

US 20050044609A1

(19) United States (12) Patent Application Publication (10) Pub. No.: US 2005/0044609 A1

(10) Pub. No.: US 2005/0044609 A1 (43) Pub. Date: Mar. 3, 2005

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(54) POLYVINYL CHLORIDE GLOVE HAVING IMPROVED CHEMICAL RESISTANCE

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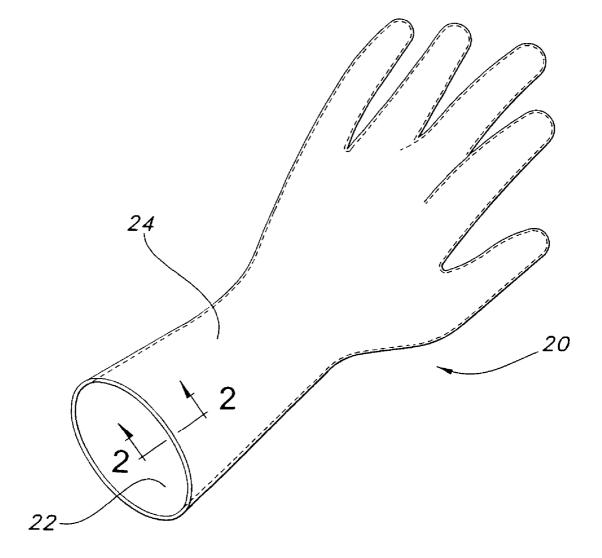
- (73) Assignce: Kimberly-Clark Worldwide
- (21) Appl. No.: 10/649,549

(22) Filed: Aug. 27, 2003

Publication Classification

(57) ABSTRACT

A glove having improved chemical permeation resistance includes a substrate body formed from polyvinyl chloride and a barrier layer overlying at least a portion of the substrate body, where the barrier layer is formed from an acrylic polymer having a glass transition temperature of from about -30° C. to about 30° C.



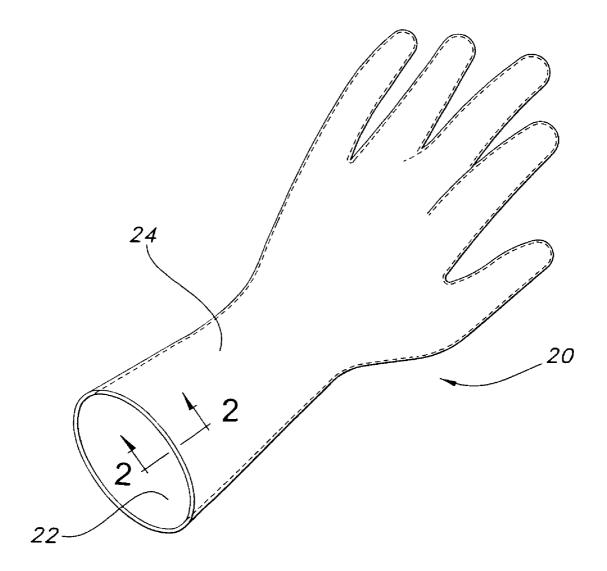


FIG. 1

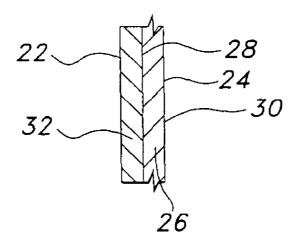


FIG. 2A

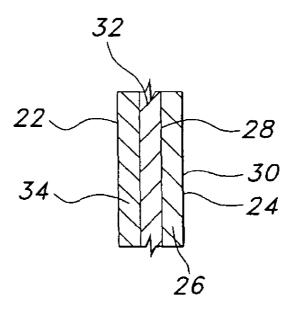


FIG. 2B

BACKGROUND

[0001] In recent years, there has been an increasing emphasis in the medical community on developing gloves that offer various degrees and types of protection. Medical practitioners are frequently exposed to solvents such as isopropyl alcohol and other chemicals that may puncture the glove and compromise the barrier afforded by the glove. Gloves formed from thermoplastic resins, such as polyvinyl chloride (PVC), have a history of poor permeation resistance to some chemicals relative to gloves formed from a coagulated rubber latex, such as natural rubber or nitrile rubber. As such, there is a recognized need for a PVC glove with improved resistance to chemical permeation.

