

- [54] **PROCESS FOR TREATING FABRICS**
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- [22] Filed: **Sept. 24, 1971**
- [21] Appl. No.: **183,371**

- [52] U.S. Cl. .... **156/85**, 28/76 P, 117/8.5, 117/11,  
117/15, 156/277, 161/63, 161/64, 161/67
- [51] Int. Cl. **B29c 27/00**, B32b 31/00, D03d 27/00,  
D04h 11/00
- [58] **Field of Search** ..... 28/76 P;  
161/62-67; 117/8.5, 9, 11, 12, 15, 33;  
156/84, 85, 86, 72, 279, 277; 8/1, 115,  
115.5, 116

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[57] **ABSTRACT**  
 The process for producing unusual texturized effects in a three-component laminate having a facing component having upstanding fibers, a backing component and a water-insoluble interlayer component securing the facing component to the backing comprising applying a chemical shrinking agent to the fibrous component in a pre-determined design pattern, drying the fabric and washing the fabric. Also disclosed is a process for producing multi-color effects in such laminates by dyeing the laminate, applying a chemical shrinking agent to the fibers in a pre-determined design pattern, said shrinking agent being capable of changing the color of said dye, drying the laminate and then washing the laminate. Laminates obtained are described.

**9 Claims, 3 Drawing Figures**

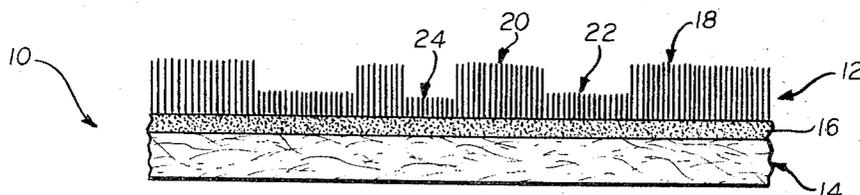


FIG. 1.

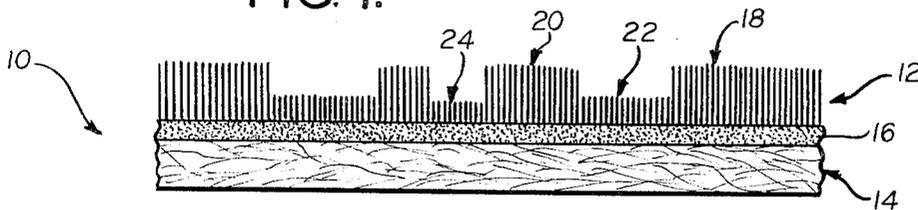


FIG. 2.

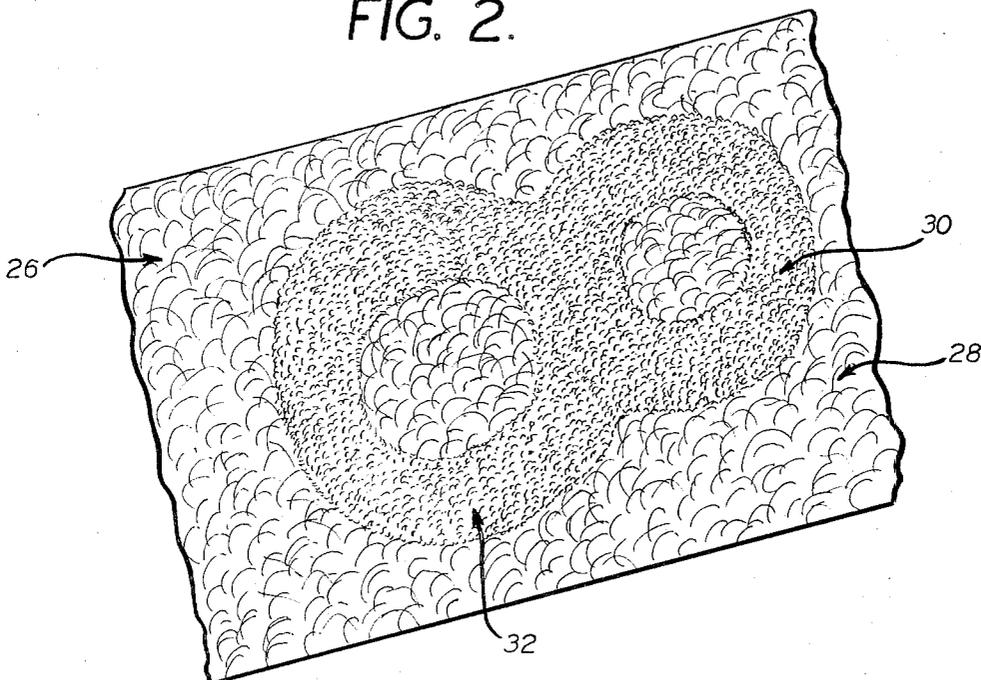
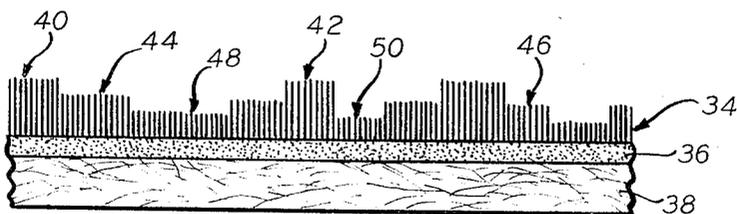


