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METHOD OF PRODUCING MULTI-LAYER TRANSFERABLE CASTINGS

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2 Sheets-Sheet 1

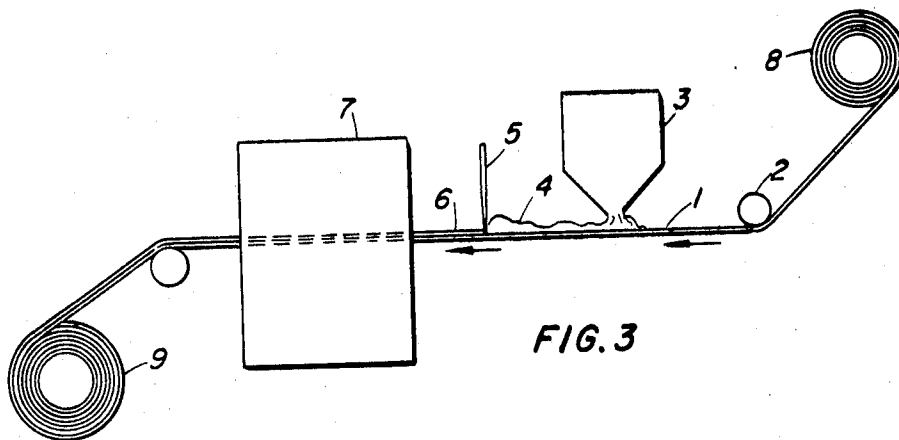


FIG. 3

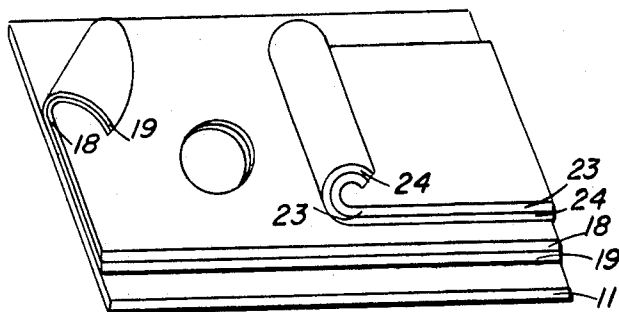


FIG. 2

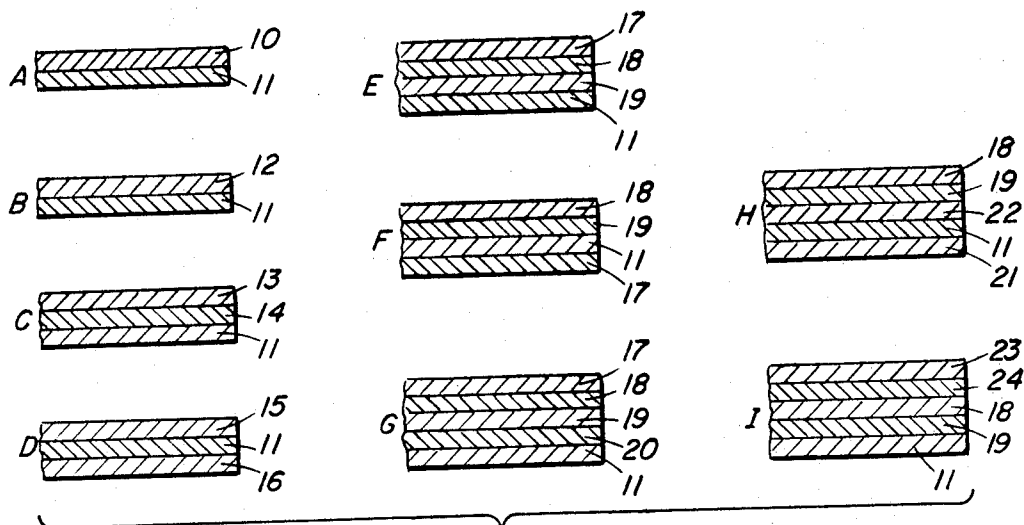


FIG. 1

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3,574,029 METHOD OF PRODUCING MULTI-LAYER TRANSFERABLE CASTINGS

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June 25, 1964. This application Apr. 4, 1968, Ser.
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U.S. Cl. 156—231 9 Claims

ABSTRACT OF THE DISCLOSURE

A process for making a multiple-layer transferable unfired casting supported on a temporary substrate. The layers are separately cast on temporary substrates and are then brought together and bonded, after which one of the temporary substrates is stripped away. The resulting multiple-layer casting can be transferred to a permanent substrate and fired.