SUMMARY OF THE INVENTION

[0002] The present invention generally relates to a glove having improved chemical permeation resistance. The glove includes a substrate body formed from polyvinyl chloride, and a barrier layer overlying at least a portion of the substrate body, where the barrier layer is formed from an acrylic polymer having a glass transition temperature of from about -30° C. to about 30° C. The barrier layer may be present in any suitable amount, and in some instances, may be present in an amount of from about 3 mass % to about 8 mass % of the glove. In other instances, the barrier layer may be present in an amount of from about 4 mass % to about 6 mass % of the glove. The barrier layer may be a skincontacting layer. In some instances, the barrier layer may be visually distinct from the substrate body. The glove may also include a donning layer overlying at least a portion of the barrier layer, where the donning layer is a skin-contacting layer.

[0003] The present invention further relates to a glove having improved chemical permeation resistance including a substrate body formed polyvinyl chloride, a barrier layer overlying at least a portion of the substrate body, where the barrier layer is formed from an acrylic polymer, and a donning layer overlying at least a portion of the barrier layer, where the donning layer is formed from a polyurethane. In some instances, the acrylic polymer may have a glass transition temperature of from about -30° C. to about 30° C. In other instances, the acrylic polymer may have a glass transition temperature of from about -20° C. to about 20° C. In yet other instances, the acrylic polymer may have a glass transition temperature of from about -10° C. to about 10° C. The glove is generally resistant to 70% isopropyl alcohol for at least 90 minutes using ASTM F739-99a. In some instances, the glove may be resistant to 70% isopropyl alcohol for at least 100 minutes using ASTM F739-99a. In other instances, the glove may be resistant to 70% isopropyl alcohol for at least 110 minutes using ASTM F739-99a. In yet other instances, the glove may be resistant to 70% isopropyl alcohol for at least 120 minutes using ASTM F739-99a.

[0004] The present invention also relates to a method of forming a glove having improved chemical permeation resistance. The method includes preparing a substrate body from a polyvinyl chloride plastisol, and forming a barrier layer over at least a portion of the substrate body, where the

barrier layer is formed from a barrier layer composition comprising an acrylic emulsion. The method may include forming a donning layer over at least a portion of the barrier layer. The method may further include rendering the barrier layer visually distinct from the substrate body by, for example, adding a colorant to the barrier layer composition.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. 1 is a perspective view of a glove that may be formed according to the present invention;

[0006] FIG. 2A is an exemplary cross-sectional illustration of the article of **FIG. 1** taken along a line **2-2**, the article including a substrate body and a barrier layer; and

[0007] FIG. 2B is an exemplary cross-sectional illustration of the article of **FIG. 1** taken along a line 2-2, the article including a substrate body, a barrier layer, and a donning layer.

DESCRIPTION

[0008] The present invention generally relates to an article having improved resistance to chemical permeation, and a method of forming such an article. The article of the present invention features improved resistance to chemical permeation through use of a barrier layer formed from an acrylic emulsion. In particular, the article of the present invention features improved permeation resistance to isopropyl alcohol as measured by ASTM F739-99a entitled "Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact". The glove is generally resistant to 70% isopropyl alcohol for at least 80 minutes using ASTM F739-99a. In some instances, the glove may be resistant to 70% isopropyl alcohol for at least 85 minutes using ASTM F739-99a. In other instances, the glove may be resistant to 70% isopropyl alcohol for at least 90 minutes using ASTM F739-99a. In other instances, the glove may be resistant to 70% isopropyl alcohol for at least 100 minutes using ASTM F739-99a. In yet other instances, the glove may be resistant to 70% isopropyl alcohol for at least 110 minutes using ASTM F739-99a. In yet other instances, the glove may be resistant to 70% isopropyl alcohol for at least 120 minutes using ASTM F739-99a.

