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BREATHABLE FABRIC WITH A LAYER OF WATER-SWELLABLE ELASTOMER

Filed Nov. 20, 1962

FIG. 1

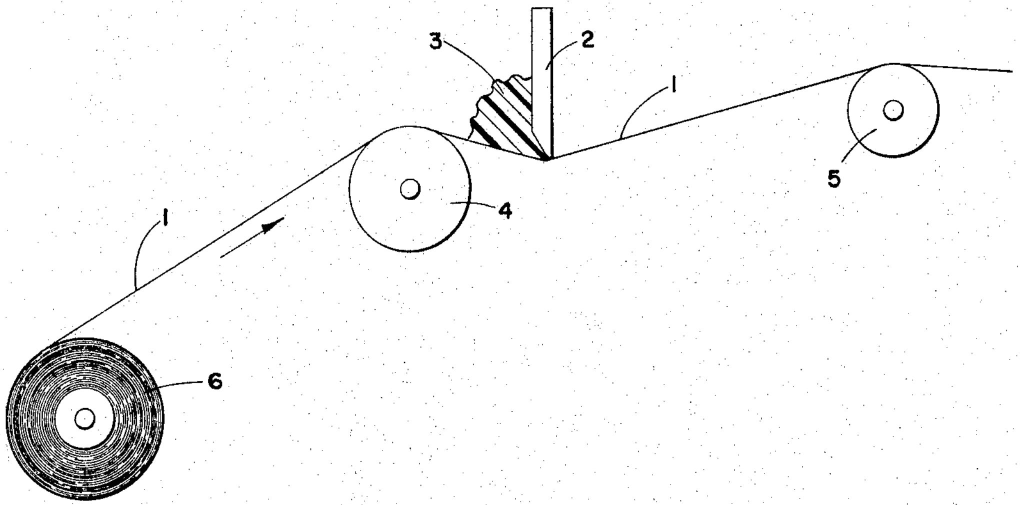
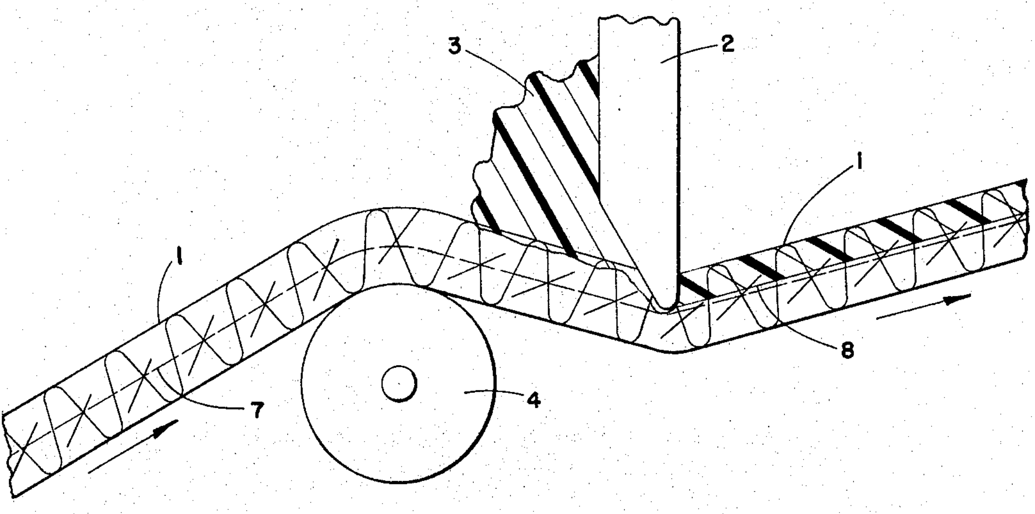


FIG. 2



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BREATHABLE FABRIC WITH A LAYER OF WATER-SWELLABLE ELASTOMER

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6 Claims. (Cl. 117—135.5)

This invention concerns waterproof coatings which are vapor permeable, more particularly rainwear including fabrics which have been prepared employing these coatings.

Rainwear has customarily been prepared by coating various types of fabrics wth some flexible hydrophobic material such as rubber or the like. However, when a person has worn this type of rainwear for a period of time, the body becomes wet due to the condensation of vapor on the inside of the rainwear and, consequently, uncomfortable. Accordingly, it has been desirable to find coatings which can be applied to fabrics which will be relatively impermeable to liquid water but which will readily transmit water vapor or other gases.

Many solutions to the problem of providing water impregnable coatings which are vapor permeable have been suggested. For instance, mechanical devices have been employed in which finely pointed instruments such as a needle or the like are used to make small punctures or holes in the fabric through which the vapor can escape. These holes are normally of such small size that they are relatively impermeable to liquid water.

Another solution to the problem employs hydrophilic pigments which are suspended in hydrophobic binders such as rubber, styrene-butadiene copolymers, and the like.

The problems inherent in obtaining a satisfactory coating include those of providing a flexible coating which will withstand wear when incorporated into fabrics and which will have the desirable hydrophilic feel which is normally associated with comfortable garments. In addition, the coating must be relatively inexpensive and must be easily applied using customary coating methods. The coating must have satisfactory adhesion to the fabric and must be relatively resistant to the solvents used for drycleaning purposes.

We have found a coating composition which is impermeable to liquid water but which satisfactorily transmits water vapor such as that resulting from body perspiration which is based on an entirely different principle, that of employing a swellable elastomer. These elastomers are hydrophilic and are also employed for impregnating the fabrics rather than coating the fabric or treating it on the surface.

One object of this invention is to provide impregnated fabrics which are waterproof to liquid water but which remain water vapor permeable. Another object of the invention is to provide a process for making waterproof fabrics using elastomers which are swellable in water. A further object is to describe elastomers which are hydrophilic and which are suitable for impregnating fabrics for use as rainwear. Another object is to provide rainwear which is suitable for garment wear, which has a pleasant hand, which is flexible, wear resistant, moisture vapor permeable and relatively water impermeable.

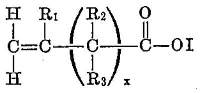
The above objects are obtained by coating the fabric with an elastomer which is able to swell rapidly on contact with water and which, in most instances, will swell so as to close the interstices in an environment of high relative humidity. These elastoms must have the swelling reaction toward water, but at the same time they must be suitable for application to fabrics. The suitability is determined by the elastomers' appearance, flexibility, abrasion resistance and adherence.

There are two general methods of practicing the invention. They are (1) prepare and apply to a fabric a water-swellable elastomer which consists of an interpolymer of 2 or more monomeric species at least one of which is a polar, hydrophilic component that is susceptible to water, and (2) to modify an elastomer which is not hydrophilic or insufficiently swollen by water with a polymer or interpolymer which is affected by water and which can be made compatible with the elastomeric matrix by primary chemical bond or by physical intermolecular forces sufficiently powerful that the two polymers are essentially inseparable in practical applications of the end use product.

The elastomers useful to the practice of the invention are polymers, copolymers and interpolymers, as well as mixtures of polymers if the mixtures of polymers result in a single graft polymer composition after curing, which will render the final composition swellable in water. The elastomers useful to the practice of the invention are polymers, copolymers, interpolymers and mixtures of polymers derived from monomers illustrated by, but not limited to, the following list: butadiene, chloroprene or isoprene copolymerized with monomers which produce homopolymers that are swollen or soluble in water are preferred examples of useful polymers. However, all other open-chain conjugated dienes having from 5 to 8 carbon atoms, such as 2,3-dimethylbutadiene-1,3; 1,4-dimethylbutadiene-1,3; piperylene and the like, are also useful.

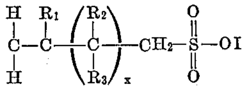
These monomers may be copolymerized with a monomer which will render the elastomer water swellable, such as monomers from the following list which illustrate but are not intended to limit the scope of the invention. Included are unsaturated polymerizable carboxylic acids, sulfonic acids, and phosphoric acids as illustrated by the following generalized formulas:

I.



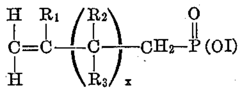
$$CH_2{=}C(R_1)-\left(C(R_2)(R_3)\right)_x-C({=}O)-OI$$

II.



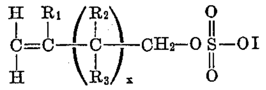
$$CH_2-C(R_1)-\left(C(R_2)(R_3)\right)_x-CH_2-S({=}O)_2-OI$$

III



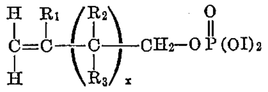
$$CH_2{=}C(R_1)-\left(C(R_2)(R_3)\right)_x-CH_2-P({=}O)(OI)_2$$

IV



$$CH_2{=}C(R_1)-\left(C(R_2)(R_3)\right)_x-CH_2-O\,S({=}O)_2-OI$$

V



$$CH_2{=}C(R_1)-\left(C(R_2)(R_3)\right)_x-CH_2-O\,P({=}O)(OI)_2$$

where:

R_1=H, CH_3, or —CH_2—CH_3
R_2=H, —CH_3, or —CH_2—CH_3
R_3=H, —CH_3, or —CH_2—CH_3
x=0, 1, 2, 3 or 4
I=H^+, NH_4^+, or any monovalent metal ion

Maleic acid and fumaric acid are also included. Polymerizable unsaturated molecules which contain more than one sulfonic, sulfate, phosphoric, or phosphate group are also included.

Elastomeric copolymers containing monomers having water susceptible groups such as amides, amines and hydroxyl are also useful. A partial list of such monomers includes fumaramide, acrylamide, methacrylamide, mono

N-substituted acrylamide and methacrylamide, di N-substituted acrylamide and methacrylamide, vinylpyridine, substituted vinylpyridine, vinylpyrrolidinone, substituted vinylpyrrolidinone, allyl alcohol, and β-hydroxyethyl esters of acrylic and methacrylic acid.

The water swellability of the elastomer can be obtained by copolymers, terpolymers, etc., of any combination of the above monomers with monomers containing conjugated unsaturation or it may be obtained indirectly by copolymerizing the elastomeric engendering monomer with monomers that may be reacted to provide water swellability. Such polymers are illustrated by copolymers of diene monomers with acrylonitrile, acrylate esters and amides, methacrylate esters and amides, and maleic anhydride. These copolymers can be hydrolyzed to provide copolymers containing unsaturated chemical units and carboxylic acid units. Other reactions to provide valuable elastomers include reactions on polymers such as hydrolysis of copolymers of vinyl acetate to give hydroxyl groups, ammonolysis of ester groups to give amide groups, and sulfonation to give elastomers which have sulfonic acid groups.

The hydrophilic groups may be made a part of the final elastomer by adding certain polymers. These polymers are those which become chemically bound by the curing reaction after the elastomer is applied to the fabric. The polymers which are useful in this method of practicing are those which contain some unsaturated monomer units but also large numbers of hydrophilic components. These polymers are usually water soluble. They include copolymers of open-chain diene monomers which have 4 to carbon atoms with one or more of the hydrophilic monomers listed above. This method of practicing the invention uses copolymers containing from 40 to 99% hydrophilic monomer units. As described above, it is usually desirable that the hydrophilic polymer be reacted or grafted on the elastomeric polymer. The reason for bonding the two polymers together is to prevent the hydrophilic polymer, which is always greatly swollen by water and is usually water soluble before incorporation in the elastomer matrix, from being extracted from the elastomer during contact with water. The reaction which grafts the polymers together may also be a curing or cross-linking reaction for the entire matrix. If the cross linking does occur at this time, then it is necessary that this reaction is done after the elastomer has been applied to the fabric.

