Aug. 16, 1960 F. C. MERRIAM ET AL 2,949,443

SURGICAL DRESSINGS

Filed Sept. 2, 1955

Fig. 1

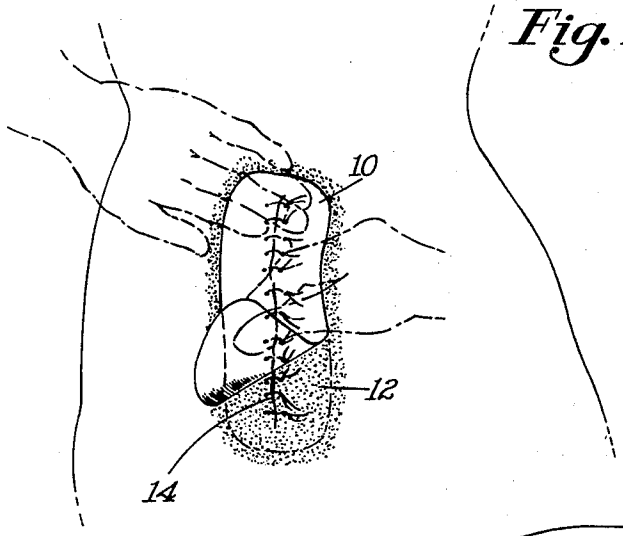


Fig. 2

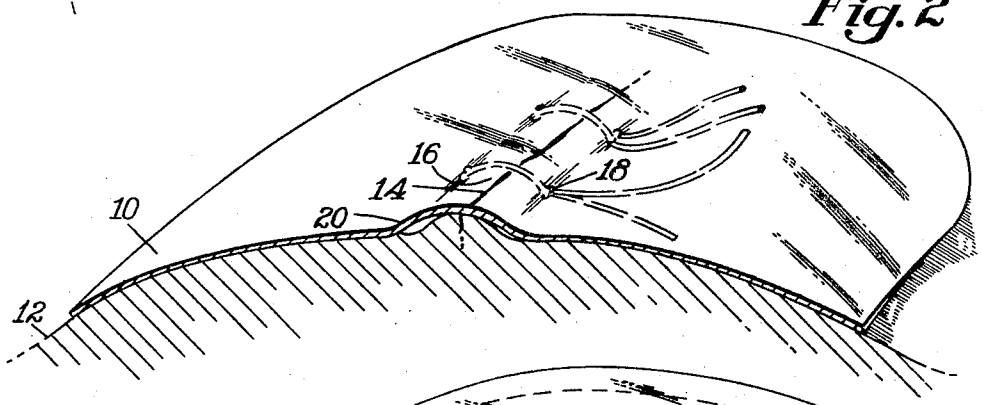
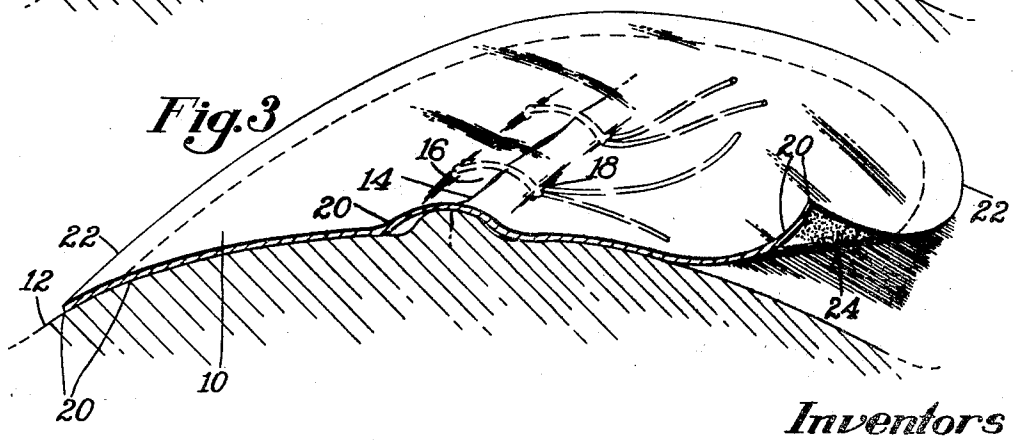


Fig. 3



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SURGICAL DRESSINGS

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This invention relates to a novel resinous material and particularly to a water vapor permeable, water-resistant, resinous sheet material.

