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PROCESS OF MAKING COATED TEXTILE MATERIALS AND THE ARTICLES PRODUCED THEREFROM

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The present invention relates in general to waterproof textiles. More particularly, it relates to waterproof textiles of the class of oil cloth, artificial leather, raincoats and the like, and to a process for producing the same.

Heretofore, in the manufacture of waterproof textiles, such as oil cloth, artificial leather, raincoats, and the like, it has been customary to apply a multiplicity of coatings to a fibrous sheet material, such as fabric, felts and paper. The trade would prefer to avoid the use of such multiple coatings but heretofore this has not been possible because (a) the fibrous materials, such as textiles, felts and papers are extremely porous, and the first two or three coatings applied tend merely to sink into the sheet without forming a film thereover; (b) such fibrous materials are characterized by having a substantial nap, the fibres of which tend to protrude through the coatings and impart an uneven surface to the product; and (c) due to the porosity, certain pin holes continue to exist even after the application of two or more coatings. Accordingly, the trade has found that these disadvantages can be overcome only by the application of a multiplicity of coatings, it being common in the trade to apply as many as seven or eight coatings in the manufacture of oil cloth, artificial leather and shoe fabric. It is obvious that the application of such a large number of coatings which must be separately dried is expensive, time consuming, and necessitates the use of a large amount of labor and equipment.

It is a general object of the present invention to provide a fibrous material with a waterproof and/or moistureproof coating which will tenaciously adhere to the material even during immersion in water for an unlimited length of time.

It is another object of the present invention to provide a coated textile, of which the coating will be non-tacky, flexible and waterproof and strongly adherent.

A further object of the present invention is to provide a simple and efficient method of applying a waterproof coating to fibrous sheet materials.

Other objects of the invention will be apparent to those skilled in the art from the following detailed description.

According to the present invention, there is provided a multi-coated fibrous sheet material comprising a layer of textile sized with an alkali-soluble water-insoluble cellulosic material and having a moistureproof top coating, and a water-resisting intermediate coating disposed between

the sized textile and the moistureproof top coating to anchor the top coating to the sized textile. In the now preferred embodiment the textile is sized with an alkali-soluble water-insoluble cellulose ether, the anchor coating is a lacquer containing as the film-forming base a urea-formaldehyde resin, and the top coating consists of a cellulose derivative, a plasticizer, a wax and a wax blending agent.

The invention accordingly comprises a process having the steps and relation of one or more of such steps with respect to each of the others, and an article of manufacture possessing the features, properties and the relation of elements which will be exemplified and hereinafter described and the scope of the invention will be indicated in the claims.

By the term "water resisting" is meant the ability of the coating material to remain adhered to the base sheet during immersion in water for an unlimited period of time.

The textile material

For the textile material there may be employed any textile fabric, felt or paper made of natural or artificial fibres or mixtures thereof. In the following detailed description and in the appended claims the expression "textile" is used to include both felts and papers as well as textile fabrics formed by knitting, weaving and braiding.

The sizing composition

The sizing composition comprises in general an aqueous alkaline dispersion of a non-fibrous cellulosic colloid, such as the alkali-soluble water-insoluble cellulose ethers as a class, such, for example, as alkyl cellulose ethers, hydroxy-alkyl cellulose ethers, and carboxy-alkyl cellulose ethers; also, natural or degraded cellulose dissolved in inorganic or organic cellulose solvents, such, for example, as alkaline zincate and alkaline stannate solutions, sodium hydroxide, alkali metal perchlorates, cuprammonia, quaternary ammonium bases, and the like. Also, there may be used viscose which is a solution of cellulose xanthate dissolved in aqueous sodium hydroxide solution. The use of the alkali-soluble water-insoluble cellulose ethers is preferred over the other cellulosic colloids because they give stronger films than the solutions of natural or degraded cellulose and they do not require desulfurization as is necessary when viscose is used.

The sizing composition may contain optional ingredients, such, for example, as pigments, dyestuffs and mineral fillers, fireproofing agents,

plasticizers, and the like. The textile material is sized by spraying, padding, backfilling or otherwise coating and/or impregnating the textile with the composition after which the cellulosic colloid is coagulated on the textile by treating the textile with a coagulant of the colloid, such, for example, as an aqueous solution of an acid, an acid salt or an acid gas. When using the cellulose ethers, they may be coagulated additionally by hot water. After the cellulosic colloid is coagulated on the fabric, it may be washed, soured or dried preferably while maintaining the textile at a predetermined width. When penetration of the textile is not necessary as in making a product coated on one side only, the sizing composition is applied by backfilling, using a composition of high viscosity to retard penetration and to cause a filming-over or "window-paning" of the spaces between the yarns or fibres. Before and/or after coagulation the sized textile is calendered or passed between doctor blades to lay the nap fibres into the size.

