Aug. 10, 1971 K. S. ETTRE ET AL 3,598,679

METHOD OF MAKING A PRESSURE-TRANSFERRABLE TAPE

Filed March 4, 1968 2 Sheets-Sheet 1

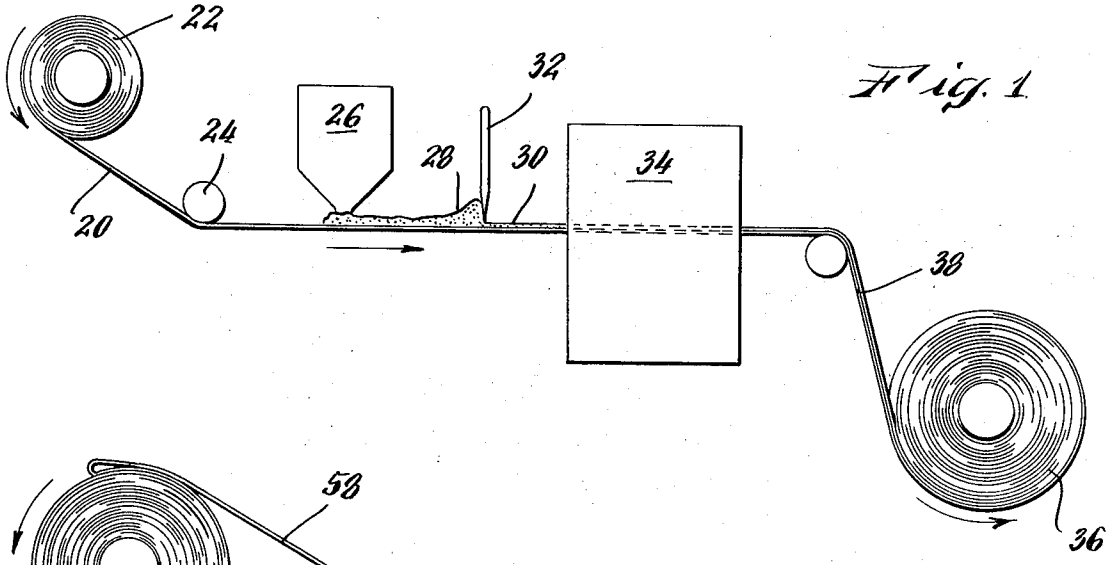