FIG. 3.



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## PROCESS FOR TREATING FABRICS

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

This invention pertains to the field of texturization of laminates. More particularly, this invention concerns methods for chemically affecting unusual texturization and color effects in three-component laminates having a facing component of upstanding fibers backing component and a water insoluble interlayer securing the facing component to the backing component.

## 2. Description of the Prior Art

The use of chemical shrinking agents to shrink woven and non-woven fabrics is known. Techniques for applying such shrinking agents as well as the preferred shrinking agents for various types of textiles fibers are also known. (See for example Bull. Inst. Textile France No. 102, pages 871-885 (1962)).

A type of laminate or fabric which such chemical shrinking techniques have not been applied are three-component laminates. Such laminates are generally composed of a facing component as hereinabove described, a base or backing component which provides the fabric with its structural strength and a water-insoluble interlayer, usually an adhesive substance, which interlayer secures the facing component to the backing component.

Because of the three-component nature of such laminates, the texturization processes used heretofore have been limited generally to physical methods, such as, for example, mechanically cutting, compressing or compacting areas of the upstanding fibers of the facing component. These methods, however, tend to require complicated equipment resulting in relatively high production cost.

## SUMMARY OF THE INVENTION

We have discovered a new three-component laminate comprising a facing component of upstanding shrunken and unshrunken fibers, the shrunken fibers being shorter than the unshrunken fibers, and wherein the combination of such shrunken and unshrunken fibers form a pre-selected design pattern in the facing component; a backing component; and a water-insoluble, substantially continuous interlayer disposed between the facing component and the backing component and securing the facing component to the backing component.

Thus, the tops of those fibers which are unshrunken define a level or plateau which is higher than that defined by the tops of the shrunken fibers resulting in the novel texturized effect.

We have also found a method for producing such laminates which comprises applying a chemical shrinking agent to the upstanding fibers in a pre-determined design pattern, drying the laminate, and washing the laminate. When such laminates are dyed subsequent to the washing step, not only are unusual texturized effects obtained, but also the shrunken areas of the fibers are a different shade from the unshrunken areas thereby imparting an unusual color effect to the laminate.

Additionally, we have discovered a new multi-colored laminate and method for producing such laminates which comprises dyeing the facing component of the above described three-component laminate, apply-

ing a chemical shrinking agent to the fibers in a pre-determined design pattern, said shrinking agent being capable of changing the color of said dye, drying the laminate and washing the laminate. The laminate thus obtained possesses not only the texturized effect described above, but also, those areas of the facing component to which the shrinking agent was applied exhibit a color different from the color of the untreated areas of the facing component.

We have further discovered that the three components of the laminate may be dyed independently of one another either before or after the shrinking step as described hereinabove, whereby a large range of unusual and highly desirable color and shade effects may be obtained.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view of a laminate in accordance with the present invention.

FIG. 2 is a perspective view of a laminate in accordance with the present invention.

FIG. 3 is a view similar to that of FIG. 1 of another embodiment of the invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to the drawings, and particularly FIG. 1, the present invention comprises a three-component laminate designated generally at 10, having a facing component 12, a backing component 14 and an interlayer component anchoring the facing component to the backing component.

