Cl. 117

Published May 11, 1943

Serial No. 333,249

ALIEN PROPERTY CUSTODIAN

PROCESS FOR WATER-REPELLING IMPREGNATION OF TEXTILES, PAPER, SKINS, AND LEATHER

Adalbert Müller, Augsburg, Germany; vested in the Alien Property Custodian

No Drawing. Application filed May 3, 1940

For rendering materials water-repellent and waterproof, there are used aqueous emulsions of paraffin, waxes, resins and soaps of polyvalent metals, together with aluminum salts. The emulsions contain protective colloids and emulsifiers, such as gelatine, glue and other albumins, or sulphonation products of aromatic and aliphatic hydrocarbons. All these compounds serve to stabilize the emulsions, i. e. to maintain the emulsified substances in the finely dispersed state. However, they are not necessary for obtaining the water-repellent effect; on the contrary, they may even impair that effect. There is also the danger of re-emulsification when cleaning the impregnated materials.

The emulsions and the aluminum salts are either used in two baths, or the aluminum salts are added to the diluted emulsions. An improvement was obtained by proposing to combine all substances in a concentrated emulsion which, after being diluted, served to prepare the treating bath.

The degree of the impregnating effect inter alia depends on the quantity of aluminum salts used. However, large quantities of aluminum salts are difficult to incorporate in commercial emulsions containing protective colloids, becausc the viscosity of the solution of the protective colloid or of the emulsion increases very much. a great force or high temperatures being required for continue mixing. On the other hand by a high temperature the mostly used protective colloids are decomposed, hardened or impaired. The stability of the obtained emulsions has suffered or the emulsions are difficult to dilute.

All these difficulties may be avoided if for rendering materials water-repellent there are used aqueous emulsions which contain no protective colloids, but, practically, only the impregnating substances, viz. aluminum salts or salts of tetravalent metals and fatty substances. The quantity of the aluminum salts used in such emulsions may vary within wide limits, according to the desired effect.

Furthermore, the emulsions have the advantage of much less changing the feel of the materials treated therewith than those containing protective colloids, at the same time producing generally equal and often even better impregnating effects. Especially the waterproofness is considerably increased according to pressure tests by Schopper's method.

The absence of a protective colloid avoids also that the treated fabrics are subjected to the risk of mould and damp stain formation.

In addition, the emulsions used according to the present invention may be readily diluted with water, whereas the commercial emulsions containing protective colloids often have to be melted before they can be diluted, as gelatine or glue, which are mostly used as protective colloids for such purposes, will jellify when becoming cool.

Finally, impregnations with emulsions according to the present invention will to a great extent often stand laundering or dry cleaning.

In preparing the emulsions it is, of course, necessary to adapt the properties of the fatty substances and of the aluminum salts to one another. The aluminum salts or the salts of tetravalent metals must be basic, i. e. they must contain less than the equivalent quantity of acid, whereas the fatty substances should have a low acid value of about 10 to 25; otherwise it is necessary to add fatty acids, their alkaline soaps, alkaline salts of soap-like, capillary-active substances or their free acids in quantities of about 10% or less of the weight of the fatty substances. This may be effected by addition to the fatty substance or also to the metal salt solution, but should in any case precede the emulsification.

Suitable fatty acids are especially such with 16 or more carbon atoms. They may also be unsaturated or they may contain oxy-groups. Examples of "soap-like, capillary-active substances" are compounds such as sulphonated oils, fats or fatty alcohols, aliphatic, aromatic or hydroaromatic sulphonic acids, condensation products of fatty acids with oxy- or amino-ethane sulphonic acid or their derivatives or homologues, or with albumin cleavage products.

By "fatty substances" there are to be understood saponifiable waxes, fats, oils and resins, as well as fatty alcohols, paraffin hydrocarbons or mineral oils or soaps of polyvalent metals. The most important substances are waxes and paraffin hydrocarbons, but the other fatty substances are also of importance, particularly as additions to these compounds.

The emulsification is effected by mixing the melted fatty substances with a warm aqueous solution of the metal salts. It is facilitated if organic solvents are also added to the fatty substances, especially in the amount of 50% to 100% of their weight. This causes at the same time an increased wetting-out effect of the treating baths prepared with the emulsions so that the impregnation may be effected more rapidly and at a lower temperature. As solvents there are preferably used chlorinated hydrocarbons, such

as carbon tetrachloric, trichlorethylene, chlorbenzol, but also many others solvents, as benzol, benzene, tetralene or diethylene-dioxide are suitable.