Fig. 1

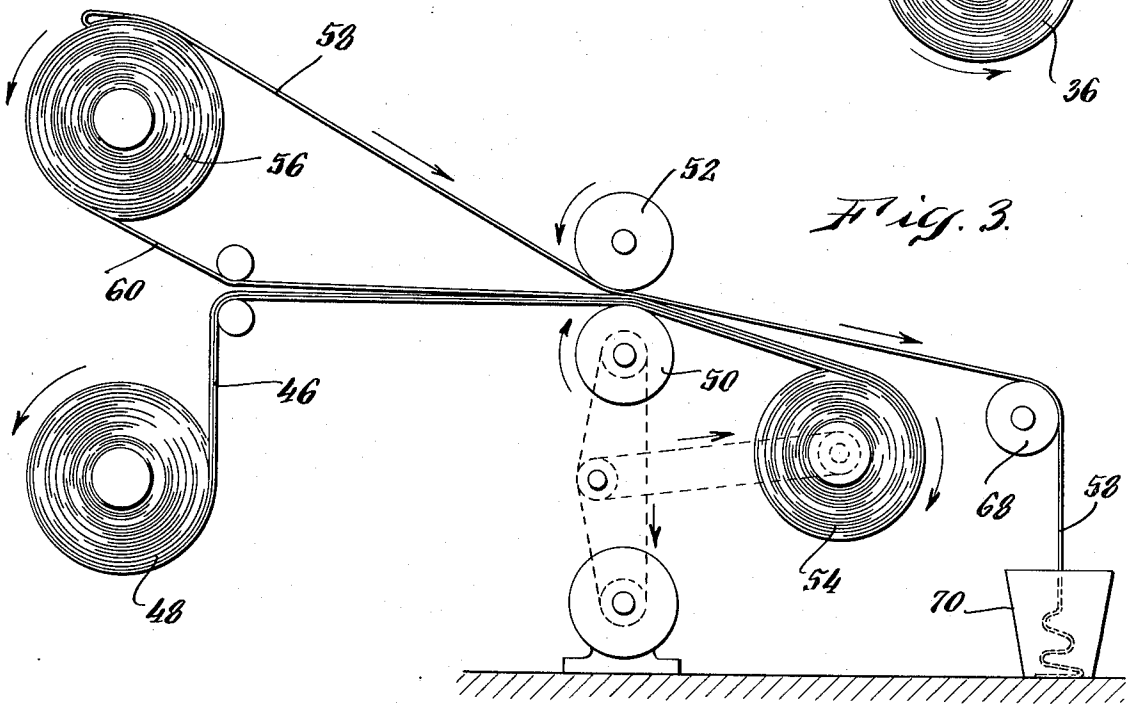


Fig. 3

Fig. 2

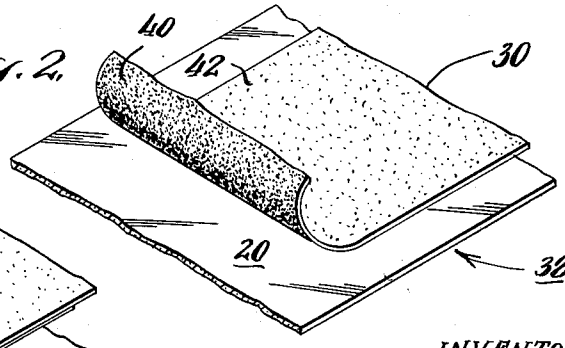
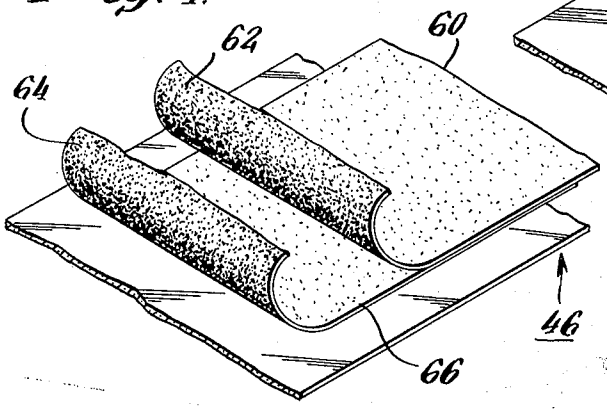