The facing component may be any type of upstanding or raised fibers and while single fibers are shown in FIG. 1, it is understood that the upstanding fibers can be in the form of loops and the like. Additionally, certain areas of the facing component such as those designated at 22 and 24, have been shrunken, resulting in unshrunken areas, such as, 18 and 20. Such shrinking is produced in a pre-determined design pattern so that the combination of the shrunken areas and the unshrunken areas result in a sculptured or texturized effect on the face of the laminate.

This effect is shown clearly in FIG. 2 which is a perspective view of just such a laminate showing the design of a figure eight on the face. Thus, in FIG. 2, the areas depicted at 26 and 28 are the unshrunken portions whereas the areas depicted at 30 and 32 are shrunken area.

As used herein, the term texturized effect or texturization effect means the production in the facing component of a three-dimensional or sculptured effect thus resulting in a design pattern appearing on the face of the laminate.

Referring again to FIG. 1, suitable materials for use as the facing component include rayon, cotton, nylon, polyester, wool, mohair, silk, acrylics, modacrylics, and the like. The type of textile material used is not critical so long as it can be shrunken.

The most well known form for the fibers in the facing component is that of a flock which comprise short fibrous or filamentary material generally less than a one-fourth of an inch in length. This flock is usually deposited upon an adhesive coated base. However, as noted hereinabove, the laminate of the present invention include those having facing components which would not necessarily be within the description of flock generally

known to the skilled art worker. For example, the raised fibers may be looped, or longer than a conventional flock material. Thus, types of laminates which are suitably within the framework of the present invention are velvet fabrics, flocked fabrics, wallcoverings, etc., carpeting or other type of three-component floor covering, etc.

The production of flocked fabrics are well known to the art (see for example U.S. Pat. No. 3,079,212 incorporated herein by reference.)

Backing component 14 may be either flexible or rigid. Suitable flexible backings include polyvinyl and urethane films; non-woven fabrics, and fabrics composed of cellulose-based fibers, e.g., rayon or cotton, and synthetic and natural fibers. Particularly preferred blends are those of cellulose-based fibers, wool, mohair, silk, acrylics, modacrylics, and the like.

Suitable rigid backings include such materials as Masonite, wood, glass, metals, fiberglass laminates, and the like.

Suitable materials for the interlayer component 16 include adhesives normally used to bind fibrous material to backings. Such adhesives are generally classified as water base and solvent base adhesives.

Water base adhesives consist of a binder, generally an emulsion polymer, and a viscosity builder. They may also contain plasticizers, thermosetting resins, curing catalysts, stabilizers and other additives well known in the art.

The emulsion polymers generally used include acrylic, vinyl-acrylic, vinyl, urethane and styrene-butadiene latexes. In order that the upstanding fibers be held in the desired position until the adhesive is fully cured, it is generally necessary to raise the viscosity of the latex to about 30 to 100 thousand centipoises. The viscosity is dictated by the nature of the backing and the method of contacting the upstanding fibers with the adhesive layer. For example, where the backing is a loose weave fabric and the beater bar method is employed, a viscosity of from 70 to 100 thousand centipoises or higher will be necessary to prevent undue penetration of adhesive into the backing which would result in a boardy hand and would leave insufficient adhesive on the surface to securely bind the fibers. On the other hand where a relatively impervious backing such as hard board is used, a much lower viscosity, e.g., about 20 to 30 thousand centipoises is sufficient.

Suitable thickeners include water soluble polymers such as carboxymethyl cellulose, hydroxyethyl cellulose, polyoxyethylenes, and natural gums as well as alkali swellable polymers such as highly carboxylated acrylic emulsion polymers.

Plasticizers may be added to alter the hand of the finished goods or to improve the flow and leveling characteristics of the adhesives. Where the primary goal is the latter, fugitive plasticizers such as the phthalate esters may be employed. If the intent is to alter the hand of the finished goods, then more permanent plasticizers such as low molecular weight polyesters may be used.

Thermosetting resins such as methylol-melamines, urea formaldehyde condensates or phenol-formaldehyde condensates may be incorporated to improve durability or abrasion resistance of the finished goods.

Catalysts such as oxalic acid or diammonium phosphate can be used to increase the rate of cure of the adhesive.

More specialized additives include ultra-violet absorbers where the backing, such as urethane foam, is subject to photo degradation and dyes or pigments to impart a color to the adhesives may be chemically or mechanically foamed.