Although many reactions can be used to cause this combination or grafting together of the two polymers, the following types are preferred. They are classified and explained as follows:

A. *Reactions between unsaturated sites in both polymers*

In these instances both polymers contain ethylenic unsaturation in the main polymer chains due to the use of a monomer having more than one ethylenically unsaturated site as a comonomer at the time of preparation of the two polymers. For instance, an elastomer made from butadiene is combined with a copolymer of butadiene and acrylic acid. These polymers are curable using peroxides, sulfur type curing, heat, or certain transition metal ions such as cobalt, manganese, or chromium or a combination of these ions with peroxides.

B. *Reactions of elastomers which contain anhydride or acid chloride groups*

Polymers and copolymers which contain readily reactive groups such as anhydride groups or acid chloride groups can be made water swellable by certain suitable reactants. For instance, copolymers of maleic anhydride with such monomers as butadiene can be reacted with sodium hydroxide solutions to obtain the sodium salt of the copolymer of sodium maleate and butadiene and thereby become a water swellable elastomeric composition. An alternate use of the maleic anhydride copolymers could depend on the reaction of such polymers with polyether terminated with hydroxyl groups. The final composition and properties of the elastomer can be varied by regulating the amount of maleic acid or by using polyethers of different chain lengths. A skillful use of these techniques will provide numerous compositions which could be useful in the practice of the invention. Other polymers which are illustrative of these reactions are:

(a) The copolymerization of elastomeric engendering monomers with acrylic and methacrylic anhydride so that the anhydride portions give linear polymers with cyclic anhydride structures

(b) The copolymers of unsaturated acid chlorides such as acryloyl chloride and methacryloyl chloride

(c) The copolymers of anhydrides of unsaturated acids with saturated acid such as the mixed anhydride of acrylic and acetic acids.

The number of active reaction sites may be varied in the copolymer to suit the particular application. For instance, relatively fewer sites will be required if a high molecular weight water soluble polymer such as a polyether terminated with hydroxyl groups is used. On the other hand, a relatively large number of sites would be required if a low molecular weight polymer is used. Empirical experiments have shown that the final elastomeric composition must have groups or segments which are susceptible to water and comprise 10—60% of the total polymer weight.

C. *Reaction between carboxyl groups*

If both polymers contain carboxyl groups either as the free acid or as a solubilizing alkali metal salt, the polymers may be chemically combined or grafted to each other by reaction with a multivalent insolubilizing metal ion. For instance, an elastomeric copolymer composition of butadiene and acrylic acid may be combined with a copolymer of acrylamide and acrylic acid by adding to the mixture an ion such as calcium, aluminum or magnesium. Since this reaction results in cross-linking of both polymers, it is necessary that the multivalent metal ion be added as a final treatment of the coated fabric. It is also preferred that only a portion of the carboxyl groups should be rendered insoluble by this reaction if the water susceptibility of the composition depends on alkali metal salts of carboxyl groups or free carboxyl groups.

The hydrophilic polymers which are useful for the practice of this invention can be any polymers which are soluble or swollen by water and which can be attached to the elastomeric composition by any or all of the techniques described above. Also included are naturally occurring hydrophilic polymers. Examples of these polymers are addition polymers and copolymers which have 20% or more of monomer constituents of acrylic, methacrylic, maleic, and fumaric acids; substituted and unsubstituted amides of these acids; β-hydroxyethyl esters and amides of these acids; the alkali metal salts and free acids of sulfonated aromatic derivatives of ethylene such as sulfonic acid derivatives of styrene, and polymers which have been obtained by hydrolysis of poly(vinyl esters) such as poly(vinyl alcohol) which can be obtained by hydrolysis of poly(vinyl acetate). Also included are sulfate, sulfonic phosphonic and phosphate derivatives of unsaturated organic radicals and other monomers as outlined by the structural formulas shown above. Particularly valuable examples of use of the above monomers are the interpolymers of one or more of the above monomers with monomers having more than one reactive double bond such as butadiene. The presence of unsaturation in the hydrophilic polymer is used to cause attachment of the hydrophilic polymer to the elastomeric polymer.

D. *Cross-linking using formaldehyde*

The elastomeric composition may be cured and grafted to the hydrophilic composition by means of a series of reactions using formaldehyde or methylol derivatives of formaldehyde.

These are well-known reactions and are discussed in "Polymer Processes," Chapter VIII, 1956, edited by C. E. Schildknechkt, published by Interscience Publishers. For example, an elastomer composed of a copolymer of butadiene and acrylamide may be cross-linked and chemically bound to a hydrophilic copolymer composed of acrylamide and acrylic acid by heating the mixture with formaldehyde or any substance capable of yielding formaldehyde under these conditions. Other examples of the use of this method of curing and combining polymers will be illustrated by specific examples.

The exact composition of the copolymer or mixture of polymers is dependent on the following factors:

(1) The nature of the fabric,
(2) The desired degree of swelling of the elastomer, and
(3) The amount of swelling which a particular monomer will cause when copolymerized with butadiene, chloroprene, or isoprene.

The preparation of suitable diene copolymers is discussed in Calvin E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, 1952. The copolymers with acrylonitrile which then may be hydrolyzed are discussed on pages 256–322.

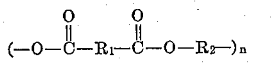
However, the copolymers are polymerized, separated and purified, the next step is to prepare the copolymer prior to treatment of the fabric. These copolymers are similar to other butadiene type elastomers in that they may be cured with standard accelerator and curing agents known to the art. An example of such curing agents is a combination of zinc oxide, sulfur, and thiocarbanilide present at approximately 5% in the dry, deposited elastomer.

In some applications it may be desirable to use an uncured elastomer but in most applications the elastomer will be cured which will reduce the water susceptibility. The curing agents, accelerators, and curing conditions for these elastomers are similar to those described for vulcanization of rubber. Typical sulfur curing systems are discussed in "Vinyl and Related Polymers," by Calvin E. Schildknecht. In addition, cures using organic peroxides are useful. The desired range of swellability of the elastomer after it is applied to the fabric is 50–500% volume increase. In addition to curing the elastomer, it is sometimes desirable to add water repellant agents such as silicone resins or waxes and the like. This addition provides an initial repellancy to liquid water, thereby providing a time in which the elastomer may swell after initial contact with the water so that the initial contact does not penetrate the interstices before swelling.

The invention is also related to the use of a water swellable elastomer made from the condensation-type polymers. The term "condensation polymers" includes any polymer whose structure indicates that it could have been prepared by a condensation reaction. This type polymer is described in "Preparative Methods of Polymer Chemistry," pages 57–147 by W. R. Sorenson and T. W. Campbell. Particular attention is directed to page 58. The invention is also related to the use of condensation polymers which are swellable upon contact with water in the range of 50 to 500%.

The condensation-type polymers which are suitable for the practice of this invention are illustrated by the following generalized formulas:

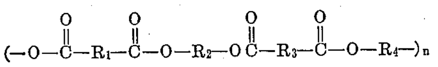
1. *Polyesters.*—



$$(-O-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-O-R_2-)_n$$

Where R_1=straight or branched chain hydrocarbon radical of 2 or more carbon atoms or cyclic hydrocarbon radicals of not more than 12 carbon atoms comprising the cyclic rings. Where R_2=water susceptible long chain ether configurations as can be obtained by the polymerization of ethylene oxide, propylene oxide, butylene oxide or mixtures or R_2=any organic radical providing elastomeric properties to the composition.

2. *Copolyesters.*—

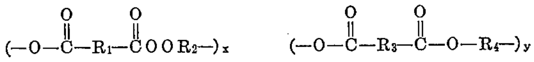


$$(-O-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}-O-R_2-O\overset{O}{\overset{\|}{C}}-R_3-\overset{O}{\overset{\|}{C}}-O-R_4-)_n$$

Where R_1=hydrocarbon radicals of 2 or more carbon atoms or cyclic hydrocarbon radicals of not more than 12 carbon atoms comprising the cyclic rings or mixtures of these radicals.

Where R_2=water susceptible long chain ether configurations such as can be obtained by the polymerization of ethylene oxide, butylene oxide or mixtures or R_2=any organic radical providing elastomeric properties to the composition. Where R_3=any organic radical but the acid derived from this radical will comprise less than 50% of the total dicarboxylic acid used to make the polyesters. Where R_4=any straight or branched chain hydrocarbon radical of 2 or more carbon atoms or a cyclic hydrocarbon radical of not more than 12 carbon atoms, comprising the cyclic rings.

3. *Mixed or block polyesters.*—



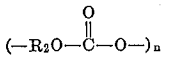
$$(-O-\overset{O}{\overset{\|}{C}}-R_1-\overset{O}{\overset{\|}{C}}OOR_2-)_x \qquad (-O-\overset{O}{\overset{\|}{C}}-R_3-\overset{O}{\overset{\|}{C}}-O-R_4-)_y$$

Where R_1, R_2, R_3, and R_4 are the radicals described above for copolyesters. x=20 through 200 repeating units. y=20 through 200 repeating units. These elastomers may contain ethylenic unsaturation to provide curing reactions for the final elastomer. Polyesters containing maleic or fumaric acid are examples of such polymers. The unsaturation may be a part of the glycol units as, for instance, if a portion of the glycol includes, for example, 2-butene-1,4-diol. The number of components which contain unsaturation is variable and is determined by the properties desired in the final elastomer. Usually if the unsaturation is used only to provide sites for cross-linking, the number of unsaturated groups may vary from 1% to 50% of acid or glycol units. This unsaturation may be obtained by including either unsaturated acids or glycols or both. In some instances, the inclusion of unsaturated acids or glycols is made to provide active sites to react sodium bisulfite to obtain greater water susceptibility. In these instances, the amount of unsaturation may be increased to the extent that all of the glycol or up to 50% of the acid and glycol components are unsaturated units.

Another very useful means of rendering the polymer susceptible to water involves the use of sulfonated aromatic dicarboxylic acids. In this instance, the acids in the generalized formulas R_1 and R_3 may have one or more groups of alkali metal salt of a sulfonic acid attached directly to the ring or rings.

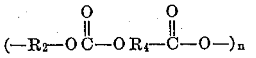
A special class of polyesters are the polycarbonate polyesters having the general formulas:

1)



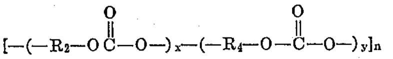
$$(-R_2O-\overset{O}{\overset{\|}{C}}-O-)_n$$

(2)



$$(-R_2-O\overset{O}{\overset{\|}{C}}-OR_4-\overset{O}{\overset{\|}{C}}-O-)_n$$

(3)

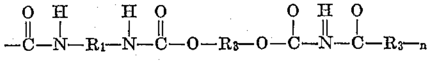


$$[-(-R_2-O\overset{O}{\overset{\|}{C}}-O-)_x-(-R_4-O-\overset{O}{\overset{\|}{C}}-O-)_y]_n$$

n=any number of units to give elastomeric properties
x=blocks from 500–4000 molecular weight
y=blocks from 500–4000 molecular weight

(4) *Polyurethanes and polyureas.*—Polyurethanes and polyureas are also useful and are illustrated by the following formulas:

(1)



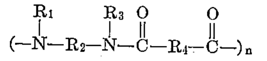
$$-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R_1-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R_8-O-\overset{O}{\overset{|}{C}}-\overset{H}{\overset{\|}{N}}-\overset{O}{\overset{|}{C}}-R_3-_n$$

Where R_1 is an alkylene or arylene group which has 2 to 30 carbon atoms. Where R_2 and R_3 are polyethers obtained from polymerization of ethylene oxide, propylene oxide, or butylene oxide or alkylene or arylene groups of 2 to 30 carbon atoms. Where R_2 and R_3 are any organic radicals capable of making the final composition elastomeric.

