade) does not cause delamination of the plastics layer from the enamelled-steel panel.

20 In a further embodiment of the invention, a thermal-shock resistant composite structure comprises a

metal substrate having a ceramic enamel layer on at least one side thereof;

the ceramic enamel layer having bonded thereto by means of a silane coupler a layer of plastics to form a reinforced laminate;

the plastics layer having a thickness of at least 1/8 in. (3.175 mm) and having a density between about 20 lbs. per cu. ft. and about 125 lbs. per cu. ft. (320 and 2000 kg m⁻³) whereby the composite structure is resistant to delamination when subjected to a sudden temperature change of at least about 180 degrees Fahrenheit (100 degrees Centigrade).

In another embodiment, a high-impact composite structure comprises a metal substrate having a ceramic enamel layer on at least one side thereof;

the ceramic enamel layer having bonded thereto by means of a silane coupler a layer of plastics material to form a high-impact-resistant laminate;

the plastics layer having a thickness of at least 1/8 in. (3.175 mm) and a density of between about 20 lbs. per cu.ft. to about 125 lbs. per cu.ft. (320 and 2000 kb m⁻³) whereby the finished layer of the composite structure is resistant to delamination when subjected to an impact of at least about 2.0 ft.-lbf. (2.71 Joules) applied to the finished layer and when an impact of at least about 3.0 ft.-lbf (4.07 Joules) is applied to the surface of the plastics layer.

The plastics layer in any of the above-described embodiments may be porous, or non-porous, or a combination of those, some parts being porous and some non-porous.



CLAIMS:

1. A thermal-shock resistant composite structure comprising:
 - a metal substrate having a ceramic enamel
 - 5 layer on at least one side thereof;
 - the ceramic enamel layer having bonded thereto by means of a silane coupler a layer of plastics to form a reinforced laminate;
 - the plastics layer having a thickness of at
 - 10 least 1/8 in. (3.175 mm) and having a density between about 20 lbs. per cu. ft. and about 125 lbs. per cu. ft. (320 and 2000 kg m⁻³) whereby the composite structure is resistant to delamination when subjected to a sudden temperature change of at least about 180
 - 15 degrees Fahrenheit (100 degrees Centigrade).
2. A high-impact resistant composite structure comprising:
 - a metal substrate having a ceramic enamel
 - layer on at least one side thereof;
 - 20 the ceramic enamel layer having bonded thereto by means of a silane coupler a layer of plastics to form a high-impact-resistant laminate;
 - the plastics layer having a thickness of at
 - least 1/8 in. (3.175 mm) and a density between about 20
 - 25 lbs. per cu. ft. and about 125 lbs. per cu. ft. (320 and 2000 kg m⁻³) whereby the finished layer of the composite structure is resistant to delamination when subjected to an impact of at least about 2.0 ft.-lbf. (2.71 Joules) applied to the finished layer and when an
 - 30 impact of at least about 3.0 ft.-lbf (4.07 Joules) is applied to the surface of the plastics layer.
3. A composite structure as claimed in claim 1 or claim 2, in which the substrate is enamelled steel.
4. A composite structure as claimed in claim 1 or
- 35 claim 2, in which the composite structure has the



configuration of a plumbing fixture.

5. A composite structure as claimed in claim 4, in which the substrate is an enamelled-steel bathtub.
6. A composite structure as claimed in claim 4, in which the substrate is an enamelled-steel sink.
7. A composite structure as claimed in claim 4, in which the substrate is an enamelled-steel shower tray.
8. A composite structure as claimed in claim 3, in which the substrate is a ceramic enamelled wall panel.
9. A composite structure as claimed in any one of claims 1 to 8, in which the coupler is a 3[2(vinyl benzylamino) ethylamino] propyltrimethoxy silane.
10. A composite structure as claimed in any one of claims 1 to 9, in which the plastics is a foam having a packing factor between about 20% and about 100% by volume.
11. A composite structure as claimed in claim 10, in which the plastics is either a solid or a foamed unsaturated polyester containing a vinyl monomer.
12. A composite structure as claimed in any one of claims 1 to 9, in which the plastics material is an unsaturated polyester-polyurethane copolymer.
13. A composite structure in accordance with any one of claims 1 to 12, in which the plastics material is reinforced by a material selected from the group consisting of glass spheres, glass fibres, glass weaves, ceramic fibres, ceramic spheres, boron, carbon and graphite fibres, wollastonite and aromatic polyamide fibre.
14. A composite structure as claimed in claim 13, in which the plastics material is a glass-reinforced unsaturated polyester-polyurethane copolymer.
15. A composite structure as claimed in any one of



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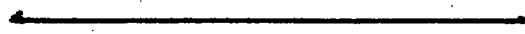
claims 1 to 14, in which the plastics material is an unsaturated polyester-polyurethane copolymer foam and in which the layer is porous or non-porous or a combination thereof.

5 16. A composite structure as claimed in any one of claims 1 to 15, in which the plastics material contains a surfactant.

10 17. A composite structure substantially in accordance with any one of the embodiments as specifically described herein with reference to the drawings.

18. A method of making a composite structure substantially in accordance with any one of the embodiments as specifically described herein.

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