[0009] An article made according to the present invention, for example, a glove 20, generally includes an inside surface 22 and an outside surface 24 (FIG. 1). As used herein, the "inside surface" refers to the surface of the article that contacts the body of the wearer. As used herein, the "outside surface" refers to the surface of the article that is distal from the body of the wearer. The glove includes a substrate body 26 having a first surface 28 and a second surface 30 (FIGS. 2A-2B). As used herein, "first surface" refers to the surface of the substrate body proximal to the body of the wearer. As used herein, "second surface" refers to the surface of the substrate body body of the wearer.

[0010] The article of the present invention may include a single layer or multiple layers as desired. In a single layer glove including only the substrate body, the first surface may form the inside surface of the glove. However, in a multi-layer glove having additional layers proximal to the body of the wearer, the additional layer or layers may each form a portion of the inside surface, or the entire inside surface, as

desired. Likewise, in a single layer glove including only the substrate body, the second surface may form the outside surface of the glove. However, in a multi-layer glove having additional layers distal from the body of the wearer, the additional layer or layers may each form a portion of the outside surface, or the entire outside surface, as desired.

[0011] For example, as depicted in FIG. 2A, the article may include a barrier layer 32 overlying at least a portion of the first surface 28 of the substrate body 26. In such an article, the barrier layer 32 forms at least a portion of the inside surface 22 of the glove 20. As depicted in FIG. 2B, the article may also include other layers, such as a donning layer 34 that overlies at least a portion of the barrier layer 32. In such an article, the donning layer 34 forms at least a portion of the inside surface 22 of the glove 20.

[0012] The substrate body **26** (FIGS. **2A-2B**) is generally formed from a polymeric material, and in some instances, may be formed from a thermoplastic polymer resin. In one such embodiment, the substrate body may be formed from a polyvinyl chloride (PVC) resin. While articles formed from a PVC resin are described in detail herein, it should be understood that any other suitable polymeric material or combination of polymeric materials may be used with the present invention.

[0013] The barrier layer 32 (FIGS. 2A-2B) may be formed from any suitable polymer that provides increased chemical resistance, and in some embodiments, may be formed from an acrylic polymer. While any suitable acrylic polymer may be used as desired, it has been discovered that use of an acrylic polymer that has a glass transition temperature of from about -30° C. to about 30° C. provides a barrier layer that is durable even after donning or manipulation of the article. In some embodiments, an acrylic polymer having a glass transition temperature of from about -20° C. to about 20° C. may be used to form the barrier layer of the present invention. In other embodiments, an acrylic polymer having a glass transition temperature of from about -10° C. to about 10° C. may be used to form the barrier layer of the present invention. In one such embodiment, an acrylic polymer having a glass transition temperature of about -3° C. may be used to form the barrier layer of the present invention.

[0014] The acrylic polymer may be provided in any suitable manner, and in some instances, may be provided as an acrylic emulsion. In some instances, it may be desirable to select an acrylic emulsion that readily forms a film without use of crosslinking agents, curatives, or the like. In some such instances, the acrylic emulsion may form a film at room temperature. This provides a significant process advantage over other polymer coatings that require curing to form a durable coating.

[0015] One such acrylic emulsion that may be suitable for use with the present invention is commercially available from Noveon, Inc. (Cleveland, Ohio) under the trade name HYCAR® 2679 Emulsion ("HYCAR® 2679"). HYCAR® 2679 has a glass transition temperature of about -3° C. and is believed to contain about 50 mass % TSC, less than 50 mass % water, and a small amount of formaldehyde. Another acrylic emulsion that may be suitable for use with the present invention is commercially available from Noveon, Inc. (Cleveland, Ohio) under the trade name HYCAR® 2671 Emulsion ("HYCAR® 2671"). HYCAR® 2671 is believed to contain about 53 mass % TSC, less than 47 mass % water, and a small amount of formaldehyde. Yet another acrylic emulsion that may be suitable for use with the present invention is commercially available from Noveon, Inc. (Cleveland, Ohio) under the trade name HYCAR® 26349 Emulsion ("HYCAR® 26349"). HYCAR® 26349 has a glass transition temperature of about 15° C. and is believed to contain about 49 mass % TSC, less than about 51 mass % water, and a small amount of formaldehyde.