This is a continuation-in-part of my copending application, Ser. No. 377,998, filed June 25, 1964 and now abandoned.

This invention relates to method for preparing multiple-layer transferable castings. More specifically, it relates to the preparation of a multiple-layer casting on a temporary substrate, which casting can be fully or partially transferred to a particular permanent substrate to be coated. The casting contains selected inorganic powders in a binder of selected type, and is normally fired or fused onto the permanent surface.

Prior art fireable or fusible layers are commonly produced by any of the "wet" techniques such as spraying, brush painting, silk screening or roller coating. All of these methods have similar characteristics. In each type of technique the powdered glass, glaze or ceramic material is dispersed as a slurry in a liquid, containing binder, solvent and plasticizer besides the powders. This slurry is then applied to the surface to be coated. These "wet" methods, however, have many disadvantages, one of which is that the concentration and viscosity of the suspension changes from time to time due to the evaporation of the organic solvents. This makes reproducibility of the applied layer variable not only from day to day but also from hour to hour during production. Further, the drying of the coating on the ceramic surface presents a problem. It has been found that the combination of the liquid, its concentration and viscosity of the fluid are of considerable importance in obtaining a uniform coating of the right thickness on the desired surface. Glazed ceramics used as micro-circuit boards are particularly sensitive to any variation in the thickness, density and smoothness of the glaze layer.

Another disadvantage is that the thickness and density and the amount of deposited powdered material cannot be determined until after the layer is fired, which makes quality control of the process very difficult. As the thickness and density cannot be controlled in advance, the finished product frequently has to be rejected and if tested the testing can be only destructive; so, reproducibility is always a great problem.

Other methods which could be used for depositing patterns of non-conductive layers are the methods called decalcomania. In this process the required exact pattern has to be printed on a carrier film and transferred from there to the desired surface. This method utilizes some of the known printing processes which could be silk screening or other types utilizing a printing press. The disadvantage of this method is that the exact pattern

must be printed on the carrier and the transfer must be made by utilizing exact positioning tools so that the pattern should come exactly to the desired place on the permanent substrate.

Another disadvantage of this printing-type decalcomania process is that the thickness of the consecutive prints cannot be accurately reproduced.

It is another disadvantage that if the entire surface has to be coated such a technique is not very useful, especially if the surface is large.

The two foregoing types of methods have a further common disadvantage, namely, that the thickness of the coating cannot be varied readily below 1 mil or above 2 mils.

Another method is to prepare self-supporting films utilizing suitable binders and powdered materials and applying this self-supporting film to the surface by punching out suitable preforms and placing it to the desired location on the permanent substrate. The disadvantage of this technique is that thin layers cannot be produced this way and that the production of preforms requires utilization of tools in connection with sometimes precious and sensitive films. Other disadvantages are that the storing and protecting of the sensitive layers cannot be well achieved in this way.

Accordingly, a primary objective of this invention is to provide a process for producing a multiple-layer transferable casting which is protected during the storage, can be produced in exact thickness and density and in which thickness and density can be tested before the utilization of the layer.

Another objective is to produce transferable castings in a variety of exact thicknesses in the range desired for the specific application.

Another objective is that the casting be transferable to the entire surface or only a selected area on the permanent substrate.

Another objective is to provide a method for producing a multiple-layer transferable casting with a uniformly smooth surface.