When a degraded cellulose ether or a degraded cellulose is employed as the size, the dried sized textile is preferably submitted to a calendering operation or ironing at an elevated temperature, such, for example, as 50 to 100° C. The application of heat and pressure in this manner serves two purposes, (a) to smooth the fabric (b) to cause a substantial flow of the cellulosic colloid. While such degraded cellulosic colloids have been heretofore considered by those skilled in the art, as non-thermoplastic materials, nevertheless, it has been found that they exhibit a substantial thermoplastic flow when subjected to heat and pressure. This novel characteristic is taken advantage of in the present invention to lay the nap fibres and to smooth the surface of the fabric whereby one is enabled to produce an impermeable and waterproof material by the application of only two coatings upon the sized and calendered textile. The textile is now ready for the application of the intermediate or anchor coating.

The anchor coating

The film-forming agent used in the anchor coating is a film-forming water-resisting material selected from the class consisting of drying oils, drying-oil-modified resins, thermosetting resins, natural and synthetic rubber, and rubber derivatives, all of which materials are characterized by forming strongly adherent continuous films which do not substantially swell in water and are not soluble in the solvents of the top coating. Among the drying oils there may be employed linseed oil, perilla oil, soy bean oil, and the like; among the drying-oil-modified resins there may be used perilla-oil-modified-alkyd, castor-oil-modified-alkyd, and soy bean-modified-alkyd resins; among the thermosetting resins there may be used phenol-formaldehyde resins, urea-formaldehyde resins, melamine-formaldehyde resins, and the like; and among the synthetic rubbers there may be used co-polymer of butadiene and styrene, e. g. "Buna-S," polymer of chloroprene, e. g. "neoprene," co-polymer of isobutylene and butadiene, e. g. "butyl" rubber, polymer of ethylene dichloride and sodium tetrasulfide, e. g. "Thiokol"; also halogenated natural rubber and the product of treating rubber with stannic chloride e. g. "Pliolite," and the like. However, in the now preferred embodiment, the film-forming agent in the anchor coating is a thermosetting resin in the thermoplastic heat-hardenable state.

To the anchor coating there is also added a hardening agent or latent catalyst for the heat-hardenable resin, and a plasticizer.

Various methods for forming the anchor coating have been discovered, for example, the anchor coating may be obtained by (a) applying the synthetic resins to the sized textile from an aqueous solution containing either the individual compounds such as urea and formaldehyde, which will condense, upon heating with an acid catalyst, to form the resin, or containing a water-soluble intermediate condensate of the resin-forming compounds, e. g. dimethylol urea, the condensate being polymerized on the textile by heating to form a water-resisting non-tacky resin, the top coating being subsequently applied; (b) by applying to the textile an organic solution comprising an intermediate condensate of the resin-forming compounds which is tacky and soluble in organic solvents, the polymerization being continued on the textile until the coating is tack-free and water insoluble, the top coating then being applied.

The foregoing heat-hardenable resins are added to the coating solution in the incompletely polymerized heat-hardenable state, which means that they are capable of later being further polymerized or hardened to a tack-free, substantially insoluble stage while included in the coating, for example, of the magnitude of about 0.0001 of an inch in thickness, by the application of heat and/or a catalyst for a period of not longer than several minutes and at a temperature not exceeding 125° C. The heat-hardenable resins are cured to give products which are non-tacky and substantially insoluble in water or the organic solvents used in the top coating. At the same time, they do not embrittle the coating but enable it to remain soft and pliable and capable of undergoing shrinkage and swelling as the moisture content of the hydrophilic pellicle changes with variations in atmospheric humidity.

The hardening agent for the heat-hardenable resin may comprise any material which tends to accelerate the polymerization or hardening of the resin, as, for example, by the release of acid upon the application of heat. Among the hardening substances which are capable of use for this purpose are ammonium thiocyanate, p-toluene sulfonic acid, and maleic acid, salts of chloroacetic acid, and the like. In some cases an alkaline catalyst may be employed, such, for example, as sodium hydroxide, potassium hydroxide, sodium carbonate, or an organic amine.

The plasticizer employed in the intermediate coating composition is preferably of the plasticizing resin type, for example, a resin of the soft type such as polymerized unsaturated hydrocarbons, for example, polymerized isobutylene, which is commonly sold under the trade name "Vistanex," or soft alkyl resins. In addition to the plasticizing resins, or in place thereof, organic plasticizers may be employed such as dibutyl sebacate, dibutyl phthalate, tricresyl phosphate, cyclohexyl butyl phthalate, and the like, or mixtures of these plasticizers.