Solvent adhesives include both fully reacted soluble polymers such as acrylic homo and copolymers, polyesters, polyimides, or polyurethanes and two package systems such as polyester polyols with diisocyanates or isocyanate prepolymers and epoxies with polyamines. The polymer or prepolymer is dissolved in a suitable preferably low boiling, solvent and thickened to the proper viscosity as for the water base adhesives. Catalysts, crosslinking agents, stabilizers, pigments, or dyes may also be incorporated.

The texturized laminate of the present invention may be prepared by first applying a shrinking agent to the facing component of the fabric in a preselected pattern design. The shrinkage agent may be applied in the form of a paste composition by printing the paste onto the fibers. Methods for formulating such pastes as well as the printing thereof are well known in the art. Thus, for example; the printing may be carried out on conventional color and dye printing machines, such as, rotary silk screen, rollers, etc.

Alternatively, the shrinkage agent may be applied to the raised component in a selected design pattern by spraying. Such spraying techniques are also conventional.

Many types of well known chemical shrinking agents may be used depending on the nature of the fibers comprising the facing component, the interlayer, and the nature of the backing component. Thus, it is understood that the shrinking agent should be a material which will not chemically attack either the interlayer or the backing component. Moreover, in all cases, the residue of the shrinking agent should be readily removable in a back washing step, such as, for example, a mildly alkaline back wash which would be used to remove acidic agents from a facing component made of nylon.

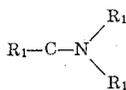
Additionally, shrinking agents should be avoided which would readily diffuse through the adhesive layer and would permit the agent to contact the backing component or cause a weakening of the securement of the facing component to the backing component.

When the raised component is nylon, the shrinkage agent should be an acidic material having a dissociation constant greater than about  $2 \times 10^{-5}$ . Suitable acidic materials include strong mono and polybasic inorganic acids and organic acids having the formula  $R-COOH$  wherein R is hydrogen, lower alkyl having 1 to 5 carbon atoms or halogen substituted lower alkyl. Particular suitable acids include acrylic acid, formic acid, monochloroacetic acid, dichloroacetic acid, alpha-chloropropionic acid, bromoacetic acid, trifluoroacetic acid, o-chlorobenzoic acid, 3, 5-dinitrobenzoic acid, sulfonic acids, such as, p-toluenesulfonic acid, benzenesulfonic acid, and phenols, such as, m-cresol, and p-chlorophenol.

The mineral acids, such as, hydrochloric and sulfuric acids are also suitable providing they are utilized in a sufficiently diluted form to minimize fiber degradation.

When the raised component is a polyacrylic material, the shrinking agent may be an acid such as defined hereinabove as being suitable for nylon; a salt formed from cations selected from the group consisting of  $Zn^{++}Ag^{+}$ ,  $Ni^{++}$ ,  $Co^{++}$ ,  $Mn^{++}$ , and an anion selected

from the group consisting of  $\text{SCN}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{Cl}^-$ ; di-substituted amides having the formula



wherein  $\text{R}_1$  is hydrogen or lower alkyl having from 1 to 5 carbon atoms, or lower alkyl carbonates, the alkyl portions of which contain 1 to 5 carbon atoms.

Particularly suitable shrinking agents for polyacrylics include alpha-chloroacetic acid, trifluoroacetic acid, hydrochloric acid, nitric acid, sulfuric acid, zinc iodide, silver iodide, ethylene carbonate, propylene carbonate and dimethyl acetamide.

When the facing component is a cellulosic derived material, the shrinking agent should be a basic material. Suitable shrinking agents for cellulose include inorganic bases such as sodium hydroxide, potassium hydroxide, barium hydroxide, ammonia, strong organic bases having a dissociation constant greater than about  $2 \times 10^{-5}$ , such as benzyltrimethylammonium hydroxide and tetraethylammonium hydroxide, and organic amines such as, ethylamine, triethyl amine, diisopropyl amine, dibutyl amine, ethylene diamine, triethylene tetramine, and the like.

The shrinking agent is generally applied in the form of a paste so as to prevent migration of the agent outside of those areas of the facing component which are to be treated. The concentration and viscosity of the shrinking agent will vary depending on the amount of shrinkage and color effects desired. Although generally the shrinking agent is in an aqueous solution or mixture, it is possible depending on the laminate used and the shrinking agent to use other solvents.

