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WATER VAPOR PERMEABLE RESINS

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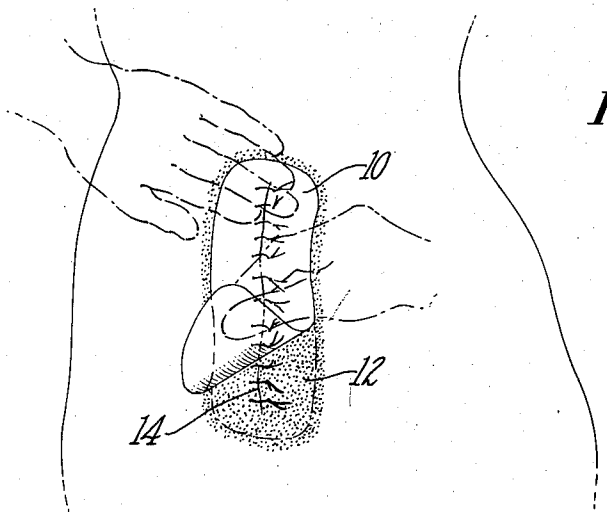
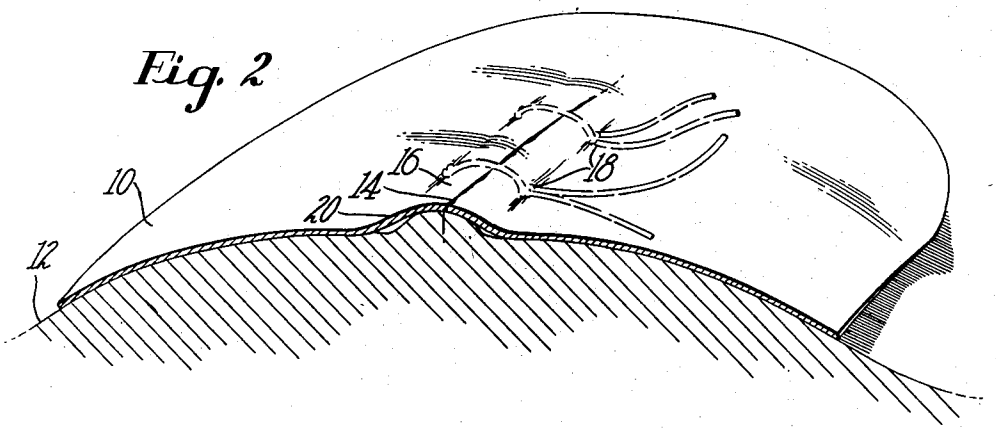


Fig. 1

Fig. 2



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By His Attorney

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WATER VAPOR PERMEABLE RESINS

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14 Claims. (Cl. 260—86.1)

This invention relates to a novel resinous material and particularly to a water vapor permeable, water-resistant, resinous sheet material and its use as a surgical dressing.

In the copending application Serial No. 344,416, filed March 24, 1953, now abandoned, entitled Plastic Film for Surgical Dressings, in the names of Merriam and Weiderhorn, there is disclosed water vapor permeable resinous material useful in sheet form for providing a water vapor permeable protective dressing for skin areas. As disclosed in that application, certain copolymers of acrylic (including methacrylic) acid esters with acrylic or methacrylic acids or acrylamide possess an unusual combination of water vapor permeability with water resistance, flexibility and toughness together with the ability to form a self bond to skin moistened with certain organic liquids. Such resinous films when applied to skin provide a transparent or translucent resinous protective layer which is water vapor permeable so that skin beneath it is not harmed and at the same time the layer is resistant to water so that the dressing itself and the skin areas surrounding it may be washed without injury or contamination.

It is a feature of the present invention to provide other water vapor permeable resinous materials useful for forming water vapor permeable protective dressings for skin areas and possessing improved toughness and flexibility characteristics.

It has now been discovered that a resinous copolymer of certain esters of alkoxy monohydroxy alcohols with acrylic or methacrylic acid, and acrylic acid, methacrylic acid or acrylamide possess when in thin layers and without the need of plasticizers or other additives a combination of water vapor permeability, water resistance, and improved flexibility and toughness together with ability to form a self bond to skin moistened with certain organic liquids which render the material useful as a protective dressing for skin areas. To obtain the desired properties it is important that the constituents be combined within a special range of relative proportions.

This invention will be further described in connection with the accompanying drawings forming part of the disclosure of the present application.

