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Parker et al.

[11] **4,403,004**

[45] **Sep. 6, 1983**

[54] **SANDWICH METALIZED RESIN LAMINATE**

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[73] Assignee: **Transfer Print Foils, Inc.**, East Brunswick, N.J.

[21] Appl. No.: **314,314**

[22] Filed: **Oct. 23, 1981**

[51] **Int. Cl.**[3] **B60R 13/00**; B29C 19/00; C09J 7/02

[52] **U.S. Cl.** **428/31**; 156/243; 156/244.27; 428/332; 428/335; 428/337; 428/339; 428/343; 428/347; 428/913; 428/914

[58] **Field of Search** 428/31, 343, 335, 337, 428/347, 339, 421, 463, 913, 914; 156/244.27, 243

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,152,950	10/1964	Palmquist et al.	428/335
3,720,567	3/1973	Shanok et al.	428/31
3,811,989	5/1974	Hearn	156/244.27 X
4,101,698	7/1978	Dunning et al.	428/31
4,235,949	11/1980	Van Manen et al.	428/31
4,275,099	6/1981	Dani	428/31

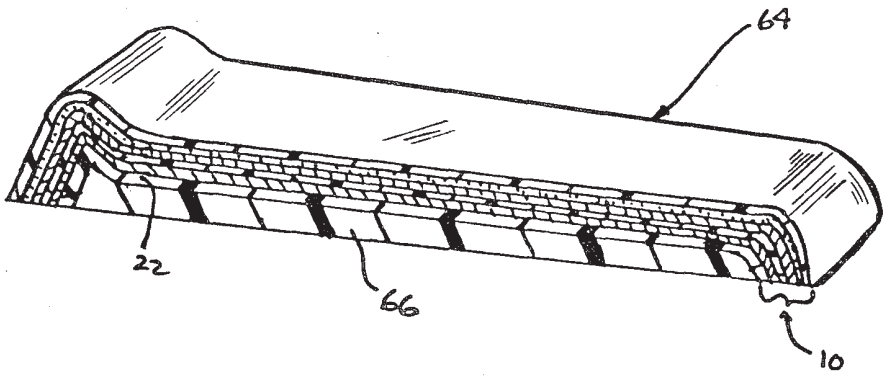
Primary Examiner—Thomas J. Herbert, Jr.
Attorney, Agent, or Firm—David A. Jackson; Daniel H. Bobis

[57] **ABSTRACT**

A decorative metallized laminate having improved brilliance, reflectance and weatherability comprises a base layer prepared from a thermo-formable resin film, with both surfaces thereof coated with vapor deposited metal layers. An outer protective capping layer prepared from a film having at least one surface treated for receptivity to adhesive bonding and resistance to attack by ultra-violet radiation, is adhesively bonded to one of the metallized surfaces of the base layer. A pressure and heat sensitive elastomeric adhesive coating is disposed between the capping layer and the metallized surface of the base layer, to form the bond between the two layers. A compatible thermo-formable resin backing layer may be laminated to the free metallized surface of the base layer, to provide a composite laminate suitable for thermo-forming and injection molding to manufacture a variety of products.

A method for preparing the metallized laminate is also disclosed.