A polyurea link is formed if R_3 is the adduct of water to the isocyanate. In this instance, R_1 and R_2 have the meaning as described above.

A discussion of the experimental conditions suitable for producing polyurethanes and polyureas may be found in "Preparative Methods of Polymer Chemistry," pp. 133-139, Interscience Publishers, Inc. (1961), by W. R. Sorenson and T. W. Campbell.

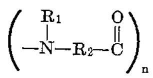
(5) *Polyamides.*—Certain types of polyamides and copolymers of polyamides are also useful. These polymers are illustrated by the following general formulas:



$$(-\overset{\overset{R_1}{|}}{N}-R_2-\overset{\overset{R_3}{|}}{N}-\overset{\overset{O}{\|}}{C}-R_4-\overset{\overset{O}{\|}}{C}-)_n$$

where R_1 and R_3 are —H, $—CH_3$, $CH_3—CH_2—$ or $(CH_2—CH_2—O)_xH$. Where R_2 and R_4 are alkylene or arylene radicals of from 2 to 30 carbon atoms or polyether segments of 200 to 20,000 molecular weight as could be made from ethylene oxide, propylene oxide, or butylene oxide. The final composition of polymer must be swellable in water in the range of 50 to 500%. This range is obtainable if the polyamides contain more than 50% by weight of polyether segments either as a part of the main polymer chain or as a side chain.

The polyamides made from certain amino acids and lactams of amino acids are also useful when they contain polyether side chains as shown by the general formula:



$$\left(-\overset{\overset{R_1}{|}}{N}-R_2-\overset{\overset{O}{\|}}{C}\right)_n$$

Where R_1 is a polyether segment as can be made by polymerizing ethylene oxide, propylene oxide, or butylene oxide. Where R_2 is $(—CH_2—)_m$; where m=3, 4, 5, 6, 7, 8, 9, 10, or 11.

An adequate discussion of this chemistry is reported in "Preparative Methods of Polymer Chemistry," pp. 60–80 by W. R. Sorenson and T. W. Campbell.

(6) *Polysulfides.*—The elastomers which contain sulfur in the main polymer chain are also useful elastomers for the practice of this invention if they are water swellable due to copolymerization with hydrophilic components or if the elastomer is mixed with a hydrophilic polymer. There are several classes of these useful materials such as polythioethers, polythioesters, polydisulfides, and the like. The chemistry of these polymers is summarized in "Polymer Processes," Chapter XI, edited by C. E. Scheldknecht, 1956, published by Interscience Publishers, Inc.

A mixture may be used composed of an elastomeric composition which is a condensation polymer and which contains a modifying hydrophilic polymer which may be a condensation, addition, or natural polymer or resin. The modifying polymer can compose any part of the final composition in the range of 5 to 80%. In some instances, it may be desirable that both polymers be hydrophilic and elastomeric. However, the final composition must be swollen by water in the range of 50–500% volume increase. These polymers are usually curable and capable of chemically combining with each other.

Some examples of polymers which are suitable modifiers for condensation-type elastomers are those derived from the following monomers used to make addition polymers. Included are acrylic, methacrylic, fumaric, maleic, and crotonic acids; amides of these acids; mono-nitrogen substituted amides of these acids; di-nitrogen substituted amides of these acids; ammonium and metal salts of these acids; β-hydroxyethyl esters of these acids; anhydrides of these acids; and acid chlorides of these acids. Also included are interpolymers of the above monomers with any other monomer capable of polymerization. A few examples of such monomers include vinyl chloride, acrylonitrile, vinyl acetate, styrene, acrylate and methacrylate esters, and polymerizable unsaturated hydrocarbons.

Also included are polymerizable monomers that contain one or more hydrophilic groups such as sulfonic, phosphonic, sulfate, phosphate, hydroxyl, or pyridinium lactam. Also included are polymers which may be reacted to become hydrophilic such as vinyl acetate, acrylonitrile, esters of acrylic and methacrylic acid which can be hydrolyzed to provide polymers having hydroxyl or carboxyl groups. Polymers such as styrene and cellulose which can be sulfonated are also included.

Hydrophilic condensation polymers may be used to modify condensation-type elastomers. These hydrophilic elastomers can contain such hydrophilic groups as sulfate, sulfonic, phosphate, or phosphonic acids or salts of these acids. They can have long chain polyether segments derived from ethylene or propylene oxide as side chains or as part of the main polymer chain. In some instances, the hydrophilic nature may be imparted by hydroxyl groups. In other instances, the hydrophilic nature of the polymer can be an inherent property of the polymer due to a large number of amide groups in the main chain or as side chain configuration.

The above discussion serves to describe the general types of polymers and polymer mixtures that are useful to the practice of the invention. Many other combinations of materials are possible in this rather complex field. The scope of the invention is not limited by a particular polymer combination except that the final composition must be insoluble in water but affected by water so as to cause the polymer to swell 50–500%. The water swellable composition must be capable of being extended 200% and to show an elastic recovery of at least 50%.

The techniques for applying all of the above polymers to suitable fabrics include applications from solutions of polymers, suspensions of polymers, and mixed systems such as an emulsion of a water soluble polymer, suspended in a solution of an organic solvent containing dissolved polymer. Examples of suspensions are the so-called organosols or plastisols. In most instances, the water swellable elastomer is applied from a solution of the elastomer in an organic solvent. The concentration of the elastomer in the solvent can have any value but the usual concentrations will be in the range of from 10 to 50% solids. The choice of solvent depends on the particular elastomer which is being applied, as for instance in the case of a modified nylon-type, the solvent could consist of low molecular organic acids or mixtures of alcohol and water. The solvent required for a polyester type on the other hand would generally consist of chlorinated hydrocarbons, alcohols, esters, ketones, and mixtures of these solvents with other organic liquids or water. Since the invention is particularly concerned with the use of water swellable materials, it is an advantage in many instances to use water in the solvent systems for the application of these elastomers.

The instances which involve the use of suspensions including organosols or plastisols employ organic liquids to suspend from 20 to 80% solids which may be applied by means of the usual coating techniques or by first coating a film to be formed on a metal blade or cylinder which is later applied to the fabric by a calendering technique. Again it may be desirable to use various amounts of water to aid in the suspension of the elastomer in the organic liquid or to cause the elastomer to be deposited in its water swollen state. It may be necessary therefore, in a few instances, to apply a particular composition from a suspended state in water. The elastomers preferred by this invention have a mixed behavior toward solvent systems and it may therefore be necessary in some instances to reduce the polymer particle size by mechanical means followed by suspension of the smaller particles in water.

The application of the elastomer to a fabric may be done by coating solutions, suspensions, by calendering cast films, padding operations, or by spraying solutions or suspensions onto the fabric. The particular method used will depend on the nature of the elastomer and the nature of the solvent. These methods are well known to the coating trade and the particular choice will be obvious to one skilled in the art.

Although any fabric, paper, leather, or other porous material can be rendered waterproof and water vapor permeable by application of these water swellable elastomers, the materials which are best suited are fabrics, papers, and leathers which have sufficient thickness that the elastomer can be deposited in the interior of the porous material. For example, fabrics which have a relatively close weave or construction and weigh more than 1½ oz./yd.^{2} are preferred. Similar consideration is required if the elastomer is applied to papers, leathers, and the like. The amount of elastomer which is applied is dependent on the original porosity of the material to be coated and its weight. For instance, a fabric which weighs 1½ oz./yd.^{2} will require more elastomer than a fabric which weighs 3 oz./yd.^{2}. On the other hand as the fabric becomes heavier than 3 oz./yd.^{2}, the coating weight is again decreased. The following table illustrates an approximate coating weight for a particular or given fabric weight and a comparison of air and water vapor permeability.

Fabric wt., oz./yd.^{2}	Average air permeability of base fabric, $\Delta P=11.58$ mm. Hg g./m.^{2}/hr.	Average water vapor permeability, $\Delta P=11.58$ mm. Hg g./m.^{2}/hr.	Lower limit elastomer wt., oz./yd.^{2} (tight weave)	Upper limit elastomer wt., oz./yd.^{2} (far-open weave)	Average air permeability of coated fabric. $\Delta P=11.58$ mm. Hg g./m.^{2}/hr.	Average water vapor permeability of coated fabric $\Delta P=11.58$ mm. Hg g./m.^{2}/hr.
1.5	300	200	1.00	2.00	150	65
2.0	275	190	0.80	2.50	160	67
2.5	250	170	0.70	2.50	170	70
3.0	225	150	0.60	2.50	180	72
3.5	200	135	0.50	2.00	190	77
4.0	175	120	0.50	1.75	150	78
4.5	125	100	0.40	2.00	125	80
5.0	125	100	0.40	2.50	125	83
5.5	----------------	----------------	0.50	3.00	----------------	----------------
6.0	----------------	----------------	0.50	3.50	----------------	----------------
7.0	----------------	----------------	0.50	3.50	----------------	----------------
>10.0	----------------	----------------	0.50	3.50	----------------	----------------

Stepwise, the preferred treatment of the fabric by impregnating with the elastomer is as follows:

(1) The swellable copolymer is dissolved in a suitable solvent such as toluene or mixtures of toluene with solvents such as ethylacetate. The exact nature of the solvent is not important to the invention and can be any organic liquid or mixture of liquids which will dissolve the elastomer. The exact percent solid of the elastomer in the solvent may vary between 5–70%. The usual range is from 20–35%.

(2) The curling agents, pigments, plasticizers, or inhibitors are then added to the elastomer solution using techniques which are well known in the rubber and coating trades.

(3) The final mixture of curing agents and other additives with the hydrophilic elastomers is applied to the fabric by any technique which will cause the elastomer to be deposited below the surface of the fabric. The usual procedure using standard coating equipment known to the art is to coat what is called a "tight coat." The amount of coating applied by any technique is dependent upon the nature of the fabric being treated, the nature of the elastomer being applied, the degree of waterproofness and the degree of the air permeability which is desired. A considerable range of compositions is useful and a high degree of air permeability may be obtained if the end use does not require a high degree of waterproofness. The exact amount of elastomer which is applied is best described as the amount necessary to produce a degree of waterproofness with a particular fabric which is able to withstand from 5–50 inches of hydrostatic head. For instance, if a 2.5 oz. cotton fabric with a basket weave is treated or impregnated with an elastomer capable of swelling 100%, the fabric will have 30 inches of hydrostatic head resistance if 0.9 oz. per square yard of the elastomer has been deposited. If it is readily apparent that the variations in elastomer composition, fabric composition, fabric construction, fabric weight, and the desired hydrostatic head resistance permits a great many variations and almost any fabric can be rendered waterproof and remain vapor permeable to meet almost any desired end use.

(4) The final step in the preparation of the impregnated fabrics involves the curing of the elastomer. The exact timing and conditions of cure are dependent on the elastomer and the type curing agents which are mixed with the elastomer. The curing conditions and the type of cure are also dependent on the type of the fabric. For instance, whereas it may be desirable to cure a cotton fabric impregnated by a water-swellable elastomer for 45 minutes at 150° C., it may be necessary to cure some other impregnated fabric at a lower temperature at a longer period of time. The usual curing conditions for butadiene and butadiene copolymers are 145° C. for 45 minutes. These conditions provide a tight cure which renders the elastomer insoluble but in no way prevents it from swelling on contact with water. Of course, the exact curing conditions are also dependent on the amount of curing agents and other additives and may be adjusted by greater or lesser additions of such curing agents.