In the drawings,

Fig. 1 is a representation of the application to a surgical abdominal incision of a resinous sheet surgical dressing according to the present invention to protect the incision and the areas surrounding it; and

Fig. 2 is a partial section of an incision protected by a dressing according to the present invention showing the close engagement maintained between the surgical dressing and the skin areas surrounding the incision.

The resinous material of the present invention, like that in the copending application referred to above, possesses a substantial degree of "water vapor permeability." As explained more fully in that application, the term "water vapor permeability" is used to refer to a physico-chemical transmission by which water molecules are passed from hydrophilic radical to hydrophilic radical in a body of material even though the material itself may be non-porous and impervious to mechanical transmission of water. "Water vapor permeability" of resinous materials depends on a number of important factors among which are the presence in the material of radicals having an affinity for water which serve to pass along water molecules through a body of the material. In the present resin the acid component is believed to function in this manner; and it has been found that the "water vapor permeability" of a copolymer, including the acid component, is very substantially greater than the "water vapor permeability" of a homopolymer of the ester.

The water vapor permeable resinous copolymers of the present invention are useful in situations where strength, flexibility, and water-vapor permeability are needed as for example in shoe parts such as shoe upper material, and in coatings for textiles for use in foul weather gear. They are also useful in adhesives for special purposes where their unusual combination of properties will eliminate difficulties inherent in the usual adhesives.

Other factors than the water vapor permeability of a material, however, are of at least equal importance in rendering a material useful for relations, i. e., in surgical dressings, in which it is in close engagement with living skin. The material must be capable of application by standardized technique under the variety of conditions encountered, and must cling to and flex and stretch with the skin and in general act as much as possible like skin itself. Also, it is important that these factors be obtainable without the aid of plasticizers because of possible harmful effects of plasticizers on the skin.

It has been found that copolymers containing from 70 to 30 mol percent of acrylic acid, methacrylic acid or acrylamide and from 30 mol percent to about 70 mol percent of an ester of acrylic or methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms are resinous materials possessing water vapor permeability together with flexibility, toughness and stretchability without requiring a plasticizer. The carbon chain of the alkoxy or alcohol components of the ester may be straight or branched.

The relative proportions of acid and ester to give the most satisfactory resin depends on the ester employed. Esters of alkoxy monohydroxy alcohols containing a total of 4 to 6 carbon atoms have a superior plasticizing effect and hence can be used in smaller proportions than simple alkyl esters.

It has also been found that coploymers useful for the protection of wounds should not contain more than a total of 60 mol percent of methacrylic acid or methacrylic ester constituents. Excess of methacrylic components over this value leads to brittle polymers which are not suitable without addition of plasticizing agent.

Preformed sheet materials, preferably from 0.003 to 0.010 inch in thickness, of these resins possess satisfactory ability to transmit moisture vapor given off from the skin and possess a stretchiness and a flexibility such that a thin sheet of the resin adapts itself to changes in shape of the skin and also is capable of stretching with the skin. Additionally, these materials possess such water insolubility that the covered area can be washed along with the surrounding uncovered area without harm to the covering.

The mol percent of ester for any given ester and acid or amide copolymer is important and for preformed sheet materials should be in the range of 35 to 65 mol percent of ester. Relatively small departures from this range give a material unfitted for this special use. Increase of the percentage of ester does not adversely affect

the stretchiness or flexibility of the sheet but the water vapor permeability is reduced to a value which may give rise to discomfort upon extended contact with the skin. It has also been observed that excess of ester causes the sheet material to separate or peel off from the skin within a relatively short time, that is, a day or two. Higher percentages of the acid give a material possessing satisfactory water vapor permeability but introduces a whole new series of difficulties. Thus a material may be entirely satisfactory in stretchiness and flexibility on a warm, moist day, due possibly to take-up of moisture from the air and the plasticizing action of the moisture on the film, but may become brittle on dry days so that the material may crack during application or when in place. That is, the stretchiness, brittleness and other characteristics of the higher acid content material are so much affected by humidity conditions that difficulty is encountered in developing methods of application uniformly adapted for all weather conditions.

Within the given range of relative proportions, a preformed copolymer resin sheet material possesses the special property that it can be activated to a condition capable of bonding firmly to skin by a simple treatment of the skin with a solvent for the resin such as ethyl alcohol or an alcohol solution. Other solvents capable of dissolving or activating the resinous materials include the lower primary alcohols such as methanol or ketones such as acetone and methyl ethyl ketone. The resin materials are insoluble in ethers and in hydrocarbons. The ability to be activated to skin adhesive condition is an extremely valuable characteristic since it enables a rapid and secure fixing of the dressing material over a wound. Likewise, this property permits partial removal of a portion of the dressing and resecuring the portion to skin by swabbing the skin with solvent and pressing the dressing back in place.

