May 1, 1973 BUHEI NAKANE 3,730,825

DECORATIVE SHEET MATERIAL HAVING PLURAL ADHESIVE LAYERS

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FIG. 1

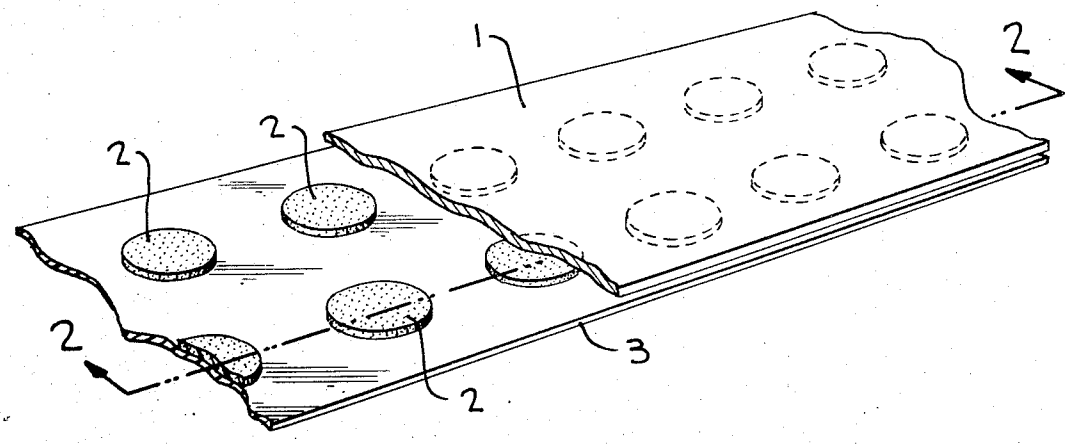
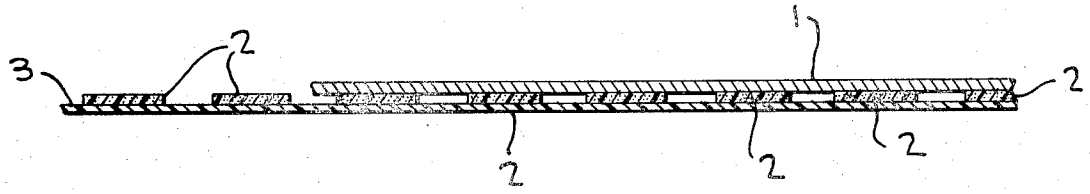


FIG. 2



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DECORATIVE SHEET MATERIAL HAVING PLURAL ADHESIVE LAYERS

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Continuation-in-part of abandoned application Ser. No. 288,513, June 17, 1963. This application Apr. 7, 1970, Ser. No. 24,420
Claims priority, application Japan, June 21, 1962, 37/26,021
Int. Cl. B32b 3/10
U.S. Cl. 161—148 4 Claims

ABSTRACT OF THE DISCLOSURE

A decorative material for adhesive attachment to a solid surface by wetting one surface of the decorative material consisting essentially of a decorative sheet material selected from paper and textile fabrics, a pressure- and thermosensitive adhesive agent coated on one surface of this decorative sheet in a series of spaced areas in a repeating pattern of a selected design and a self-supporting film of a water- and thermosensitive adhesive agent bonded to these spaced areas on the side opposite the decorative sheet, the areas being so spaced from each other that when the self-supporting film is in contact with water both adhesive agents comingle to form a single adhesive layer.

This application is a continuation-in-part application of our co-pending application Ser. No. 288,513 filed June 17, 1963, now abandoned.

This invention relates to decorative construction materials and process for manufacture thereof. More particularly, this invention relates to decorative construction materials which exhibit a strong adhesive property to various materials upon being wetted on their reverse side, for example, wall paper, wall cloth, flooring, and furniture decoration materials, and a process for manufacture thereof.