In most applications the invention is practiced by applying the water swellable elastomer from solutions of the elastomer in organic liquids or mixtures of organic liquids. For example, a copolymer of butadiene containing less than 10% acrylic acid or potassium acrylate units is readily applied from a solution in toluene whereas if the polymer contained more than 10% of such units, mixture of toluene and some polar liquid such as the lower alcohols, ketones, or acids might be required. In some instances it may be desirable to add small quantities of water which will be emulsified or dissolved in the coating mixture. The use of water in the coating mixture is resorted to if the elastomer contains more than about 15% of metal ion salts of acidic groups such as salt groups of carboxylic, sulfonic, sulfate, phosphonic or phosphate acids. In some instances the elastomer may be applied from suspensions of the elastomer in organic liquids or from mixtures of organic liquids and water. This method of applying the elastomer is particularly valuable because a relatively discontinuous layer of the elastomer is desired. If a suspension of the water swellable elastomer is applied to the fabric, curing results in a crosslinked network of particles which have been sintered together. In this instance the film has discontinuities because the fibers of the fabric are incompletely impregnated and because the elastomer contains microscopic holes. Both types of holes are permeable to water vapor and are closed to liquid water when the elastomer is swollen by water. Regardless of the solvent or suspending agent used, the nature of the process requires that volatile liquids be used. The practice of the invention is limited to the use of water and organic liquids which can be removed by evaporation. Solvents or liquids which boil below 160° C. may be used except that some higher boiling substances may be used if they are left in the final coating to serve as plasticizers or softeners.

In the practice of our invention, the type fabric for a specific application is important in that the fabric and the elastomer must provide a suitable combination of swelling by the elastomer and closeness of weave of the fabric which will permit interstices of the fabric to be closed when the elastomer has swollen approximately 100%. The composition of the fabric can be any composition which does not interfere with the curing of the elastomer. Examples of suitable compositions are fabrics made from cotton, nylon, cellulose esters, regenerated cellulose, and polyester fibers such as Dacron fibers and Kodel fibers. Also included are mixtures and blends of the above-mentioned fabrics as, for example, the fabric composed of 50% cotton fibers and 50% Kodel fibers. The fabric construction can be any construction but it is usually important to have a relatively tight weave as, for example, a poplin of a twill-type weave.

The technique of applying the water swellable elastomer to the fabric is important but the design of the machine is not. The invention describes an elastomer that is applied to a fabric to give a discontinuous film or layer. This film becomes continuous because the elastomer swells and closes the small holes left by the coating operation. Any machine that will spread the coating medium and cause a partial penetration of the fabric is suitable. A "floating knife" is particularly suitable but in some instances a 3 roll coater, knife against roll, or pinch roll might be used.

Regardless of the process used, the final deposition of the elastomer must be in the interior of the fabric. It is also desirable that the elastomer should be in a thin layer above the center plane of the fabric. Maximum flexibility and good hand are obtained only if elastomer is essentially confined to the volume bounded by the midplane of the fabric and another plane half the distance between the midplane and the upper surface. For example, if a floating knife is used these results may be obtained if the coating blade has an open angle of about 8°, and a thickness of about ¼″. Of course, other angles and thicknesses may be used. The open angle faces the uncoated fabric and serves to force the coating solution below the surface of the fabric. The tension of the fabric is also adjusted so as to cause a certain amount of compression of the fabric during the coating operation. This compression of the fabric against the coating blade also helps to deposit the elastomer in the proper position. Finally, each layer of elastomer is applied from alternate directions so that the interstices of the fabric are filled in a more or less uniform manner. However, they are not completely closed during the coating operation.

The application of the water-swellable elastomer using a floating knife is shown by diagram in FIGS. 1 and 2. FIG. 1 shows the fabric being removed from a storage roll **6** over a roll **4** which supports the viscous solution of elastomer **3**. The knife **2** is shown as depressing the fabric **1** as it spreads and forces the elastomer **3** into the fabric.

FIG. 2 is an enlarged diagrammatic illustration showing a cross-sectional view of the fabric **1** as it is impregnated with the polymeric material. The open angle on coating knife **2** is shown as metering a thin layer of elastomer solution **3** onto the surface of the fabric **1**. The knife **2** also compresses the fabric **1** and forces the elastomer **3** to be deposited in the fabric **1** but above the center plane **7** of the fabric **1**. A layer **8** of elastomer **3** is deposited in the fabric **1** above the center plane **7**. It is readily realized that by adjusting the blade angle, fabric tension, elastomer solution solids and viscosity, and rate of fabric movement that varying amounts of elastomer can be deposited within any volume of the fabric. Other methods of applying the elastomer present special problems but the principle is essentially the same as described above.

After the elastomer is applied to the fabric in a suitable solvent, curing is accomplished by heat. This heating can be done in autoclaves, festoon ovens, or continuous roll ovens. The exact time and temperature required for an adequate cure depends on the elastomer, the fabric, and the curing system. In most instances the elastomer is deposited below the surface of the fabric and what is known to the art as a "tight cure" is not as important as for a surface deposited rubber coating. However, if peroxides are used in the range of from 0.5 to 5 parts based on the rubber, curing conditions of 100° C. to 200° C. for 1 minute to 2 hours may be used. Sulfur cures can be obtained using from 0.5 to 8 parts sulfur and compounds containing sulfur. The useful temperature ranges include 100° C. to 200° C. for 10 minutes to 2 hours. Other curing systems include metal oxides and sulfur which are well known curing systems for chlorinated elastomers such as neoprene.

In the practice of our invention the copolymers used to provide the water swellable elastomers contain 50–95% of a monomer selected from the class consisting of butadiene, chloroprene, isoprene or the like. The monomers whose homopolymers are water soluble or greatly swollen by water are employed in a range of 5–50%.

The following examples are intended to illustrate our invention but not to limit it in any way:

EXAMPLE 1

An elastomer having the composition of 75% butadiene and 25% acrylic acid was dissolved in a mixture of 75% toluene and 25% ethyl acetate. Based on the dissolved elastomer, 5% finely divided zinc oxide, 1% sulfur and 0.5% thiocarbanilide were added. Based on the elastomer weight, 2% of 2,6-(1-methylheptadecyl)-p-cresol was added as a stabilizer. This mixture was then applied to a 2.5 oz./sq. yd. cotton fabric by passing the fabric between a roll and a doctor blade where 0.8 oz. of the elastomeric solids in solution was deposited on each sq. yd. The coating mechanism was adjusted to tension the fabric and the angle of the doctor blade with the fabric caused the elastomer to be deposited through the surface of the fabric. However, the elastomer solution did not strike entirely through the fabric. The elastomer was cured by placing the fabric in an oven heated to 150° C. After 45 minutes, the fabric was removed and was found to be proof to a 30-in. head of liquid water. Samples of the fabric were then tested for water vapor permeability, and it was found that the fabric was able to transmit 65 g./sq. m./hr. under conditions of 50% relative humidity on one side of the fabric and 100% relative humidity on the other side of the fabric. The temperature during the transmission test was 26° C. This fabric had a good appearance and good hand.

EXAMPLE 2

An elastomer having a composition of 75% butadiene and 25% acrylic acid was dissolved in a solvent mixture composed of 80% toluene and 20% methyl ethyl ketone. The polymer was present in solution at the level of 26%. Based on the dissolved polymer, 1% of a water-repellent silicone resin was then added to the solution. As in Example 1, curing agents and accelerators were then added, and the elastomeric solution was used to impregnate 3½ oz. cotton fabric. Based on the elastomer weight, 2% of 2-tert. butyl-4-glycidyloxy phenol was added to stabilize the cured elastomer. After solvent evaporation, the fabric contained 1.05 oz./sq. yd. of deposited elastomer. The elastomer was cured by oven treatment as in Example 1. After curing, the fabric was tested, and it was found that it could withstand a hydrostatic head of 47 in.

and that it was able to transmit 60 g./sq. m./hr. of water vapor. The conditions during the transmission test were 50% relative humidity on one side and 100% on the other at the temperature of 26° C.

EXAMPLE 3

One hundred grams of elastomer having a composition of 60% butadiene and 40% N,N-dimethylacrylamide were dissolved in 250 g. of toluene mixed with 150 g. of ethanol. As in Example 1, curing agents and accelerators were added to the solution. As in Example 2, a water-repellent silicone resin was added to the solution, and the final mixture was used to impregnate a 2.4 oz./sq. yd. nylon fabric. Nine-tenths ounce dry coating weight was deposited on the fabric. After curing, the fabric would withstand a hydrostatic head of 23 in. and was able to transmit 72 g./sq. m./hr. under the same conditions as in Example 2. The air permeability was 165 g./sq. m./hr. or 66% of the untreated fabric.

EXAMPLE 4

One hundred grams of an elastomer having the composition of 60% butadiene and 40% N-isopropylacrylamide were dissolved in 25 g. toluene mixed with 150 g. ethanol. Five grams of finely divided zinc oxide, 1 g. of sulfur, and 0.5 g. 2-mercaptoimidazoline were added. As in Example 2, a water-repellent silicone resin was added to the solution, and the final mixture was used to impregnate a 3 oz./sq. yd. cotton fabric. On a dry weight basis, 1.25 oz./sq. yd. of coating were deposited in the fabric. This impregnated or treated fabric was then cured in an oven at 150° C. for 45 minutes. After curing, the fabric was tested and it was found that the fabric was waterproof to a hydrostatic head of 42 in. and was able to transmit 65 g./sq. m./hr. under the same test conditions as described in Example 2.

EXAMPLE 5

One hundred grams of an elastomer having a composition of 70% butadiene and 30% acrylamide were dissolved, coated, and cured as in Example 4. The fabric was tested and was found to transmit 69 g./sq. m./hr. and to withstand a hydrostatic head of 38 in.

EXAMPLE 6

One hundred grams of an elastomer having a composition of 70% butadiene and 30% β-hydroxyethyl acrylate were dissolved, coated and cured as in Example 4. The fabric was tested and was found to transmit 69 g./sq. m./hr. and to withstand a hydrostatic head of 38 in. The air permeability was 183 g./sq. m./hr. or 68% of the untreated fabric.

EXAMPLE 7

One hundred grams of an elastomer having a composition of 70% butadiene and 30% vinyl pyridine were dissolved, coated, and cured as in Example 4. The fabric was tested and was found to transmit 69 g./sq. m./hr. and to withstand a hydrostatic head of 38 in.

EXAMPLE 8

One hundred grams of an elastomer having a composition of 70% butadiene and 30% methacrylic acid were dissolved, coated, and cured as in Example 4. The fabric was tested and was found to transmit 69 g./sq. m./hr. and to withstand a hydrostatic head of 38 in.

EXAMPLE 9

One hundred grams of an elastomer having a composition of 70% butadiene and 30% methacrylamide were dissolved, coated, and cured as in Example 4. The fabric was tested and was found to transmit 69 g./sq. m./hr. and to withstand a hydrostatic head of 38 in.