Various preparing methods are described in applicants copending patent application, dated 23rd February, 1940, "Aqueous emulsions and process for their production."

The emulsions according to the present invention are throughout oil-in-water-emulsions with an acid reaction, containing in excess basic salts of aluminum and tetravalent metals. The proportions of all the fatty substances and the metal salts, expressed as aluminum oxide, are such that to one part of the latter there may be about ½ to 7 parts of the fatty substances. The quantities of fatty acids, soaps, or soap-like, capillary-active substances, as far as at all present, amount to about 10% or less of the weight of the fatty substances.

The aluminum salts and the salts of tetravalent metals may both be present. Highly suitable of the latters are zirconium, thorium, uranium and titanium.

Furthermore, salts, acids or dressing agents may subsequently be added to the emulsions or to the diluted treating baths if special effects are desired.

Advantageously, the treating baths are prepared with concentrated emulsions diluted with a multiple quantity of water. Apart from lower costs of transportation and production, the concentrated emulsions also have the advantage that the proportions of the salt and fatty substances may fluctuate within considerably wider limits which also makes it possible to obtain a better adaption of the composition to the desired impregnating effect.

The impregnating methods are those which are customarily applied with aqueous emulsions. Drying may also be effected in the usual manner.

The following examples are to illustrate the process without, however, limiting its scope.

Example 1.—An emulsion prepared by intimately mixing 30 kgs. of a solution of basic aluminum formate (22% Al_2O_3 and 31% of formic acid) and 60 litres of hot water on the one hand and a melted mixture of 20 kgs. of paraffin, 10 kgs. of paraffin oil, and 3 kgs. of oleic acid, on the other hand, is diluted with warm water in the proportion of 1 to 25 and placed in a jigger or a padding machine. Gabardine cloth consisting of wool or of wool and rayon staple fibre is treated therewith by repeated passage at a temperature of 30° to 40° C, squeezed out and dried. It possesses very good water-repellent properties and also a good waterproofness.

Example 2.—4 kgs. of an emulsion containing 5,7% Al_2O_3, 6,3% of formic acid and 14,3% of hard wax (melting point 70° C, acid value 19), and prepared by intimately mixing the melted wax with a solution of basic aluminum formate, are diluted with 100 litres of warm water. On a jigger or a padding machine there is treated mantle cloth by repeated passage at 30° C and then finished as usual.

The cloth may also be impregnated, after dyeing and rinsing, on a washing machine with 5% of the above emulsion, calculated on the weight of the article. The article runs for an hour through such a bath, whereupon it is dried and finished. In this way too, there is obtained a very good water-repellent and waterproof impregnation. If for the bath there is used water of a higher temporary hardness or alkaline reacting water, a prealable addition of a small quantity of acetic of formic acid is of advantage in order to avoid the flocculation of the highly diluted emulsion. The effect may be still more increased by adding to the emulsion, for example, 2% of crystallized zirconium oxychloride or thorium nitrate and a corresponding quantity of sodium acetate in order to neutralize the mineral acid.

Example 3.—Wool yarn or mixed yarn of wool and rayon staple fibre is impregnated on the vat or in a yarn dyeing apparatus with a bath prepared by diluting 2 kgs. of an emulsion containing 25% of wax and 6% of zirconium oxide in the form of the basic acetate with 100 litres of water. The impregnation is effected at 30° to 40° C after the dyeing. The emulsion may be prepared by emulsifying a wax having an acid value of 20 with a solution of basic zirconium acetate.

Example 4.—A concentrated emulsion is prepared by emulsifying a solution of 6,5 kgs. or paraffin in 1,5 litres of carbon tetrachloride with 80 litres of an aqueous solution of basic aluminum formate (8% Al_2O_3) which also contains 0,3 kgs. of sodium salt of tetralene-sulphonic acid. A 2% to 4% dilution of this emulsion may be used for impregnating paper and is, for this purpose, sprayed on the paper sheet by means of a suitable device. Thereupon the paper sheet is dried and then possesses water-repellent properties and an increased tearing quality so that it is suitable as packing material.