The resinous materials of the present invention may be prepared by various means including copolymerization of mixtures of the acid or amide and the ester, the partial saponification of a polymer of the ester, the partial esterification of polymerized acid, or the polymerization of a mixture comprising a partially polymerized acid and an ester or various combinations of these procedures.

As illustrated in Figs. 1 and 2, a resin sheet protective dressing **10** having a length and width for covering skin areas **12** surrounding a wound **14** may be secured to the skin areas **12** in protective relation to the wound by activating the surfaces of the resin sheet **10** with a solvent such as alcohol and pressing the sheet against the skin surface **12**. As shown in Fig. 1, the preferred method of application is to moisten the skin area **12** surrounding the wound **14** with a solvent, as indicated by stippling, and manually to place and press the sheet **10** against the solvent moistened skin **12** and hold the sheet in place for a brief period after it has been applied. The resin sheet dressing **10** adheres promptly and firmly and conforms smoothly to the surface of the skin to provide a transparent, flexible, protective cover.

Alternatively, a protective film may be formed in situ to cover the wound and the area around the wound by applying a solution of the resin in a volatile solvent. In either case, there is provided after removal of the solvent a tough, water vapor permeable, flexible, stretchable dressing **10** on the wound which will protect it from contamination and which will, because of its transparency, permit observation of the progress of healing of the wound.

As shown in Figs. 1 and 2, the preformed resin sheet dressing **10** adapts itself to the shape of the skin surface **12** to be covered and adheres closely to the skin. The flexibility and stretchability of the material are such that even relatively sharp ridges, such as the puckered area **16** where skin is brought together as by stitching **18**, cause only a very limited bridging **20** in the sheet dressing.

Various antiseptic, bactericidal, or treatment agents may be used in combination with the surgical dressing of the present invention. These agents may be combined with the film or sheet **10** when it is cast or may be joined as a coating to the surface of the dressing material where the dressing material is a preformed sheet. An advantageous procedure is the application of a very thin deposit of silver to the surface of a resin sheet dressing which is to be in contact with the wound.

The following examples are given to aid in understanding the invention and it is to be understood that the invention is not restricted to the specific materials, proportions or procedures set forth in the examples other than as defined in the appended claims.

Example I

	Parts by weight
Butoxyethyl methacrylate (33 mol percent of mixture)	10
Acrylic acid	8
Methanol	13
Butyraldehyde	0.1
Benzoyl peroxide	0.1

The materials were introduced into a glass reaction vessel and nitrogen gas was introduced beneath the surface to maintain a nitrogen atmosphere over the reacting materials. Heat was supplied to the reaction vessel by placing it on a steam bath. After reaction had begun, the temperature was kept at a value sufficient to cause a gentle reflux action by heating or cooling the reaction vessel as necessary. After 15 minutes of reaction, considerable thickening occurred in the reaction mixture and the mixture was diluted with an equal volume of methanol. Reaction was then continued for an additional 45 minutes.

The reaction mixture was combined with 20 volumes of petroleum ether and precipitated from the ether. The precipitated polymer was then dissolved in methanol and reprecipitated in a 20 volume suspension of equal parts of water and petroleum ether. The precipitated polymer was removed, was air dried and was subjected to a short vacuum drying. The partially dried polymer was dissolved in methanol (7% solution) and cast as a film on a silicone treated level glass plate. On titration of a portion in dimethyl formamide using standard alkali, the polymer was found to contain approximately 58 mol percent of ester. The film was flexible and extensible and could be applied to the skin using alcohol as the activating agent.

The water vapor permeability of the film $D=29\times10^{-8}$ grams/hrs.×cm.×mm. of Hg water vapor pressure, as determined by the method disclosed in Industrial and Engineering Chemistry, vol. 28, pages 1255–1263, 1936, in an article by Taylor, Herrmann and Kemp.

