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METHOD OF INTEGRATION OF PARTICULATE MATERIAL WITHIN A METAL SUBSTRATE AND THE PRODUCT THEREOF

Filed Sept. 3, 1968 2 Sheets-Sheet 1

Fig. 1.

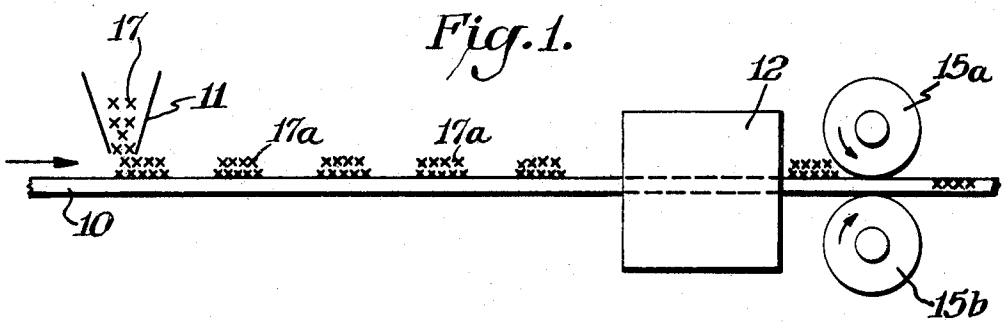


Fig. 2.

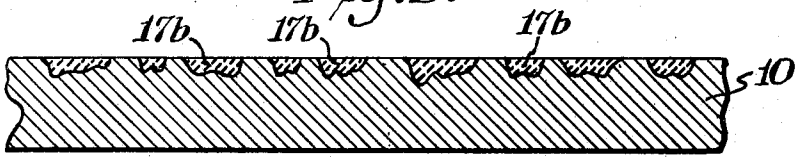
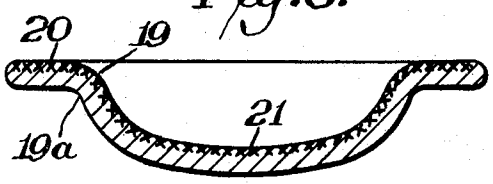


Fig. 3.



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Fig. 4.

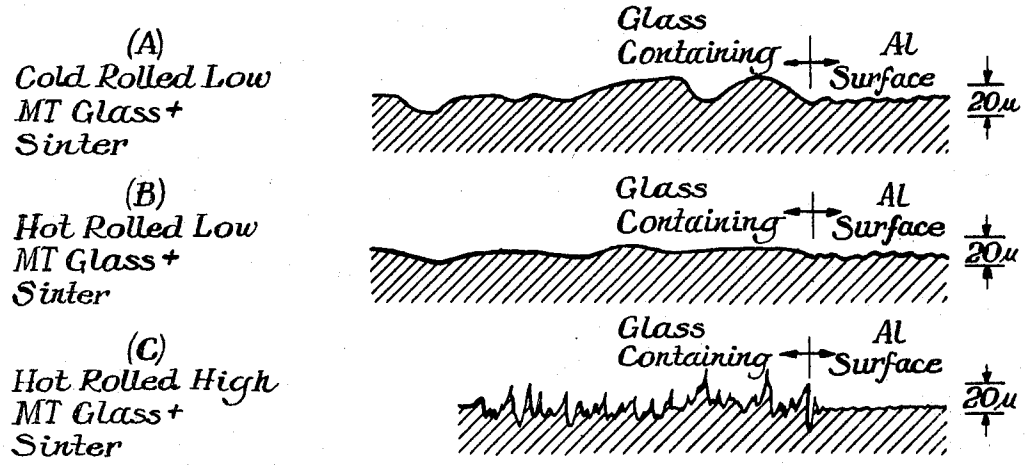
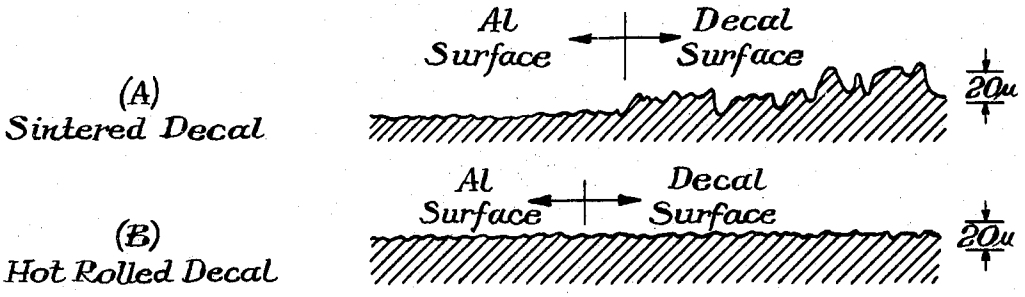


Fig. 5.



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METHOD OF INTEGRATION OF PARTICULATE MATERIAL WITHIN A METAL SUBSTRATE AND THE PRODUCT THEREOF

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Continuation-in-part of application Ser. No. 403,020, Oct. 12, 1964. This application Sept. 3, 1968, Ser. No. 756,891

Int. Cl. C03c *17/06*

U.S. Cl. 117—22 24 Claims

ABSTRACT OF THE DISCLOSURE

A non-porous metal substrate having embedded within its surface and substantially coplanar therewith attached particulate glass, glass-metal mixtures or glass-metal composites, and a method for the production thereof.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application Ser. No. 403,020, filed Oct. 12, 1964, now abandoned.

BRIEF SUMMARY OF THE INVENTION

Generally, this invention comprises an article of manufacture of the type taught in application Ser. No. 403,020 comprising a non-porous metal substrate carrying within its surface a particulate substance from the class consisting of glass, glass-metal mixtures and glass-metal composites impressed into the surface to a degree such that the particulate substance is firmly embedded in, and attached to, the substrate with the outwardly facing surfaces of the particulate substance substantially co-planar with the surface of the substrate, and a method for the production thereof.

DRAWINGS

The subject matter of this invention together with important characteristics thereof and a preferred apparatus for its production are detailed in the following drawings, in which:

FIG. 1 is a schematic drawing illustrating a preferred method of producing the manufacture of this invention utilizing a compaction roll set for the embedding of the particulate material which it is desired to join with the metal substrate,

FIG. 2 is a schematic vertical sectional representation of the manufacture produced by this invention,

FIG. 3 is a schematic vertical sectional representation of a manufacture according to this invention after subjection to cold draw forming,

FIG. 4 is a comparative surface profilometer plot, with individually distinctive representations of glass and metal phases omitted, in which tracing (A) is that of a metal substrate having impressed therein a low maturing temperature (abbreviated MT in the drawing legends) particulate glass by cold rolling followed by a sinter treatment, (B) is that of a hot-rolled low maturing temperature particulate glass product according to this invention which has also been subjected to a final sinter treatment and (C) is that of a hot-rolled high maturing temperature particulate glass product according to this invention, sintered as a final step, and

FIG. 5 is a comparative surface profilometer plot in which tracing (A) is that of a glass decalcomania applied solely by sintering, without any rolling, and (B) is that of a hot-rolled glass decalcomania.