There may be added to the intermediate or anchor coating certain optional ingredients, in particular a secondary film-forming agent, a moistureproofing agent, such as a wax blending agent, and slip agent. Slip agents in the anchor coating are advisable when the pellicle has to be rewound before application of the top coating thereon.

The secondary film-forming base of the anchor

coating may be one or more of the film-forming organic solvent-soluble cellulose derivatives as a class, among which may be mentioned cellulose nitrate, cellulose acetate, ethyl cellulose and benzyl cellulose; or film-forming thermoplastic synthetic resins as a class, such, for example, as the resin resulting from the reaction of polyhydric phenols with aliphatic polyhalides, methacrylate resins, vinyl polymers, and the like; and rubber-like materials, such as chlorinated rubber, rubber hydrohalides, and cyclized rubber derivatives.

The top coating

The top coating comprises, in general, a film-forming moistureproof material, but if the film-forming material is not inherently moistureproof or sufficiently flexible there is added a moistureproofing agent, a plasticizer and, optionally, a blending agent. The film-forming base of the top coating may comprise (a) film-forming organic-solvent soluble cellulose derivatives as a class, among which may be mentioned cellulose nitrate, cellulose acetate, ethyl cellulose, benzyl cellulose and the like; or (b) film-forming thermoplastic synthetic resins as a class, such, for example, as the resin resulting from the reaction of polyhydric phenols with aliphatic polyhalides, polymers of esters of acrylic acid and methacrylic acid, polyvinyl resins and the like, in particular a copolymer of vinylidene chloride and vinyl chloride; or (c) drying oils and drying-oil-modified resins, or a mixture of these classes of bases; or (d) natural and synthetic rubber and rubber-like materials, such as halogenated rubber, rubber hydrohalides, cyclized rubber derivatives, and the like.

In the now preferred embodiment the film-forming agent employed as the top coating comprises nitrocellulose combined with a plasticizer and a moistureproofing agent.

In the top coating composition there may be employed a compatible plasticizer such, for example, as a soft alkyd resin or a non-volatile organic plasticizer, such, for example, as tricresyl phosphate, dibutyl phthalate, cyclohexyl butyl phthalate, dibutyl sebacate, and the like.

The moistureproofing agent may comprise a high-melting wax or a wax-like material. A high melting paraffin wax is preferred for this purpose, that is, a paraffin wax melting between 62° and 65° C. is preferred, although other waxes and wax-like materials may be used, for example, ozokerite, ceresin wax, carnauba wax, and the like.

If desired, a suitable wax-blending agent may be added to the coating. As wax-blending agents, there are used substances which are characterized, in general, by a low melting point and a solubility in both hydrocarbon solvents and hydroxyl-containing solvents and by compatibility with molten paraffin wax, for example, ester gum, a blown vegetable oil, wax-free dammar, japan wax, and castor oil phthalates.

The foregoing ingredients are suitably dissolved in a solvent or a mixture of solvents for all of the materials present. Suitable solvents are mixtures of aromatic hydrocarbons, alcohols and esters, such as xylene and butanol, or toluene and butyl acetate.

Generally speaking, the organic solvent or both the intermediate coating and the top coating is evaporated at an elevated temperature and when a moistureproofing wax is present in either of the coatings, the temperature employed is

preferably above the melting point of the particular wax employed.

There may be added to the top coating a suitable slip-inducing agent which is added in accordance with well-known practices to enable one finished sheet to slide over another when stacked. Suitable slip agents are, for example, any comminuted solid which is insoluble in the ingredients of the anchor coating, such, for example, as starch, talc, zinc oxide, calcium carbonate, and the like.

By way of explanation of the invention and not in limitation thereof, the following specific examples of an anchor coating composition for use in the production of a moistureproof waterproof article of the present invention will be given:

Example 1.—A cotton fabric is first wet with an aqueous solution containing $\frac{1}{8}\%$ of Tergitol. After squeezing the wet fabric by means of a water mangle, the wet fabric is coated on both sides with an aqueous alkaline solution of a hydroxy ethyl cellulose ether containing 7% of cellulose ether and 7% of sodium hydroxide, the solution having a viscosity of 9 compared to pure glycerine. The cellulose ether is coagulated on the fabric by passing it into a 5% aqueous solution of sulfuric acid. It is then washed in water and treated with a solution of $\frac{1}{2}\%$ soda ash, washed, and then treated with $\frac{1}{2}\%$ acetic acid solution to neutralize any residual alkali. Thereafter the fabric is plasticized with an aqueous solution containing from 3 to 10% monoethanolamine sulfamate. The material is then dried on a tenter frame to a desired width. In the dried product the percent of plasticizer on the weight of the dry cellulose ether is from 20 to 40%.