Example II

		Parts by weight
Acrylic acid		23
Ethoxyethyl acrylate / Butyl acrylate	58 mol percent	14 / 43
Methanol		80
Benzoyl peroxide		0.15

Using the technique outlined in the preceding example, this mixture was reacted under dry nitrogen for 2 hours at a temperature maintained to provide a gentle reflux action. The polymer was recovered, purified and cast as a film by the procedure given in the preceding example. By titration a figure of 60 mol percent ester of the polymer was obtained based on the assumption that the ratio of one ester to the other in the charge and polymer remained constant. The water vapor permeability of the film $D=39\times10^{-8}$.

A film of the polymer 6 to 7 mils in thickness was found satisfactory for a surgical dressing.

Example III

	Parts by weight
Ethoxyethyl acrylate / n-Octyl acrylate } 43 mol percent	20.2 / 5.8
Acrylic acid	16.4
Methanol	42
Benzoyl peroxide	0.1

Using the technique outlined in the first example, this mixture was reacted under dry nitrogen for 2½ hours at a temperature maintained to provide a gentle reflux action. The polymer was recovered, purified and cast as a film by the procedure given in the first example. By titration a figure of 46 mol percent ester of the polymer was obtained based on the assumption that the ratio of one ester to the other in the charge and polymer remained constant. The water vapor permeability of the film $D=100\times10^{-8}$.

Example IV

	Parts by weight
2-ethoxyethyl acrylate (50 mol percent)	20
Acrylic acid	10
Methanol	30
Benzoyl peroxide	0.1
Butyraldehyde	0.1

Using the technique outlined in the first example, this mixture was reacted under dry nitrogen for 45 minutes at a temperature maintained to provide a gentle reflux action. The polymerization mixture was diluted with methanol (100 parts) and the diluted solution was precipitated in 10 vol. of petroleum ether. The precipitate was redissolved in methanol and reprecipitated in 10 vol. of a petroleum ether-water (equal parts) dispersion. The product was air dried and vacuum dried and the dried material was dissolved in methanol and cast as a film on silicone treated level glass plates. On titration with standard alkali the polymer was found to contain 52 mol percent of ester. The film cast from this material was rubbery and somewhat sticky and although it adhered to the skin fairly well it was rather sensitive to water showing a tendency to swell at the edges and to separate from the skin.

Five (5) grams of this polymer were dissolved with 21 grams of a copolymer of butyl acrylate and acrylic acid containing 53 mol percent of ester. The two polymers were compatible both in solution and in a film cast from the solution, and the film was considerably more plastic than a film of the butyl acrylate-acrylic acid copolymer alone. The 2-ethoxy ethyl acrylate acrylic acid copolymer exercised a desirable plasticizing action on the butyl acrylate-acrylic acid copolymer, while on the other hand the sheet material showed a very substantial improvement in its resistance to water.

Example V

	Parts by weight
Ethoxyethyl acrylate	15
Acrylamide	7.5
Methanol	18
Benzoyl peroxide	0.1

Using the technique outlined in the first example, this mixture was polymerized under nitrogen for one-half hour at a temperature providing gentle reflux action. The reaction mixture was then precipitated with 20 vol. of petroleum ether, redissolved and added to a dispersion of equal parts of water and petroleum ether. At this stage an emulsion of the polymer was formed, however; some of the polymer could be precipitated and was air dried, dissolved in methanol and cast as a film. The film showed good adhesion to skin but was sensitive to water and humidity, being somewhat soft and sticky on a humid day but leathery on a dry day. The water vapor permeability value $D=230\times10^{-8}$. This value approaches

the value $D=260\times10^{-8}$ for water soluble polyvinyl alcohol (78% hydrolyzed vinyl acetate).

Example VI

	Parts by weight
Butoxyethyl acrylate (44% mol ester)	13
Acrylic acid	7.0
Methanol	20
Benzoyl peroxide	.08

Using the technique outlined in the first example, this mixture was polymerized under nitrogen for one hour at a temperature providing gentle reflux action. The polymer was recovered, purified and cast as a film by the procedure given in the first example. By titration a figure of 41 mol percent ester of the polymer was obtained. The polymer was soft and readily adhesive to the skin and could be used as a skin covering. The water vapor permeability $D=46\times10^{-8}$.

Example VII

	Parts by weight
2-ethylhexoxyethyl acrylate (39% mol ester)	12
Acrylic acid	6
Methanol	16
Benzoyl peroxide	0.06

Using the technique outlined in the first example, this mixture was polymerized under nitrogen for one hour at a temperature providing gentle reflux action. The polymer was recovered, purified and cast as a film by the procedure given in the first example. By titration a figure of 37 mol percent ester of the polymer was obtained. The polymer was flexible and extensible and could be used as a skin covering. The water vapor permeability $D=26\times10^{-8}$.