Wounds such as surgical incisions, cuts and other breaks in the skin are usually covered with pads of absorbent fibrous material such as gauze or cotton which must be secured in place over the wounds by tape or special bandage holders. These dressings serve to protect the wounds from contamination to reduce the danger of infection and also guard the area against mechanical factors which might interfere with healing or even reopen a partially healed wound. The fibrous pad surgical dressing is necessarily bulky and difficult to keep clean and to hold in place. The fibers tend to adhere to the wound and the pad is not easily removed for inspection of the progress of healing of a wound. Additionally, since the fibrous pad is absorbent, it is difficult to wash skin areas around a wound without wetting the pad.

In the copending applications Serial No. 344,416, filed March 24, 1953, in the names of Frederic C. Merriam and Norman M. Wiederhorn, entitled "Surgical Dressings" (now abandoned) and Serial No. 394,988, filed November 30, 1953, in the name of Frederic C. Merriam, entitled "Water Vapor Permeable Resins" (now Patent No. 2,870,129, granted January 20, 1959), certain acidic polyelectrolyte materials are set forth which have the properties of water vapor permeability, water resistance, flexibility and toughness, and the ability to form a self bond to skin when moistened with certain organic liquids. These materials, by reason of the indicated properties, have been found useful as surgical dressings. However, other materials having these physical properties, and materials having resistance to solvents which are commonly employed in medical applications, have been sought.

It is a feature of the present invention to provide a water vapor permeable resinous material particularly useful for forming a water vapor permeable protective dressing for skin areas.

Further features of the present invention are to provide a new transparent or translucent resinous film surgical dressing which can be applied to a skin area in a manner forming a self bond to the skin, the dressing being water vapor permeable and at the same time being resistant to water so that the dressing itself and the skin areas surrounding it may be washed without injury or contamination.

We have discovered new film forming resinous materials which possess, when in thin layers and without the need of plasticizers or other additives, a particularly satisfactory combination of water vapor permeability with water resistance, flexibility and toughness. These resinous materials may have the ability to form a self bond to skin moistened with certain organic liquids, while at the same time presenting a tack free exposed surface. These new resinous materials are the amphoteric polyelectrolytes comprised of certain acrylic acid esters of saturated alcohols, certain acrylic acids, and certain acrylic acid esters of N,N-dialkylaminoalkyl alcohols in which the constituents of the polyelectrolytes are within special ranges 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 solvent soluble, resinous sheet surgical dressing according to the present invention to protect the incision and the areas surrounding it;

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

Fig. 3 is a partial section, similar to Fig. 2, of an incision protected by a dressing according to the present invention showing a layer of adhesive bonding the dressing to the skin at the periphery of the dressing.

Water may pass through a layer of material in several ways, including passage through physical openings in the sheet material, the physical openings being either small, i.e., pores or large mechanically formed openings, and physico-chemical transmission by which water molecules may be passed from hydrophilic radical to hydrophilic radical in a body of material even though the material itself may be nonporous and impervious to mechanical transmission of water. The physico-chemical transmission is referred to in this application as "water vapor permeability."

"Water vapor permeability" of resinous materials depends on a number of important factors, among which are the presence in the material of hydrophilic radicals, i.e., radicals having an affinity for water, which serve to pass along water molecules to a body of the material. In the present polyelectrolyte resins the acidic and basic hydrophilic components of the resins are believed to function in this matter; and it has been found that the "water vapor permeability" of the polyelectrolytes, including the acidic and basic components, is very substantially greater than the "water vapor permeability" of a homopolymer of an ester.