In the past the most common means for imparting decorative effects on walls and furniture has been by applying to the surface to be finished a paste and adhering thereon a decorative paper or cloth, or by applying the paste on the back of such paper or cloth and putting them on the surface to be finished. In these cases, wheat starch is generally used as the paste. Another technique utilized is the application of a paste on the back of the decorative paper or cloth in advance of their use. The paste used in this case is a water-soluble paste, e.g., starch which is either applied to the back of the decorative material directly or in case the decorative material is a cloth, through lining paper to secure adhesion. Still in other cases, for the same purpose an adhesive agent is applied on back of a decorative material, said surface then being covered by a peelable paper through which the adhesive agent does not permeate, for example, paper applied with cellulose lacquer, or cellophane.

It is well known that when applying a paste to either the surface upon which the decorative materials are to be applied or directly upon the decorative materials each time the same is to be used, this becomes very troublesome and the operation cost is also high. Although it is convenient to use decorative materials which have applied to their back surfaces a water-soluble paste in advance of their use, it is well known that generally their adhesive property is inferior, and they adhere only to limited types of materials. Moreover when the paste is applied directly to the decorative materials without intervening paper, it tends to stain or grow moldy. This is true when using lining paper, because the decorative material and its lining

papers are easily separable, the joining portions of the decorative paper tend to come out or rise with the passage of time, and impair the appearance. Furthermore, those situations wherein a peelable paper is placed over the surface having an adhesive agent applied thereon have been found to be inconvenient in that the peelable paper must be removed at each time of the operation, and also their adhesive property deteriorates after a long period of storing.

Therefore a primary object of the present invention is to overcome the deficiencies in the prior arts, and to provide decorative construction materials of easy and cheap production and which are strongly adherable with all kinds of materials.

The objects of this invention are accomplished by applying on the entire back surfaces of decorative materials a layer of a pressure-sensitive adhesive agent and thermosensitive adhesive agent and thereafter applying on that layer another layer consisting of a water and thermosensitive adhesive agent.

The decorative sheet material of the present invention will now be further illustrated by the attached drawing wherein:

FIG. 1 is a perspective view partially broken away of the decorative material of the present invention; and

FIG. 2 is a view taken along line 2—2 in FIG. 1.

Referring to FIGS. 1 and 2 which show a plane view and cross-sectional view of the decorative material of the present invention, decorative layer **1** is coated with a series of spaced areas **2** of a pressure- and thermosensitive adhesive agent. Bonded to the pressure- and thermosensitive adhesive agent is a self-supporting film **3** of a water- and thermosensitive adhesive agent. The areas **2** of the adhesive are spaced from each other in a repeating pattern of pre-selected design to that when self-supporting film **3** is contacted with water, film **3** comingles with the adhesive in spaced areas **2** to form a single adhesive layer.

The terminology "pressure- and thermo-sensitive adhesive agent" as used in this application defines those adhesive agents which exhibit adhesive property or stickiness upon being subjected to pressure and/or heat. This type of adhesive agent is well known in the prior art. The pressure- and thermosensitive adhesive agents disclosed in the examples of this application are merely illustrative of said adhesive agents.

In accordance with this invention any known pressure- and thermosensitive adhesive agent composed of, as the chief component, various synthetic adhesive materials such as, for example, cellulose derivatives, polyethylene, acrylic acid derivatives, polyamides, polyvinyl acetate, vinyl acetate-acrylate copolymers, polyvinyl butyral, polyisobutylene, butadiene-acrylonitrile copolymers, cyclorubber, chloroprene rubber, vinyl chloride-vinyl acetate copolymers, polyvinylidene chloride and its copolymers; and a minor amount of natural adhesive material such as rubber and glue optionally blended therewith, may be used. Furthermore, if desired, additives such as a plasticizing agent may also be blended with the above described compositions. These pressure- and thermosensitive adhesive agents are applied on decorative materials by being dispersed in water or dissolved in a solvent.