[0016] In some embodiments, the barrier layer may be visually distinct from the substrate body. For instance, the barrier layer may include a colorant that enables the wearer to recognize the existence of multiple layers in the glove. Alternatively, the substrate body may include a colorant to create visually distinct layers. In one embodiment, the substrate body and the barrier layer may each include a colorant, so that the inside of the glove is predominantly one color, while the outside of the glove is another color.

[0017] Any suitable colorant may be used to create a visual distinction between layers as desired. One such colorant that may be suitable for use with the present invention is commercially available from Sun Chemical Corporation (Amelia, Ohio) under the trade name FLEXIVERSE® Phthalo Blue Dispersion ("FLEXIVERSE®"). FLEXI-VERSE® is a resin based aqueous dispersion that is believed to contain an acrylic resin, phthalocyanine blue, and water.

[0018] Additionally, the glove of the present invention may include a donning layer 34 (FIG. 2B). The donning layer may be formed from any polymeric material that facilitates donning of the article, and in some instances, may include a polyurethane. One such polyurethane that may be suitable for use with the present invention is available from Soluol Chemical Co., Inc. (West Warwick, R.I.) under the trade name SOLUCOTE® 117-179. SOLUCOTE® 117-179 is provided as a waterborne polyurethane dispersion having from about 10-20 mass % total solids content (TSC).

[0019] In other embodiments, the donning layer may be formed from a blend of an acrylic polymer and a polyurethane. One such blend that may be suitable for use with the present invention is available from Jatrac, Inc. (Kyoto, Japan) under the trade name SMOOTHER Anti-Stick Agent ("SMOOTHER"). SMOOTHER is believed to contain about 5 mass % polyurethane latex, 3 mass % polyacrylic latex, 2 mass % polyvinyl chloride latex, 3 mass % mica, and water.

[0020] While exemplary donning layer materials are set forth herein, it should be understood that any suitable donning layer material may be used as desired. Furthermore, various lubricating materials may be added to the donning layer composition as desired or needed to enhance donning. Some such materials may include a flattening agent, a lubricant, for example, a wax or a silicone, or particulate matter, for example, silica.

[0021] The glove of the present invention may be formed using a variety of processes, for example, dipping, spraying, tumbling, drying, and curing. An exemplary dipping process for forming a glove is described herein, though other processes may be employed to form various gloves having different characteristics. Furthermore, it should be understood that a batch, semi-batch, or a continuous process may be used with the present invention.

[0022] A glove is formed on a hand-shaped mold, termed a "former". The former may be made from any suitable

material, such as glass, metal, porcelain, or the like. The surface of the former defines at least a portion of the surface of the glove to be manufactured.

[0023] In general, the glove is formed by dipping the former into a series of compositions as needed to attain the desired glove characteristics. The glove may be allowed to solidify between layers. Any combination of layers may be used, and although specific layers are described herein, it should be understood that other layers and combinations of layers may be used as desired. Thus, in one embodiment, the glove may include a substrate body 26 and a barrier layer 32 (FIG. 2A). In another embodiment, the glove may include a substrate body 26, a barrier layer 32, and a donning layer 34 (FIG. 2B).

[0024] In one embodiment, the substrate body may be formed from a plastisol using a dipping process. As used herein, a "plastisol" refers to a dispersion of fine resin particles in a plasticizer. The plastisol is formed by mixing the resin particles into the plasticizer with sufficient shear to form a stable system. Any suitable resin may be used as desired, and in some instances, the resin includes polyvinyl chloride (PVC). While articles formed from PVC are described in detail herein, it should be understood that any other suitable thermoplastic material or combination of thermoplastic materials may be used with the present invention. Thus, for example, the resin may include a styreneethylene-butylene-styrene block copolymer, a nitrile butadiene polymer, or any other polymer capable of forming a film without use of a coagulant. Furthermore, while exemplary process conditions are described herein, it should be understood that such conditions depend on the desired thickness of the article, the viscosity of the composition, the time required to gel the article, and so forth.