DETAILED DESCRIPTION

The compositing of metal subtrates, particularly those which are relatively non-prous, such as rolled sheet stock and the like, with particulate glass, mixed glass-metal or glass-metal composites is a difficult task. Porous metal articles have been coated with ceramics by hot forging processes such as those described in U.S. Patents 2,826,512 and 2,858,235, and some success has been achieved in the cold compositing of ceramics to metals by the heavy size-reduction process taught in U.S. Patent 3,087,240; however, smooth, flush, highly adherent particulate glass, glass-metal mixtures, or glass-metal composite surface intergration with nonporous metal substrates of the type represented by sheet stock, castings, electroplates and similar smooth, continuous surfaces has hitherto not been attained.

A primary object of this invention is to provide a manufacture consisting of a non-porous metal substrate carrying within its surface highly adherent particulate glass, glass-metal mixtures, or glass-metal composites embedded within the metal to a degree such that substantial coplanarity is achieved as regards the metal substrate and the particulate substance. Other objects include the provision of a manufacture of the type described which is adapted to employment as a cold-drawing stock, and the provision of a method of producing the manufacture described which does not necessitate the use of extremely high temperatures nor the application of compositing forces reducing the thickness of the metal substrate stock by a large percentage, or otherwise working the metal to an extent altering its as-received physical properties.

The invention calls for first heating the metal substrate and the particulate substances to be embedded therein sufficiently to effect a secure bond therebetween. The heating can be separately conducted for each where the processing temperatures are widely different, or can be concurrently effected where the temperatures overlap.

Compositing according to this invention requires that the temperature of the glass employed either as the particulate substance per se or as a component of the particulate glass-metal mixtures or glass-metal composites be such that the viscosity of the glass, when brought into contact with the metal substrate and thereafter impressed into its surface, be in the range of about $10^{2.8}$ to 10^{7} poises. If the viscosity is higher than about 10^{7} poises, the glass has a tendency to pulverize rather than flatten under the compressive force accomplishing the embedding, and little or no compositing with the substrate surface occurs. On the other hand, if the glass viscosity is too low, the glass will smear under compaction without entering into the substrate metal, and no compositing will be achieved.

The determination of viscosity of glass melts is a time-consuming and laborious task which can be avoided in many instances by use of the maturing temperature test as an approximate check on glass viscosity. It happens that the observable viscosity attained in the course of determining maturing temperature as hereinafter described lies within the middle part of the permissible viscosity range $10^{2.8}$ to 10^{7} poises for the practice of this invention.

Determination of maturing temperature is effected by grinding the glass under test to a fineness of —325 mesh.

Each ground glass sample consists of 10–20 gms. of the glass powder distributed as a layer about 3 mils thick on a 16 gage stainless steel support plate. Individual samples are placed in the test furnace maintained at a stable test temperature for 10 minutes each. The maturing temperature is that temperature at which the particulate glass sinters to form a continuous coating and, after a little practice, it is possible to duplicate maturing temperature measurements within about 15° C.

Satisfactory compositing, especially where coplanarity is an objective, also requires that the metal substrate surface be soft enough to accept the particulate substance under compressive forces which are limited in magnitude so as to effect only small substrate gage reductions, and thus the metal substrate must be heated. Generally, the temperature at which the metal substrate is supplied to the process should be within, or adjacent to, a preselected band of the conventional metal hot working temperature range. Greatest convenience in compositing is attained where the metal substrate temperature can be brought to about the same level as the temperature of the glass component to be joined therewith at which the glass viscosity is in the range of about $10^{2.8}$–10^{7} poises hereinbefore detailed. However, it is not always practicable to match the substrate temperature with the glass temperature, as, for example, where the metal might melt, or even vaporize, at a high glass maturing temperature, and then separate heating of each can be resorted to with good results.

It is convenient to consider metal substrates as falling into two general classes for the purpose of this temperature selection, the first being the relatively low melting point metals, melting in the range of about 400–800° C., typified by aluminum, magnesium, zinc and alloys of these metals, whereas the second is the high melting point group, melting in the range of about 800–1900° C., typified by copper and its alloys, stainless steel, low carbon steel, titanium and nickel, and alloys of these latter two metals.

As to the low melting point metals we have found that a temperature lying within the hot metal working temperature range for extrusion to about 120° C. thereabove is satisfactory when these metals are employed as substrates. High melting point metal substrates are generally satisfactorily composited at temperatures lying within the hot metal forming range for rolling to about 100° C. therebelow.

The following is a tabulation in degrees C. of hot working temperatures of typical metals of both low-melting and high-melting type compiled from "Metals Handbook" (1948 Edition) American Society of Metals, 7301 Euclid Avenue, Cleveland, Ohio, and "Aerospace Structural Metals Handbook," Syracuse University Press, Box 87, University Station, Syracuse 10, N.Y., which consolidates the hot metal working temperature ranges for the three operations forging, rolling and extrusion as a guide in the practice of this invention. It should be mentioned that the low temperature limit of each of the several tabulated ranges is applicable to the lowest melting metal or alloy to which the Handbook data extended, whereas the high temperature limit applied to the highest melting. Specific temperatures suited to specific compositions are obtainable by reference to the primary information sources given.

HOT WORKING TEMPERATURES OF METALS (° C.)

Metal	Melting Point Of Elemental Metal	Forging Range	Rolling Range	Extrusion Range
Low Melting Point:				
Al and Alloys	660	360–450	150–450	400–480
Zn and Alloys	420	[1] 200	[1] 200	250–300
Mg and Alloys	650	340–450	300–450	360–440
High Mlting Point:				
Cu and Alloys	1,083	620–870	680–870	650–1,090
Ti and Alloys	1,820	----------	430–950	----------
Stainless Steel	[2] 1,540	815–1,260	----------	----------
Carbon Steel	[2] 1,540	700–1,300	700–1,260	----------
Ni and Alloys	1,455	----------	650–1,260	----------

[1] Approximately.
[2] Fe.

It will be understood that only the immediate surface of the metal substrate need be heated to a plasticity permitting reception of the particulate substance therein, so that relatively thick metal masses can be surface-impregnated according to this invention by localized heating of the surface limited very precisely both in area and in depth, as by high frequency electric induction heating techniques, or the like. Under these circumstances the interior metal mass remains in non-plastic hard condition throughout the impregnation, thereby providing firm backup opposed to the compressive forces effecting the embedding.

This fact also makes it possible to coat a metal foundation mass without subjecting it to objectionably severe temperature or pressure conditions through the agency of a particularly receptive metal substrate, such as one of the low-melting metals, adhered to the outside surface of the foundation metal in accordance with the technique hereinafter taught in Examples 8 and 9.

Finally, where particulate glass-metal mixtures constitute the substance to be surface-integrated, the metal component should be heated to its sintering temperature.

From the foregoing, it will be seen that the temperature ranges for metal substrate processing are quite broad and thus permit the compositing of a wide variety of glasses having over-lapping temperature-viscosity equivalents therewith, so that concurrent heating of the particulate substance and the metal substrate is practicable in many cases, which is particularly convenient in the practice of this invention. Similarly, metal sintering temperatures are broad range, so that this additional requirement for glass-metal mixture powder compositing is not seriously limiting.