The terminology "water- and thermosensitive adhesive agent" as used in the present application relates to adhesive agents having the property of exhibiting adhesive property or stickiness upon being wetted with water and undergoing chemical and physical changes such as polymerization upon being subjected to heat, where the adhesive properties or stickiness are strengthened. More specifically, they are adhesive agents composed of polyvinyl alcohol or its derivatives. For example: polyvinyl alcohol of 85–97% saponification, particularly 88–90%,

partially acetalized product of entirely saponified polyvinyl alcohol with 3–15% acetalization, partially urethenized polyvinyl alcohol with 3–15% urethanization obtained by reacting polyvinyl alcohol with urea, and polyvinyl alcohol type copolymers which are obtained by saponifying copolymers of vinyl acetate with crotonic acid, isopropenyl acetate, ethylene oxide, etc. Mixtures of not less than 80 parts of weight of these polyvinyl alcohols or their derivatives with less than 20 parts by weight of other high molecular materials are also useful in this invention. Examples of such high molecular materials are: polyvinyl acetal, polyvinyl methylether, polyacrylates, vinyl acetate-maleic acid anhydride copolymer, vinyl methylether-maleic acid anhydride copolymer, glue, gelatin, dextrin, soluble starch, and wheat starch.

When polyvinyl alcohol is used, its degree of saponification is within the range of 85–97%, as indicated above the reason being that if the degree of saponification is less than 85–97%, it is very difficult to prepare a satisfactory film-formed material and aqueous solution and if the film is formed it has poor water-sensitivity. Although it is possible to form films with polyvinyl alcohols having higher degrees of saponification than (85–97%) the film that is formed has inferior water sensitivity.

The terminology "decorative sheet materials" not only covers wall paper and wall cloth used in buildings, but also manufactured articles such as furnitures; decorative materials applied on covers of books, albums, etc., as well as floorings and ceilings.

Therefore the decorative materials useful as decorative construction materials for the present invention, e.g. as the substrate, may be a wide variety of shaped articles, for example, woven, knitted, and non-woven fabrics of animal, vegetable, and mineral natural fibers, synthetic fibers, or semi-synthetic fibers; plastics in forms of sheet, board, tile, and film; fictile tile; synthetic leather; wooden board, etc.

Various techniques may be utilized in forming the first layer of pressure- and thermosensitive adhesive agent as well as the second layer of water- and thermosensitive adhesive agent on the back surfaces of decorative materials to produce the decorative construction materials of the present invention.

The most preferred process is first daubing on the whole back surface of a decorative material a pressure- and thermosensitive adhesive agent by means of, for example, spray rolls, and thereafter before said adhesive agent dries completely, pressing against the daubed surface film of water- and thermosensitive adhesive agent, drying and so adhering the two. By this process, decorative construction materials are obtained, whereby the two layers of pressure- and thermosensitive adhesive agent and of water- and thermosensitive adhesive agent are mutually adhered by one entire surface.

Decorative construction materials of similar structure may be prepared, alternatively, instead of daubing a pressure- and thermosensitive adhesive agent on the back surface of a decorative material, daubing the same onto one side of the film of water- and thermosensitive adhesive agent, and pressing the same against the back of a decorative material followed by daubing; or by daubing a pressure- and thermosensitive adhesive agent on the back of a decorative material, drying, and thereafter daubing onto the dried surface an aqueous solution of water- and thermosensitive adhesive agent followed by drying. The former process is preferred when the decorative material is loose fabrics, or fabrics composed of only warps or lace. However in order to avoid any melting of the film of water- and thermosensitive adhesive agent at the time of daubing the pressure- and thermosensitive adhesive agent, the latter must be daubed in the form of a solution in an organic solvent.

Moreover, when using the latter process the water- and thermosensitive adhesive agent should be limited to polyvinyl alcohols of a degree of saponification (i.e. the percent of polyvinyl acetate converted to polyvinyl alcohol) of from 85 to 97% preferably 88–90%, partially urethanized polyvinyl alcohol, and copolymers of partially saponified polyvinyl alcohol with crotonic acid, isopropenyl acetate, or ethylene oxide.