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

The solvent soluble materials of the present invention possess properties fitting them for special uses, such as in surgical dressings, in which they may be in close engagement with living skin. Thus the materials are capable of application to the skin by simple techniques under the variety of conditions encountered, flex and stretch with the skin, and are permeable to moisture vapor. Also, it is an important advantage that these factors are obtainable without the aid of plasticizers because of the harmful effects of plasticizers on the skin.

The solvent soluble, amphoteric polyelectrolytes of the present invention are composed of from 50 to 80% by weight of an ester of one of certain acrylic acids with a saturated alcohol containing from 1 to 10 carbon atoms, and the remainder substantially comprised of a mixture of an acrylic acid and an ester of one of certain acrylic acids with a N,N-dialkylaminoalkyl alcohol. The alkyl alcohol group esterified with the acrylic acid has from 2 to 4 carbon atoms, and the remaining alkyl groups

have from 1 to 4 carbon atoms. These latter monomers are employed in the ratios of 25 to 47% by weight of acid and 75 to 53% by weight of the amino acrylate. The new amphoteric polyelectrolytes are resinous materials possessing a desirable combination of water vapor permeability, flexibility, toughness and stretchability without requiring a plasticizer. The carbon chain of the alcohol component of the ester may be straight or branched. These materials also are activatable to skin adhesive condition with alcohol for application to the skin, and therefore meet the need for a dressing which may be applied simply to skin.

The relative proportions of the ingredients of the present amphoteric polyelectrolyte which will give the most satisfactory resin depend on the saturated alcohol ester and the aminoacrylate employed and on the conditions of reaction. For example, with a given saturated alcohol ester to acid ratio, copolymers containing esters of the higher alcohols are more flexible than those containing esters of the lower alcohols but have somewhat lower water vapor permeability. The esters of higher alcohols may be used in small proportions along with esters of the lower alcohols to give a tougher, more flexible product than might result from copolymerization of the ester of the lower alcohol and the acid. Toughness and flexibility of a copolymer from a given ratio of ester to acid may be improved by including a chain termination agent such as a mercaptan or aldehyde in the polymerization reaction mixture. The same considerations apply to the N,N-dialkylaminoalkyl esters, with higher molecular weight alkyl group containing materials providing flexibility and lower water vapor permeability to the resin.

The acrylic ingredients most useful herein are the unsubstituted acrylics, i.e., those having neither alpha nor beta substitution. However, the alkyl substituted acrylates, e.g., methacrylates, may be employed to the extent of about 40 mol percent of the acrylic ingredients, i.e., the acrylic acid or the acrylic esters described. As regards the ester ingredients, i.e, the saturated alcohol ester and the N,N-dialkylaminoalkyl alcohol ester, they may each be replaced in small part, e.g., up to 30%, with acrylonitrile. Also, a small amount of acrylamide may be added to the formulation. However, the major portion of the resin should be composed of the preferred ingredients, i.e., the alkyl acrylate, acrylic acid and N,N-diethylaminoethyl acrylate. This is for the reason that the substitute materials impart somewhat less satisfactory characteristics, e.g., rigidity in the case of the alpha substituted acrylics, to the resin.

These solvent soluble amphoteric polyelectrolytes may be prepared by various means, including copolymerization of mixtures of the acid, the ester, and the aminoacrylate, and the polymerization of a mixture comprising partially polymerized ingredients. It should be noted that the copolymers obtained may vary somewhat from the composition of the charge but that such variation is not great and does not render the copolymers obtained unsuitable for use as surgical dressings.

Preformed sheet materials, preferably from 0.003 to 0.010" in thickness, of these resins possess satisfactory ability to transmit moisture vapor given off from the skin and possess a stretchiness and flexibility such that a sheet having a thickness within this range 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 surrounding uncovered area without harm to the covering.

Relatively small departures from the range of ingredients specified above, give a material unfitted for this special use. Increase of the percentage of saturated alcohol 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 and amino acrylate components 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 and/or amino acrylate 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 amphoteric polyelectrolyte resin sheet 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, or even by contact with the alcohol which might be present in tincture of iodine swabbed on an area of the skin. 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 actuated 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.

