

# UNITED STATES PATENT OFFICE

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## WATERPROOFED FABRIC AND METHOD OF PRODUCING IT

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4 Claims. (Cl. 117-161)

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This invention relates to compositions useful in film formation, and for coating textile fabrics, and to new coated fabrics capable of transmitting water vapor. More specifically, the invention relates to water-impermeable, water-vapor-permeable fabrics having a coating of polydiene rubber.

The application of water-proof coatings to cloth is well known and many satisfactory methods have been devised for effecting this objective. However, when the cloth, thus treated is to be used for garments such as raincoats, these coating compositions are not wholly satisfactory because they do not transmit the water vapor resulting from body perspiration. As a result, the comfort of the wearer is greatly impaired. To overcome this objection, light-weight fabrics of closely woven fibers are widely used for the manufacture of so-called rain-proof garments because they do transmit water vapor, but these fabrics are not sufficiently water-proof to prevent the penetration of liquid water when subjected to rainfall for long periods of time or to substantial hydrostatic pressure. Rain-proof garments have also been made by treating woven fabrics with organic silicon compounds, such as the silanes, or other compounds which render the fabric hydrophobic, or water-repellent, but these also do not withhold water under the hydrostatic pressures experienced in normal usage.

The primary purpose of this invention is to provide new water-proof fabrics capable of excluding liquid water under substantial hydrostatic pressures and yet which are quite pervious to gases, and especially to water vapor. A further purpose is to provide water-proof compositions useful in the preparation of films and coatings, capable of transmitting water vapor while being impervious to liquid water.

In accordance with this invention films are prepared, or woven fabrics are coated, with a specially compounded polymerized diene synthetic rubber. Useful rubbers of this type are polyisoprene, polymerized butadiene-1,3, polymers of other conjugated diolefinic hydrocarbons and the polymers of chlorine-substituted diolefinic hydrocarbons, such as 2-chloro-butadiene-1,3. The coating of cloth with polydiene rubbers is not new and such practice will not, of itself, yield a water vapor pervious fabric.

In order to secure the desired result, the coating compositions are specially compounded with large proportions of a hydrophilic diatomaceous earth or other similar naturally occurring fossil remains of microscopic marine animals, including diatoms and other photophyta. These minerals

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are known as infusorial earth, diatomaceous silica, and kieselguhr and are available in various states of refinement under the trade names of "Sil-o-cel," "Celite," and "Superfloss." For the purpose of this patent application all of these minerals in their natural state and in purified form are intended to be included within the generic expression "diatomaceous earth."

The different minerals vary substantially in their densities and for the purpose of defining the invention it has been found that the volume ratios of the diatomaceous earth are more significant than the weight ratios. A useful composition can be prepared by compounding the polydiene rubber with at least two volumes of diatomaceous earth, the volume being based on the so-called "apparent density" measured by pouring the pigment into a graduate or other volume measuring device. The preferred compositions will contain from three to five volumes of diatomaceous earth. If more than six volumes of the pigment are used, many compositions become too rigid or viscous for ready application to cloth, especially when the latex technique, hereinafter described, is used.

A preferred method for preparing the new compositions involves the use of the latex as it is obtained by the emulsion polymerization of the diene. The latex so prepared is usually an aqueous suspension of finely-divided solid particles of polymer, the emulsion being usually stabilized by the presence of soap or other wetting agent. The latex may be used directly in this form, or it may be concentrated by creaming, agglomerating or centrifuging in any manner well known to the art. The solid rubber content of these aqueous suspensions may vary between 30 and 55 percent solids. In the practice of this invention the polydiene latices are compounded with antioxidants, accelerators, plasticizers and coloring agents in the manner well known to the art. Suitable antioxidants for use in the polydiene rubbers are phenyl-beta-naphthylamine, butyraldehyde-aniline derivative and di-beta-naphthyl-para-phenylene diamine. The conventional accelerators used in these compositions are hexamethylene ammonium hexamethylene-dithio-carbamate, potassium salt of mercapto-benzothiazole, zinc oxide, and magnesia and litharge. To improve the visual appearance colored pigments and dyes may also be incorporated. In addition to the conventional modifying agents, the diatomaceous earth is added in substantial amounts. When so compounded the latex is a viscous liquid or a semi-solid paste.