Fig. 4

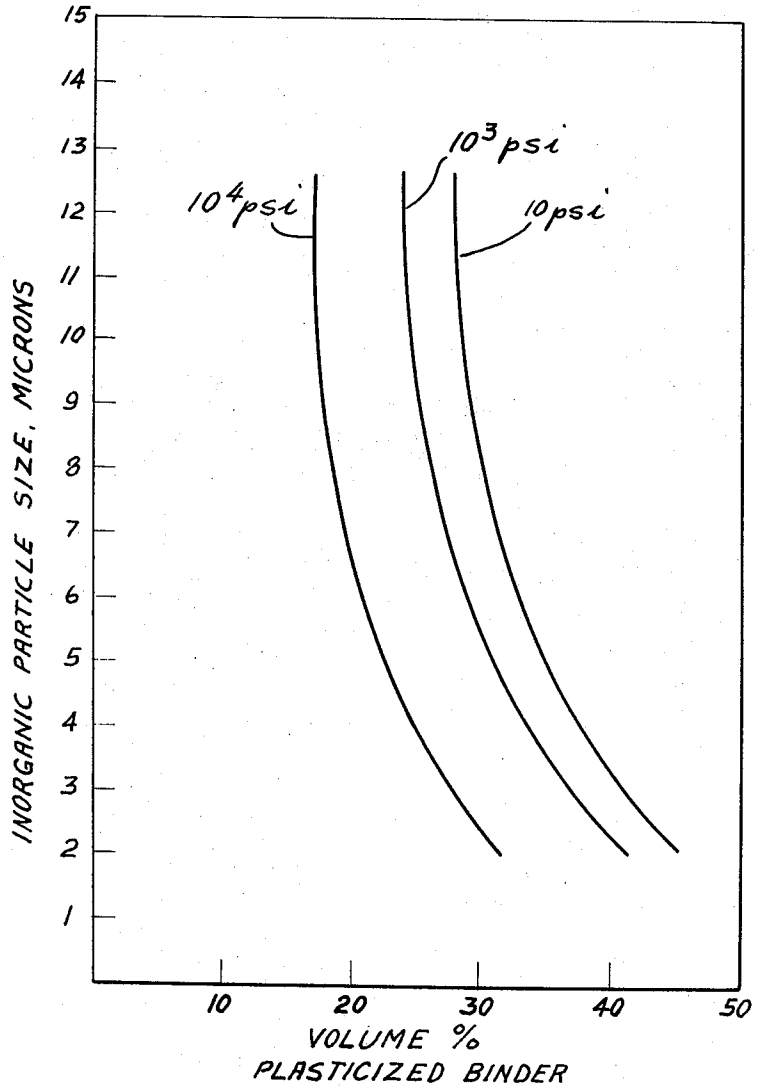


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METHOD OF MAKING A PRESSURE-TRANSFERRABLE TAPE

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Fig. 5.



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METHOD OF MAKING A PRESSURE-TRANSFERRABLE TAPE

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ABSTRACT OF THE DISCLOSURE

A flexible transferrable filmlike casting. Individual thin films are cast onto the flexible supporting substrate by doctor-blading a heavily loaded slurry of a solid inorganic powder mixed with a plasticized binder. The exposed surface of the resulting slurry casting is dried, while the surface contacting the substrate remains tacky and can be used as an adhesive. One casting may be stripped from its substrate and the tacky surface applied to the exposed dry surface of another casting. The superimposed castings are then bonded together solely by pressure.

The invention relates to flexible films or castings of the type which may be transferred from a temporary substrate to another surface and then fired to set the casting and bond it to a permanent substrate. More particularly, it relates to such castings which have a tacky surface contacting the temporary substrate, which tacky surface is used to adhere the casting to the new supporting surface.

It is known to produce transferrable fireable castings by doctor-blading a slurry of inorganic powder in a binder onto a temporary substrate and drying it, to form a transferrable casting. Such known transferrable castings are then typically coated with adhesive to assist the transfer of the casting from the temporary substrate to the final substrate. The addition of such an adhesive is undesirable for many types of transferrable casting. Known adhesives may react with some constituent of the casting, and usually leave some sort of residue during the firing operation, which residue may interfere with uniformity of the casting or with the bonding of the casting to the final substrate. Additional problems arise if it is desired to produce a transferrable casting having a thickness greater than approximately ten mils, since the drying time increases considerably faster than the increase in casting thickness.

With castings greater than ten mils in thickness, air drying at ambient temperatures can take as long as an hour or more. If heated in ovens or by other sources of externally applied heat, the heat must be carefully controlled to avoid cracking of the casting or other defects. Other problems are known to be associated with the use of heat for drying the castings.

Such thick castings according to the prior art, can only be successfully formed on a rigid, non-shrinkable supporting substrate such as stainless steel. If an organic temporary substrate (such as polyethylene film) is used for preparation of thick castings, the organic solvent used to prepare the slurry will have time to penetrate slightly into the surface of the organic substrate, which effect becomes more pronounced as the wet thickness is increased. Such penetration of the solvent into the organic substrate tends to distort the casting and substrate. This renders necessary the use of a rigid, non-shrinkable material such as stainless steel, if a thick casting is to be made in one casting step.

If such a rigid material is used for the substrate, the casting is separated from the temporary substrate after drying. The removed casting has only a limited storage life, however. If the casting is stored on a rigid temporary substrate, the film can be stored for a very much longer period, but cannot be conveniently rolled for shipping and storage. Shipping costs and the required inventory of rigid temporary substrate are serious disadvantages of storing the castings on rigid temporary substrate.