[0025] The former may first be heated to a temperature of about 100° F. (38° C.) to about 200° F. (93° C.), for example, 150° F. (66° C.). The former is then dipped into a plastisol containing a suitable thermoplastic resin, for instance, PVC, and a plasticizer. The composition may be maintained at any suitable temperature, and in some instances, is maintained at a temperature of from about 75° F. (24° C.) to about 175° F. (79° C.), for example, 105° F. (40° C.).

[0026] The formers are then removed from the composition to drain. The time permitted to drain ("drain time") determines the mass of the glove, its thickness, and so forth, based on the temperature of the former and the viscosity of the plastisol. The formers are then advanced to a fusion oven where the substrate body fuses on the former. In one instance, the fusion oven may be maintained at about 300° F. (149° C.) to about 500° F. (260° C.), for example, 450° F. (232° C.), and the former may be in the oven for about 3 to about 8 minutes, for example, 6 minutes.

[0027] The fused PVC substrate body on the former is then cooled to a temperature of about 100° F. (38° C.) to about 200° F. (93° C.), for example, 150° F. (66° C.), by exposing the formers to one or more cooling fans, as appropriate.

[0028] The former is then dipped into a composition to form the barrier layer. As stated herein, the barrier layer may be formed from any suitable material, and in some instances, may be formed from an acrylic emulsion. One such acrylic emulsion that may be suitable is HYCAR® 2679, described

in detail above. Where desired, the composition may include other additives. In one embodiment, the composition may include a colorant to render the barrier layer visually distinct from the substrate body. Where other layers are present, the barrier layer may also be visually distinct from such other layers as desired.

[0029] The barrier layer is then dried in an oven maintained at a temperature of about 350° F. to about 450° F., for example, 392° F. (200° C.) for about 60 seconds to about 120 seconds, for example, 90 seconds, and cooled to a temperature of about 100° F. (38° C.) to about 200° F. (93° C.), for example, 150° F. (66° C.), by exposing the formers to one or more cooling fans, as appropriate.

[0030] The barrier layer may be present in the finished article any suitable amount, and in some embodiments, the barrier layer may be present in an amount of from about 3 mass % to about 8 mass % of the article. In other embodiments, the barrier layer may be present in an amount of from about 4 mass % to about 6 mass % of the article. In yet another embodiment, the barrier layer may be present in an amount of about 5.7 mass % of the article.

[0031] Where no separate donning layer is desired, various lubricating materials may be added to the barrier layer composition as desired or needed to enhance donning. Some such materials may include a flattening agent, a lubricant, for example, a wax or a silicone, or particulate matter, for example, silica. As used herein, the term "silicone" generally refers to a broad family of synthetic polymers that have a repeating silicon-oxygen backbone, including, but not limited to, polydimethylsiloxane and polysiloxanes having hydrogen-bonding functional groups selected from the group consisting of amino, carboxyl, hydroxyl, ether, polyether, aldehyde, ketone, amide, ester, and thiol groups. In some embodiments, polydimethylsiloxane and/or modified polysiloxanes may be used as the silicone component in accordance with the present invention. For instance, some suitable modified polysiloxanes that can be used in the present invention include, but are not limited to, phenylmodified polysiloxanes, vinyl-modified polysiloxanes, methyl-modified polysiloxanes, fluoro-modified polysiloxanes, alkyl-modified polysiloxanes, alkoxy-modified polysiloxanes, amino-modified polysiloxanes, and combinations thereof.