Other very effective coating compositions may

be prepared by compounding solid polydiene rubber on a rubber mill with the conventional antioxidants, plasticizers, and accelerators, as above described. The rubber so compounded is then dissolved or dispersed in organic solvents, such as benzene, toluene, methyl ethyl ketone, ethylene, dichloride, chlorobenzene, high naphthenic petroleum fractions. Although sometimes regarded as true solutions, the mixtures of organic solvents and polydiene rubbers are believed to be colloidal dispersions of rubber particles in the organic liquids in which the organic liquid is the exterior phase, or dispersion medium, just as the water is the exterior phase of a latex, or aqueous dispersion. The dispersion of the polydiene rubber in the solvent is effected by adding the compounded rubber to the solvent in a dough mixer or other conventional mixing device. Sufficient solvent is added to make a thin cement and the desired amount of the diatomaceous earth is thereafter added to yield a thick cement which can be fabricated by the same methods useful in the fabrication of the compounded latex, by painting, spraying, calendering, spreading or other methods well known to the art.

The principal use of the above-described coating compositions is in the coating of fabrics which may be woven or knitted of animal fiber, such as wool, silk, fur and hair, vegetable fibre, such as cotton, linen and hemp, mineral fibre, such as glass and asbestos, and synthetic fibre, such as rayon or nylon. Matted fabrics, such as felt and paper may also be coated. The apparatus and method used for impregnating or coating the fabrics are well known and are not a part of this invention.

The preferred method of applying the coatings involves the "spreading" technique, in which cloth is drawn tightly over a series of rolls or other devices and the compounded latex or solvent dispersion is applied using a doctor blade or other straight edge to control the thickness. The blade may be set up perpendicularly to the fabric or at an angle so as to force the coating composition into the interstices. Frequently it is desirable to apply several successive layers, allowing each to dry wholly or partially before applying the next layer. The first layer is sometimes applied with the spreader knife set at zero clearance so that only the interstices are filled on the first application, the desired covering layers being put on subsequently by separate spreading operations. After each coating, or after several coatings have been applied, the composition is dried, by heating, if necessary, to remove the water or other liquid present in the rubber dispersion. The dried coating is then vulcanized by heating the coated fabric to the vulcanization temperature of the particular compound.

The new compositions may also be used without the fabric base in the form of films. Such films will have the same properties of water-imperviousness and water-vapor-permeability as the cloth laminates, but generally do not have the tensile and flexural strengths. They are, however, useful for the fabrication of items not intended to be subjected to severe stress.

The coated fabrics and the films may be used in the fabrication of coats, gloves, boots and shoes, and other wearing apparel as well as tents, sleeping bags, hospital sheeting, bandage wrappers, tarpaulins, furniture coverings or other structures adapted for enclosing or contacting the human body.

The water vapor perviousness of the coated

fabrics may be tested by any of several standard methods. In the examples below the coated fabrics were tested by cementing a sample of the fabric to the top edge of a glass Petri dish containing water, the level of which is  $2.3 \pm .05$  cm. below the fabric, and measuring the water evaporated during a predetermined period of time. The water vapor transmitted, which is expressed in grams per hour per square meter, is corrected for variations in temperature and humidity by running a control with a standard balloon cloth (Sak or pima cotton,  $2.0 \pm 0.1$  oz./yd.<sup>2</sup>, warp count 133, fill count 134, plain weave) and multiplying the measured moisture vapor transmission of the test sample by 47.5, the average moisture vapor transmission of the standard cloth, and dividing by the control measurement of the standard cloth. This method of testing gives accurate reproducible test data. Conventional fabrics water-proofed by rubber coatings usually have moisture vapor transmissions of less than 5 grams per hour per square meter, while fabrics prepared in accordance with this invention will have moisture vapor transmissions in excess of 15 grams per hour per square meter and preferably in excess of 20 grams per hour per square meter.

The hydrostatic head of a film or fabric is the pressure, usually measured in height of water, which is required to force water through the film or fabric. The hydrostatic head may be measured by the method, ASTM D583-40T, procedure B, section 6. Water-proof fabrics should have hydrostatic heads of over 125 cm. of water and preferably over 200 cm. of water, whereas the hydrostatic heads of water-repellent fabrics do not exceed 75 cm. of water.

Although fabrics have been prepared with hydrostatic heads within the above defined preferred range, it has been accomplished by sacrifice of the moisture vapor transmission rate. Similarly fabrics of the desired moisture vapor transmission rates have been prepared but only by giving up the desirable resistance to liquid water under pressure. This invention makes it possible to achieve both of the desired properties to an effective extent.

Further details of the preparation of the coating compositions and the laminated fabrics prepared therefrom are set forth with respect to the following specific examples.

#### Example 1

A polychloroprene latex containing approximately 50 percent rubber solids (Neoprene 571) was mixed with the following materials, the quantities being based on 100 parts by weight of the polychloroprene:

60	Casein .....	5
	Water glass.....	15
	Calcium carbonate.....	25
	Zinc oxide .....	25
	Hexamethylene tetramine .....	3
65	Agerite white <sup>1</sup> .....	3
	Methyl cellulose.....	3

<sup>1</sup> Antioxidant sym. dibetanaphthyl-p-phenylene diamine.