The viscosity of the mixture or paste is usually varied by adding a thickening agent in a manner well known in the art. The preparation of such pastes are well known to the art and, of course, the rheology of the paste will depend on the thickening agent used.

After the application of the shrinking agent to the facing component, the laminate is dried. The conditions of drying will depend not only on the reactivity and the concentration of the shrinking agent, but also on the nature of the heating mechanism and the type laminate being shrunk. Thus for example, when conventional laboratory ovens are used to affect shrinkage of cellulose, the sodium hydroxide shrinking agent concentration is preferably in the range from about 30% to 50% and the heating is preferably carried out at a temperature in the range from about 80 to 125°C. When high pressure steam-heated, can dryers of the conventional type normally found in textile mills are used, the preferred concentration range for sodium hydroxide when treating a cellulosic material is from about 10 to 25%.

When a volatile shrinking agent is used, it is generally preferable to heat the material with the shrinking agent thereon in an autoclave. Of course, if a more reactive shrinking agent is used, the drying may be carried out at a lower temperature. Thus, for example, with very reactive shrinking agents, it is possible to dry at room temperature.

Consequently, the drying operation can be carried out in a temperature range from about ambient to a temperature limited only by the degradation tempera-

ture of the components of the laminate. Usually, the preferable operating temperature would be in the range from about 80 to 160°C.

After the drying step, the laminate is washed to remove any remaining or residual shrinking agent. The components and pH of the backwash, will, of course, depend on the nature of the shrinking agent. Usually it is most desirable for economic reasons that the back washing solution be aqueous.

When the shrinking agent is an acid having a dissociation constant greater than about  $2 \times 10^{-5}$ , an aqueous wash solution containing a relatively weak base such as for example, sodium carbonate, trisodium phosphate, or ammonia can be used. When the shrinking agent is a weak acid such as phenol, a more alkaline washing solution may be required.

If the shrinking agent is an alkaline material having a dissociation constant greater than about  $2 \times 10^{-5}$ , an aqueous solution containing any inorganic acid with a dissociation constant greater than about  $1 \times 10^{-5}$  can be used. It is understood, of course, that the washing solution must not contain any materials which will either degrade the materials comprising the laminate or attack the adhesive interlayer.

It is also possible, when the shrinking agent is an organic solvent, to remove any residual shrinking agent by steaming or volatilization as by passing the laminate through ovens or over hot cans.

The laminate resulting from the foregoing process possesses a textured face which exhibits a 3-dimensional sculptured effect. It is further possible, if desired, to enhance the 3-dimensional effect by dyeing the laminate with appropriate dyes. Such dyeing can be carried out either before the application of a shrinkage agent or subsequent to the washing step. Moreover, inasmuch as each of the components of the laminate is susceptible to dyeing, it is possible by independent dyeing of the components, to achieve many combinations of effects as well as unusual effects. Thus, for example, it is possible to subject the textured laminate to a dyeing step wherein only the adhesive interlayer is dyed. Usually this is carried out with dispersed dyes. Alternately, it is possible to union dye the laminate by subjecting it to a mixture of one or more dyes, each of the dyes having an affinity for a different component of the laminate.

Additionally, inasmuch as many of the adhesive interlayers known to the art are essentially colorless or transparent, it is possible to dye the backing component, with one color of dye and dye the facing component with different color dye. As a result of the variation in levels of the fibers in the facing component, one obtains an unusual variation in color shades between the shrunken and unshrunken portions of the facing component.

If the facing layer is dyed one color, for example blue, and the interlayer is dyed a different color, for example yellow, the unshrunken areas of the facing layer will appear bluish and the shrunken areas will appear greenish (combination of blue and yellow). Also, the fabric will take on different color effects depending on its angle to the light.

When the dyeing step is carried out subsequent to the washing step, a multi-shade effect is obtained. As used herein, the term multi-shade means an effect wherein the shrunken portion of the facing component is a different shade from the unshrunken portion, the color,

however, of both portions being the same. As noted hereinabove, additional effects can be obtained by independently dyeing the various components of the laminate which enhance the multi-shade effect.

Also, as described hereinabove, when different color dyes are used for the different components, variations in apparent color of the facing layer can be obtained.

In yet another embodiment of the present invention, it is possible, when the appropriate combinations of dyestuffs and fibers are used, to obtain a multi-color effect in the laminate. As used herein, the term multi-color effect means that the shrunken areas of the facing component of the laminate are a different color of the unshrunken areas of the laminate.