As illustrated in Figs. 1 and 2, preformed solvent soluble, amphoteric polyelectrolyte sheet material **10** may be secured to skin **12** surrounding a wound **14** for protective purposes by activating the surfaces of the sheet material **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 material **10** against the solvent moistened skin **12** and hold the sheet material in place for a brief period after it has been applied. The sheet material **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 film **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 film.

One method useful for attaching dressings of these materials to skin is shown in Fig. 3 and comprises applying to the dressing **10** in an area **20** adjacent to the outer edge **22** thereof an adhesive layer **24** of a solvent soluble acrylic polyelectrolyte, and bonding the adhesive layer to the skin **12** while it is in skin adhesive condition by reason of the presence of solvent. Other adhesive materials, obviously, may be employed in this fashion. Another method useful for adhering the polyelectrolyte to

skin is placing a dressing on the wound and applying a common adhesive tape over the edges of the dressing and onto the skin.

Various antiseptic, bactericidal, or treatment agents may be used in combination with the solvent soluble polyelectrolyte surgical dressing of the present invention. These agents may be combined with the films when the film 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

A mixture of 13 parts by weight of methyl acrylate, 4 parts by weight of acrylic acid, 3.5 parts by weight of N,N-diethylaminoethyl acrylate, 12 parts by weight of acetone, 12 parts by weight of glacial acetic acid and 0.1 part by weight of benzoyl peroxide was introduced into a long reaction tube. Nitrogen was bubbled through the reaction mixture to provide a stirring action and to maintain a nitrogen atmosphere above the mixture. The reaction tube was heated at a temperature of approximately 68 to 70° C. for ¾ of an hour to initiate polymerization, and then cooled to room temperature. The mixture of polymer and nonreacted materials which resulted was dissolved in an equal volume of a 50/50 by weight acetone-glacial acetic acid mixture, and the resulting solution was poured into 15 volumes of petroleum ether (ligroine, a petroleum fraction boiling in the range of 30° to 60° C.) to precipitate the polymer. The precipitated material was redissolved in 10 volumes of a mixture of 2 parts by weight of glacial acetic acid, 2 parts by weight of acetone and 1 part by weight of methanol and reprecipitated in 15 volumes of water. The precipitated material then was separated from the water and vacuum dried for 2 hours at 20 mm. of mercury pressure at room temperature.

The dried material then was dissolved in a 50/50 by weight mixture of glacial acetic acid and acetone to provide a 15% by weight solution of a polymer which was poured on a level silicone treated glass plate, covered and allowed to dry slowly. After the solution was dried overnight, a film was derived from it which was baked in a vacuum oven at approximately 20 mm. of pressure for approximately 2 hours at 60° C. to drive off residual solvent. The resultant film had a thickness of .007" and was relatively tough and flexible.

Moisture vapor permeability of the film was determined by a method similar to the procedure described by Taylor et al. in Industrial and Engineering Chemistry 28, 1255–63 (1936). According to this method, a piece of the film was sealed over the mouth of an aluminum cup containing 75 cc. of water, and the cup was placed in an atmosphere having a relative humidity of 50% and a temperature of 70° F. The cup was weighed at intervals until the weight loss became constant. The water vapor permeability factor D, expressed as grams of water vapor transmitted per hour through a centimeter cube of the plastic under a water vapor differential of 1 mm. of mercury at a constant temperature of 70° F., was 57×10^{-8}. For purposes of comparison, a similar determination of the water vapor permeability of polymethyl methacrylate gave a factor D of less than 3×10^{-8}.

A strip of the material was cut to a size to project beyond the edges of a wound. The area of skin surrounding the wound was swabbed with ethyl alcohol and the strip of material pressed against the moistened area and held in place for a few seconds. The strip thereafter adhered firmly to the skin and provided a transparent protection for the wound and the surrounding area.