These and further problems of the prior art are avoided according to one aspect of the present invention by provision of self-adhesive tapes which do not require a separate adhesive. By selection of proper combinations of inorganic fireable powder, binders, plasticizers and solvents, the face of the casting which contacts the temporary substrate remains tacky after the exposed surface of the casting is dry. The casting can therefore be used as a pressure-sensitive adhesive casting after removal of the temporary substrate, without the use of a separate adhesive.

According to another aspect of the invention, the temporary substrate can be a flexible organic film, permitting ease of storage and shipping. According to another aspect of the invention, individual castings are laminated together using the tacky side as the adhesive, to produce castings of any desired thickness. The lamination process is effected solely by the use of pressure, i.e., without the use of mechanical vibration, externally applied heat, additional adhesive, solvents, or the like.

Accordingly, a primary object of the invention is to provide a tape including a pressure transferrable casting.

A further object is to provide a tape of the above character wherein the transferrable casting is supported on a flexible temporary substrate.

A further object is to provide a tape of the above character wherein the casting does not require a separate adhesive.

A further object is to provide a tape of the above character wherein the casting is tacky on the side contacted by the temporary substrate, and is substantially non-tacky or dry on the opposite surface.

A further object is to provide a tape of the above character wherein the casting has excellent storage life.

A further object is to provide a tape of the above character wherein the casting is formed of superimposed laminated layers bonded together by pressure.

A further object is to provide a method for making tapes of the above character.

A further object is to provide apparatus for making tapes of the above character.

A further object is to provide preferred casting compositions for making tapes of the above character.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, the apparatus embodying features of construction, combinations and arrangement of parts which are adapted to effect such steps, and the article which possesses the characteristics, properties and relation of elements, all as exemplified in the detailed disclosure hereinafter set forth, and the scope of the invention will be indicated in the claims.

For a more complete understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawings, in which:

FIG. 1 is a schematic side elevation view of exemplary apparatus forming a tape according to one aspect of the invention.

FIG. 2 is a perspective view of the tape produced by the FIG. 1 apparatus, showing a flexible, self-adhesive casting carried on the flexible temporary substrate;

FIG. 3 is a schematic side elevation view of apparatus for laminating a casting from a first tape onto a casting on a second tape;

FIG. 4 is a perspective view of the laminated tape produced by the FIG. 3 apparatus; and

FIG. 5 is a graph showing the effect of inorganic particle size on the required amount of plasticized binder.

Suitable tapes according to the invention may be produced by the exemplary apparatus illustrated in FIG. 1, wherein a flexible, temporary substrate in the form of continuous polyethylene film **20** is withdrawn from feed roll **22**. Film **20** passes under guide roll **24** and beneath slurry supply tank **26**. Slurry **28** is fed from tank **26** onto the upper surface of film **20**, to form a casting layer **30** thereon. Doctor blade **32** is vertically adjustable to control the thickness of casting **30**. The laminated tape consisting of film **20** and slurry casting **30** is fed through dryer **34** and collected on take-up roll **36**. In dryer **34**, the film is subjected to a flow of air, preferably at or near room temperature, to drive off the volatile solvent and render the exposed surface of casting **30** dry to the touch.

The resulting tape **38** is shown in FIG. 2, wherein a portion of casting **30** has been peeled back. As will be further discussed below, upper surface **42** of casting **30** is substantially dry, while lower surface **40** is still sufficiently tacky to render the casting pressure-transferrable. "Pressure-transferrable," as used in the specification and claims, means that when surface **40** (of a casting **30** which is at least approximately 1 mil thick) is pressed for 1 second against a surface such as fire-polished glass with a pressure of about 10 to about 10,000 pounds per square inch (p.s.i.), casting **30** will adhere so strongly that it cannot be readily stripped off again without tearing. If surface **40** will thus adhere at a pressure substantially less than about 10 p.s.i., the casting will be too soft and rubbery for the uses according to the present invention. The dry surface **42** should require at least 100 times the pressure, and preferably at least 1,000 times the pressure, to similarly adhere to the polished glass surface. Thus, if the tacky side will adhere at 10 p.s.i., the dry side should not similarly adhere at less than 1,000 p.s.i. and preferably should not adhere at less than 10,000 p.s.i. Accordingly, castings according to the invention have a tackiness differential on opposite sides of at least 100 times, and preferably at least 1,000 times.