Another objective is to provide a tape or film of the above characteristics wherein the organic binder material therein will be substantially completely eliminated at elevated temperature without leaving wastes which would destroy the uniformity of the film, and will not leave any undesirable residue on the surface and which will not result in cracks or peeling of the layer after heating.

Other objectives and advantages of the invention will become apparent from the following descriptions taken in connection with the accompanying drawings wherein:

FIG. 1 is a sectional view of exemplary transferable tapes made in accordance with this invention;

FIG. 2 illustrates the removability of the casting from its carrier film or temporary substrate;

FIG. 3 is a schematic side elevation view illustrating a method of making the transferable casting in accordance with this invention;

FIG. 4 shows the different applications of glass transferable tapes to various bodies in accordance with this invention;

FIG. 5 shows a ceramic dielectric insulator layer over both sides of a disc;

FIG. 6 shows a metal cylinder where the outside surface is glazed in accordance with this invention;

FIG. 7 is an elevational view of a micro-circuit board where the glazing and insulators are made utilizing this invention;

FIG. 8 shows a semiconductor coated for protection with a glaze according to this invention; and

FIG. 9 shows a ceramic wafer sealed to metal conductors by utilizing a glaze in accordance with this invention.

A slurry containing selected inorganic powder, binder, plasticizer and solvent is deposited on a carrier film in a uniformly thick and smooth layer to form a transferable casting in a manner to be described hereinafter. A third layer using an adhesive which is selected plastic materials dispersed in a solvent medium is laminated over the prepared double layer.

The carrier film utilized in the process must be inert towards the organics and inorganic materials used for the casting preparation and for the adhesives, and must have good mechanical properties. The carrier film must have uniform surface qualities so that the heavily loaded casting is uniform and its release can be accomplished in a uniform manner. It was found that several carriers are suitable for this purpose; for example, such carriers are polyethylene, Teflon or paper.

The heavily loaded casting contains the inorganic powdered material, a binder and a plasticizer. In the glazing of ceramics, for example, it was found that the role of the binder and the plasticizer is of considerable importance. Cellulose nitrates or ethyl cellulose have been commonly used as binders for glazing liquids deposited by painting or spraying methods. Although nitrocellulose can be used in glazing castings or films of the presently described type, nitrocellulose does not support as a binder large amounts of the selected glass powders. This results in a somewhat low density glazing which is undesirable in some cases. Furthermore, nitrocellulose film also is inclined to become brittle and to harden slightly during aging or under influence of light, affecting storing qualities of the prepared film. We have found that over the common organic resins having better film forming characteristics polyvinylalcohol and polymethacrylates give particularly excellent results as binders. For example, for using poly-n-butyl methacrylate as a binder, it is possible to prepare high density glazing film with as little as about 2% binder and the resultant film will be substantially unaffected by light or aging. Not more than 16% binder is preferred for the best results. We found in this respect that the transfer from the carrier to the object to be coated is influenced to a considerable degree by the binder, its concentration and also by the plasticizer.

It is desirable in many cases that the binder completely decompose or evaporate during the firing process so as to leave no solid organic residue in the coating. This is particularly true in connection with the manufacture of glass-to-metal seals and micro-circuit components. In such cases polymethacrylates are particularly desirable as binders because during the glazing or sintering processes the polymethacrylates leave as gaseous products with little or no solid organic residue remaining in the coating.

A plasticizer is used as a part of the binder to render the casting flexible. It is preferable that the plasticizer should also leave the casting at elevated temperatures without leaving an organic residue. The concentration of the plasticizer is extremely important and the percentage of the plasticizer relative to the binder must be very exactly chosen in order to achieve this effect. For different types of applications a different composition of the layer is necessary. It was found that the percentage of the plasticizer to the binder must be changed if the layer is made to be transferred to large areas or if it has to adhere only to a minuscule pattern.

In accordance with this invention plasticizers such as sucrose acetate isobutyrate, dibutyl phthalate and diethyl-oxalate may be used successfully with poly-n-butyl methacrylate and glycerine with polyvinyl alcohol. The plasticizers specified above decomposed completely and have an excellent softening effect on the binder. It was also found that utilizing these plasticizers in combination with the mentioned binders, the desired change in the transfer characteristics of the tape can be achieved.