Finally, separate heating of the metal substrate or the glass-containing component has proved feasible, even where substantially different temperatures must be utilized in order to achieve the necessary glass viscosities and metal plasticities required. With this technique, the components to be composited are brought into contact at the different temperatures required for each and immediately compacted to form a composite before substantial changes in temperature can occur. Since the thermal conductivity of glass is approximately two orders of magnitude less than that of most metals, compositing can be readily achieved before temperature exchange between the metal substrate and the glass has time to proceed to a degree where the characteristics of either are brought outside the range of practicable compositing as hereinbefore described. Additionally, glass can be supplied in considerably coarser particle sizes where a higher temperature of glass than metal substrate is necessary, as for a high maturing temperature glass, for example, thereby avoiding rapid quenching of the glass by the colder substrate metal before compositing can be effected. Similar particle size adjustment is practicable for the reverse situation where the substrate metal supplied is hotter than the glass.

It will be understood, of course, that separate heating of metal substrate and particulate materials to be composited therewith is often useful even where approximate temperature equality therebetween is sought, as, for example, where a protective atmosphere oven is desirable to avoid surface oxidation or other deleterious effects as regards one, but where the same conditions cannot be tolerated for the other.

Embedding is effected before substantial cooling occurs by applying compressive force to the particulate substances distributed over the metal substrate in sufficient amount to embed and attach the particulate substances firmly within the surface of the metal substrate with outwardly-facing surfaces of the particulate substances substantially coplanar (i.e., within ± 10 microns of coplanarity with the surface of the metal substrate, after with the metal substrate incorporating the particulate substance therein is cooled to room temperature.

The density of population of the particulate embedded material can vary within a wide range from, typically, only about 1% or less of the final product surface area consisting of glass, glass-metal mixture, or glass-metal composite, to virtually 100% being the embedded material, with just enough of the metal substrate phase showing as to effect secure interlocks around the embedded material. Also, the particle sizes of the substances to be embedded can vary from extremely fine decalcomania powders to relatively coarse 100-mesh grade, or even coarser material, so that a great variety of decorative effects as well as surface-protective properties are readily attainable.

It is preferred, however, to obtain a visually perceptible island-like pattern of embedded material resembling that indicated by the multiple particle clusters of FIG. 1. Also, if the thickness of the particle clusters deposited on the substrate prior to embedding is relatively small and uniform, the compressive force application is correspondingly more uniform, which permits control of the surface appearance of the product as well as improves the adherence of the particulate material to the supporting metal matrix.

Referring to FIG. 1, a preferred method of preparing manufactures according to this invention where the essential temperatures of glass and metal overlap, so as to permit concurrent heating of the substrate and the particulate substance to be embedded therein, comprises the continuous processing of the substrate as a clean strip or other web **10**, passed from left to right and in sequence under a particulate substance applicator **11**, such as a spray gun or the like. Strip **10**, with solids distributed over its upper surface, then passes through an oven **12** and, immediately thereafter, before the metal substrate or the particles to be affixed thereto have had an opportunity to cool, past the particle-embedding pressure-applying means, which, in this instance, comprises a power-driven roll set **15***a*–**15***b*, between the nip of which strip **10** is threaded. The particulate material **17** can conveniently be applied as a slurry, e.g., a 30 volume percent suspension of solids in a suitable liquid adhesive, so that there is obtained a thin island-like distribution of multiplicities of particles over the surface of the metal substrate, as denoted at **17***a*. A typical adhesive which has given good results is a 50% methanol-50% epoxy resin mixture (e.g., that marketed as "Plastibond" by National Engineering Products, Inc., Washington, D.C.) The heat of oven **12** burns off the great bulk of the resinous binder, so that the strip exiting from the oven consists essentially of the hot substrate to which the particulate substance is temporarily adhered, clean of all else.

In the majority of the examples which follow, simultaneous obtainment of satisfactory compositing temperatures for both the particulate substance and the metal substrate was practicable in the range of 390° C. to 610° C. detailed, and, thus, this operation is the one concentrated on. As has already been described, separate heating of one or more of the materials involved before bringing the materials into contact for integration under compression is entirely feasible is satisfactory compositing temperature matching of the particulate glass and metal components cannot be had with the particular metal substrate used, although operation in this manner is somewhat less convenient.

Oven **12** can usually operate in an air atmosphere, although, if the metal substrate is susceptible to oxidation an inert gas atmosphere, such as argon, hydrogen or a similar gas, can be resorted to. The oven capacity should, of course, be sufficiently large to accommodate the substrate for a period of time long enough to effect full high-temperature attainment. In this regard, an oven residence time of 0.1–20 minutes is usual, depending upon the gage of the stock as-received, whether any preheating of strip **10** preceded entrance to oven **12**, and the final temperature desired.

The suitably heated strip **10** passes, without delay, from oven **12** to power-driven roll set **15***a*, **15***b* so that both metal and glass phases are in hot workable state under the compaction effect of the rolls. The inter-roll clearance is carefully set to produce only a nominal thickness reduction of substrate **10**, 0.5–4 mils reduction being best practice but somewhat greater reduction being tolerable. Compactions of this order have been found entirely adequate, as shown in FIG. 2, to firmly embed the particulate material **17***b* as individual particles, or interbonded agglomerates of several particles, within the substrate in substantially coplanar relationship with respect to the latter. This coplanarity is facilitated by flattening deformation of the particulate substance at the surface confronting the roll or other embedding mechanism, as can be clearly seen in FIG. 2. If the substrate layer heated to plasticity is of relatively small depth, e.g., less than the as-received diameters of the particles which are embedded, microscopic examination has revealed that similar deformation occurs at the bottom surfaces of the particulate material abutting against nonplastic interior metal. This is also true where a thin substrate overcoat is employed in conjunction with a high-melting foundation metal strip as backing, as taught in Examples 8 and 9 hereinafter set forth.

The attachment of embedded material to substrate metal is not limited to mechanical keying solely, it having been verified that there is also obtained extensive glass to metal bonding as regards embedded glass and receiving substrate. In this regard, it will be understood that the particulate attachment is not necessarily directly to the substrate as regards individual particles but, commonly, indirectly through adjacent particles or particulate agglomerates to which a given individual particle is itself bonded. In addition, abutting particles of concurrently embedded glass and metal bond together strongly under the heat and pressure at which the embedding is effected, so that integral agglomerates of high strength in themselves form and are immediately embedded as entities along with individual particles as indicated by the varied sizes of the embedded materials **17***b*, FIG. 2. After cooling to room temperature, embedded material **17***b* is thus anchored into the metal substrate as matrix with a strong enough bond to resist very severe mechanical stresses, such as those of deep drawing and the like, without objectionable spalling loss and with essentially zero deleterious effect on product appearance.

Thus, referring to FIG. 3, dish-shaped draws of flat composited stock to the relative degree shown are easily obtainable, it being observed that the tendency toward embedded particle separation is most noticeable at the inflectional points **19** and **19***a* existing between flange **20** and central portion **21**. The compressional, or inside bend **19***a* on the flange underside, is prone to the greatest flaking where the underside flange surface contains embedded material and, of course, the flaking propensity is increased with reduction of bend radii. In sharp contradistinction, enameled surfaces are capable of very little deformation without large-scale visible cracking or loss of the enamel coat. The improved results with this invention are probably due to the fact that the metal matrix surrounding each individual mass of embedded substance **78***b* takes most of the bending stress, with only a relatively minor tendency to pop the embedded material from their secure emplacements within substrate **10**.