EXAMPLE 10

One hundred grams of an elastomer having the composition of 70% chloroprene and 30% methacrylamide were dissolved, coated, and cured as in Example 4. The fabric used was a 3½ oz./sq. yd. basketweave construction made from the synthetic fiber, Kodel (Kodel fiber is a polyester fiber made by Tennessee Eastman Company). After curing the fabric was tested and was found to transmit 65 g./sq. m./hr. and to withstand a hydrostatic head of 38 in. The air permeability of the sample was 196 g./sq. m./hr. or 72% of the untreated fabric.

EXAMPLE 11

One hundred grams of an elastomer having the composition of 70% isoprene and 30% acrylic acid were dissolved, coated, and cured as in Example 4. The fabric for this example was a 4 oz./sq. yd. fabric made from a blend of fibers. This blend was composed of 50% Kodel fibers (made by Tennessee Eastman Company) and 50% cotton fibers. The finished fabric was tested and was found to transmit 66 g./sq. m./hr. and to withstand a hydrostatic head of 41 in.

EXAMPLE 12

The elastomer prepared in Example 4 was used to coat a 3½ oz./sq. yd. fabric made from Dacron fibers (essentially a fiber made from poly(ethylene terephthalate) made by DuPont). After curing the fabric was tested and was found to transmit 72 g./sq. m./hr. and to withstand a hydrostatic head of 32 in.

EXAMPLE 13

The elastomer and the procedure of Example 2 were used to impregnate a fabric consisting of a blend of Dacron fibers and viscose rayon. The fabric was tested and was found to transmit 63 g./sq. m./hr. and to withstand a hydrostatic head of 46 in.

EXAMPLE 14

An elastomer having a composition of 70% butadiene and 30% sodium acrylate was dissolved in a solvent mixture composed of 80% toluene and 20% methyl ethyl ketone. The polymer was present in solution at the level of 26%. Based on the dissolved polymer, 1% of a water-repellent silicone resin was then added to the solution. As in Example 1, curing agents and accelerators were then added, and the elastomeric solution was used to impregnate 3½ oz. cotton fabric. After solvent evaporation, the fabric contained 1.05 oz./sq. yd. of deposited elastomer. The elastomer was cured by oven treatment as in Example 1. After curing, the fabric was tested, and it was found that it could withstand a hydrostatic head of 47 in. and that it was able to transmit 60 g./sq. m./hr. of water vapor. The conditions during the transmission test were 50% relative humidity on one side and 100% on the other at the temperature of 26° C.

EXAMPLE 15

150 g. of a copolymer of butadiene and acrylonitrile having a composition of 32% acrylonitrile and 68% butadiene were dissolved in 650 g. of toluene. This solution was stirred at 80° C. and 45 g. of potassium hydroxide dissolved in 250 g. of ethanol was added. Stirring was continued for one hour and 36 g. of water were added. The stirring was continued for another 12 hrs. and 36 g. of water were added. After 24 hrs. analysis showed that 90% of the acrylonitrile units of the original copolymer had been converted to potassium acrylate units. The final polymer had the composition of 67% butadiene, 29.8% potassium acrylate and 3.2% acrylonitrile. Films were cast of this composition, and it was found that these films swelled up to 400% in the presence of water. Cured films which were prepared by adding 1.5% dicumyl peroxide based on the rubber and by heating to 110° C. for 45 min. were found to swell about 300% in the presence of water.

This elastomer was used to impregnate poplin fabric weighing 4.5 oz./yd.^{2} made from a blend of fibers. Before coating the elastomer was modified with 1.5% of dicumyl peroxide based on the solids in the coating solution. The fibers were a mixture of 55% Kodel fibers (a polyester fiber made by Tennessee Eastman Company) and 45% Topel (a cellulosic fiber made by Courtaulds Limited). This fabric was impregnated with .9 oz. of the elastomer per sq. yd. and was caused to be impregnated so that virtually none of the elastomer was on either surface. This impregnation was done with a coating blade pressed against the unsupported fabric in what is known to the coating trade as a floating knife. The impregnation was accomplished in two passes over the fabric in opposite directions. The impregnated fabric was cured by heating in an oven for 45 min. at 110° C. After curing the impregnated fabric was tested, and it was found that the elastomer was air-permeable but waterproof. The fabric on contact was the water swelled due to the hydrophilic nature of the elastomer and after swelling was no longer air-permeable. Because of the hydrophilic nature of the elastomer, the impregnated fabric was readily wet; and therefore, the final step in the preparation of the fabric for use as a waterproof material was to treat the surface with a silicone resin. This was done using a water emulsion of a silicone resin.

After the surface had been treated with the silicone resin, the fabric was again tested and it was found that on contact with water where no hydrostatic head was involved that the fabric did not wet. It was also observed under these conditions that the elastomer did swell and was therefore able to support a column of water 55 cm. high. The moisture vapor transmission rate was measured and found to be 65 g./sq. meter/hr. at 25° C. with a vapor pressure differential equivalent to 11.5 mm. of Hg.

EXAMPLE 16

Using the technique of Example 15, a copolymer of butadiene and methylacrylate was hydrolyzed and coated. The composition of the copolymer was 35% methylacrylate and 65% butadiene. The physical properties and characteristics of this polymer were similar to the hydrolyzed polymer of Example 15. A fabric impregnated as in Example 15 had the same hydrostatic head resistance and air permeability. The moisture vapor transmission rate was measured and found to be 65 g./sq. meter/hr. at 25° C. with a vapor pressure differential of 11.5 mm. of Hg.

EXAMPLE 17

Using the technique as described in Example 15, a copolymer composed of 72% butadiene and 28% acrylonitrile was hydrolyzed and coated and was impregnated on 7.5 oz./sq. yd. cotton duck fabric. A silicone finish was applied to the surface of the fabric as described in Example 15, and the fabric was evaluated for use in the manufacture of tents. The fabric was found to withstand a hydrostatic head of 75 cm. and to be permeable to water vapor. The water vapor transmission rate was found to be 45 g./sq. meter/hr. at 25° C. with a pressure differential of 11.5 mm. of Hg.

EXAMPLE 18

A copolymer of butadiene and maleic anhydride having the composition of 80% butadiene and 20% maleic anhydride was dissolved in toluene so as to make a solution having 25% dissolved solids. Water was added to the solution to hydrolyze the anhydride thereby producing a solution of the copolymer of butadiene and maleic acid. Films were cast of this polymer and were found to be swellable in the presence of water. 4.5 oz./sq. yd. cotton poplin fabric was impregnated as in Example 15, and this fabric was found to be air and water vapor permeable but waterproof to liquid water. After being treated with a silicone resin, this fabric was suitable for rainwear.

EXAMPLE 19

100 g. of a copolymer composed of 70% isoprene and 30% acrylonitrile were dissolved in 200 g. of toluene. 40

g. of potassium hydroxide dissolved or suspended in 100 g. of ethanol were added. This mixture was stirred and heated to 70° C. for 36 hours. During this time ammonia was evolved and the final product consisted of a copolymer of potassium acrylate and isoprene. This copolymer was coated on a 3.5 oz./yd.^{2} cotton fabric in a manner that deposited 1.1 oz./yd.^{2} of dry rubber below the surface of the fabric. This coating or impregnation was air and water vapor permeable but was proof against liquid water equal to 26" of hydrostatic head. Under test conditions of 50% relative humidity at 75° C. the fabric transmitted 70 g./m.^{2}/hr. of water vapor.

EXAMPLE 20

100 g. of a copolymer composed of 70% isoprene and 30% methylacrylate was dissolved, hydrolyzed and coated as in Example 19. The resulting coated fabric was waterproof to a hydrostatic head of water equal to 25" and transmitted 70 g./m.^{2}/hr. with a vapor pressure differential equivalent to 11.5 mm. Hg.

EXAMPLE 21

100 g. of a copolymer composed of 30% sodium acrylate and 70% isoprene were dissolved in 200 g. of toluene=100 g. of ethanol. 2.5 g. benzoylperoxide were added and this mixture was coated on a fabric made from polyethylene terephthalate. This fabric weighed 2.8 oz./yd.^{2}. The coating was applied by a floating knife technique which caused coating to be deposited in the interstices of the fabric in a discontinuous film. The solvent was evaporated and the fabric was heated to 145° C. for 30 minutes. The final product was a fabric which contained a discontinuous layer of cured swellable elastomer which transmitted 65 g./m.^{2}/hr. of water with a water vapor pressure differential equivalent to 11.5 mm. Hg.

EXAMPLE 22

The elastomer described in Example 21 was dissolved in 1 pt. toluene+2 pt. methylethylketone. Based on the rubber 1.0 pt. sulfur, 1.5 pt. 2-mercaptoimidazoline and 5 pt. of zinc oxide were added. This mixture was applied to a fabric which weighed 8 oz./yd.^{2}. The weight of the dry elastomer after coating was 2.1 oz./yd.^{2}. As in Example 21, the elastomer was applied below the surface of the fabric in a discontinuous layer which was cured by heating at 145° C. for 45 minutes. This fabric was water vapor permeable but waterproof. The coated fabric was further processed by passing the fabric through a water suspension containing 1.6% emulsified silicone resin. The fabric was dried and the final product was water resistant to limited exposure to rainfall. Extended exposure to simulated rainfall equivalent to 1" of rainfall/hr. demonstrated that the silicone water resistance of the fabric surface was destroyed. However, the fabric remained proof against the rainfall because the water swellable elastomer had swelled and closed the interstices of the fabric.

EXAMPLE 23

100 g. of a copolymer composed of 95% isobutylene and 5% butadiene were dissolved in 200 g. of toluene. 33 g. of a polyethylene oxide, molecular weight 2400 and chain terminated with acrylic acid by esterification of the terminal hydroxyl groups, were dissolved in 33 g. of methylethylketone. This solution was added to the toluene solution. 3.0 g. of sulfur, 5 g. of zinc oxide, 3.0 g. of stearic acid and 1 g. teteramethyl thiuram disulfide were added as a fine dispersion in toluene. This mixture was then used to coat or impregnate a cotton poplin fabric which weighed 3.6 oz./yd.^{2} by a knife suspended over a revolving drum. Three coating passes were made. After the solvent was evaporated 0.9 oz./yd.^{2} of elastomer was found to be deposited within the fabric and on the surface of the fabric. This fabric elastomer combination was then heated to 145° C. for 1 hr. to crosslink or cure the elastomer. Treatment of the impreg-

nated fabric with methylethylketone showed that the polyethylene oxide was chemically bound to the rubber since no resin was extracted even though the modified elastomer was very greatly swollen. The fabric was also exposed to water and again the polymer was swollen. Tests of the fabric by subjecting the fabric to a hydrostatic head of 20" showed that the elastomer was a continuous barrier to water in the swollen state. After drying the fabric was permeable to air and water vapor. This fabric was further processed by spraying a solution of silicone resin (DC–ZO18, made by Dow Corning Corporation) onto the surface. After evaporation of the solvent the fabric was found to be surface water repellent, waterproof, and water vapor permeable.

EXAMPLE 24

100 g. of a copolymer composed of 5% piperylene and 95% isobutylene were dissolved in 300 g. of toluene. 33 g. of a copolymer composed of 10% butadiene and 90% lithium acrylate were dissolved and 100 g. of water were added. This mixture was stirred until a smooth viscous 2-phase dispersion was obtained. 2.0 g. tertiary butyl hydroperoxide were added and the mixture was applied to a fabric made from Kodel polyester fibers (manufactured by Tennessee Eastman Co.). This fabric weighed 3.65 oz./yd.^{2} and was a poplin weave. The application was done using a floating knife technique and 1.5 oz./yd.^{2} of elastomer was found to be deposited below the surface of the fabric after the solvent was evaporated. The fabric was then heated to 160° C. for 20 minutes to crosslink or cure the elastomer. Attempts to extract the copolymer of butadiene-lithium acrylate with water were unsuccessful although the elastomer was greatly swollen by the water. The fabric was waterproof to a hydrostatic head of 41" but was air and water vapor permeable. Tests showed that the water vapor transmission rate was 58 g./m.^{2}/hr. with a water vapor pressure differential equal to 11.5 mm. Hg.