The object of the present invention is accomplished not only with the decorative construction materials having a structure as defined above wherein a layer of pressure- and thermosensitive adhesive agent and a layer of water- and thermosensitive adhesive agent are mutually adhered together as one entire surface, but also with decorative construction materials having a structure wherein on the back surface of a decorative material, a film of water- and thermosensitive adhesive agent is adhered at certain areas by means of a pressure- and thermosensitive adhesive agent applied in a certain pattern, e.g., in spots, or in lines. Decorative construction materials of such a structure can be manufactured by applying on certain portions of the back surface of a decorative material a pressure- and thermosensitive adhesive agent, and before the same dries applying a film of water- and thermosensitive adhesive agent and then drying both layers. Or, alternatively, it may be manufactured by daubing intermittently on one side of a film of a water- and thermosensitive adhesive agent, and a pressure- and thermosensitive adhesive agent and before the same dries out, adhering the same to back surface of a decorative material.

By any of the above processes, the resultant decorative construction materials of the present invention can be readily adhered onto any surface to which is to be applied, upon wetting of the layer of water- and thermosensitive adhesive agent on the backs of the materials with water.

The underlying concept is that, by applying water, the layer of water- and thermosensitive adhesive agent dissolves, and simultaneously due to the water the layer of the pressure- and thermosensitive adhesive agent becomes white, swollen and consequently, sticky, with the result that the two adhesive agents are commingled and exhibit strong adhesive property. Because the water- and thermosensitive adhesive agent will melt at 110–117° C. and thus have an increased crystallinity, the material may be heated, after its application if necessary, so that the adhering strength may increase with the increase in crystallinity of the adhesive agent.

Of the two types of the decorative construction materials described above, the particular type wherein the decorative material is partially adhered with a film of water- and thermo-sensitive adhesive agent by a pressure- and thermosensitive adhesive agent, will, when the layer of water- and thermosensitive adhesive agent is wetted with water, dissolve on direct contact with the back surface of the decorative material. On the other hand, when the water- and thermosensitive adhesive agent has in its molecule many hydroxyl groups and consequently has a high affinity with cellulosic materials. On the other hand, the decorative material may be a cellulosic type material such as a cloth or paper. Therefore, in general this type of decorative construction material has a higher adhesive strength compared with the other types of decorative construction material wherein the two adhesive agents are stuck over the whole surface. This can be observed from the data set forth in the later-appearing Example 5 wherein a staple fiber fabric was used as the decorative material. Again in the former type of decorative construction material, the portions of the film of water- and thermosensitive adhesive agent which are not in contact with a pressure- and thermosensitive adhesive agent are more easy-soluble, and therefore this type of material become quickly effective, that is, the time length between the wetting of the back applied with the adhesive agents and the material's exhibiting of stickiness is short, and also its initial adhesive strength is great. This fact is also illustrated in the later-appearing Example 5.

The invention shall now be explained with respect to the following examples, it being understood that the invention shall in no way be limited thereby.

EXAMPLE 1

An adhesive composition was prepared by mixing the following three at the indicated ratio.

	Parts by weight
Vinyl acetate-butyl acrylate copolymer (ratio of co-polymerization 8:2)	50
Urea-melamine precondensate	30
Tricresyl phosphate	20

The composition was evenly daubed over the entire back surface of a non-woven fabric (a long, continuous material of unit weight 130 g./m.^{2}, and width 1 m.) by means of a roll-coater, and while the daubed surface still remained moist, a film of partially urethanized polyvinyl alcohol of 6% urethanization was adhered thereto, and the material was dried. Said film of the adhesive agent having acid- and alkali-resistant properties, thus prepared decorative construction material is very useful when applied on concrete surface.

EXAMPLE 2

An adhesive composition was prepared by mixing the following:

	Parts by weight
Polyvinyl acetate (degree of polymerization 500)	50
Glue (6.7% aqueous solution)	20
Methylcellulose (6.7% aqueous solution)	10
Glyoxal	15
Dibutyl phthalate	5

(This composition shall be hereafter referred to as the adhesive agent A.)