If heated rolls **15***a*–**15***b* are employed in the compressive embedding, little or no unattached powder residue survives the passage of sheet **10** through the roll set. However, where water-cooled roll sets are utilized, a post-compaction annealing treatment of 10–20 minutes duration at a temperature of about 600° C. for all examples except Examples 4 and 13 serves to bond any residual loose surface powder to the substrate without much loss of coplanarity as hereinbefore taught.

In the following examples, except Example 12, the hot rolling was effected exclusively by a power-driven

roll set **15***a*–**15***b* of the type shown in FIG. 1 wherein the bearings were cooled by water circulation through cooling passages provided in the bearing housings. Since the rolling mill was small in size, incorporating rolls of 8½" dia. by 10" free length (exclusive of the 4" neck diameter at each roll end journaled for lengths of approximately 6" within the water-cooled sleeve bearings), the cooling of the bearings simultaneously chilled the roll surfaces to at least room temperature, and sometimes below, as evidenced by condensate droplet formation thereon. The samples processed were all of such small mass, and were passed through the mill at such a relatively high speed of 40 ft./min., that the rolls remained at substantially constant surface temperature throughout the entire experimental program.

EXAMPLE 1

It was desired to obtain a product surface comparison between hot compaction according to this invention and cold compaction practiced by the prior art as separate procedures for the attachment of particulate glass to smooth metal substrates.

Accordingly, a lead borosilicate glass containing iron cobalt black sintered inorganic pigment and having a low maturing temperature of about 525° C. (corresponding to a viscosity of approximately 10^4 poises) was employed in both instances, the glass being ground to a fineness of 100% through a 100-mesh screen. The glass was applied with methanol-thinned epoxy resin adhesive as a thin, well-distributed layer in the form of a 1" wide strip on a Type 1100 aluminum substrate of 4" nominal width, 1/16" thick.

Specimen (B) was hot-rolled immediately after heating to 580° C. by passage between the power-driven roll set **15***a*–**15***b*. An over-all reduction in thickness of 2 mils resulted, and the composited strip was finally annealed at 580° C. for 20 minutes.

Specimen (A) was prepared in identical manner with Specimen (B), except that the particulate glass was cold-rolled into the metal, after which the same anneal was performed as for Specimen (B).

Referring to FIG. 4, profilometer traces were taken transverse a width of ¼" to either side of one edge boundary of each composited strip on both of the specimens, denoted by the same letters (A) and (B) as hereinbefore assigned them. As can be seen in the right-hand regions of both tracings, the neighboring aluminum displayed only a small peak-to-valley variation of about 2 microns maximum. Specimen (B), in the composited region to the left of its tracing, evinced only a slight elevation over the adjoining aluminum averaging but 2.7 microns, with the maximum peak detected being about 5 microns.

In sharp contrast, cold-rolled specimen (A) was relatively rough in surface quality, averaging 7.5 microns above the aluminum surface, with a detected maximum peak-to-valley variation of 17.5 microns.

This test demonstrates that substantially coplanar embedding of particles is truly achieved according to this invention.

EXAMPLE 2

Several hot-rolled and cold-rolled circularly-shaped specimens of 4¼" diameter were made up as described in Example 1 using the same aluminum substrate as therein taught but, as the particulate embedded material, an intimate mixture of 75 volume percent ground glass and 25 volume percent powered aluminum, both of a fineness passing 100% through a 100 mesh screen. This glass, which had a maturing temperature of about 540° C. (corresponding to a viscosity of approximately 10^4 poises), was of the following composition by weight: PbO 34.3%, SiO_2 27.3%, Li_2O 2.2%, Na_2O 13.6%, K_2O 2.2%, TiO_2 13.4%, Sb_2O_3 2.7% and BaO 4.3%. The hot-rolled specimens were prepared by rolling conducted at about 580° C., followed by annealing at 580° C. for 20 minutes.

Each specimen was subjected to deep-drawing conducted at room temperatures producing dished products in which a distention of approximately ⅝" was produced within a diameter of 2½", duplicate specimens being utilized and the surfaces containing embedded particles including both convex and concave bends. The dished products so formed were of the general shapes shown in FIG. 3, with the side walls of the depression oriented at an angle of approximately 60°.

In the hot-rolled samples, no spalling but moderate cracking visible at 20 magnifications occurred in the regions corresponding to point **19**, FIG. 3. A profilometer measurement of maximum peak-to-valley roughness on flange **20**, where the material is subjected to pronounced lateral displacement in the course of drawing, gave a reading of only 7.5 microns maximum peak-to-valley roughness. There was no visually detectible difference in surface appearance between deformed and undeformed specimen areas where inspection was made without the aid of magnification.

The cold-rolled samples spalled heavily in drawn regions of the sample and, in addition, there was general spalling and cracking throughout the entire sample area apparent to the eye without magnification. A profilometer measurement on the flange 20 point corresponding to that chosen for the hot-rolled sample indicated a maximum peak-to-valley roughness of about 11 microns.

EXAMPLE 3

This test was conducted to evaluate the adhesion of manufactures according to this invention when subjected to the standard test of the ceramic industry, namely, exposure for 96 hours at room temperature to a 5% aqueous solution of ammonium chloride.

The two specimens were prepared using the same compositions and hot-rolling conditions as described in Example 2, and in one there was a concentration of embedded material approximately 10% of the surface area, whereas the other had approximately 100% embedded material surface coverage.

A lengthened test exposure of 112 hours total failed to develop any loss of embedded material in the vicinity of exposed edges, where accelerated attack could normally be expected, nor was there loss elsewhere in the samples.

EXAMPLE 4

The purpose of this test was to determine the surface quality obtainable where the particulate glass to be embedded in the metal substrate possessed a viscosity at the rolling temperature somewhat outside of the $10^{2.8}$ to 10^7 poise range found critical for the practice of this invention.

The glass utilized was a bottle glass ground to −100 mesh particle size having the analysis SiO_2 74.2%, Na_2O 17.7%, MgO 3.2%, CaO 4.3%, which possessed a viscosity of 10^8 —10^9 poises at a temperature of 650° C.

The metal substrate was Type 1100 aluminum sheet 50 mils thick, the ground glass being adhered thereto at room temperature as a 1" strip with a methanol-thinned epoxy resin adhesive and dried for 30 mins. before placement in an oven.

The metal substrate with attached strip was then heated to 650° C. for 10 mins. after which it was immediately passed hot through a roll set effecting a 2 mil reduction. The product was later given an annealing treatment by reheating to 650° C. for 10 mins. and then cooled to room temperature.

The strip formed by the particulate glass particles was well-defined on the metal substrate, but the particles were not securely embedded in the substrate, so that the strip was upraised to the touch and the particles were so loosely attached that they dislodged under light finger

brushing incident to testing the fact that the particulate glass strip was upraised instead of coplanar.

The surface was evaluated by profilometer was described in Example 1, and the tracing (C) of FIG. 4 obtained. It was found that pronounced roughness with a maximum peak-to-valley span in excess of 24 microns existed.

EXAMPLE 5

The efficacy of the method of this invention in the affixing of intricate glass decalcomanias to one of the low-melting metals, in this instance Type 1100 aluminum sheet, was appraised by this example.