This effect is obtained by first dyeing the facing component of the laminate and then applying a shrinking agent to the facing component in the manner as described hereinabove in a predetermined pattern design, which shrinking agent is capable of changing the color of the dye. Understandably, the selection of the dye depends upon the type of fiber comprising the facing component of the laminate. In turn, the shrinking agent selected depends on the dye used. Thus, the fiber comprising the facing component must be receptive to the dye and the shrinking agent must be capable of changing the color of the dye.

Many combinations of fibers, dyes, and shrinking agents which meet the foregoing requirements are well known to the skilled art worker.

Preferably, the facing component of the laminate is composed of a cellulosic containing material such as, for example, rayon, cotton, and blends of such cellulosic materials with synthetic materials such as, for example, nylon, polyesters, acrylics, modacrylics, vinyl acetate, and the like.

Dyes which are particularly suitable for use in this embodiment of the invention includes those to which the aforescribed cellulosic materials are susceptible, such as, sulfur dyes, naphthol dyes, vat, direct or dispersed dyes. Particularly, such dyes produce the here-indescribed multi-color effect upon treatment with suitable shrinking agents, such as, for example, sodium hydroxide, potassium hydroxide and the like or the strong organic bases described hereinabove, such as, for example, ethylenediamine, choline, etc.

Of course, it is understood that in order to achieve the multi-color effect, it is easily within the skill of the art worker to select a proper combination of fiber material, dye and shrinking agent so long as they meet the requirements described hereinabove.

The laminate obtained from the foregoing process exhibits a 3-dimensional sculpture effect and a multi-color effect inasmuch as those areas of the facing component which were treated with a shrinking agent are a color different from the areas which were not so treated.

Additionally, as noted hereinabove, the other components of the laminate may be independently dyed so as to produce even more unusual color effects.

As shown in FIG. 1, a textured effect is obtained as a result of given areas of the facing component 12 being shrunken, all of the shrunken fibers being shrunken the same amount. However, a different type of sculptured effect can be obtained by varying the shrinkage of the shrunken areas of the facing component.

Thus, shown in FIG. 3 is a laminate comprising a facing component 34, interlayer component 36 and backing component 38 similar to that described with reference to FIG. 1. However, those of the upstanding fibers comprising the facing component which are shrunken are shrunken in varying amounts. Thus, for example, the areas at 40 and 42 are unshrunken. The areas at 44 and 46 are shrunken, and the areas at 48 and 50 are shrunken even a greater amount than those at areas 44 and 46. Consequently, the facing layer possesses a three-leveled sculptured effect, wherein the shrunken fibers are composed of at least two portions, the shrinkage of each of the portions being different from that of any other portion.

A laminate possessing such a three or more layered sculptured effect as exemplified in FIG. 3 may be prepared by treating a laminate as described with reference to FIG. 1, with the exception that more than one application of shrinking agent is used, the applications differing in the strength of shrinking agent used. The strength of the shrinking agent may be varied by using a different shrinking agent or varying the concentration of the same shrinking agent.

Thus, for example, the laminate may be printed with a certain concentration of the shrinking agent in a given design. Then, the laminate is again printed with a higher concentration of the same shrinking agent or a different, more powerful, shrinking agent, in a different design. On drying and washing, the areas printed with the more concentrated or reactive shrinking agent are shrunken a greater amount than those areas wherein the less concentrated or reactive shrinking agent was applied. The different applications may be carried out in separate steps or in a single step by using several printing rollers in sequence.

Even more complicated sculpturing effects can be obtained by using additional shrinking agent application steps.

The following examples illustrate our invention (Unless otherwise indicated, in the following examples, the adhesive used was an aqueous based acrylic binder.)

#### EXAMPLE 1

A fabric composed of 1 mm. rayon flock and a woven rayon backing material with the flock being anchored to the backing material by an adhesive was dyed with a sulfur dye of a yellow color, (Sodyesul Yellow YCF - C. I. Name: Sulfur Brown 3) and with a fiber reactive dye of a blue color (Procion Blue M3RS - C. I. Name: Reactive Blue 9) in the second step. The dyed fabric exhibited an overall green color.

A design was printed onto the rayon flock with a printing paste composed of 30% sodium hydroxide, 3% carboxymethylated starch as a thickening agent and 67% water. The printed fabric was dried for 5 minutes at 125°C., washed in water (50°C), rinsed in a 5% acetic acid solution, rinsed in cold water and dried.