Castings **30** having these properties are produced according to one aspect of the invention by the proper slurry compositions and drying conditions. Slurry **28** includes a major portion of the desired inorganic fireable powder, intimately mixed with a plasticized binder which is dissolved in sufficient temporary volatile solvent to permit flow of slurry **28** onto film **20**.

The inorganic powder can include any of the known

fireable glasses, ceramic, or metals, or mixtures of these materials. Selection of suitable inorganic powders or loading materials is well within the scope of one skilled in the art, and will depend upon the desired end use for the casting. One suitable specific example of inorganic loading materials is a boro-silicate glass material having the following approximate chemical composition: SiO_2 80%, B_2O_3 14%, Na_2O 4%, and Al_2O_3 2%. A suitable lead oxide solder glass contains PbO 71.40%, ZnO 16.24%, B_2O_3 10.11%, Al_2O_3 0.28%, Na_2O 0.05%, and CaO 1%. A suitable ceramic material includes: Al_2O_3 92%, CaO 3%, SiO_2 3%, and $H_2Mg_3(SiO_3)_4$ 2%. Another exemplary material is $BaTiO_3$. An exemplary metallic loading material is a mixture of 80% molybdenum and 20% manganese. All references in the specification and claims to percentages refer to percentages by weight, where not otherwise specified.

The function of the binder according to the prior art is to provide a matrix for binding together the inorganic powder until it is fired. According to the present invention, the plasticized binder also renders the casting pressure-transferrable. The binder may be selected from a wide variety of known organic film-forming materials, depending on the desired properties of the casting. Suitable exemplary binder materials include polyvinyl butyral, cellulose acetate, polyvinyl alcohol, and the polymethacrylates, such as poly (n-butyl methacrylate). The polymethacrylates are particularly desirable because during the firing of the casting onto the final substrate the polymethacrylates decompose into gaseous products, leaving virtually no organic residue in the final fired casting.

The plasticizer must be chosen to be compatible with the selected binder, so as not to separate into a separate phase, and must be present in the proper amount. If too much plasticizer is present, both surfaces of the casting will be tacky and the casting will not readily strip from the temporary substrate. On the other hand, if the amount of plasticizer is too low, surface **40** will not develop sufficient tackiness to make casting **30** pressure-transferrable. Suitable plasticizers for polymethacrylates include dibutyl phthalate, diisodecyl phthalate, diisobutyl adipate, diethyl oxalate, sucrose acetate isobutyrate, and fatty acid type plasticizers. Glycerine is a suitable exemplary plasticizer for polyvinyl alcohol.

Temporary substrate **20** must be chemically inert to slurry **28**, and must have appropriate surface characteristics for temporarily lightly bonding to surface **40** so that casting **30** can be readily stripped therefrom when desired. Suitable substrate materials include untreated polyethylene, certain papers, Tedlar (polyvinyl fluoride) and Mylar (a glycol-terephthalic acid polyester).

The volatile solvent should preferably wet the surface of temporary substrate **20**, and should dissolve the binder and plasticizer without chemically reacting with the slurry components. Exemplary solvents include acetone, amyl acetate, benzene, ethanol, and a mixture of ethanol and water. Preferably the solvent is sufficiently volatile to readily evaporate at room temperature, so that drying can be accomplished without the need for heaters in dryer **34**.

The proportions of the various slurry components are determined by several considerations. Ordinarily the inorganic powder constitutes at least about 75% by weight of the slurry (exclusive of the solvent), and preferably constitutes a considerably higher portion. To obtain the desired tackiness and pressure-transferable properties as above defined, the ratio of plasticized binder to inorganic powder must be selected within certain ranges, which will vary somewhat depending on the particle size of the inorganic powder and the properties of the binder and plasticizer selected.