Here the decalcomanias were conventional products in the form of different antique automobile designs marketed for the decoration of glass tumblers and the like by Commercial Decal, Inc., Mount Vernon, N.Y. The maturing temperature of the decalcomania glass was measured as 540° C., at which the corresponding viscosity was approximately 10^4 poises.

The advantage of hot-rolling as compared to merely hot application of the decalcomanias was investigated here.

Referring to FIG. 5, Specimen (A), the profilometer tracing to the right of the aluminum metal demarcation boundary showed marked roughness with maximum peak-to valley span of the order of 17 microns for the decalcomania which was merely applied and thereafter sintered at 580° C.

In contrast, FIG. 5, Specimen (B), shows the profilometer trace obtained for the decalcomania applied to the metal substrate heated to a temperature of 580° C. and immediately thereafter rolled while hot. This decalcomania pattern was impressed essentially coplanar with the adjacent metal, in that the maximum surface roughness was limited to only approximately 5 microns peak-to-valley. Surprisingly, there was no discernible distortion of the design at all as a result of the hot rolling, and an exceedingly adherent decalcomania application was obtained. Moreover, because of the embedded material coplanarity with the matrix metal, there was much less tendency of the impressed design to foul with dust or other foreign material in the environment.

This example demonstrated, too, that multiple superposed glass layers, such as the different-colored layers making up the decalcomania designs, could be laid down in very satisfactory manner by the hot compaction method of this invention without relative lateral displacemnet of the layers one from another, and without objectionable sacrifice of coplanarity in the final product.

EXAMPLE 5A

Glass decalcomania application in three different manners was compared in this example, using decalcomanias of the same characteristics as those of Example 5 and one of the high-melting metals as substrate, in this instance 65 mil metallic nickel strip.

In all cases the decalcomanias were applied by adhering the moist representation to the metal substrate and drying for 30 mins. at room temperature.

Specimen (A) was heated to 550° C. for 15 mins. to burn off the decal polymer backing, after which it was cooled and rolled at room temperature with a 6 mil reduction in thickness. The decalcomania pattern flaked off extensively under this treatment and was obviously of unacceptable quality.

Specimen (B) was heated to 800° C. for 10 mins. and thereafter immediately rolled hot to a 3 mil reduction in thickness. The rendition obtained was visually perfect and a profilometer trace revealed excellent coplanarity.

Specimen (C) was heated to 600° C. for 10 mins. and thereafter cooled. The decalcomania rendition was good but the design was upraised and, thus, exposed to dislodgement abrasion as well as dust and foreign material accumulation.

EXAMPLE 6

The disadvantages of excessive application of glass embedded material are demonstrated by this example, where a continuous dense coverage of blue glass powder over the surface of 50-mil thick Type 1100 aluminum was obtained as follows:

The blue-glass powder was Du Pont J784 enamel consisting of lead-free alkali borosilicate glass (maturing temperature approximately 538° C., corresponding to a glass viscosity of approximately 10^4 poises), containing blue cobalt silicate calcined inorganic pigment. The powder had a particle size of —200 mesh and was mixed with a 50% methanol-50% epoxy resin adhesive to produce a thin slurry. The slurry was sprayed on the aluminum substrate to a heavy, continuous, porous thickness of approximately 0.010", after which the coating was air-dried for 30 minutes at room temperature and the coated sheet placed in an oven heated to 600° C. for 7 minutes, during which time the carrier substance burned off and the metal and glass were simultaneously heated to oven temperature. The sheet was then removed from the oven and immediately hot-rolled to reduce the composite to a final thickness of 0.047". The thick coating was non-adherent and poorly bonded, flaking off very easily. The sample was finally annealed at 650° C. for 15 minutes to sinter the embedded glass particles into a relatively continuous surface coating.

The finished sample possessed a rather unpleasing flat-black appearance, with small diameter pin holes noticeable throughout the surface. Both the color deterioration and the pinhole formation were due to the relatively dense coverage of the metal surface by the initially applied particulate glass layer, which precluded the development of coplanarity under compaction and, at the same time, necessitated extensive post-heating via the final annealing, which was destructive of the cobalt-containing coloring ingredient.

EXAMPLE 7

An attempt was made by this example to test the desirability of diluting the powdered glass with powdered metal, particularly where the composite sought to be developed is concentrated to the extent of approximately 100% surface coverage.

Thus, an intimate mixture of 25 volume percent of aluminum powder (—100 mesh) with 75 volume percent of —100 mesh Du Pont J784 enamel of the composition and softening temperature reported in Example 6 was made up in a cone blender. This mix was dispersed in an excess of methanole-epoxy resin adhesive solution and sprayed on a 50-mil thick Type 1100 aluminum sheet to a depth of 0.008" as a full length dense particle distribution, continuous coating strip 1" wide centrally disposed in the middle of the 4" wide aluminum substrate strip, the remainder of the sheet being protected from deposition by masking tape.

The sprayed-on coating was air-dried for 30 minutes at room temperature, after which the masking tape was removed from the sheet. The metal sheet with its adhered glass-metal stripe was then placed in an oven and heated at 580° C. for 7 minutes in order to burn off the temporary carrier adhesive and heat the glass and metal to inter-bonding temperature.

The sheet was then removed from the oven and immediately hot-rolled, production a final sheet thickness of 48 mils. The product was finally annealed at 600° C. for 10 minutes.

The resulting stripe was of pleasing soft blue, pastel quality appearance, substantially coplanar with the adjacent aluminum. The durability was tested by bending the strip around a ¼" radius, which neither removed nor cracked the colored stripe.

EXAMPLE 8

This example was devised to test the application of this invention to aluminum-coated steel (gage 50 mils), such as that represented by Armco Steel Corporation's Grade No. 2.

The particulate additive consisted of 50% by volume Du Pont J405 enamel, which is a lead-free alkali borosilicate glass of −100 mesh particle size and 538° C. maturing temperature (corresponding to approximately 10^4 poises viscosity), and 50% by volume −100 mesh aluminum powder, applied as a thin slurry in 50% methanol-50% epoxy resin adhesive solution. The slurry was sprayed on to the surface of the aluminized sample and dried in air at room temperature for 30 mins., after which the sample was placed in an oven heated to 600° C. for 10 minutes and then immediately hot-rolled to a final gage of 49 mils.

The specimen was reheated twice to 600° C. within the oven, and thereafter hot-rolled each time with a gage reduction of about one mil on each rolling, following which the sheet was finally annealed by heating to 580° C. for 10 minutes. A smooth, highly adherent, substantially coplanar attachment of the glass-metal mixture was obtained on the aluminized surface, which resulted in a greatly improved appearance.

Example 9

The encouraging results of Example 8 led to an attempt to coat a commercial zinc-galvanized steel using glass-aluminum powders in the same proportions, particle sizes and adhesive solution as detailed in Example 8, except that a lower melting glass, namely, Du Pont J–150, consisting of a low-melting alkali lead silicate glass of 516° C. maturing temperature (corresponding viscosity approximately 10^3–10^4 poises) was utilized as the glass component. The glass was colored black by the incorporation of Du Pont K929 pigment.

The steel sheet was 52 mils thick, galvanized on both sides with a coating of zinc about one mil thick, making an overall thickness of 54 mils.