EXAMPLE 25

100 g. of polybutadiene were dissolved in 200 g. of toluene. 20 g. of maleic anhydride and 0.5 g. of benzoyl peroxide were added and the mixture was heated to 50° C. for 24 hours in a stirred reactor. The mixture was cooled and 2 g. of benzoyl peroxide were added. This mixture was then coated as in Example 24 on the fabric described in Example 24. After evaporation of the solvent the elastomer was cured by heating the fabric to 145° C. for 20 minutes. The fabric was then passed through a 10% water solution of sodium hydroxide. After drying this fabric was found to be impregnated with a water swellable elastomer which was waterproof but permeable to water vapor. A fluorinated hydrocarbon finish (Scotchgard FC208, made by Minnesota Mining and Manufacturing Co.) was applied by passing the fabric through an emulsion of the fluorinated hydrocarbon. The final product was a porous fabric which had a water repellent surface but was also waterproof because the maleic acid, sodium salt, modified polybutadiene was swollen on contact with liquid water. This fabric withstood a hydrostatic head of 24" but transmitted water vapor at a rate equal to 65% of the untreated fabric.

EXAMPLE 26

The copolymer described in Example 25 was converted to the sodium salt of the maleic acid-butadiene coplymer before coating by adding sodium hydroxide dissolved in ethanol to the toluene solution before the elastomer was applied to the fabric. After application, evaporation of solvent and curing, the fabric was found to be identical to that prepared by Example 25.

EXAMPLE 27

33 g. of a copolymer composed of a 1:1 molar ratio of styrene and maleic anhydride were dissolved in 50 g. of acetone and 50 g. of toluene. 5 g. of allyl alcohol were added and the mixture was heated to cause the alcohol to form ester groups with a portion of the anhydride units. Next, 5 g. of water were added to hydrolyze the remainder of the anhydride structure. The resulting polymer was a copolymer of styrene and maleic acid which contained allyl alcohol esters of a portion of the carboxylic groups. This polymer still in solution was added to 100 g. of natural rubber dissolved in 200 g. of toluene. 2.0 g. of acetyl peroxide were added and the mixture was applied to a cotton fabric weighing 4 oz./yd.^{2}. A knife over roll technique was used to incompletely close the openings in the fabric with 0.7 oz./yd.^{2} of dry elastomer. This elastomer was cured by heating to 125° C. for 1 hour. Analysis showed that the maleic acid-styrene copolymer was chemically grafted to the natural rubber by the reaction of the allyl ester groups. The elastomer was water swellable and therefore tended to become a continuous barrier to water when the fabric was wet. The fabric was water and air vapor permeable when dry.

EXAMPLE 28

The maleic acid-styrene copolymer described in Example 27 containing a few allyl alcohol ester groups was converted to the sodium salt by adding a molar quantity of sodium hydroxide based on the free carboxyl group. This conversion was done before the polymer was added to a solution of natural rubber as in Example 27. A similar fabric was treated as in Example 27 and the results were similar.

EXAMPLE 29

100 g. of a copolymer composed of 80% butadiene and 20% sodium allyl sulfonate were prepared using the following polymerization recipe:

	Pts.
Butadiene-1,3	80
Sodium allyl sulfonate	20
Water	180
Emulphor ON870 (a polyethylene oxide surfactant)	3
Potassium persulfate	2
Sodium meta bisulfite	0.5

This mixture was agitated and heated to 50° C. for 24 hours. No attempt was made to prevent crosslinking. The polymer was obtained as suspended particles. 300 g. of toluene were added and the water was removed by refluxing the water azeotrope and collecting the water in a Dean-Stark tube. After removal of the water the product consisted of an organosol of the particles of the original emulsion. These particles were swollen by the toluene to a semi-rigid gel-like structure. Based on the polymer 2 pts. dicumyl peroxide were mixed in the suspension. This organosol was then applied to a cotton fabric which weighed 10.25 oz./yd.^{2} using a scraper type blade suspended between and below 2 rolls so as to cause the fabric to be depressed below line formed by the top surfaces of the rolls. The angle formed by the V of the depressed fabric was about 160°. The coating was applied using 3 passes under the scraper. The total weight of elastomer after evaporation of the solvent was 2.4 oz./yd.^{2}. This elastomer was cured by heating to 175° C. for ½ hr. The final elastomer was found to be deposited almost entirely in the interstices of the fabric. That the elastomer was microporous was demonstrated by casting a film on a metal plate which resulted in a film which was porous to air under a slight pressure. In this example air and water vapor permeability were obtained by 2 mechanisms. That is, the elastomer was microporous in the areas between the woven fibers and the incompletely impregnated fiber bundles were permeable. Both types of micropores were closed by swelling when the elastomer was contacted by water. The fabric prepared by this technique was waterproof to a hydrostatic head of 58" and transmitted water vapor at 50 g./m.^{2}/hr. with a vapor pressure different equivalent to 11.5 mm. Hg.

EXAMPLE 30

200 g. of the copolymer composed of 29.8% potassium acrylate, 67% butadiene, 3.2% acrylonitrile was prepared by hydrolysis of the copolymer of butadiene and acrylonitrile using the technique described in Example 15. The toluene-ethanol-water suspension of the hydrolyzed elastomer was then blended with a toluene solution of 100 g. of unhydrolyzed polymer composed of 68% butadiene and 32% acrylonitrile. This mixture of polymers was then catalyzed, coated, and cured as described in Example 15. The final coated fabric was water vapor and air permeable but was waterproof. The blending of a water swellable elastomer with a non-swelling elastomer resulted in an impregnated fabric which had an improved flexibility.

The fabric was treated with a silicone finish as described in Example 15. This final product transmitted 73 g./m.^{2}/hr. of water vapor and 165 g./m.^{2}/hr. of air with a vapor pressure differential equivalent to 11.58 mm. Hg. The original untreated fabric transmitted 102 g./m.^{2}/hr. of water vapor and 225 g./m.^{2}/hr. of air under the same conditions. The hydrostatic head resistance of the untreated fabric was zero but the treated fabric withstood a hydrostatic head of 45".

EXAMPLE 31

100 g. of elastomeric material composed of polybutadiene was dissolved in 200 g. of toluene. 30 g. of a copolymer composed of 20% butadiene and 80% sodium acrylate was dissolved in 50 g. of water. The water solution was then emulsified or dispersed in the toluene solution of the elastomer. Next, 2 g. of dicumyl peroxide was added and thoroughly mixed. This mixture was then applied to one surface of a fabric which weighed 4.5 oz./yd.^{2} The method of application consisted of a straight edge or spreading knife which extended across the width of the fabric and was in contact with the fabric surface. The viscous polymer mixture was poured on the fabric just before the fabric (which was moved by a system of rotating drums) passed under the spreading knife. The solvents were removed by evaporation over steam-heated coils. This operation was repeated twice to produce a fabric which had 1.1 oz./yd.^{2} of dry elastomer deposited more or less in the interstices of the fabric. This deposition constituted a discontinuous layer due to carefully regulated adjustments of the spreading equipment. The treated fabric was then cured by heating to 145° C. for 45 min. Tests were made by treating the impregnated fabric with various liquids including water. These treatments showed that neither polymer could be removed from the matrix combination. The elastomer was swollen by water to such an extent that in the swollen state the layer became essentially continuous and would therefore resist the penetration of liquid water. The dry fabric was air and water vapor permeable. The fabric was flexible and was suitable for use as rainwear. Specifically, this fabric would withstand a hydrostatic head of 30" and would transmit water vapor at the rate of 72 g./m.^{2}/hr. at a vapor pressure differential equivalent to 11.58 mm. Hg. The air permeability was 165 g./m.^{2}/hr. or 66% of the untreated fabric.

EXAMPLE 32

100 g. of polybutadiene dissolved in 200 g. of toluene was mixed with 75 g. of a 50% water solution of an interpolymer which had the composition of 36.8% styrene, 53.0% sodium maleate and 10.0% mixed allyl ester-sodium salt of maleic acid. 1.75 g. of benzoyl peroxide was added and this mixture was applied by the technique described in Example 1 to a 3.2 oz./yd.^{2} cotton fabric. This treated fabric transmitted water vapor at the rate of 65 g./m.^{2}/hr. at 75° F. and a vapor pressure differential equivalent to 11.58 mm. Hg. It withstood a hydrostatic head of 35". The air permeability was 183 g./m.^{2}/hr. or 68% of the untreated fabric.

EXAMPLE 33

100 g. of polychloroprene dissolved in 200 g. of toluene was mixed with 100 g. of a toluene suspension containing 50 g. of a copolymer composed of 33.8% styrene, 53% potassium maleate, and 13.5% mixed allyl ester potassium salt of maleic acid. 1.75 g. of cumene hydroperoxide was added and the final mixture was applied to a 5.5 oz./yd.^{2} nylon fabric by the technique described in Example 1. The final fabric was water vapor permeable but would withstand a hydrostatic head of 72". The air permeability of the sample was 130 g./m.^{2}/hr. or 78% of the untreated fabric.

EXAMPLE 34

100 g. of a copolymer having the composition of 68% butadiene and 32% acrylonitrile dissolved in 200 g. of toluene was mixed with 100 g. of a copolymer having the composition of 70% butadiene and 30% acrylic acid which was dissolved in 200 g. of methylethylketone. 2.5 g. of dicumyl peroxide was added and using the methods and similar conditions to those described in Example 1, a 10 oz./yd.^{2} cotton duck fabric was treated. This fabric was air and water vapor permeable but was waterproof to all types of natural precipitation. This treated fabric was particularly suitable for use as tentage and tarpaulins.

EXAMPLE 35

100 g. of a copolymer containing 95% isobutylene and 5% butadiene was dissolved in 200 g. of toluene. This solution was mixed with 100 g. water solution of 25 g. of poly(vinyl alcohol) which had been reacted with 10 g. of acrylic anhydride to form ester groups from a portion of the hydroxy group. 2.5 g. of dicumyl peroxide was added and after mixing to obtain an emulsion of the water phase in the toluene phase the mixture was applied to a fabric by the technique described in Example 1. This fabric weighed 4.6 oz./yd.^{2} and was made from a polyester fiber (Kodel). The final fabric transmitted water vapor and air at a rate equal to 66% of the untreated fabric. The treated sample was waterproof to a 50" head of water. This fabric was suitable for use as rainwear.

EXAMPLE 36

The treated fabric of Example 5 was further treated by applying a water resistant finish by passing the fabric through a water emulsion of silicone type resin containing unreacted epoxide groups. After curing by heat the fabric was water vapor permeable but remained waterproof as in Example 5 and was in addition resistant to surface wetting.

EXAMPLE 37

100 g. of a copolymer composed of 95% isobutylene and 5% butadiene was dissolved in 250 g. of toluene. 40 g. of a copolymer composed of 60% hydroxyethyl acrylate and 40% chloroprene was dissolved in 150 g. of a 1:1 mixture of isopropyl alcohol and toluene. The two solutions were mixed with 1.25 g. of cumene hydroperoxide and the final solution was applied to a 3.5 oz./yd.^{2} cotton fabric as described in Example 1. After curing, this fabric was water vapor permeable and waterproof to liquid water. This fabric was suitable for use as sports and hunting jackets and other sportswear.