For tapes transferable to large areas a ratio of 85% solid powder, 9% binder and 6% plasticizer gave satisfactory results while for tapes utilized for transferring small

patterns this ratio had to be changed to 85% solid powder, 7.5% binder and 7.5% plasticizer.

Another example is when 94% solid powder was used; then tapes utilized to be transferred on large areas contained about 4% binder and 2% plasticizer and this was changed to a composition of 94% solid powder, 3% binder, and 3% plasticizer for tapes transferable in fine pattern.

These examples demonstrate that the transferable tape can be adapted to produce low or high density coating on large areas or in fine patterns by changing the solid content of the tape in the range of 60% to 98% of the total and by changing the binder to plasticizer ratio in the range of 1:2 to 5:1, where the first number relates to the amount of binder relative to the amount of plasticizer which is represented by the second number.

Furthermore, it was also found that using a combination of different binders or plasticizers may be also very helpful for producing tapes transferable in different patterns. As example with 92% solid powder is 4% poly-n-butyl methacrylate, 2% sucrose acetate isobutyrate and 2% dibutyl phthalate mixture.

It is understood that the above examples and ratios are merely exemplary, and other ratios and amounts can as well be used to achieve transfer of the castings.

The solvent utilized to produce the slurry can be acetone, but amyl acetate, benzene, water or other common solvents may also be used. It was also found that mixtures of different solvents such as acetone and ethyl alcohol, ethyl alcohol and benzene, or water and ethyl alcohol, are very useful and the casting of films with different thickness values requires a different composition of these solvents.

The preparation of thick castings (where the thickness is above 10 mil) cannot be satisfactorily achieved in most cases by a single solvent such as acetone. A mixture of acetone and amyl acetate is more suitable for this purpose. On the other hand, for thin layers (where the thickness is below 1 mil), ethyl alcohol is an extremely useful solvent medium.

It is particularly pointed out that the term solid powder is used herein to include any of the components which are known to be used as fireable or fusible materials, such as glazes utilized for preparing glazed ceramic substrates, protective coatings, conductive films, or glass-to-metal seals. The ceramic materials refer to insulator ceramic materials, dielectric ceramic materials, piezo-electric materials or Ferrite materials. Also the term glaze or ceramic material is intended to encompass a combination of these materials such as alumina oxide or SiO_2 or barium titanate. One example of a glazing material is a lead glass which can be described with the following chemical forms SiO_2 68%, PbO 15%, Na_2O 10%, K_2O 6% and CaO 1%. Another example is a boro silicate glass material which can be described by the following chemical forms SiO_2 80%, B_2O_3 14%, Na_2O 4%, and Al_2O_3 2%. An example of dielectric material is barium titanate which can be described with the following chemical form BaTiO_3 . Another example is a ceramic material which is a mixture of different inorganic oxides as described with the following chemical forms Al_2O_3 92%, CaO 3%, SiO_2 3% and $\text{H}_2\text{Mg}_3(\text{SiO}_3)_4$ 2%. An exemplary conductive casting may contain 80% molybdenum and 20% manganese. It is understood that other materials and a combination of these can also be prepared in tape form and the actual amounts of the ingredients may be varied within wide ranges.

One casting may be produced wherein the mixture is a film forming product containing about 90% by weight of the selected glass, about 7% by weight of the poly-n-butyl methacrylate, and about 3% by weight of plasticizer. This composition was homogenized by continuous agitation using acetone as a solvent and then spread evenly upon a temporary substrate of polyethylene film, as depicted in FIG. 3.

The glazing tape described above can be applied to a

ceramic surface by first separating it from the carrier film and using it as a self-supporting film or it can first be applied to the ceramic surface after which the carrier may be removed. The glazing film itself may be secured to the ceramic surface by thermal sealing or by the use of a suitable solvent to form a bond to the substrate and achieve the transfer. Both polar and non-polar organic solvents are suitable for use with this technique.