Because of the low vaporization point of the zinc substrate metal, it was desired to keep the compositing temperature as low as practicable while still effecting good surface incorporation of the particulate material. Zinc is soft enough at 380° C.–400° C. to receive the particulate impregnant, even though the temperature of the latter, when simultaneously heated with the metal substrate, is in the upper part of the permissible viscosity range required for compositing according to this invention.

Accordingly, the particulate material in adhesive suspension was deposited on the upper surface of the galvanized steel and dried in air at room temperature for 30 mins., leaving accumulations of particulate material about 8 mils thick distributed at random over the substrate. The sheet was then heated to 390° C. in an oven for 10 minutes, after which it was immediately hot-rolled to a final overall gage of 52 mils.

The specimen was reheated twice to 390° C. and thereafter hot-rolled each time with a gage reduction of about one mil on each rolling, following which it was annealed at 390° C. for 10 minutes.

Microscopic examination and profilometer readings confirmed the fact that the particulate material was firmly embedded in the zinc coating overlying the steel substrate with substantial coplanarity obtainment. The firm backing support provided by the underlying steel, which was not raised to working temperature at the low temperature levels preserved, contributed importantly to the even incorporation of the particulate material throughout the zinc overcoat. The product had a greatly improved surface appearance as compared with the galvanized-coated starting material, which was further enhanced by the black color of the glass component, retained with great fidelity in the hot-rolled specimen.

Cuttings were removed from the specimen and examined microscopically, revealing that there was considerable flattening of the embedded particles confronting the steel foundation sheet. This was to be expected, since the particles embedded were substantially larger in as-received average diameter than the one mil thick zinc overcoat (e.g., 325 mesh corresponds to about 1.7 mil).

This, and the preceding example, demonstrates the feasibility of surface attachment of particulate material to practically any metal sheet material via the use of a binding receptor metal coated over the metal sheet. Using this technique, there is great freedom of choice of compositing temperatures, compacting pressures and conditions, and the combination of different particulate metals, glasses and substrates one with another.

Example 10

This example was directed to the surface integration of particulate premanufactured glass-metal composites of the type taught in U.S. Patent 3,165,821 within smooth-surfaced metal substrates.

The same glass-metal composite was used in each of the following tests, this consisting of 50 volume percent of −100 mesh Aluminum Association Type 1100 aluminum powder mixed with 50 volume percent of the glass having the composition reported supra in Example 2, except that calcined chrome cobalt inorganic pigment of turquoise blue color was added for color impartation. The intimate mixture was pressed at 8000 lbs./sq. in. into 2" x 1.5" x 1" billets, which were then sintered by heating at 580° C. for 2 hours. The billets were thereafter crushed and ball-milled to pass 100% through a 150 mesh screen.

In Test A the metal substrate was 16 gage yellow brass overlaid with masking tape to expose a 1" wide strip upon which was sprayed a 30 volume percent slurry of −150 mesh composite suspended in 50% methanol-50% epoxy cement as hereinbefore described. The sprayed-on coating was air-dried for 30 mins. at room temperature, after which the masking tape was removed. The brass substrate carying the particulate material on its surface was heated in a furnace at 580° C. for 10 minutes, after which it was immediately hot-rolled with an overall gage reduction of only one mil. A 10 minute anneal at 580° C. was conducted to adhere any loose powder, after which the product was cooled an examined. Substantial coplanarity over the full 1" width strip was verified. Excellent color rendition was obtained, and a very attractive product secured.

In Test B the identical compositing procedure followed in Test A was adhered to, except that an aluminum metal substrate (Aluminum Association Type 1100) of 50 mil thickness was substituted for the brass, and the hot rolling resulted in a somewhat greater overall gage reduction of 3 mils. Excellent coplanarity was obtained and, again, the visual appearance was extremely attractive.

EXAMPLE 11

This example was devised to show that overlaid hot compositing is practicable.

Here the substrate was a piece of Type 1100 aluminum metal 2¾" x 3⅝", 50 mils thick.

The first stripe applied was a 1" wide 50 volume percent turquoise-colored glass—50 volume percent aluminum sintered composite prepared as described in Example 10. The following procedure was employed:

(a) A 50% methanol—50% epoxy cement adhesive was utilized to adhere the −150 mesh composite to a 1" wide open strip of the substrate defined by masking tape.

(b) The substrate with adhered glass-metal composite was heated to 580° C., after which the specimen was immediately rolled hot to a gage of 48 mils, which produced a coplanar inlay in the substrate.

(c) The cooled product from (b) was given a second stripe of 50% light blue glass—50% metal composite

prepared as described for the first stripe (a), but oriented at 90° to the first stripe to produce a 1" wide overlay therewith, the final pattern then being a cross.

(d) The specimen was finally reheated to 580° C. and rerolled to a final thickness of 47 mils.

Excellent color rendition was preserved and the entire surface was coplanar, including the area of overlap for the two stripes.

EXAMPLE 12

In this example the objective was to ascertain the effect on compositing of hot rolling using heated rolls.

The glass employed was —200 mesh brown pigmented glass of the same composition as that of Example 2 (maturing temperature about 540° C.) in mixture of 50 volume percent glass with 50 volume percent of —100 mesh aluminum powder.

The substrate was 50 mil thick Type 1100 aluminum sheet.

The particulate glass-metal mixture was adhered to the substrate at room temperature as a masking tape—defined 1" wide strip with methanol thinned-epoxy resin adhesive and then dried for 30 mins.

The specimen was then heated to 580° C. for 10 mins., after which it was immediately passed through a power-driven roll set at a speed of about 40 ft./min. with a gage reduction of 3 mils. This roll set utilized rolls 6" in diameter with a stock-receiving width of 6", the rolls being provided with internally mounted, longitudinally arrayed, slip-ring current supplied, resistance heating rods, so that the roll surface temperature was maintained at 230° C. even though water-cooled sleeve bearings supported the rolls at both ends. The specimen was thereafter cooled to room temperature.

The strip was found to be coplanar, adherent and non-powdery, so that no post-annealing treatment was necessary.

EXAMPLE 13

This example involved the compositing of a high maturing temperature (approx. 1100° C.) glass with a substrate metal plastic at temperatures considerably below that necessary to achieve a glass viscosity in the range $10^{2.8}$–10^{7} poises.

The glass had a composition close to that of the bottle glass of Example 4, whereas the substrate was a strip of Type 1100 aluminum 1¼" x 2¾" x ⅛" thick.

The procedure was as follows:

The substrate was heated to 600° C. and a short rod of the glass measuring about 3/32" diameter x 2" long was held over the substrate and heated at one end by playing a blow torch thereover until the glass at this end was visibly softened. The temperature of this soft glass was 800–850° C., corresponding to a glass viscosity of approximately $10^{5.5}$ poises.

The entire glass piece was then dropped onto the substrate in longitudinal alignment therewith and the specimen immediately passed between the rolls of the water-cooled roll set employed for Examples 1–11, inclusive, with the hot glass end of the rod leading.

The highly heated glass end composited with the aluminum substrate smoothly and with good coplanarity, whereas the cooler trailing end composited to only an unsatisfactory degree, in that it fragmented to partially adhered particles of completely different appearance from the predecessor material.