Example VIII

	Parts by weight
Ethyl acrylate / 3-ethoxypropyl acrylate } 60 mol percent	9.6 / 3.8
Acrylic acid	5.8
Methanol	18
Benzoyl peroxide	.08

Using the technique outlined in the first example, this mixture was polymerized under nitrogen for one hour at a temperature providing gentle reflux action. The polymer was recovered, purified and cast as a film by the procedure given in the first example. By titration a figure of 63 mol percent ester of the polymer was obtained based on the assumption that the ratio of one ester to the other in the charge and polymer remained constant. The polymer was flexible and extensible and could be used as a skin covering. The water vapor permeability $D=80\times10^{-8}$.

Having described the invention, what is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A film forming water-insoluble, water vapor permeable, resinous copolymer of at least one member of the group consisting of acrylic acid, methacrylic acid, and acrylamide and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 30 to 70 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

2. A water vapor permeable, water-insoluble, thin, tough, flexible resin protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, said dressing comprising a resinous copolymer of at least one member of the group consisting of acrylic acid, methacrylic acid, and

acrylamide and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 30 to 70 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

3. A water-insoluble, water vapor permeable, thin, tough, flexible resin protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, said dressing comprising a resinous copolymer of acrylamide and an ester of methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 30 to 70 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

4. A water vapor permeable, water-insoluble, thin, tough, flexible resin protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, said dressing comprising a resinous copolymer of acrylic acid and an ester of acrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol partion has from 2 to 4 carbon atoms, the ester component constituting from 30 to 70 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

5. A water vapor permeable, water-insoluble, thin, tough, flexible resin protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, said dressing comprising a resinous copolymer of acrylic acid and an ester of methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 30 to 70 mol percent of the copolymer, said copolymer, not containing more than 60 mol percent of methacrylic components.

6. A water-insoluble, water vapor permeable, thin, tough, flexible resin protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, said dressing comprising a resinous copolymer of acrylamide and an ester of acrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 30 to 70 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

7. A thin, tough, flexible water-insoluble, water vapor permeable, resin protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, said dressing comprising a resinous copolymer of methacrylic acid and an ester of acrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 30 to 70 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

8. A thin, tough, flexible, water-insoluble, water vapor permeable, resinous sheet material, the film forming component of said resinous sheet material comprising a copolymer of at least one member of the group consisting of acrylic acid, methacrylic acid, and acrylamide and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 35 to 65 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

9. A water vapor permeable, water-insoluble, thin, tough, flexible resin sheet protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, the film forming component of said resinous sheet dressing comprising a copolymer of at least one member of the group consisting of acrylic acid, methacrylic acid, and acrylamide and an ester of an acid selected from the group consisting of acrylic acid and methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 35 to 65 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

10. A water vapor permeable, water-insoluble, thin, tough, flexible resin sheet protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, the film forming component of said resinous sheet dressing comprising a copolymer of acrylic acid and an ester of ethoxy propyl alcohol with acrylic acid, the ester component constituting from 35 to 65 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

11. A water vapor permeable, water-insoluble, thin, tough, flexible resin sheet protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, the film forming component of said resinous sheet dressing comprising a copolymer of acrylic acid and an ester of butoxy ethyl alcohol with methacrylic acid, the ester component constituting from 35 to 65 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

12. A water vapor permeable, water-insoluble, thin, tough, flexible resin sheet protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, the film forming component of said resinous sheet dressing comprising a copolymer of acrylic acid, and an ester of methacrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 35 to 65 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

13. A water vapor permeable, water-insoluble, thin, tough, flexible resin sheet protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, the film forming component of said resinous sheet dressing comprising a copolymer of methacrylic acid and an ester of acrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms, the ester component constituting from 35 to 65 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

14. A water vapor permeable, water-insoluble, thin, tough, flexible resin sheet protective dressing having a length and width for covering skin areas and being solvent activatable to skin adhesive condition, the film forming component of said resinous sheet dressing comprising a copolymer of acrylamide, and an ester of acrylic acid with a saturated alkoxy monohydroxy alcohol in which the alkoxy group has from 1 to 8 carbon atoms and the remaining alcohol portion has from 2 to 4 carbon atoms,

the ester component constituting from 35 to 65 mol percent of the copolymer, said copolymer not containing more than 60 mol percent of methacrylic components.

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