EXAMPLE 38

100 g. of polychloroprene was dissolved in 250 g. of toluene. 50 g. of a copolymer composed of 85% acrylamide and 15% chloroprene was dissolved in water. The two polymer solutions were mixed with 1.25 g. of dicumyl peroxide and the water solution was emulsified in the toluene solution by vigorous agitation. After a smooth dispersion had been obtained, the mixture was applied to a 11.5 oz./yd.^{2} cotton fabric as described in Example 1. After curing, the fabric was surface treated with a fluorocarbon-type resin (Scotchgard, made by Minnesota Mining and Manufacturing Company). The final fabric was

water vapor permeable but was waterproof to liquid water.

EXAMPLE 39

100 g. of a copolymer composed of 91% butadiene-9% acrylamide was dissolved in 300 g. of toluene. 50 g. of a copolymer composed of 90% sodium acrylate and 10% acrylamide was dissolved in 65 g. water. The two solutions were mixed together to form an emulsion of the water phase in the toluene phase. 2 g. of potassium carbonate and 10 g. formaldehyde were added and this mixture was heated to 70° C. for 0.5 hr. The mixture was cooled and made acidic by adding 2.0 g. acetic acid. This mixture was then used to impregnate a 4.65 oz./yd.^{2} fabric with a poplin weave. 1.1 oz./yd.^{2} of elastomer was deposited below the surface of the fabric in 3 coating passes under a floating knife. After evaporation of the solvent, the elastomer impregnated fabric was heated in an oven at 150° C. for 0.5 hr. The final product was a fabric containing an elastomer which was insoluble in all solvents because it was cross-linked. The elastomer was swollen by water and although the layer of elastomer in the fabric was a discontinuous layer when dry the fabric was waterproof.

The fabric was finished with a silicone resin so that the surface resisted wetting. The final product was air and water vapor permeable but waterproof to liquid water.

EXAMPLE 40

100 g. of polyethylene which had been modified by chlorosulfonation (Hypolon 20, made by Du Pont) was dissolved in 250 g. of toluene. 50 g. of a copolymer composed of 50% potassium acrylate-50% butadiene suspended in 100 g. of a 1:1 mixture of toluene-methylethylketone was added to the solution. 0.75 g. cumene hydroperoxide was added and this mixture was used to treat a cotton fabric which weighed 4.2 oz./yd.^{2} so that the fabric had deposited in the interstices about 1.6 oz./yd.^{2} of the dry elastomer. After curing as in Example 1, this fabric transmitted 38 g./m.^{2}/hr. of water vapor with a vapor pressure differential equivalent to 11.6 mm. Hg. The fabric withstood a hydrostatic head of 150 cm. after the elastomer was swollen by water. The fabric was suitable for tarpaulins, tents, and the like.

EXAMPLE 41

A polyester having poly(ethylene oxide) segments was prepared using poly(ethylene oxide) terminated with hydroxyl groups and having a molecular weight of 500. The exact composition was 1 mole of adipic acid, 0.5 mole ethylene glycol, and 0.5 mole of the poly(ethylene oxide). This polymer had elastomeric properties sufficient for the practice of this invention and was capable of being swollen by water approximately 300%. The polymer was dissolved in a mixture of toluene and ethyl alcohol to produce a viscous solution consisting of 33% solids. The polymer was then applied to a fabric which weighed 3.5 oz./yd.^{2}. The elastomer was applied using a knife over roll technique in such a manner that 3 passes were required to deposit an 0.8 oz. of the elastomer/yd.^{2} of the fabric. After evaporation of the solvent, the fabric was tested for permeability to water vapor. With a water vapor pressure differential equivalent to 11.58 mm. Hg this fabric transmitted 80 g./m.^{2}/hr. The uncoated fabric under the same conditions transmitted 105 g./m.^{2}/hr. The coated fabric was tested for hydrostatic head resistance and was found to resist a column of water 32" high. This coated fabric had excellent properties of flexibility and abrasion resistance. Further tests showed that the treated fabric transmitted air at the rate of 75% of the value obtained for the untreated fabric.

EXAMPLE 42

A copolymer was prepared using 0.5 mole adipic acid, 0.5 mole succinic acid, 0.5 mole of 1,4-butenediol and 0.5 mole poly(ethylene oxide) terminated with hydroxyl groups which had a molecular weight of 1200. This polymer was dissolved in a mixture of methylethylketone and toluene to produce a solution which contained 40% solids. A 3.5 oz./yd.^{2} cotton fabric with a simple poplin weave was coated in 4 passes using a knife or spreader blade. This blade was positioned in contact with the fabric by means of 2 rolls before and behind the coating blade with reference to the direction in which the fabric was passing beneath the blade and in such a manner that the fabric was depressed by the coating blade positioned between the rolls. Intimate contact of the fabric with the blade was made by applying tension to the fabric as it passed beneath the blade. This particular coating blade was beveled on the forward side with a 20° bevel and positioned so as to depress the fabric so that the angle formed by the fabric with the back of the blade was 75°. After coating, a microscope examination of the fabric showed that the elastomer had been deposited between the 2 sides of the fabric in a discontinuous layer. Due to these discontinuities the fabric was permeable to water vapor under the conditions described in Example 1 and was waterproof to a 45" head of water. The air permeability was found to be 190 g./m.^{2}/hr. or 73% of the untreated fabric.

EXAMPLE 43

A block polymer was made by preparing prepolymers of relatively low molecular weight. Prepolymer A was composed of 0.25 mole of adipic acid and 0.3 mole of poly(propylene oxide) terminated with hydroxyl groups having a molecular weight of 2500. Prepolymer B was prepared using an 0.3 mole succinic acid and 0.25 mole of poly(ethylene oxide) terminated with hydroxyl groups and having a molecular weight of 3000. The prepolymers were mixed together and subjected to heat and vacuum to give a high polymer consisting of blocks or segments of prepolymer A alternating with segments of prepolymer B. The final polymer was dissolved in a mixture of acetone and toluene in a ratio of 60/40. This solution which consisted of 15% solids was used to coat or impregnate a 6 oz./yd.^{2} cotton fabric so that the fabric after evaporation of the solvent contained 1.5 oz./yd.^{2} of block polyester. This polyester was swellable in water and the coated or impregnated fabric was found to be resistant to a 29" head of water although the layer of elastomer was discontinuous and therefore was water vapor permeable. The coated fabric was tested and it was found that it transmitted 76 g. of water vapor/m.^{2}/hr. under the same conditions described in Example 1. The air permeability under the same test conditions was found to be 145 g./m.^{2}/hr. or 63% of the untreated fabric.

EXAMPLE 44

A polyurethane was prepared from toluene diisocyanate and a poly(ethylene oxide) terminated with hydroxyl groups and having a molecular weight of 3000. This polymer was prepared in solution in a mixture of toluene and methylethylketone. The solution was composed of 26% solids and was a viscous fluid which was applied to a 4.65 oz./yd.^{2} fabric. This fabric was a blend of a polyester fiber and a cellulosic fiber. The fabric was coated or impregnated in 3 passes so as to provide a discontinuous film deposited between the fabric surfaces. This discontinuous film which weighed 0.9 oz./yd.^{2} was water swellable but due to the discontinuous nature of the film, the coated fabric was water vapor permeable and under the conditions described in Example 1 transmitted 73. g. of water vapor/m.^{2}/hr. This coated sample withstood a hydrostatic head of 57". The air permeability was tested and was found to be 125 g./m.^{2}/hr. or 76% of the untreated fabric.

EXAMPLE 45

A polymer made from toluene diisocyanate, 1,4-butene-2-diol and a poly(ethylene oxide) terminated with hydroxyl groups and having a molecular weight of 500 was dissolved in a mixture of toluene and methyl alcohol so as to produce a solution composed of 30% solids. The polymer was water swellable and could be used to coat or impregnate fabrics, paper, or leather. Such coated or impregnated materials could be rendered water resistant to hydrostatic heads varying from 5 to 100″ depending on how much polymer was deposited on the porous material. If the elastomer were deposited as a discontinuous layer as in the previous examples, the porous material was vapor permeable. This polymer had the additional feature that it contained ethylenic unsaturation and could therefore be cured or cross-linked. The curing or cross-linking was done by adding peroxides, certain metal drying agents such as cobalt, naphthenate or by adding sulfur or certain sulfur bearing organic compounds to the elastomer before it is applied to the fabric. For example, to a portion of the above elastomer in solution was added 1½% dicumyl peroxide based on the weight of the elastomer. This portion of elastomer solution was then used to impregnate or coat various fabrics to produce waterproof, water vapor permeable materials. After evaporation of the solvent, the elastomer was cured or caused to cross-link by heating the sample in an oven for 45 min. at 150° C. The resulting elastomer could not be removed from the fabric by action of solvents such as would be used in dry cleaning operations. The curing or cross-linking process in no way affected the performance of the coated fabric with respect to its hydrostatic head resistance or its water vapor permeability. Another portion of the elastomer solution was made curable by adding 1½% manganese naphthenate based on the weight of the dissolved polymer. This solution was used to impregnate a fabric and after evaporation of the solvent was cured or cross-linked by heating it in an oven at 110° C. for 1 hr. Another portion of the elastomer, in solution, was catalyzed by adding 1 part of sulfur and 1 part 2-mercapto imidazoline based on the dissolved polymer. After coating and evaporation of the solvent, the elastomer was cured by heating in an oven at 145° C. for 45 min.

EXAMPLE 46

A polyester composed of 0.25 mole of terephthalic acid, 0.25 mole maleic acid, and 0.5 mole of poly(ethylene oxide) terminated with hydroxyl groups and having a molecular weight of 1200 was dissolved in a mixture of methylethylketone and alcohol to give a solution containing 36% polymer. Based on the dissolved polymer, 2% benzoyl peroxide was added and the resulting mixture was used to coat a 3.5 oz. cotton fabric in 2 passes of the fabric under a coating blade so as to cause to be deposited 0.93 oz. of elastomer/yd.^{2} of fabric. After evaporation of the solvent, this coated fabric was heated in an oven to 120° C. for 30 min. The coated fabric was tested and was found to be water vapor permeable. It transmitted 62 g./yd.^{2}/hr. of water vapor at 60° F. with 55% relative humidity on one side of the fabric and 100% relative humidity on the other. The coated fabric was tested for hydrostatic head resistance and was found to withstand a head of 49″. The fabric was then tested by soaking samples in various organic liquids which originally were solvents for the polymer. Although these solvents swelled the elastomer, it was not dissolved due to the cross-links formed during the curing process.

EXAMPLE 47

A polyamide made from equal moles of hexamethylene-diamine and adipic acid was reacted with ethylene oxide to produce a polyamide having polymeric ether chains attached to the nitrogen atom. The reaction was carried out in such a way so that 75% of the weight of the final polymer was due to the attached poly(ethylene oxide)segments. This polymer was readily swollen in water, and was soluble in mixtures of water and methyl alcohol. A solution of the polymer was prepared containing 25% dissolved polymer. This solution was a viscous mass and could be coated or applied to a fabric using a doctor blade or roll technique. A 4 oz. polyester fabric (Dacron) was coated in 3 passes and in such a fashion that 1.1 oz. of dry elastomer was deposited in the interstices of the fabric. This amount of elastomer deposited in this particular fashion was a discontinuous layer embedded in the fabric so as to form a porous layer which was water vapor permeable. Since the elastomer was readily swollen by water, the interstices of the fabric were closed when contacted with water. The swollen elastomer fabric combination was therefore waterproof and would resist a hydrostatic head of 42″. It was found that the fabric would transmit 67 g. of water vapor/m.^{2}/hr. with a vapor pressure differential equivalent to 11.58 mm. Hg. Raincoats and sport jackets prepared from this coated fabric were excellent barriers to rain and had increased comfort due to their permeability to water vapor.