The well-composited glass, even though possessed of a coefficient of thermal expansion considerably less than half that of the aluminum substrate metal (i.e., 9 x 10^{-6}/° C. as compared with 21 x 10^{-6}/° C.) was firmly embedded in the aluminum with a very smooth transitional boundary over much of the periphery and only a slight groove throughout the remainder.

EXAMPLE 14

This example confirmed the fact that compositing according to this invention can be accomplished at low glass contents as well as at 50% or higher glass contents.

The glass component employed was 325 mesh Du Pont J405 colorless glass enamel, such as that used in Example 8, analyzing: 1% Sb_2O_3, 11.25% $BaCO_3$, 2.5% boric acid, 21.5% SiO_2, 3.5% $(Li)_2CO_3$, 10.25% K_2CO_3, 27% Na_2CO_3, 2.75 $NaNO_3$ and 20.5% TiO_2, the maturing temperature of which was 538° C. (corresponding to approximately 10^4 poises viscosity).

The particulate glass was mixed with minus 100 mesh aluminum powder to give the five final proportions in volume per cent glass of 5, 10, 20, 30 and 40. These individual mixtures were applied to separate pieces of Type 1100 aluminum substrate measuring 4" square by 1/16" thick, utilizing acetone-thinned epoxy resin adhesive as the binder, laydown being as thin layers 1" wide. After heating for 20 minutes at 580° C. in air, the samples were rolled between a pair of rolls heated to a surface temperature of 100° C., to reduce the overall thickness 2 mills. Finally, the samples were annealed at 580° C. for 20 minutes. The laid-down strips were exceedingly smooth and imperceptible to the touch at the substrate-strip boundaries, thus evidencing the absence of crevices at these points.

Surprisingly, even though a colorless glass component was employed, the strips impressed in the samples were all clearly perceptible visually, as frosty-like coatings, which increased in darkness with increase in particulate glass content.

Profilometer measurements were made on all five specimens and it was verified that the surface roughness was well below ±10 microns, the criterion for coplanarity hereinbefore defined.

The coatings obtained were highly adherent, emphasizing the importance of matching the viscosity of the glass to the hot working temperature of the metal substrate. By way of comparison, a high melting point ground bottle glass (100% glass, no metal) of the type hereinbefore reported in Example 4, having a viscosity of 10^8–10^9 poises at a temperature of 650° C., was impressed on the same metal substrate by the identical rolling and annealing procedure hereinabove described; however, the bottle glass composite was powdery, flaking off at the finger's touch, nor was it smooth in the sense of an integral coplanar integration.

EXAMPLE 15

This example confirmed the fact that compositing according to this invention can be accomplished using prefabricated glass-metal composites of relatively low glass content, i.e., far below 50 volume percent glass, as the particulate substance integrated with the substrate.

The glass-metal composites were first made up as described in Example 1, U.S. Patent 3,165,821 supra, by taking —100 mesh Aluminum Association Type 1100 Al powder which was mixed as separate batches in the proportions hereinafter reported with ground glass (100% through a 100 mesh screen) of the following composition by weight: PbO 34.3%, SiO_2 27.3%, Li_2O 2.2%, Na_2O 13.6%, K_2O 2.2%, TiO_2 13.4%, Sb_2O3 2.7% and BaO 4.3%, maturing temperature 500° C. The glass had previously been mixed with cobalt oxide blue pigment in the weight ratio of 5 parts of glass to 1 of pigment. The mixture was cold-pressed at 15,000 lbs./in.^{2} into 2" x 1½" x 1" billets, which were then heated to 560° C. and forged to final shape. The specimens were then cleansed by surface grinding with 600-grit paper and thereafter immersed for 10 minutes in a 3.2% $Ca(OH)_2$ slurry in water containing, also, 2% NaOH, followed by rinsing and drying.

Three separate compositions were made up analyzing as follows:

Sample (vol. percent)	Surface appearance
Al+10% pigmented glass	Light blue, rough surface.
Al+20% pigmented glass	Do.
Al+30% pigmented glass	Darker blue, surface less rough.

The different composition billets were then separately crushed to −100 mesh size and individually applied as a slurry in acetone-thinned epoxy resin adhesive as binder in 1" wide strips approximately 5 mils thick to single surfaces of separate pieces of Type 1100 aluminum substrate measuring 3" x 4" x 1/16" thick. After heating for 20 minutes at 580° C. in air, the samples were immediately passed between roll pairs heated to 100° C. to reduce the overall thickness about 2 mils. The specimens were then annealed for 20 minutes at 580° C.

Excellent adherence of the glass-metal composites to the substrates was achieved for all three compositions, and the stripe boundaries with the substrates were undetectable to the touch. Profilometer readings of surface quality were made for all three specimens and these conformed in all respects to that of FIG. 4(B), with the aluminum substrate glass-metal compoite boundaries practically indistinguishable, confirming that excellent coplanarity within the ±10 micron standard of this invention was readily obtained.

Preferred metal substrates, employed as such without any external binder coatings, include aluminum, magnesium, zinc and alloys of these metals, because of their relatively low hot metal working temperatures. However, the invention is operable with high melting metals per se, including low carbon steel, stainless steel, copper, nickel, titanium and alloys thereof, and, of course, through the agency of appropriately selected substrate coatings adhered to foundation metals, to practically any metal or alloy which it is desired to benefit by surface compositing.

A great variety of vitreous compositions are available as the glass component of the invention, borosilicate, alkali lime and lead silicate glasses being particularly preferred because of the disposition of their temperature-viscosity criticalities within the same general region as the working temperature of the preferred metals hereinbefore detailed.

It is entirely practicable to incorporate the particulate solids within the exterior surface of the substrate metal in the course of the conventional extrusion forming of the substrate metal. Unique streaking effects can be thereby obtained as a function of draw ratio and the amounts of particulate material supplied per unit time interval. Also, because the embedding of particles is essentially independent of the extrusion forming itself, there is little necessity to alter the conventional forming techniques in order to accommodate the particle compositing.

The advantages of this invention are not limited purely to decorative aspects, since a very substantial corrosion-protective effect is obtained by the mere presence of embedded glass or glass-metal composites throughout the metal surface. The composite secured is in numerous respects a very satisfactory substitute for conventional enameled structures, because it is possible to dispense with many of the most expensive essential ingredients of these enamels, such as opacifiers, adhesion-improving additives and the like with great accompanying economies, due to the high strength bond of metal to glass achieved by this invention. Also, it is, of course, entirely practicable to improve the corrosion resistance of the composite products even further by the incorporation of water-leachable corrosion inhibitors in the glass phase as carrier, all as taught in issued U.S. Patent 3,205,566.

It is feasible to coat both sides of a metal substrate according to this invention, and this can be done by adhesive attachment of particulate material to both exterior surfaces at room temperature, followed by a hot roll which composites the particulate material on opposite sides of the sheet simultaneously. Alternatively, since rerolling as shown by the examples is not at all detrimental, and, in fact, is beneficial as an improvement in uniform particle distribution and coplanarity achievement, attachment can be had to one surface via one hot rolling and to the opposite surface by a second independent hot rolling. It is additionally possible to incorporate either the same or different, e.g., differently colored glass components, by superposing a plurality of particulate material layers one over another, as by a silk screen process or the like, each applied by a single hot compaction reserved to itself. Varicolored patterns of unique design and coloration are thereby reproducibly obtained, to give results varying from precise decalcomania patterns on the one hand to random dispositions on the other.