The modified fabric exhibited a flock shrinkage of approximately 50% in the printed areas and a three-dimensional effect. The shrunken regions exhibited a color change from the original green color to a yellow color.

#### EXAMPLE 2

A fabric composed of 1 mm. rayon flock and a woven rayon backing material with the flock being anchored to the backing substrate by an adhesive was dyed with

a green vat dye (Ponsol Jade Green - Du pont - C. I. Name: Vat Green 1, C. I. Number 59825) and with a red fiber reactive dye (Procion Red H7BS - C. I. Name: Reactive Red 4) in a second step. The dyed fabric exhibited an overall violet color.

A design was printed onto the rayon flock with a printing paste composed of 50% sodium hydroxide, 4% carboxymethylated starch, and 66% water. The printed fabric was dried for 5 minutes at 125°C., washed in water (50°C), rinsed in a 5% acetic acid solution, rinsed in cold water and dried at 100°C.

The modified fabric exhibited a flock shrinkage of approximately 50% in the printed regions, a textured appearance, and a green color (in the shrunk regions) on a violet background (non-shrunk regions).

#### EXAMPLE 3

A fabric composed of 1 mm. rayon flock and a woven rayon backing substrate with the flock being anchored to the backing substrate by an adhesive was dyed with a blue fiber-reactive dye (Procion Blue M3RS - C. I. Name: Reactive Blue 9) and with a dispersed orange dye (Amacron Orange BL-American Aniline - C. I. Name: Dispersed Orange 5, C. I. Number 11100) in a second step. The fabric exhibited an overall dark blue color.

A design was printed onto the rayon flock with a printing paste composed of 50% sodium hydroxide, 5% carboxymethylated starch as a thickening agent, and 45% water. The printed fabric was dried 4 minutes at 100°C., and washed as outlined in Example 1.

The modified fabric exhibited a flock shrinkage of approximately 50-60% in the printed regions, a textured effect and a color change from the original dark blue to a light reddish brown color.

#### EXAMPLE 4

A woven rayon fabric to which a 1½mm. rayon flock was bonded by an adhesive was locally treated with liquid ammonia on the flocked side. The fabric was air dried and conventionally dyed with sulfur dye (Sodyesyl Yellow YCF - C. I. Name: Sulfur Brown 3). The treated fabric exhibited a textured and two-toned effect.

#### EXAMPLE 5

A commercially obtained urethane/nylon laminate was coated with a flock binder on the urethane side and flocked with 1½mm. rayon flock. A pattern was printed onto the flock with a paste composed of 30% potassium hydroxide, 4% carboxymethylated starch and 66% water. The printed substrate was dried for 10 minutes at 100°C. The substrate was washed and dried as outlined in example 1 and then dyed with Sodyesul Brass 5024 (Sulfur Brown 37 and Sulfur Brown 3) according to conventional methods.

The flocked laminate exhibited textured flock and a two-toned effect.

#### EXAMPLE 6

Commercially obtained Masonite was coated with a urethane based flock binder and flocked with ¼ mm. rayon flock. The flocked Masonite was printed with a 20% sodium hydroxide paste on the flocked side. The printed material was dried for 3 min. at 120°C., washed in warm water (50% ) until all of sodium hydroxide was removed and was then dried.

The treatment produced a textured flock surface and a two-toned effect.

#### EXAMPLE 7

A design was printed onto a nylon carpet comprising a woven cotton backing substrate and a nylon flock 2 mm. in length with the flock being anchored to the backing substrate by an adhesive. The printing paste was composed of 80% formic acid, 10% fumed silica. The printed carpet was dried for 1 minute at 80°C. The dried paste was removed by brushing.

The finished carpet exhibited a three-dimensional pattern.

#### EXAMPLE 8

A fabric comprising a woven cotton backing substrate and a 1½mm. rayon flock with the flock being anchored to the backing substrate by an adhesive was printed in pre-selected areas with a paste composed of 10% sodium hydroxide, 4% carboxymethylated starch, and 36% of water. The fabric was dried over a series of hot cans, and was then steamed for 8 minutes. Subsequently the fabric was washed as outlined in Example 1.