18 Claims, 4 Drawing Figures



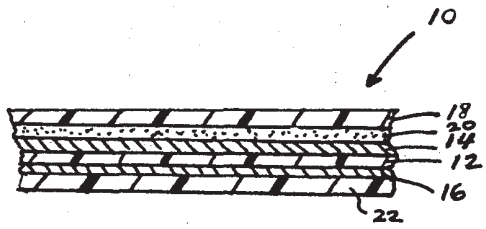


FIG. 1

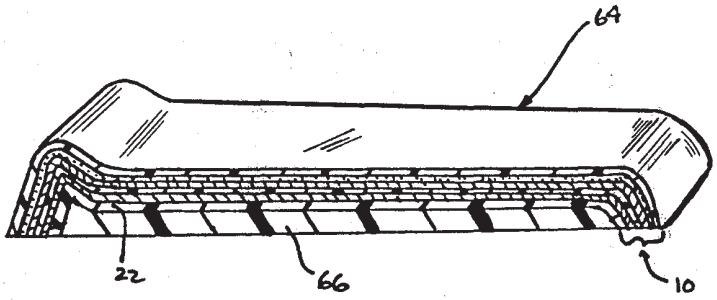


FIG. 4

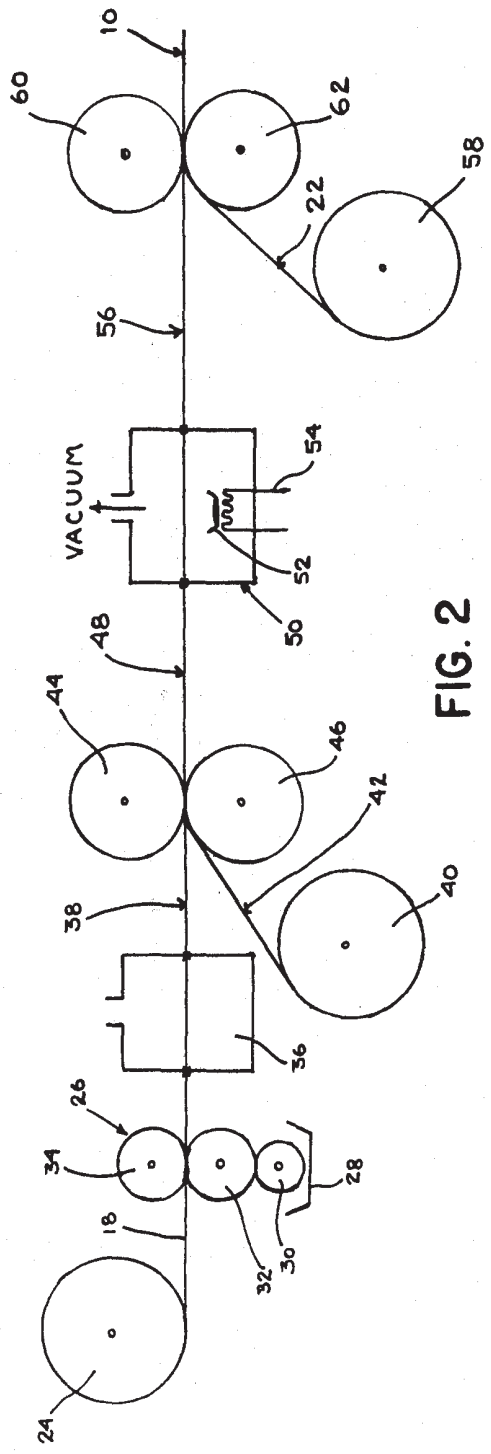


FIG. 2

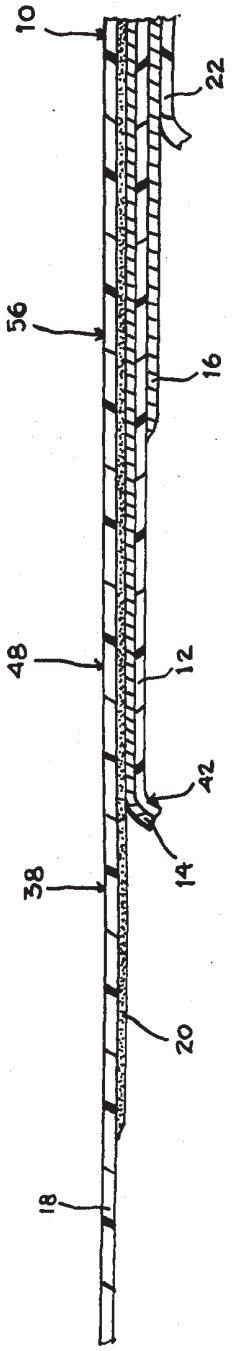


FIG. 3

SANDWICH METALIZED RESIN LAMINATE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to reflective decorative laminates, and more particularly to such laminates as are useful in applications requiring exposure to mechanical stress and environmental extremes.

2. Description of the Prior Art

A variety of decorative, reflective laminates prepared with a variety of resin materials, have been developed and in existence for some time. With the increasing concern for safety and weight reduction, that has developed in the automotive industry, for example, the use of such reflective laminates in place of reflective articles prepared entirely from metal, has been on the increase. Thus, structures such as bumpers, side trim, grill work and the like, previously prepared from relatively rigid and heavier chromium-plated metals, are being replaced by the lighter weight resinous materials.

While wide-spread employment of resinous materials exists, their use has been primarily in the instance where pigmented non-reflective hardware such as bumpers, and the like, is acceptable in the design of the vehicle. In those instances where reflective surfaces are desired, however, the manufacturers tend to continue their use of the conventional plated metal, because they find that the reflective surfaces prepared from resinous laminates tend to be of inferior brightness and reflectivity, and frequently exhibit surface defects when exposed to mechanical impact, as well as deterioration of the metallic layer after relatively short exposure to atmospheric air and sunlight.