Also, the compaction effecting embedding can be conducted with a wide variety of different mechanisms, including reciprocatory hammers, a single power-driven roll traversed lengthwise over a firm stationary metal bed supporting the metal substrate into which compositing is desired, and other arrangements.

From the foregoing, it will be understood that this invention is capable of relatively wide modification employing the skill of the art and in accordance with its essential spirit, and it is intended to be limited only within the scope of the appended claims.

What is claimed is:

1. A manufacture comprising a non-porous metal substrate carrying within its surface a particulate substance from the class consisting of glass, glass-metal mixtures and glass-metal composites impressed into said surface to a degree such that said particulate substance is firmly embedded in, and attached to, said substrate with the outwardly-facing surfaces of said particulate substance substantially co-planar with said surface of said substrate.

2. A manufacture according to claim 1 wherein said glass, glass-metal mixtures and glass-metal composites are disposed within said metal substrate in a predetermined geometrical pattern.

3. A manufacture according to claim 1 wherein said glass, glass-metal mixtures and glass-metal composites contain colorants integral therewith.

4. A manufacture according to claim 1 wherein said metal substrate is a metal having a melting point in the range of about 400° C.–1900° C.

5. A manufacture according to claim 4 wherein said metal substrate is a metal having a melting point in the range of about 400° C.–800° C.

6. A manufacture according to claim 1 wherein said metal substrate is one of the class consisting of aluminum, magnesium, zinc and alloys thereof.

7. A manufacture according to claim 1 wherein said metal substrate is one of the class consisting of low carbon steel, stainless steeel, copper, nickel and their alloys.

8. A manufacture comprising a non-porous low-melting metal substrate adhered to an underlying high-melting metal mass as backing carrying within the surface of said metal substrate a particulate substance from the class consisting of glass, glass-metal mixtures and glass-metal composites impressed into said surface to a degree such that said particulate substance is firmly embedded in, and attached to, said metal substrate with the outwardly facing surfaces of said particulate substance substantially co-planar with said surface of said metal substrate.

9. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate comprising in sequence heating said particulate substance and said metal substrate as follows: (a) said glass and glass-metal composites to a temperature at which the glass viscosity is in the range of about $10^{2.8}$ to 10^{7} poises and (b) said metal substrate to a tem-

perature at which said surface becomes soft enough to accept said particulate substance under the application of compressive force to said particulate substance, before substantial cooling occurs applying compressive force to said particulate substance and to said metal substrate with said particulate substance distributed over said surface of said metal substrate in sufficient amount to embed said particulate substance firmly within said surface of said metal substrate with outwardly-facing surfaces of said particulate substance substantially coplanar with said surface of said metal substrate, and cooling said metal substrate and said particulate substance embedded therein.

10. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate according to claim **9** wherein said application of compressive force is via a squeeze roll pair rotating in the direction of feed of said metal substrate therebetween.

11. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate according to claim **9** wherein said particulate substance is distributed over said surface of said metal substrate in a predetermined pattern.

12. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate according to claim **9** wherein said particulate solid is applied to said metal substrate as a decalcomania.

13. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate having a melting point in the range of about 400° C.–1900° C. comprising in sequence heating said particulate substance and said metal substrate as follows: (a) said glass and glass-metal composites to a temperature at which the glass viscosity is in the range of about $10^{2.8}$ to 10^{7} poises and (b) said metal substrate to a temperature at which said surface becomes soft enough to accept said particulate substance under the application of compressive force to said particulate substance, before substantial cooling occurs applying compressive force to said particulate substance and to said metal substrate with said particulate substance distributed over said surface of said metal substrate in sufficient amount to embed said particulate substance firmly within said surface of said metal substrate with outwardly-facing surfaces of said particulate substance substantially coplanar with said surface of said metal substrate, and cooling said metal substrate and said particulate substance embedded therein.

14. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate according to claim **13** wherein said non-porous metal substrate has a melting point in the range of about 400° C.–800° C.

15. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate according to claim **9**, wherein temperatures (a) and (b) overlap, in which said particulate substance is distributed over said surface of said metal substrate prior to effecting said heating, said heating is thereafter conducted concurrently as regards said particulate substance and said metal substrate, and then said compressive force is applied to said particulate substance and said metal substrate.

16. A method of compositing a particulate substance from the class consisting of glass and glass-metal composites within the surface of a non-porous metal substrate according to claim **9**, wherein temperatures (a) and (b) do not overlap, in which said heating is effected separately as regards said particulate substance and said metal substrate, following which said particulate substance is distributed over said metal substrate and then said compressive force is applied to said particulate substance and said metal substrate.

17. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of a non-porous metal substrate comprising in sequence heating said particulate substance and said metal substrate as follows: (a) said glass-metal mixture to the sintering temperature of the metal component thereof and (b) said metal substrate to a temperature at which said surface becomes soft enough to accept said particulate substance under the application of compressive force to said particulate substance, before substantial cooling occurs applying compressive force to said particulate substance and to said metal substrate with said particulate substance distributed over said surface of said metal substrate in sufficient amount to embed said particulate substance firmly within said surface of said metal substrate with outwardly-facing surfaces of said particulate substance substantially co-planar with said surface of said metal substrate, and cooling said metal substrate and said particulate substance embedded therein.

18. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of a non-porous metal substrate according to claim **17**, wherein said application of compressive force is via a squeeze roll pair rotating in the direction of feed of said metal substrate therebetween.

19. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of a non-porous metal substrate according to claim **17** wherein said particulate substance is distributed over said surface of said metal substrate in a predetermined pattern.

20. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of a non-porous metal substrate according to claim **17** wherein said particulate substance is applied to said metal substrate as a decalcomania.

21. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of a non-porous metal substrate having a melting point in the range of about 400° C.–1900° C. comprising in sequence heating said particulate substance and said metal substrate as follows: (a) said glass-metal mixture to the sintering temperature of the metal component thereof and (b) said metal substrate to a temperature at which said surface becomes soft enough to accept said particular substance under the application of compressive force to said particulate substance, before substantial cooling occurs applying compressive force to said particulate substance and to said metal substrate with said particulate substance distributed over said surface of said metal substrate in sufficient amount to embed said particulate substance firmly within said surface of said metal substrate with outwardly-facing surfaces of said particulate substance substantially coplanar with said surface of said metal substrate, and cooling said metal substrate and said particulate substance embedded therein.

22. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of a non-porous metal substrate according to claim **21** wherein said non-porous metal substrate has a melting point in the range of about 400° C.–800° C.

23. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of a non-porous metal substrate according to claim **17**, wherein temperatures (a) and (b) overlap, in which said particulate substance is distributed over said surface of said metal substrate prior to effecting said heating, said heating is thereafter conducted concurrently as regards said particulate substance and said metal substrate, and then said compressive force is applied to said particulate substance and said metal substrate.

24. A method of compositing a particulate substance consisting of a glass-metal mixture within the surface of

a non-porous metal substrate according to claim 17, wherein temperatures (a) and (b) do not overlap, in which said heating is effected separately as regards said particulate substance and said metal substrate, following which said particulate substance is distributed over said metal substrate and then said compressive force is applied to said particulate substance and said metal substrate.

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