Example II

A mixture of 13 parts by weight of butyl acrylate, 3.7 parts by weight of acrylic acid, 4.4 parts by weight of N,N-diethylaminoethyl acrylate, 15 parts by weight of methanol, 10 parts by weight of distilled water and 0.1 part by weight of potassium persulfate was polymerized by the same procedure employed in Example I, with the exception that in this case the temperature of heating was 80° C. and the time was 3 minutes followed by a 1 hour cooling period during which time a nitrogen stirring was continued. The polymer mixture was dissolved in 3 volumes of methanol and precipitated in 15 volumes of water. The precipitate was removed quickly from the water and emulsified in fresh water with stirring, following which it was purified by electrodialysis between cellophane membranes. The polymer plated out on the negative membrane, from which it was collected. It then was dried at room temperature for about two hours in an evacuated atmosphere, i.e., approximately 20 mm. of Mercury. The dried material then was stirred into methanol, in which it dispersed and a small amount of water was stirred in causing it to form a clear solution. The solution was cast as a film according to the method employed in Example I. The D value of this film was 157×10^{-8}.

A sheet of this material was applied to cover a skin area by a procedure involving swabbing the surrounding area with ethanol and pressing the film in place. The film adhered firmly to the skin, and when removed two days later showed no maceration of the skin, i.e., whitening of the skin due to retained moisture.

Example III

A mixture of 10.3 gms, of butylacrylate, 8.1 gms. of ethyl acrylate, 2.9 gms. of acrylic acid, 4.8 gms. of N,N-diethylaminoethyl acrylate, 31.3 gms. of a 5 to 1 by weight t-butyl alcohol-glacial acetic acid mixture and 0.065 gm. of 2,2'-azobisisobutyronitrile was charged into a long reaction tube. Nitrogen was bubbled through the reaction mixture to provide a stirring action to maintain a nitrogen atmosphere above the mixture. The reaction tube was heated in a water bath for two hours at 60 to 75° C. After polymerization, the mixture was allowed to cool for one-half hour and was diluted with about an equal volume of methanol. Following this the polymerization mixture was subjected to steam distillation in an open container for one hour to remove unreacted monomer. Near the end of this period the polymer precipitated, and the liquid surrounding it was decanted. The precipitate was comminuted and steamed further for five hours, and then was dried in a freeze drying apparatus. The polymer was then placed in a small flask having a cold trap comprising a flask containing Dry Ice and acetone at its mouth, and the flask containing the polymer was evacuated with a vacuum pump to a pressure of less than 1 mm. of mercury. The flask containing the polymer was heated with steam for about eight hours as a further purification measure. The purified polymer then was dissolved in methanol and cast as a 15% solution on a silicone treated glass plate. The resulting .007" thick film was then baked for one hour at 60° C. The D value of this film was 70×10^{-8}.

Example IV

A mixture of 16.3 gms. of 2-ethylhexyl acrylate, 4.9 gms. of acrylic acid, 3.3 gms. of N,N-diethylaminoethyl acrylate, 20 ml. of methanol, 3 ml. of 5 molar hydrochloric acid, and 0.07 gm. of potassium persulfate were charged into a long reaction tube. Nitrogen was bubbled through the tube to stir the mixture and to provide a nitrogen atmosphere above it, and the reaction tube was heated in a water bath at 70 to 80° C. Polymerization

was complete in about one-half hour and the polymerization mixture then was dissolved in acetone, and precipitated in 10 volumes of petroleum ether. The precipitate then was dissolved in acetone and precipitated in 15 volumes of water. The polymer was filtered from the liquid and dried at 20 mms. of mercury for one hour. Following this, the polymer was dissolved in methanol to provide a 14% solution and a film of the polymer was cast from the solution on a silicone treated glass plate. The resulting film, which was approximately 0.006 of an inch thick, had a D value of 54×10^{-8}.

The film then was applied as a surgical dressing to a wound and the skin area surrounding the wound, which had been moistened with ethyl alcohol. The dressing adhered firmly to the skin and permitted passage of water vapor as evidenced by no signs of maceration in the skin upon removal of the dressing four days following its application.