It was found that in certain cases solvents which are inert towards the glazing film can be excellently as well used. Such solvents are, for example, water, cyclohexanol or ethyl alcohol.

Pressure sensitive adhesives can also be used to facilitate the transfer. Different types of slurries which are generally known for their lasting adhesive qualities can be spread on the transferable casting.

The solvent of the adhesive slurry should wet the surface of the transferable casting and preferably should not dissolve the binder or plasticizer used in the preparation of the casting.

Another criteria of this adhesive is that it should completely decompose or evaporate at higher temperatures; it should leave the transferred casting without causing pin holes, cracks or any other residues which may be harmful in the fired casting. It shouldn't contain any material which may attack the powders dispersed in the transferable tape or the carrier. Several types of such adhesive slurries can be successfully used in combination with glass or ceramic transferable tapes. Such adhesives can be water base, solvent base or water or solvent base types. In particular, starch, polyvinyl alcohol, synthetic rubber and acrylate tapes are very useful, but other types can as well be used.

For the procedure of producing the adhesive layer as a third layer on the transferable tape, the machine shown in FIG. 3 can be well utilized. In this case the procedure is as described above except the tank 3 contains now the adhesive slurry and the spindle 8 carries the double layer tape containing the carrier and the heavily loaded transfer casting. In this case a protective paper may be utilized, and fed on to cover the tacky surface of the adhesive. This four layer tape comprising the carrier, the heavily loaded transferable casting, the adhesive layer, and the protective paper is wound up on a roll and stored. The protective paper is removed before the application of the tape. It is understood that the protective paper is not a necessary part of this process but it is necessary to have a protective layer for this type of transferable film for storage purposes if it is stored in rolled form. The protective layer can be formed, however, on the back side of the carrier film or a carrier film can be chosen which does not adhere to the adhesive layer. In this case the film can be wound up without utilizing a protective paper.

Another way to produce adhesive coated transferable tapes is that the adhesive layer is laminated on a separate carrier film, which carrier film can be polyethylene, paper, or Mylar or the same treated with a releasing agent. This laminated adhesive layer can be stored separately or brought together with the transferable casting immediately. If it is stored separately, the adhesive layer is transferred to the casting before it is utilized.

Several examples of transferable tapes are shown in FIGS. 1-A through 1-I.

FIG. 1-A shows a carrier film 11 supporting a transferable casting 10.

FIG. 1-B shows a transferable tape where a carrier film 11 supports a transferable casting 12 in which adhesive material is intermixed.

FIG. 1-C shows a transferable tape wherein 11 is a carrier film, 14 is a transferable casting with adhesive intermixed and 13 is a protective coating.

FIG. 1-D shows a carrier 11, a transferable casting 15 in which the adhesive material is incorporated and a protective layer 16 coated on the reverse side of the carrier.

FIG. 1-E shows a carrier 11 supporting a transferable

casting 19, a layer of adhesive 18, and a removable protective layer 17.

FIG. 1-7 shows an arrangement where the carrier 11 is coated with a transferable casting 19 which in turn is covered by an adhesive layer 18, and the protective layer 17 is now on the reverse side of the carrier.

In FIG. 1-G an arrangement is shown in which a carrier film 11 is coated with a surface coating 20 to facilitate the release of the casting. Casting 19 is spread on this release coating, the adhesive layer 18 is spread on the casting, while 17 is a removable protective layer.

FIG. 1-H shows a carrier film 11 according to the invention, the backing of which is coated with a protective layer 21. The carrier film is also equipped with a surface coating 22 on which the transferable casting 19 is spread which is again coated with an adhesive layer 18.

FIG. 1-I shows an arrangement where the carrier 11 is coated with casting 19 which is again coated with an adhesive layer 18. This adhesive layer is covered by a protective layer 23 which is coated to facilitate its release by release coating 24.

According to the invention these layers are not produced in consecutive slurry depositions, but each of the layers can be produced separately on individual temporary substrates and brought together at a later time in order to form the configurations shown in FIGS. 1-A to 1-I.