The fabric was dyed with a yellow sulfur dye (Sodesul Yellow YCF - C. I. Name: Sulfur Brown 3) and was then dyed dispersed blue (Terasil Blue-Ciba - C. I. Name: Dispersed Blue 56) according to methods well known in the art.

The finished fabric exhibited a textured flock surface, a brown color in the non-printed areas and a green color in the printed areas. The brown and the green color changed shade when exposed to the light at different angles thus exhibiting chambeleon type characteristics.

#### EXAMPLE 9

A fabric composed of a woven rayon backing substrate and a 1 mm. rayon flock with the flock being anchored to the backing substrate by an adhesive was printed with sodium hydroxide paste on the flocked side by using two printing rollers simultaneously. From the first roller, a 10% sodium hydroxide paste was applied and from the second roller, a 20% sodium hydroxide paste. The printed fabric was dried over a series of steam cans and was then washed as outlined in Example 1. The fabric was dyed with a blue fiber reactive dye (Procion Blue M3RS - C. I. Name: Reactive Blue 9).

The fabric exhibited a textured appearance and a three-toned effect.

#### EXAMPLE 10

A design was printed onto a 1½mm. acrylic flock with the flock anchored to a cotton fabric by an adhesive. The printing paste was composed of 25% zinc chloride, 5% carboxymethylated starch, and 70% water. The printed fabric was dried for 5 minutes at 125°C. The fabric was dyed with a dispersed dye (Terasil Blue - Ciba - C. I. Name: Dispersed Blue 56) according to conventional methods.

The finished fabric exhibited a textured effect.

Variations and modifications may, of course, be made, without departing from the spirit and scope of the present invention.

Having thus described our invention we desire to secure and claim by Letters Patent:

1. A method for producing three dimensional and variable color effects in a laminate of the type composed of a backing layer, a facing layer of upstanding fibers, and a water insoluble, substantially continuous binder inter-layer, securing the facing layer to the backing layer, consisting of:

- a. shrinking selected areas of the facing layer in a predetermined design pattern by applying a chemical shrinkage agent to said selected areas;
- b. drying the laminate; and
- c. washing the laminate.

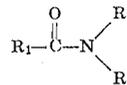
2. The process of claim 1 wherein the fibers are nylon, cellulose, or polyacrylic.

3. The process of claim 2 wherein the fiber is nylon and the shrinking agent is an acid having a dissociation constant greater than about  $2 \times 10^{-5}$  and is selected from the group consisting of strong mono and polybasic inorganic acids; organic acids having the formula R-COOH wherein R is hydrogen, lower alkyl having 1 to 5 carbon atoms, halogen substituted lower alkyl having 1 to 5 carbon atoms or a nucleus of the phenyl series; sulfonic acids; and phenols.

4. The process of claim 2 wherein the fiber is a cellulosic material and the shrinking agent is a base selected from the group consisting of alkali hydroxides, alkaline earth hydroxides, ammonia, and organic bases having a dissociation constant greater than about  $2 \times 10^{-5}$ .

5. The process of claim 2 wherein the fiber is polyacrylic and the shrinking agent is an acid having a dissociation constant greater than about  $2 \times 10^{-5}$  and is selected from the group consisting of strong mono and

polybasic inorganic acids; organic acids having the formula R-COOH wherein R is hydrogen, lower alkyl having 1 to 5 carbon atoms, halogen substituted lower alkyl having 1 to 5 carbon atoms; or a nucleus of the phenyl series; sulfonic acids, phenols; a salt formed from cations selected from the group consisting of  $Zn^{++}$ ,  $Ag^+$ ,  $Ni^{++}$ ,  $Co^{+++}$ ,  $Mn^{++}$  and an anion selected from the group consisting of  $SCN^-$ ,  $I^-$ ,  $Br^-$ , and  $Cl^-$ ; a disubstituted amide having the formula



wherein  $R_1$  is hydrogen or lower alkyl having from 1 to 5 carbon atoms; or a lower alkyl carbonate, the alkyl portion having from 1 to 5 carbon atoms.

6. The process of claim 1 wherein subsequent to washing step (c), at least one component of the laminate is dyed.

7. The process of claim 6 wherein two of the components are dyed.

8. The process of claim 1 wherein the fibers are dyed prior to applying the shrinking agent, and wherein the shrinking agent used is capable of changing the color of said dye.

9. The process of claim 8 wherein at least one of the components in addition to the facing component is dyed.

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