The adhesive agent A was evenly daubed on the back of a staple fiber textile as wall cloth (a long, continuous material of a unit weight 200 g./m.^{2}, and a width 1 m.) over the entire surface by means of a roll-coater. While the daubed surface still remained moist, a film of polyvinyl alcohol having a saponification degree 88±1, and a polymerization degree of 1725±25, was adhered thereto and dried. Thereby a decorative construction material of the invention having a structure wherein the layer of the adhesive agent A and that of the polyvinyl alcohol film were adhered by the one entire surface was obtained. (The material hereafter shall be referred to as the decorative construction material I.)

Using the similar roll-coater, the adhesive agent A was daubed on the back of the same staple fiber textile at spots, on which the same polyvinyl alcohol film as in the above was applied. Thereby a decorative construction material of the invention having a structure wherein on the back of the decorative material polyvinyl alcohol film was adhered by the adhesive agent A applied at spots was obtained. (The material hereafter shall be referred to as the decorative construction material II.)

EXAMPLE 3

A pressure- and thermosensitive adhesive agent was prepared by mixing the following five at the indicated ratio.

	Parts by weight
Polyvinyl butyral (polymerization degree 100)	10
Butadiene-acrylonitrile copolymer (synthetic rubber)	5
Toluene-alcohol mixed solvent (mixture ratio by volume 6:4)	83
Dibutyl phthalate	1
Triphenol phosphate	1

The same was daubed on an entire surface of a film of 88% saponified product of vinyl alcohol-crotonic acid (95:5) copolymer by means of a doctor-coater, and immediately thereafter the daubed film was put on the back of a loose fabric composed of straw yarn (a long, continuous material of a unit weight 150 g./m.^{2}, and a width 1 m.), and dried.

Thus obtained material is suitable for application on concrete surface, because said adhesive agent film has acid- and alkali-resistant properties.

EXAMPLE 4

An adhesive agent was prepared by mixing the following:

	Parts by weight
Vinyl chloride-vinyl acetate copolymer	70
Dioctyl phthalate	10
Tricresyl phosphate	15
Maleic acid	2
Cadmium stearate	3

The composition was evenly applied on the back of an uncut, long plastic tile by means of a doctor-coater, and dried. Thereafter an aqueous solution of polyvinyl alcohol similar to that used in Example 2 was daubed on the same surface, and dried.

EXAMPLE 5

Three test samples were prepared by evenly daubing on the backs of three sample patches of 10 cm. x 5 cm. of the same staple fiber textile as used in Example 2, each diluted wheat starch paste (viscosity 6000 cps.), thick wheat starch paste (viscosity 16,000 cps.) and the adhesive agent A of Example 2. The samples shall be called, by the stated order, each sample III, IV and V.

Next with the sample patch of the staple fiber textile of the same size, the decorative construction materials I and II as described in Example 2 were prepared, which shall be herein called test samples I and II.

The table below shows the comparison of the adhesive strength of those five test samples.

The testing method was as follows:

The diagonal sample patches of the said size each applied with different adhesive agent were stuck on the back (smooth polished surface) of a slate plate inclined by 45°, in such a manner that their shorter side lines become horizontal, and under the conditions of 23±1° C. and relative humidity of 50%, at each indicated time passage, a weight was hung from the edge of upper side line of the sample and the heaviness of the weight at the time the sample started to peel from the slate was recorded as the peeling load.

Further as to the decorative construction materials I and II of the invention, the time lapse from wetting till they showed stickiness was measured.

Sample No.	Time passed before stickiness appeared	Load (g.) at time of peeling after— 10 min.[1]	20 min.[1]	30 min.[1]	60 min.[1]	24 hr.[1]	48 hr.[1]
III		4	7	13	60	500	800
IV		8	13	30	150	600	900
V		120	160	220	800	2,000	2,500
I	120	150	200	280	1,000	2,500	3,000
II	30	300	400	500	1,200	3,500	4,500

[1] After application.