The intermediate or anchor coating composition is prepared by mixing together the following substances:

40	Film-forming agent:	Parts
	Urea-formaldehyde butanol ether resin...	39
	Plasticizer:	
	Alkyd resin.....	20
45	Hardening agent:	
	Maleic acid.....	10

This composition is dissolved in a mixture of toluene, xylene, butyl alcohol and butyl acetate, and after application to the dried sized textile, the solvent is evaporated at an elevated temperature, for example, from 75° to 98° C. During the evaporation of the solvent, the heat causes a further polymerization or hardening of the thermosetting resin to the insoluble stage and causes the coating to become firmly anchored to the textile so that it will not blister when immersed in water.

The fabric bearing the anchor coating is then coated with a composition comprising:

60	Film-forming agent:	Parts
	Nitrocellulose (5-6 sec.).....	30
	Plasticizers:	
	Dibutyl sebacate.....	13
	Alkyd resin ("Beckacite").....	25
65	Moistureproofing agent:	
	Paraffin wax (M. P. 67° C.).....	5
	Wax blending agents:	
	Esterified Congo gum.....	5
70	Rapeseed oil.....	0.5

From 10-20 parts of this composition are dissolved in 200 parts of a mixture of 70% toluene, 15% ethyl acetate and 15% butyl acetate. This solution is then applied to the sized textile bearing the anchor coating and the solvent is evap-

orated at an elevated temperature, for example, from 75 to 98° C., that is, above the melting point of the wax.

Example II.—The process of Example I is repeated using, instead of the cellulose ether solution, a solution formed by dissolving ground woodpulp in an aqueous alkaline solution of sodium zincate containing an excess of sodium hydroxide, the solution being effected by cooling the mixture to about 8° C. with cracked ice, stirring and warming. The solution thus produced is then applied by back-filling to one side of a textile felt, the cellulose coagulated immediately and the alkali neutralized by means of an acid coagulant, after which the felt is washed and dried. The dried felt is then calendered whereby the surface is rendered smooth and the nap fibres laid and bound to the body. The degraded cellulose size is sufficiently thermoplastic to flow slightly and fill the interstices between the fibres. The resulting fabric is then coated with an anchor coating as in Example I by using, instead of the urea-formaldehyde butanol ether resin, a melamine formaldehyde resin in the thermoplastic state, the resin being polymerized further during the drying of the anchor coating. To the coated felt thus produced there is applied a top coating consisting of Saran (a co-polymer of 80 parts of vinylidene chloride and 20 parts of vinyl chloride) dissolved in suitable solvents, such, for example, as a warm mixture of toluene and dioxane or a mixture of dioxane and methyl ethyl ketone. The product thus produced will be found to be highly moistureproof and resistant to loosening of the coating when the felt is soaked in water. The product thus serves admirably as a floor covering, artificial leather and the like. It should be noted that in the second example no moisture-proof wax is employed either in the anchor coating or in the top coating because the Saran is itself highly moistureproof and water-resisting.

Since certain changes in carrying out the above process and certain modifications in the composition which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description

shall be interpreted as illustrative and not in a limiting sense.

I claim:

1. In a process for forming a flexible, water-proof fabric, the steps comprising coating a porous fabric with an aqueous alkaline solution of a hydrophilic alkali-soluble cellulose ether insoluble in water; coagulating said cellulose ether to form a coating and thereafter applying pressure to said cellulose-ether-coated fabric while the coagulated cellulose ether coating is in a wet gel state to cause the coating to flow and lay the nap; applying to said coated fabric an intermediate anchor coating comprising a hydrophobic thermosetting synthetic resin in an intermediate stage of polymerization dissolved in an organic solvent, said resin being selected from the group consisting of phenol-formaldehyde resins, urea-formaldehyde resins and melamine-formaldehyde resins; said cellulose ether coating preventing penetration of the fabric by said resin solution; thereafter evaporating the organic solvent and continuing polymerization of the resin to give a non-tacky water-insoluble coating; applying to said intermediate coating a moisture-proofing composition comprising a film-forming cellulose compound dissolved in a volatile organic solvent, said cellulose compound being selected from the group consisting of cellulose ethers and cellulose esters; and evaporating said last-mentioned organic solvent to form a top coating; said intermediate coating anchoring said top coating and the cellulose ether coating anchoring the intermediate coating to the fabric, whereby the various coatings tenaciously adhere to the fabric without cracking or peeling therefrom.

2. The process recited in claim 1, wherein the top coating comprises a plasticizer and a moisture-proof wax.

3. A flexible, water-proof fabric made in accordance with the process defined in claim 1.

4. A flexible, water-proof fabric made in accordance with the process defined in claim 1, in which the top coating comprises a plasticizer and a moisture-proof wax.

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