[0032] In some embodiments, the barrier layer may include a silicone emulsion. One such silicone emulsion that may be used is DC 365, a pre-emulsified silicone (35% TSC) that is commercially available from Dow Corning Corporation (Midland, Mich.). DC 365 is believed to contain 40-70 mass % water, 30-60 mass % methyl-modified polydimethylsiloxane, 1-5 mass % propylene glycol, 1-5 mass % polyethylene glycol sorbitan monolaurate, and 1-5 mass % octylphenoxy polyethoxy ethanol. Another silicone emulsion that may be used with the present invention is SM 2140, commercially available from GE Silicones (Waterford, N.Y.). SM 2140 is a pre-emulsified silicone (50% TSC) that is believed to contain 30-60 mass % water, 30-60 mass % amino-modified polydimethylsiloxane, 1-5% ethoxylated nonyl phenol, 1-5 mass % trimethyl-4-nonyloxypolyethyleneoxy ethanol, and minor percentages of acetaldehyde, formaldehyde, and 1,4 dioxane. Another silicone emulsion that may be suitable for use with the present invention is SM 2169 available from GE Silicones (Waterford, N.Y.). SM

2169 is a pre-emulsified silicone that is believed to contain 30-60 mass % water, 60 to 80 mass % polydimethylsiloxane, 1-5 mass % polyoxyethylene lauryl ether, and a small amount of formaldehyde. Yet another silicone that may be useful with the present invention is commercially available from GE Silicones (Waterford, N.Y.) under the trade name AF-60. AF-60 is believed to contain polydimethylsiloxane, acetylaldehyde, and small percentages of emulsifiers. If desired, these pre-emulsified silicones may be diluted with water or other solvents prior to use.

[0033] In another embodiment, the barrier layer composition may contain a quaternary ammonium compound, such as that commercially available from Goldschmidt Chemical Corporation of Dublin, Ohio under the trade name VER-ISOFT® BTMS. VERISOFT® BTMS is believed to contain behnyl trimethyl sulfate and cetyl alcohol. Thus for example, in one embodiment, the lubricant layer may include a quaternary ammonium compound such as VER-ISOFT® BTMS and a silicone emulsion such as SM 2169. In other embodiments, such a barrier layer composition may include, for example, a cationic surfactant (e.g., cetyl pyridinium chloride), an anionic surfactant (e.g., sodium lauryl sulfate), a nonionic surfactant, or the like.

[0034] Where desired, the former may be dipped into a composition to form a donning layer to facilitate donning of the glove. One such donning layer composition that may be suitable for use with the present invention may include SMOOTHER Anti-Stick Agent, described in detail above. The donning layer composition may be maintained at about 100° F. (38° C.) to about 200° F. (93° C.), for example, 150° F. (66° C.). The donning layer on the former may then be dried in an oven, for example, for about 2-3 minutes at a temperature of about 200° F. (93° C.) to about 400° F. (204° C.), for example, 300° F. (149° C.).

[0035] The donning layer may be present in the finished article any suitable amount, and in some embodiments, the donning layer may be present in an amount of from about 0.1 mass % to about 2 mass % of the article. In other embodiments, the donning layer may be present in an amount of from about 0.3 mass % to about 1 mass % of the article. In yet another embodiment, the donning layer may be present in an amount of about 0.6 mass % of the article.

[0036] Alternatively, the barrier layer may be dusted with a powder to facilitate donning. One such dusting powder that may be suitable for use with the present invention is USP grade starch.

[0037] The former is then sent to a bead rolling station, where the cuff is rolled slightly and permitted to solidify. The former may then be transferred to a stripping station where the glove is removed from the former. The stripping station may involve automatic or manual removal of the glove from the former. For example, in one embodiment, the glove is manually removed and turned inside out as it is stripped from the former. By inverting the glove in this manner, the donning layer formed on the exposed surface of the substrate body on the former becomes the interior of the glove.

[0038] The resulting glove features improved barrier characteristics when exposed to isopropyl alcohol. These discoveries are evidenced by the following example, which is not intended to be limiting in any manner.

EXAMPLE

[0039] Improved chemical permeation of the glove of the present invention was demonstrated. Various competitive polyvinyl chloride gloves (Samples A-D) were compared with a glove formed according to the present invention (Sample E).