A variety of laminates specifically designed for automotive application have been developed, all of which have attempted to remedy the aforementioned deficiencies, by providing, in pertinent part, a reflective metal layer, usually vapor deposited upon a transparent resin film, with the resulting metal coated film bonded adhesively to one or more further resin films, so that the metal layer is presumably securely disposed within the resulting laminates. Variations on this construction are illustrated in the following U.S. Pat. Nos. 4,275,099; 4,235,949; 4,101,698; 3,811,989; and 3,720,567. Naturally, the foregoing listing is illustrative only, as other patents, and related publications illustrate yet further variations in construction and preparation of such laminates.

Of the patents listed, U.S. Pat. No. 4,275,099 to Dani is of particular interest, as it discloses in its general discussion, a laminate construction that is presently popular, that of the tri-laminate. Dani describes this construction as essentially three-ply, constituted of an aluminized polyester film, adhesively bonded to outer polyvinylfluoride film and bonded on its opposite side to a base layer of what patentee terms a "virgin vinyl resin." The patentee states further, that the tri-laminate maybe either heat fused or otherwise adhesively bonded to a three dimensional extrusion, to form products such as automotive trim strips and the like.

The deficiencies of this state of the art construction are also noted by Dani, in that patentee remarks that the laminated products tend to delaminate in use after relatively short exposure to outside environments. Dani notes that delamination frequently occurs at the adhesive interface between the metallized surface and the next adjacent resin film, and proposes a specific adhesive formulation that purportedly remedies this defect.

In addition to those deficiencies noted by Dani, the present inventors found that the commercial production of the known tri-laminates was exceeding difficult if not impossible, when attempts were made to adapt these tri-laminates to the preparation of automotive accessories by thermo forming techniques. Thus, it was observed that when the temperatures of the thermo forming operation fluctuated outside illustrative tolerances of about 5° F., the resulting products exhibited surface crazing, the development of a haze in the resin films that reduced brightness and reflectivity, and an effect known as "rainbow," i.e., a multi-color hue that appears due to the distortion of the polyester film during the thermo forming process. Further, the appearance of any of the foregoing defects would result in the rejection by automobile manufacturers of products having these defects.

A further problem, noted by Dani, and others in the art, comprises the susceptibility of the resin laminate to attack and rapid deterioration upon exposure to ultra-violet light. Dani proposes to include an ultra-violet inhibitor in the polyester film to remedy this defect. The present inventors have found, however, that the adhesive utilized in the laminates presently known, have generally low resistance to deterioration from exposure to ultra-violet light, and therefore fail within an unacceptably short period of time after their installation. Further, the prior art adhesives appear to attack the adjacent metal layer and to cause it to corrode, with the result that desired appearance and laminate integrity rapidly deteriorate.

A need therefore exists for the development of an improved laminate and associated method of preparation that can efficiently and economically cure the noted product deficiencies.

SUMMARY OF THE INVENTION

In accordance with the present invention, a decorative metallized laminate exhibiting improved brilliance, reflectance and weatherability is disclosed which comprises a base layer prepared from a thermo formable resin film having both surfaces thereof coated with a thin, adherent layer of metal, and an outer, protective capping layer prepared from a film having at least one surface treated for receptivity to adhesive bonding and resistance to attack by ultra-violet radiation, the capping layer adhesively bonded to one of the metallized surfaces of the base layer. A pressure and heat sensitive elastomeric adhesive coating, also resistant to attack by ultra-violet radiation and harmless to the metal layers, is disposed between the capping layer and the metallized surface of the base layer, and forms the bond therebetween. The present laminate maybe bonded to a compatable thermo-formable resin backing layer that may be laminated to the free metallized surface of the base layer.

The base layer is a non-oriented resin film prepared from material selected from the group consisting of amorphous polyester resins, polycarbonate resins, substituted and unsubstituted vinyl polymers, and their co-polymers. Preferably, the non-oriented resin comprises an amorphous polyester, such as polyethylene terephthalate and ranges in thickness from about 3 to about 8 mils. The metal layers may be applied by conventional techniques, such as vapor deposition, and may

include chromium, nickel, iron, aluminum, and others, with aluminum preferred.

The capping layer may be a material selected from the group consisting of fluorinated vinyl polymers, fluorinated polyolefins, and polyesters treated for resistance to ultra-violet radiation. Preferably, the capping layer comprises a polyvinylfluoride.

The adhesive coating maybe a silicone resin or an acrylic resin, and preferably includes a catalyst in amount ranging from about 2% to about 6% by weight of the resin solids of the adhesive. Preferrably, the adhesive is a silicone resin such as a substituted polysiloxane, and the catalyst is a silicone compound as well.