Other configurations which are variations of the above can also be used and are understood to be a part of this invention. For example, two castings may be separately produced on temporary substrates, and then laminated together using pressure, heat, solvent, adhesive or other means to bond adjacent casting surfaces together. One of the temporary substrates can then be stripped away, producing a multi-layer transferable casting supported on the other temporary substrate. The superimposed layers may be of different compositions and contain different inorganic powders. This process can be repeated to produce transferable castings with any desired number of superimposed layers. Since the thickness of the individual castings can be accurately controlled, the resulting multi-layer casting can be produced with excellent dimensional control. The individual castings can be cast and dried in a short period of time, because they have a large surface-to-volume ratio. A relatively thick casting (thicker than about 7-10 mils) can usually be produced more rapidly and economically by laminating thin castings than by directly casting and drying a slurry to the final thickness.

An illustration of one of these transferable tapes is shown in FIG. 2. In this figure, 11 shows a carrier film from which the transferable tape 19 is partially removed. The adhesive layer 18, however, is still firmly attached to the transferable tape. The protective layer 23 is removed from the adhesive but the release layer 24 is firmly attached to the protective layer. This figure shows also a place where a round shaped pattern has been transferred to a substrate according to the invention.

FIG. 3 is an arrangement for producing transferable tapes according to this invention. It can be seen that a carrier film 1 is carried by spool 8 from which it passes under a guide roller 2 and beneath a tank 3 which contains the slurry. As the carrier film 1 moves in the direction indicated by arrows, a supply of slurry 4 is deposited on its upper surface and is carried beneath a flat profile doctor blade 5 which smooths the mixture. Blade 5 is adjustable perpendicular to the surface of the film so as to provide the layer of the mixture with controlled uniform thickness. After the carrier film is thus provided with a uniformly thick and smooth layer, it is dried in any suitable means such as dryer 7 whereby the casting 6 becomes removably attached to the carrier film 1. The resultant laminated tape or film then passes to a spool 9 on which it is wound for storing. Tapes consisting of more layers can be produced by running this laminated tape several times over the machine, thus achieving any

of the layer structures shown in FIG. 1. Alternatively, the layers can be laminated consecutively in the same operation or can be made in separate manufacturing processes utilizing a spreading technique. These can then be laminated together on a single roll at the end of the last process or can be stored in separate rolls and brought together just before the usage of the tape.

FIG. 4-A is showing an arrangement in which a metal part 27 is pressed towards the casting 28, which adheres to part 27 at the contacted areas. The glazing is then produced by a subsequent firing procedure.

FIG. 4-B shows a ceramic wafer 25 which was equipped with a glaze 26 by pressing the transferable tape according to this invention to the ceramic wafer 25 and transferring the glaze casting 26 to the ceramic.

FIG. 4-C shows an arrangement where only the edge of a ceramic wedge is coated with glazing in order to produce a narrow glazed line on the ceramic. The ceramic wedge 29 was pressed against the transferable tape or the transferable tape can also be pressed against the wedges, transferring the glaze casting 30 to the wedge.

FIG. 5 shows a ceramic wafer 25 which is coated on both sides with a ceramic insulator casting 31 according to the invention. This ceramic insulator casting can be subsequently fired in order to achieve a sintered layer.

FIG. 6 shows the application of this invention to covering the outside surface of a metal tube 32 with a glaze 33.

FIG. 7 shows an application which a ceramic wafer 25 is coated with a glaze 37 according to the invention; in another step one or more ceramic materials are transferred to the glazed surface by utilizing a die and pressing a pattern to the glazed ceramic surface. In this case the pattern 34 adheres to the glazed ceramic at the points the tool is pressing the tape and not at any other points. The layer is then firmly bonded to the substrate material. In certain cases, this adhesion can be increased by a heat treatment.