The following specific example in Table I illustrate the effect on required transfer pressure of varying the amount of one particular plasticized binder:

TABLE I

		Tape type					
		Ceramic tape		Glass tape		Metal tape	
		Average particle diameter, microns					
		2–3		2–4		3–5	
		Density, g./cm.^{3}					
		3.2		6.3		9.4	
		Grams		Grams		Grams	
Inorganic substance(s)	Al_2O_3	288	Solder glass	300	Mo	240	
	Mistron [1]	12			Mn	60	
Poly(n-butyl methacrylate)		54		24		18	
Dibutyl phthalate		12		6		4.5	
Total organic		66		30		22.5	
Inorganic substance(s)	Al_2O_3	288	Solder glass	300	Mo	240	
	Mistron	12			Mn	60	
Poly(n-butyl methacrylate)		45		20		15	
Dibutyl phthalate		9.9		5		3.75	
Total organic		54.9		25		18.75	
Inorganic substance(s)	Al_2O_3	288	Solder glass	300	Mo	240	
	Mistron	12			Mn	60	
Poly(n-butyl methacrylate)		30		16		13	
Dibutyl phthalate		6.6		4		3.25	
Total organic		36.6		20		16.25	

[1] Hydrous magnesium silicate.

See the following table:

Pressure required, p.s.i.g	10	10^3	10^4
Type of roller	Rubber	Rubber	Steel
Durometer hardness	40	80	

Table II shows the effect of varying inorganic particle size on the amount of a given plasticized binder required to produce a particular transfer pressure. This effect is independent of the type of inorganic material used. It should be understood that the optimum ratios of plasticized binder to inorganic powder will vary with different binders and plasticizers.

TABLE II

	Lead oxide solder glass transfer tapes (density: 6.3 gm./cm.^{3})		
Average particle diameter, micron	2–4	4–7	10–15
Solder glass, gms	300	300	300
Poly (n-butyl methacrylate), gms	20	16	12
Dibutyl phthalate, gms	5	4	3
Total organic, gms	25	20	15

See the following table:

Pressure required, p.s.i.g	1,000
Type of roller	Rubber
Durometer hardness	80

In Table I, wherein the inorganic powders had substantially the same particle size, the samples providing a transfer pressure of 10 p.s.i. had approximately 59% inorganic powder and 41% plasticized binder, the samples having a transfer pressure of 1,000 p.s.i. had approximately 63% inorganic powder and 37% plasticized binder, while the samples having a transfer pressure of 10,000 p.s.i. had approximately 72% inorganic powder and 28% plasticized binder, expressed in terms of volume.

In Table II, the sample having an average particle diameter of 2–4 microns contained 37% plasticized binder, the sample having an average particle diameter of 4–7 microns contained 30% plasticized binder, while the sample having an average particle diameter of 10–15 microns contained 24% plasticized binder.

The results of Tables I and II are plotted in FIG. 5, showing that the volume of a given plasticized binder should be increased as particle size decreases.

The inert solvent is added in an amount sufficient to render the given composition readily flowable. Using the specific compositions disclosed in Tables I and II above, for example, approximately 15 cc. of acetone per 100 cc. of inorganic powder and plasticized binder is an appropriate amount.

The individual tapes **38**, as above described, include only a single casting **30**, having a thickness of preferably less than 10 mils. A laminated casting of any desired thickness may be produced according to a further aspect of the invention, by laminating the castings, using the tacky sides **40** to effect bonding. Suitable apparatus for performing this process is illustrated in FIG. 3 wherein a first tape **46** is withdrawn from a supply roll **48**, fed between pressure rolls **50** and **52**, and collected on take up roll **54**. A second similar tape is supplied on roll **56**. Roll **56** is rotated in the counterclockwise direction as illustrated in FIG. 3. The temporary substrate **58** of the second tape is stripped away from its casting **60**. Casting **60** is fed (see FIG. 4) with its tacky side **62** contacting the upper dry side **64** of casting **66** of tape **46**.