The casein was added as a 10 percent water solution of ammonium caseinate and the water glass was also added in water solution. The materials were mixed by means of high speed propeller type agitators, and, when thoroughly mixed, 90 parts of water were added. One hundred parts by weight (3.5 volumes) of diatoma-

ceous silica were then thoroughly mixed into the latex.

The latex paste so prepared was spread on cotton sheeting weighing 3.6 oz./sq. yd. and having 58 threads per inch in the warp and 50 threads in the fill. The fabric was coated with three layers of the material with the spreading knife set at 0.001-0.002 inch. Each layer was dried thoroughly over steam coils before applying the next layer. The coated fabric was cured in an oven for 50 minutes at 105° C. The resulting product was measured to determine its moisture vapor transmission which was found to be 22 grams/hr./m.<sup>2</sup>. The hydrostatic head was measured and found to be 200 cm. of water.

#### Example 2

A polychloroprene rubber (GR-M) was milled on a laboratory-size rubber mill with the following materials; the parts being by weight based on 100 parts of polychloroprene:

Zinc oxide.....	10
Calcined magnesia.....	10
Phenylbetanaphthylamine.....	2
Sulfur.....	2

The compounded rubber was placed in a dough mixer and thinned by 762 parts by weight of toluene. After mixing to a thin uniform cement 112 parts by weight (4 volumes) of diatomaceous silica were added.

After this, the cement was spread on a cloth fabric identical to that used in the preceding example by coating once with the doctor blades and thereafter with three coats each 0.001 to 0.002 inch in thickness. The coated fabric was then dried in hot air to evaporate the excess toluene and cured for 60 minutes at 280° F. The hydrostatic head was found to be 287 cm. of water and the moisture vapor transmission was found to be 35 grams/hr./m.<sup>2</sup>.

The method of this invention may be used to coat cloth utilizing other resins or rubbers containing high proportions of hydrophilic diatomaceous silica. Preferably in excess of three volumes of the pigment are used per volume of the rubber or resin. Thus, the following rubbers and resins may also be used: synthetic rubber including copolymers of hydrocarbodiene and 20 to 50 percent of other mono-olefinic monomers, such as styrene, acrylonitrile or the acrylates; natural rubber, including hevea and other vulcanizable natural resins; vinyl chloride resins, including polyvinyl chloride and copolymers of vinyl chloride and from 5 to 20 percent of vinyl acetate, ethyl fumarate, or the alkyl acrylates and methacrylates; the polyvinyl acetals, including polyvinyl butyral; polyvinyl alcohol; polymers of aliphatic mono-olefinic compounds including polyisobutylene and butyl rubber; linear polyamide interpolymers, including the soluble nylons; the polymerized alkyl acrylates, including polymethyl methacrylate, polymethyl chloroacrylate and polymethyl acrylate.

Although the invention has been described with respect to specific examples it is not intended that the details thereof shall be construed as limitations on the scope of the invention except to the extent incorporated in the following claims.

I claim:

1. A water-impervious and water vapor-permeable fabric which comprises a woven textile fabric coated with a continuous layer of rubberlike polychloroprene, said polymer containing intimately dispersed therein from two to six volumes, based on the polymer, of a hydrophilic diatomaceous earth.

2. A water-impervious and water vapor-permeable fabric which comprises a woven textile fabric coated with a continuous layer of rubberlike polychloroprene, said polymer containing intimately dispersed therein from three to five volumes, based on the polymer, of a hydrophilic diatomaceous earth.

3. A method of preparing a water-impervious and water vapor-permeable coated fabric which comprises mixing a latex of a rubberlike self-polymer of 2-chlorobutadiene-1,3 with from three to five volumes, based on the polymer, of a hydrophilic diatomaceous earth, and applying a continuous layer of said polymer on a woven textile fabric by spreading the mixture on the fabric, drying the coating by evaporation of the water in the latex, and vulcanizing the coating.

4. A method of preparing a water-impervious and water vapor-permeable coated fabric which comprises mixing an organic solvent dispersion of a rubberlike self-polymer of 2-chlorobutadiene-1,3 with three to five volumes, based on the polymer, of a hydrophilic diatomaceous earth, and applying a continuous layer of said polymer on a woven textile fabric by spreading the mixture on the fabric, drying the coating by evaporation of the organic solvent, and vulcanizing the coating.

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**Certificate of Correction**

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November 20, 1951

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 1, line 55, for "photophyta" read *protophyta*; column 3, line 7, strike out the comma after the syllable "ene";

and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of March, A. D. 1952.

[SEAL]

THOMAS F. MURPHY,  
*Assistant Commissioner of Patents.*