FIG. 8 shows an application where a semiconductor surface 35 is coated by a protective glaze 36

FIG. 9 shows an application where a ceramic wafer 25 is coated with the transferable casting 39, into which metal conductors 38 are pressed to achieve firmly bonded conductive lands.

These examples show a variety of applications of the transferable tapes for different devices. It was found that the devices produced by the transferable tape technique show superior characteristics compared to those produced by spraying, painting, silk screening or the decalcomania process. This is believed to be accomplished at least partly by the better control of uniformity in density, thickness and surface smoothness achieved by the presently described techniques and the adaptability of the film to the surface of various shapes and sizes with the ease of transferring. It is also to be believed that this technique makes the automation of such processes possible.

From the foregoing it will be apparent that novel means and methods have been presented in accordance with the objectives of these inventions for preforming glazing ceramics or metals or equipping them with ceramic layers or patterns. It is to be understood, however, that various changes in the means and methods described may be made by those skilled in the art but not departing from the spirit of the invention as expressed in the accompanying claims.

I claim:

1. A method of making a multiple-layer transferable unfired casting comprising, in combination, the steps of:

(A) casting a first transferable layer onto a first temporary substrate,

(B) casting a second transferable layer onto a second temporary substrate,

(1) at least one of said first and second layers being firable and comprising an organic binder

composition loaded with inorganic powdered material,

(C) laminating said first and second layers together to form said multiple layer casting, and

(D) stripping away one said temporary substrate.

2. A method as defined in claim 1 wherein said casting comprises an adhesive layer.

3. A method as defined in claim 1 wherein said temporary substrates are carrier films in the form of tapes, said laminating step comprising continuously feeding together said carrier film tapes with said layers thereon so as to contact and laminate one said layer to the other.

4. A method as defined in claim 1 wherein each said firable layer comprises from about 60% to about 98% by weight of inorganic powdered materials dispersed in an organic binder composition comprising a binder and a plasticizer, the binder to plasticizer ratio being between about 1:2 to about 5:1.

5. A method as defined in claim 4 wherein said binder is polyvinyl alcohol and said plasticizer is glycerine.

6. A method as defined in claim 4 wherein said binder is a polymethacrylate and said plasticizer is selected from the group consisting of sucrose acetate isobutyrate, dibutyl phthalate, diethyloxylate, and mixtures thereof.

7. A method as defined in claim 6 wherein said binder is poly-n-butyl methacrylate.

8. A method of making a relatively thick transferable unfired casting comprising, in combination, the steps of:

(A) casting a first transferable layer onto a first temporary substrate, said first layer comprising an organic binder composition loaded with inorganic powdered material,

(B) casting a second transferable layer onto a second temporary substrate, said second layer comprising an organic binder composition loaded with inorganic powdered material,

(C) laminating said first and second layers together to form said relatively thick casting, and

(D) stripping away one said temporary substrate.

9. A method of making a relatively thick transferable unfired casting in tape form comprising, in combination, the steps of:

(A) casting a first transferable layer onto a first carrier film tape, said first layer comprising an organic binder composition loaded with inorganic powdered material,

(B) casting a second transferable layer onto a second carrier film tape, said second layer comprising an organic binder composition loaded with inorganic powdered material,

(C) laminating said first and second layers by continuously feeding together said carrier film tapes with said layers thereon so as to contact and laminate one said layer to the other, and

(D) stripping away one said carrier film tape.

References Cited

UNITED STATES PATENTS

2,311,876	2/1943	Scheetz	117—46
2,559,649	7/1951	Little et al.	156—231
2,593,553	4/1952	Francis	156—344X
2,776,235	1/1957	Peck	117—36.1X
2,966,719	1/1961	Park	264—66
3,189,504	6/1965	Whittle et al.	156—234
3,212,959	10/1965	Vardi et al.	161—167
3,293,072	12/1966	Doolittle et al.	156—89X
3,015,574	1/1962	Gobel	117—3.6X
3,274,017	9/1966	Borrajo	117—3.6X
3,489,587	1/1970	Weingrad	161—406X
3,506,473	4/1970	Ettre	161—167X

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