The present invention includes a method for preparing the decorative metallic laminate, comprising the steps of applying the metal layer to one surface of the base layer, adhesively bonding the capping layer to the metallized surface of the base layer and thereafter metallizing the free surface of the base layer. The resulting laminate may then be bonded by standard laminating techniques, such as extrusion lamination, to a backing layer of a thermo-formable resinous material. The resulting laminate may be extrusion molded to a preformed substrate or maybe formed into a three dimensional article by injection molding with additional resinous material adhesively compatible with the composition of the backing layer. Such resinous material may include various known polyolefins, vinyl compounds such as polyvinylchloride, and others.

The present laminates are particularly useful in the instance where automotive products for exterior exposure are prepared, as the combined inertness of the adhesive and the ultra-violet resistance of both the adhesive and the capping layer, substantially extend the useful life of the laminate surface, to resist ultra-violet radiation, chemical attack from the environment, and resistance to fracture from mechanical impact. The presence of the catalyst in the adhesive of the present laminate, promotes the formation of a firm bond between the capping layer and the underlying base layer, that resists surface defect formation and delamination during subsequent thermo-forming operations, and provides improved transparency that enhances the brilliance and reflectivity of the metal layer.

Finally, the provision of the sandwich of metallized surfaces surrounding the base layer, totally eliminates the "rainbow" effect that can result from the deformation of the base layer during thermo-forming, as the two layers cooperate to provide a continuous surface regardless of the extent to which the base layer may be deformed in susequent manufacturing procedures.

The present product is easily and inexpensively prepared without resorting to rigorous processing. Product uniformity is substantially improved so that the reject rate for formed parts drop well within commercially acceptable tolerances.

Accordingly, it is a principal object of the present invention to provide a decorative metallized laminate exhibiting improved brilliance, reflectance and weatherability, that is capable of successfully undergoing thermo-forming operations.

It is a yet further object of the present invention to provide a laminate as aforesaid, which eliminates the frequency of surface defects, loss of reflectance and breakdown of the metal layer upon exposure to ultra-violet light.

It is a yet further object of the present invention to provide a laminate as aforesaid that is particularly useful for the formation of exterior automotive parts.

It is a yet further object of the present invention to provide a method for preparing a bright, metallized laminate, that is simply and inexpensively practiced without resorting to rigorous conditions.

It is a yet further object of the present invention to provide a method as aforesaid, forms a laminate product capable of successfully undergoing subsequent thermo-forming operation.

Other objects and advantages will become apparent to those skilled in the art from a consideration of the ensuing description, which proceeds with reference to the following illustrative drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic fragmentary sectional view of a laminate in accordance with the present invention.

FIG. **2** is a schematic representation of the process of the present invention.

FIG. **3** is a schematic representation illustrating the state of preparation of the laminate at the various points of the process illustrated schematically in FIG. **2**.

FIG. **4** is a schematic perspective illustrating a typical automotive product utilizing the laminate of the present invention.

DETAILED DESCRIPTION

Referring to FIG. **1**, the decorative laminate **10** is illustrated schematically and comprises a base layer **12** that is prepared from a thermo formable resin film. The base layer **12** is preferably prepared from a non-oriented film selected from the group consisting of amorphous polyester resins, polycarbonate resins, substituted and unsubstituted vinyl polymers, and their copolymers. More particularly, the amphorous polyesters may include polyethylene terephthalate, the polycarbonates may include acrylonitrile-butadiene-styrene resins, the vinyl polymers may include polyvinylchloride homo- or copolymers as well as other commercially available vacuum formable or thermo-formable materials.

A preferred material for base layer **12** comprises a polyethylene terephthalate sold by Allied Chemical Corporation, known as "Petra." The invention however is not limited to this later material, so long as the base layer is substantially non-oriented, that is to say, has not been previously mechanically treated, to enhance rigidity and "memory."

Base layer **12** may be provided in a variety of thicknesses, depending upon the specific application for the resulting laminate, however, in the instance where an automotive laminate is contemplated, that is to be formed by injection molding as described hereinafter, base layer **12** preferably possesses a thickness ranging from about 3 mils to about 8 mils, and more specifically made be utilized at a thickness of 5 mils.

Base layer **12** is provided on both of its surfaces with tightly adherent, reflective metal coatings **14** and **16**. While metal coatings **14** and **16** may be applied by a variety of well recognized techniques, it is preferable in the present invention that metal coatings **14** and **16** be applied by vapor deposition. The techniques of vapor deposition, particularly as utilized in connection with the preparation of aluminized polyester films, are well known, and are described, for example, in the Modern Plastics Encyclopedia (1970–1971), at pages 710 and following. For example, in the instance where alumi-

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