Thus in the decorative construction materials of the invention having such a structure wherein the pressure- and thermosensitive adhesive agent is sandwiched between the decorative material and the layer of water- and thermosensitive adhesive agent, the water- and thermosensitive adhesive agent layer functions as the peelable paper in the conventional products, and prevents the pressure- and thermosensitive adhesive agent from sticking to other materials and from aging. Again because the water- and thermosensitive adhesive agent needs not be peeled at the time of use unlike the conventional peelable paper, but is dissolved upon being wetted to show a strong adhesive property as mixed with the pressure- and thermosensitive adhesive agent, the decorative construction materials of the invention are very convenient for use. They also enable such a practice as applying them to still wet surfaces without first drying,

such as a concrete wall surface just poured in. Furthermore, the decorative construction materials of the invention being of the structure lined by the layer of water- and thermosensitive adhesive agent, they are rich in suppleness, have excellent hand, are free of static electricity, are beautiful and have great commercial value. Furthermore, they will not, for example, brock and stick during storage in rolled form, or curl. In case the method of adhering the film of water- and thermosensitive adhesive agent is employed for the manufacture of the decorative construction materials of the invention, there is such additional advantage that the film may be printed in advance of various trademarks, rules and arrows, or instruction for use.

Besides the aforesaid advantages that their application is simple and they may be immediately applied on wet walls, the decorative construction materials of the invention possess the following great advantages in practice and effects. That is, they are applicable not to limited types of substrate, but can adhere well to surfaces of any materials such as concrete, clay wall, metal, wood, plastics, etc. The freedom in application is also great, that is, before the adhesion completes, misplacing of the decorative construction materials or their slight distortion or shift can be freely adjusted. In case the decorative construction material employed is of the type wherein the pressure- and thermosensitive adhesive agent is partially applied, for example, at spots, vacant spaces being formed between the decorative material and the substrate, soundproof, moist-proof and heat-insulating effects are brought about. Also because the lines of junction of the decorative materials applied on a surface do not become raised up, when the materials of the invention are applied on, for example, a wall of large area, very appealing effect can be achieved, that is, the appearance is not impaired as often observed in the past. They again can achieve stronger adhesion upon being heated after application. These are the advantages unique to the invention, never expectable from the conventional decorative construction materials.

It is also possible with the invention to subject the decorative materials to such treatments as that for water-repelling with aluminum acetate, silicon, or triazine; or a soiling-resistant treatment with a polyvinyl alcohol solution of low concentration, CMC, starch paste; and anti-flammable treatment with carbonates, borates, or phosphates; or insecticidal and mold-resistant treatments with various suitable agents in advance, thereby to all the more enhance the advantages of the invention.

Since it is apparent that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited thereto except as set forth in the appended claims.

What is claimed is:

1. A decorative material adapted to be adhesively attached to a solid surface by wetting one surface of said decorative material consisting essentially of

(a) a decorative sheet material having a decorative design on one surface thereof, said sheet material being selected from paper and textile fabrics;

(b) a pressure- and thermosensitive adhesive agent coated on the surface of said decorative sheet away from said decorative design in a series of spaced areas in a repeating pattern of a selected design of an amount sufficient to attach said decorative sheet to a solid surface, said pressure- and thermosensitive adhesive being selected from the group consisting of polyvinyl acetate, vinyl acetate-butyl acrylate copolymers, polyvinyl butyral, and vinyl chloride-vinyl acetate copolymers;

(c) a self-supporting film of a water- and thermosensitive adhesive agent adhesively bonded to said spaced areas on the side opposite said decorative sheet, said water- and thermosensitive agent being selected from partially saponified polyvinyl alcohol having a degree of saponification between 85 and 97%, or copolymers of partially saponified polyvinyl alcohol having a degree of saponification between 85 and 97% with crotonic acid, isopropenyl acetate or ethylene oxide, said areas being so spaced from each other than when said self-supporting film is in contact with water, said water- and thermosensitive adhesive agent and said pressure- and thermosensitive adhesive comingle to form a single adhesive layer.

2. The decorative material of claim **1** wherein the said sheet material is paper.

3. The decorative material of claim **1** wherein said sheet material is a non-woven fabric.

4. The decorative composition of claim **1** wherein said sheet material is a woven textile fabric.

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