[0040] The experimental gloves (Sample E) were prepared by first heating the glove formers to about 65° C. The formers were then dipped into a polyvinyl chloride plastisol maintained at about 45° C. The plastisol was then fused in an oven at 200° C. for about 5 minutes. The formers were then cooled to a temperature of about 100° C. and dipped into a barrier layer composition including about 10 mass % HYCAR® 2679. The barrier layer was then dried at about 200° C. The formers were again cooled to a temperature of about 100° C. and dipped into a donning layer composition including about 1 mass % SMOOTHER. The donning layer was then dried at about 200° C. The gloves were then cooled and removed from the formers.

[0041] The gloves were tested for chemical permeation resistance according to ASTM F739-99a entitled "Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact" using 70% isopropyl alcohol as the challenge chemical. Three repetitions were performed. The results of the analysis are presented below.

Sample	Mass/unit area (g/m [^] 2)	Sample thickness (mm)	Breakthrough detection time (min)
А	154.0	0.130	67
в	131.8	0.118	47
С	143.4	0.128	77
D	150.8	0.129	77
Е	127.4	0.113	130

[0042] The results indicate that the glove formed according to the present invention (Sample E) offers a significant improvement in chemical permeation resistance when compared with several competitive products (Samples A-D). Thus, although the glove of the present invention (Sample E) has a lower mass/unit area and a lower thickness, it provides a greater barrier to isopropyl alcohol.

[0043] The invention may be embodied in other specific forms without departing from the scope and spirit of the inventive characteristics thereof. The present embodiments therefore are to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

1. A glove having improved chemical permeation resistance comprising:

a substrate body comprising polyvinyl chloride; and

a barrier layer overlying at least a portion of the substrate body, the barrier layer comprising an acrylic polymer having a glass transition temperature of from about -30° C. to about 30° C. **3**. The glove of claim 1, wherein the barrier layer is present in an amount of from about 4 mass % to about 6 mass % of the glove.

4. The glove of claim 1, wherein the barrier layer is a skin-contacting layer.

5. The glove of claim 1, wherein the barrier layer is visually distinct from the substrate body.

6. The glove of claim 1, further comprising a donning layer overlying at least a portion of the barrier layer, wherein the donning layer is a skin-contacting layer.

7. The glove of claim 6, wherein the donning layer comprises a polyurethane.

8. The glove of claim 6, wherein the donning layer is present in an amount of from about 0.1 mass % to about 2 mass % of the glove.

9. The glove of claim 6, wherein the donning layer is present in an amount of from about 0.3 mass % to about 1 mass % of the glove.

10. A glove having improved chemical permeation resistance comprising:

a substrate body comprising polyvinyl chloride;

a barrier layer overlying at least a portion of the substrate body, the barrier layer comprising an acrylic polymer; and

a donning layer overlying at least a portion of the barrier layer, the donning layer comprising a polyurethane.

11. The glove of claim 10, wherein the acrylic polymer has a glass transition temperature of from about -30° C. to about 30° C.

12. The glove of claim 10, wherein the acrylic polymer has a glass transition temperature of from about -20° C. to about 20° C.

13. The glove of claim 10, wherein the acrylic polymer has a glass transition temperature of from about -10° C. to about 10° C.

14. The glove of claim 10, wherein the glove is resistant to 70% isopropyl alcohol for at least 90 minutes using ASTM F739-99a.

15. The glove of claim 10, wherein the glove is resistant to 70% isopropyl alcohol for at least 100 minutes using ASTM F739-99a.

16. The glove of claim 10, wherein the glove is resistant to 70% isopropyl alcohol for at least 110 minutes using ASTM F739-99a.

17. The glove of claim 10, wherein the glove is resistant to 70% isopropyl alcohol for at least 120 minutes using ASTM F739-99a.

18. A method of forming a glove having improved chemical permeation resistance comprising:

preparing a substrate body from a polyvinyl chloride plastisol; and

forming a barrier layer over at least a portion of the substrate body, the barrier layer being formed from a barrier layer composition comprising an acrylic emulsion.

19. The method of claim 18, further comprising forming a donning layer over at least a portion of the barrier layer.

20. The method of claim 18, further comprising rendering the barrier layer visually distinct from the substrate body.

21. The method of claim 19, wherein the step of rendering the barrier layer visually distinct from the substrate body comprises adding a colorant to the barrier layer composition.

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