Castings **60** and **66** are pressure bonded (i.e., bonded together in the absence of added adhesives, solvents, mechanical vibration, heat, etc.) on passing between rolls **50** and **52**, so that the tape wound on roll **54** contains a laminated casting. Temporary substrate **58** preferably is passed between roll **52** and casting **60**, to strip substrate **58** from casting **60** without further apparatus. Substrate **58** then may pass over a guide roll **68** (FIG. 3) to a suitable container **70**.

Additional thin castings can be laminated onto tape **46** to produce a final laminated casting of any desired thickness, and the lamination can be carried out either in successive steps or simultaneously. Since castings less than about 10 mils thick can be made rapidly with excellent control of casting thickness, a laminated thick casting can be made having closely controlled thickness in a fraction of the time required to dry a casting of equal thickness formed directly from the slurry. It should be noted that the several laminations may include different inorganic powders if desired.

It may be seen from the above disclosure and accompanying drawings that the present invention provides a

pressure-transferrable casting exposed on a flexible temporary substrate. The resulting tape can be stored for periods of months before losing the pressure-transferrable property, and can be conveniently rolled for storage and shipping. The casting does not require the addition of a separate adhesive for its transfer property, and is thus advantageous in many uses.

In the embodiments wherein the final casting is formed from superimposed thinner castings, great precision is possible in the control of the final casting thickness. In addition, thick castings can be produced by the lamination process in a much shorter period of time than would be required if the casting were formed from slurry in a single step. In addition, the laminated construction permits production of castings wherein different layers can be of different compositions. The presently preferred methods of producing tapes of the above character are simple and efficient, as is the specifically disclosed apparatus.

It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained and, since certain changes may be made in carrying out the above process, in the described product, and in the constructions set forth without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described, and statements of the scope of the invention which, as a matter of language, might be said to fall therebetween.

Having described our invention, what we claim as new and desire to secure by Letters Patent is:

1. A method of making a thick self-adhesive unfired casting which is carried on and pressure-transferrable from a temporary substrate comprising, in combination, the steps of:

(A) producing each of at least a pair of castings by

(1) preparing a slurry comprising an organic binder composition loaded with inorganic powder,

(a) said organic binder composition comprising a volatile solvent, a binder and a plasticizer,

(2) providing a ratio of binder to plasticizer in relation to the particle size of said powder so that upon evaporation of said solvent the exposed surface of the resultant casting is substantially dry while the surface contacting the substrate remains tacky,

(3) spreading said slurry to a predetermined thickness on a temporary substrate, and then

(4) evaporating said solvent,

(B) maintaining a first one of said pair of castings adhered to its temporary substrate,

(C) stripping the temporary substrate from the second one of said pair of castings to expose the tacky surface thereof, and

(D) laminating said castings by

(1) placing said tacky surface of said second casting in contact with the dry exposed surface of said first casting and

(2) applying bonding pressure to said contacting pair of castings.

2. A method as defined in claim 1 wherein said pair of castings are each provided with different compositions.

3. A method as defined in claim 1 wherein said binder in at least one of said castings is selected from the group consisting of polyvinyl butyral, cellulose acetate, polyvinyl alcohol, and polymethacrylates.

4. A method as defined in claim 1 wherein, in at least one of said castings, said binder is a polymethacrylate and said plasticizer is selected from the group consisting of dibutyl phthalate, diisodecyl phthalate, diisobutyl adipate, diethyl oxalate, sucrose acetate isobutyrate and fatty acid type plasticizers.

5. A method as defined in claim 1 wherein said binder in at least one of said castings is poly(n-butyl methacrylate).

6. A method as defined in claim 1 wherein, in at least one of said castings, said binder is polyvinyl alcohol and said plasticizer is glycerine.

7. A method as defined in claim 1 wherein, in at least one of said castings, said binder is poly(n-butyl methacrylate) and said plasticizer is dibutyl phthalate.

8. A method as defined in claim 7 wherein the ratio of said binder to said plasticizer is between about 3.5/1 and 5/1.

9. A method as defined in claim 7 wherein the ratio of said binder to said plasticizer is between about 4/1 and 4.5/1.

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