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

1. The film forming, water insoluble, water vapor permeable, resinous amphoteric polyelectrolyte polymer of 50 to 80% by weight of at least one member of the group consisting of esters of acrylic acid and methacrylic acid with an alcohol of which the radical attached to the hydroxyl group is a saturated alkyl group containing 1 to 10 carbon atoms and substantially the remainder comprising, in the indicated ratios, 25 to 47% by weight of at least one member of the group consisting of acrylic acid and methacrylic acid and 75 to 53% by weight of an ester of at least one member of the group consisting of acrylic acid and methacrylic acid with N,N-dialkylaminoalkyl alcohols in which the carbon chain of the alkyl alcohol has from 2 to 4 carbon atoms and the remaining alkyl groups contain 1 to 4 carbon atoms, said polyelectrolyte not containing more than 40 mol percent of methacrylic components.

2. The film forming, water insoluble, water vapor permeable resinous amphoteric polyelectrolyte polymer of 50 to 80 % by weight of an ester of acrylic acid with an alcohol of which the radical attached to the hydroxyl group is a saturated alkyl group containing 1 to 10 carbon atoms, and substantially the remainder comprised, in the indicated ratios, of 25 to 47% by weight of acrylic acid and 75 to 53% by weight of an ester of acrylic acid with a N,N-dialkylaminoalkyl alcohol in which the carbon chain of the alkyl alcohol group has from 2 to 4 carbon atoms and the remaining alkyl groups contain 1 to 4 carbon atoms.

3. The film forming, water insoluble, water vapor permeable resinous amphoteric polyelectroylte polymer of 50 to 80% by weight of an ester of acrylic acid with an alcohol of which the radical attached to the hydroxyl group is a saturated alkyl group containing 1 to 10 carbon atoms, and substantially the remainder comprised, in the indicated ratios, of 25 to 47% by weight of acrylic acid and 75 to 53% by weight of N,N-diethylaminoethyl acrylate.

4. A thin, tough, flexible, water insoluble water vapor permeable, resinous sheet material capable of activation to skin adhesive condition to provide a covering for wounds, the film forming component of said resinous sheet material being an amphoteric polyelectrolyte polymer of 50 to 80% by weight of at least one member of the group consisting of esters of acrylic acid and methacrylic acid with an alcohol of which the radical attached to the hydroxyl group is a saturated alkyl group containing 1 to 10 carbon atoms and substantially the remainder comprising, in the indicated ratios, 25 to 47% by weight of at least one member of the group consisting of acrylic acid and methacrylic acid and 75 to 53% by weight of at least one member of the group consisting of esters of acrylic acid and methacrylic acid with N,N-dialkylaminoalkyl alcohols in which the carbon chain of the alkyl alcohol group has from 2 to 4 carbon atoms and the remaining alkyl groups contain 1 to 4 carbon atoms, said polyelectrolyte not containing more than 40 mol percent of methacrylic components.

5. A thin, tough, flexible, water insoluble, water vapor permeable, resinous sheet material capable of activation to skin adhesive condition to provide a covering for wounds, the film forming component of said resinous sheet material being an amphoteric polyelectrolyte polymer of 50 to 80% by weight of an ester of acrylic acid with an alcohol of which the radical attached to the hydroxyl group is a saturated alkyl group containing 1 to 10 carbon atoms, and substantially the remainder comprised, in the indicated ratios, of 25 to 47% by weight of acrylic acid and 75 to 53% by weight of an ester of acrylic acid with a N,N-dialkylaminoalkyl alcohol in which the carbon chain of the alkyl alcohol group has from 2 to 4 carbon atoms and the remaining alkyl groups contain 1 to 4 carbon atoms.

6. A thin, tough, flexible, water insoluble, water vapor permeable, resinous sheet material capable of activation to skin adhesive condition to provide a covering for wounds, the film forming component of said resinous sheet material being an amphoteric polyelectrolyte polymer of 50 to 80% by weight of an ester of acrylic acid with an alcohol of which the radical attached to the hydroxyl group is a saturated alkyl group containing 1 to 10 carbon atoms, and substantially the remainder comprised, in the indicated ratios, of 25 to 47 % by weight of acrylic acid and 75 to 53% by weight of N,N-diethylaminoethyl acrylate.

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