EXAMPLE 48

A polyamide was made from caprolactam. This polymer was reacted with ethylene oxide as described in Example 7 to produce a final polymer composed of 60% by weight of poly(ethylene oxide) segments. This polymer was readily swollen by water and was coated on fabrics from solutions in mixtures of alcohol and water similar to the technique used in Example 7. The coated fabrics have essentially the same properties as in Example 7.

EXAMPLE 49

100 g. of an elastomeric polyester composed of maleic acid, diethylene glycol, and a polyether of ethylene oxide terminated with hydroxyl groups was dissolved in 300 g. of butyl acetate. 10 g. of a copolymer composed of 80% sodium acrylate and 20% butadiene was suspended in butyl acetate. This suspension was obtained by ball milling a slurry of the polymer to obtain the polymer in a finely divided state. The average size of the particles was 0.2 micron. This suspension was then added to the solution of the elastomer. 1.2 g. of dicumyl peroxide was added and the mixture was applied to a 4.65 oz./yd.^{2} nylon fabric using the technique described in Example 1. The treated fabric was cured at 175° C. for 30 min. A silicone resin was applied to both surfaces from a water emulsion as in Example 6. After evaporation of the water, the silicone resin was fixed by heating to 150° C. for 3 min. The final product was air and water vapor permeable but was waterproof to liquid water. The surface of the fabric was also water resistant. Water vapor was transmitted at the rate of 72 g./m.^{2}/hr. with a vapor pressure differential equivalent to 11.58 mm. Hg. Further testing showed that in contact with water the elastomer swelled and closed the interstices and the fabric withstood a 65″ head of water.

EXAMPLE 50

100 g. of an elastomer made from 0.5 mole adipic acid, 0.5 mole maleic acid, 0.5 mole 1,4-butandiol and 0.5 mole of poly(ethylene oxide) terminated with hydroxyl groups and having a molecular weight of 500 was dissolved in 100 g. of toluene and 100 g. isopropyl alcohol. 50 g. of a copolymer composed of 60% methacrylic acid and 40% butadiene was dissolved in 50 g. of water mixed with 100 g. of isopropyl alcohol. The two solutions were mixed together with 2.5 g. dicumyl peroxide and the final mixture was applied to a 2.5 oz./yd.^{2} fabric as described in Example 1. After curing, the treated fabric was tested and it was found that it transmitted 63 g./m.^{2}/hr. of water vapor with a vapor pressure differential equivalent to 11.58 mm. Hg. The fabric also was waterproof to a 42″ head of water. This fabric was suitable for use as rainwear and protective covers for delicate instruments.

EXAMPLE 51

100 g. of poly(decamethyleneurea) in the form of a fine powder was suspended in dimethyl formamide. This mixture was placed in an autoclave and 50 g. of ethylene oxide was added. The mixture was heated and stirred to cause the ethylene oxide to form polymeric branch chains attached to the nitrogen atoms of the polyurea chain. The final polymer weighed 135 g. and was soluble in solvents such as methylethylketone, 1,4-dioxane, and mixtures of these solvents with toluene. 100 g. of this polymer was dissolved in 200 g. of methylethylketone and 50 g. of the copolymer composed of 80% N,N-dimethylacrylamide-20% acrylamide was added. After the second copolymer was dissolved, 5 g. of a melamine-formaldehyde resin with contained reactive methylol groups was added. This mixture was used to treat a 3.2 oz./yd.^{2} cotton fabric with 1.1 oz./yd.^{2} of dry elastomer as described in Example 1. The impregnated fabric was heated to cause a cross-linking reaction between the elastomeric polyurea, the hydrophilic polymer containing acrylamide, and the methylol containing resin. The fabric was waterproof to liquid water but was water vapor permeable.

EXAMPLE 52

100 g. of poly(hexamethylene tetrasulfide) was dissolved in 200 ml. toluene mixed with 100 ml. of methylene chloride. 50 g. of the copolymer composed of 45% butadiene-55% acrylic acid dissolved in methylethylketone was added. This mixture was used to treat a 4.75 oz./yd.^{2} fabric by the technique described in Example 1. The final fabric after heating in an oven at 145° C. for 45 minutes was capable of withstanding a hydrostatic head of 32" but was air and water vapor permeable and transmitted 68% as much water vapor as the untreated fabric.

An important aspect of the present invention is the location of the elastomer with respect to the fabric structure. The greater part of the elastomer is pushed below the fabric surface and little, if any, can be seen. Hence, the fabric retains its original texture and does not have a smooth or glossy appearance. This is a very important advantage over the "coated" fabrics known to the art. It is well known that the application of a continuous coating to the surface of a textile fabric produces two undesirable results: (a) the appearance of the fabric is changed completely and it resembles a film or sheet rather than a textile product, (b) the draping qualities are almost completely lost and stiff hand or feel is acquired. In contrast, textile fabrics treated by the process of the present invention are not changed in appearance. Furthermore, there is essentially no change in draping qualities or hand because the elastomer is present as a non-continuous structure and hence exerts a minimum of stiffening action. Therefore, it is very surprising to find that the fabrics are highly resistant to penetration by liquid water. This valuable combination of appearance and functional properties represents an entirely new concept in the art.

The amount of elastomer used to render any particular fabric waterproof but water vapor permeable is dependent on the weight of the fabric and the type of fabric construction. A relatively light fabric with an open weave will require more elastomer than a medium weight fabric. A heavy fabric will also require more elastomer than a medium weight fabric. The following table describes the limits which are useful to the practice of the invention. Fabrics made from different types of polymers require only very slight adjustments in the amount of elastomer and these small differences are included in the ranges shown by the table.

Fabric wt., oz./yd.^{2}	Lower limit elastomer wt., oz./yd.^{2} (tight weave)	Upper limit elastomer wt., oz./yd.^{2} (open weave)	Average air permeability* of coated fabric, $\Delta P = 11.58$ mm. Hg g./m.^{2}/hr.	Average water vapor permeability of coated fabric, $\Delta P = 11.58$ mm. Hg g./m.^{2}/hr.
1.5	1.00	2.00	150	65
2.0	0.80	2.50	160	67
2.5	0.70	2.50	170	70
3.0	0.60	2.50	180	72
3.5	0.50	2.00	190	77
4.0	0.50	1.75	150	78
4.5	0.40	2.00	125	80
5.0	0.40	2.50	125	83
5.5	0.50	3.00	----------------	----------------
6.0	0.50	3.50	----------------	----------------
7.0	0.50	3.50	----------------	----------------
>10.0	0.50	3.50	----------------	----------------

*The average air permeability of the impregnated fabric was found to be 60% of the untreated fabric.

The use of a water repellant finish with this elastomer is desirable to provide a time for the elastomer to swell after exposure to water. The exact nature of this finish is not important. However, the properties of the finish should be such that it can be applied to the fabric after the elastomer has been applied and before curing or after the curing step. In some instances the finish may be applied with the elastomer. Finishes which are applied from an emulsion in water may be applied to the fabric after the elastomer has been applied and either before or after the curing step. Water repellant materials which are soluble in the same organic solvents as the elastomer can be applied with the elastomer by dissolving the water repellant in the solvent for the rubber. This material may also be applied after the elastomer has been applied. These materials may be applied by dipping, spreading, or spraying techniques. The amount used depends on (1) the effectiveness of the material and (2) the technique used to apply the material. For instance, if the repellant material is added to the solvent containing dissolved elastomer the material may comprise any part of the total solids from 0.001% to 20%. From the table showing fabric and elastomer weights it can be calculated that the range of weight of water repellant finish varies from 0.0004 oz./yd.^{2} to 0.7 oz./yd.^{2} based on the weight of the fabric. If the water repellant finish is applied from a water emulsion or from a solution after the elastomer has been applied to the fabric, the amount of water repellant used can have any value from 0.0004 oz./yd.^{2} to 1.0 oz./yd.^{2}. This amount can be applied in one treatment or in multiple applications. The water repellant finishes that are suitable for this application are hydrophobic waxes, oils, metallic soaps, and the like. Especially valuable are paraffin waxes; silicone oils, waxes and polymers; fluorinated oils, waxes and polymers; and certain pyridinium compounds. The methods of applying these finishes vary with type of finish, type of fabric, and certain synergistic combinations of water repellant finish and organic resins. A discussion of these techniques may be found in the following references: E. J. Grajeck and W. H. Petersen, Textile Research Journal 32, 320–331 (1962); DeMarco, C. G., McQuade, A. J., and Kennedy, S. J., Modern Textiles 2, 50–56 (1960); and Fisman, W. A., NRL Report 4932 (May 15, 1957).

It is evident that a wide variety of water-swellable elastomers can be used to make the impregnated textile fabric products of the invention. The polymers containing amide groups, as described in U. S. Patent 3,026,293 may be employed.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A breathable fabric particularly useful as rainwear which, in contact with liquid water is water impermeable but out of contact with liquid water, is air and water vapor-permeable, which comprises a fibrous textile fabric having deposited below one surface of but above the midplane of said fabric a layer of water-swellable elastomer having an elongation of at least 200% in the dry state, which layer, out of contact with liquid water, is discontinuous and porous by virtue of the presence therein of a plurality of minute voids which permit passage therethrough of air and of water vapor, as such, but which elastomer layer, in contact with liquid water, swells from 50–500% of the volume the elastomer has out of contact with liquid water, thereby substantially and immediately to reduce the cross-sectional area or size of said voids to such an extent as to preclude the passage of liquid water, as such, through said voids and thus to remain impervious to the penetration of water for so long a time as liquid water is in contact with said layer but which, upon removal of liquid water from contact with said layer, shrinks and thereby regains its original discontinuity and porosity and its original permeability to air and water vapor.

2. The product of claim 1 in which the water-swellable elastomer is derived from a combination of vinyl monomeric constituents such that the elastomer has an elongation at least 200% in the dry condition and swells in contact with liquid water at least 50–500% of the volume the elastomer has when out of contact with liquid water.

3. The product of claim 1 in which the water-swellable elastomer is derived from a condensation polymer.

4. The product of claim 3 in which at least 50% of the condensation polymer components are connected by ester linkages.

5. The product of claim 3 in which at least 50% of the condensation polymer components are connected by amide linkages.

6. The product of claim 1 in which the water-swellable elastomer is derived from a mixture of vinyl polymers and condensation polymers.

References Cited by the Examiner

UNITED STATES PATENTS

25,110	8/1859	Goodyear	117—135.5
2,149,750	3/1939	Schwartz	117—135.5
2,317,499	4/1943	Trowell	117—135.5
2,575,577	11/1951	Beauchamp	117—135.5
2,626,941	1/1953	Habeck.	
2,673,823	3/1954	Biefeld et al.	117—135.5 X
2,917,807	12/1959	Scholl	117—135.5 XR
3,013,926	12/1961	Railsback et al.	260—821.1 XR
3,026,293	3/1962	Caldwell et al.	117—145 XR

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