The impregnation may also be effected in the beater engine by adding the emulsion to the paper pulp.

A 2% dilution of the emulsion may also be used for producing impregnated paper yarn, in which case the solution serves for moistening and damping the paper band before the cutting. The strips which are still wet are wound to the yarn in the spinning machine and subsequently dried.

Example 5.—Together with the water-repellent impregnation, textiles may also be subjected to other treating operations, for example rendering crease-resistant. For this purpose, an emulsion is used which is prepared by emulsifying 80 kgs. of hard wax (acid value 12), 25 litres of paraffin oil, and 30 litres of carbon tetrachloride or another chlorinated hydrocarbon on the one hand, and 210 kgs. of an aqueous solution of basic aluminum formate and zirconium formate (19% Al_2O_3, 2,5% ZrO_2, and 25% of formic acid) on the other hand, and subsequently stirring in of 70 litres of warm water. 6 kgs. of this emulsion, 1 kg. of urea and 2 litres of formaline are dissolved in 100 litres of water. Addition is suitably made of 300 gs. of tartaric acid. Then a rayon plush is treated by passing it twice times on the sizing machine at 40° C. Thereupon the plush is brushed, dried on the tenter at 70° C and subsequently subjected for 10 minutes to a heating of about 140° C. It possesses very good water-repellent and to a large extent crease-resistant properties.

Example 6.—The impregnating may be combined simultaneously with filling operations, such as they are necessary with canvas and tents fabrics. There is used a bath containing 8% of the emulsion according to the present invention and, furthermore, 2% of glue, 3% of dextrine and 2% of an aluminum formate solution of 12° Bé. The goods are placed into the bath in the dry state and pass twice times on the padding machine at 50°–60° C; they are subsequently dried as usual.

The emulsion used for the bath may be pre-

pared by emulsifying a mixture of paraffin, paraffin oil, copper oleate and trichlorethylene with an aqueous solution of a basic aluminum formate and the sodium salt of an alkylated naphthalene sulphonic acid, and contains 16% paraffin, 8% of paraffin oil, 1,6% of copper oleate, 24% trichlorethylene, 10% aluminumoxide and 2% of the sulphonic acid salt. The copper oleate serves as preserving agent for the glue and the dextrine.

Example 7.—Leather may be impregnated by lubricating it as usual in the fulling trough with a train-oil emulsion, then continuing the fulling for about an hour with 5% of an emulsion according to the present invention (calculated on the weight of the leather) and the required quantity of water, and then finishing as customarily. Such an emulsion contains, for example, 7,3% of Al_2O_3, 12,0% of paraffin, 4,5% of paraffin oil, 1,2% of stearic acid, and 14,1% of trichlorethylene, and is prepared by intimately mixing paraffin, paraffin oil, fatty acid, and solvent on the one hand, with an aqueous solution of basic aluminum formate, on the other hand.

Example 8.—For impregnating skins, it is advantageous to use undiluted emulsions and to spread them thereon, whereupon the skins are dried on the ironing machine, roughened up, and sheared. If required, the treatment is repeated in order to increase the effect. Finally, the skins are beaten. A suitable emulsion is, for example, one that is prepared by emulsifying 24,5 parts by weight of a mixture of paraffin and paraffin oil, to which are added 10% of oleic acid, with 72 parts by weight of a solution of basic aluminum formate, containing 7,3% Al_2O_3 and 10,1% of formic acid. There may also be added to the emulsion organic solvents for more rapidly wetting the skins, as well as glazing agents, such as are customarily in use in preparing furs, as for example adipic acid esters.

Example 9.—13 kgs. of resin are allowed to swell up for some hours in the equal quantity of perchlorethylene, dissolved by heating and mixed with 64 kgs. of melted paraffin. Thereupon the mass is intimately mixed at 50°–60° C with 120 kgs. of a basic aluminum formate solution (22% Al_2O_3, 31% of formic acid), which contains 3 kgs. of a not neutralized sulphonated oil. Finally, 52 litres of warm water are added.

A bath, containing 1% of this emulsion, may be used for impregnating acetate rayon yarn on a cheese dyeing apparatus. The yarn which is dyed and rinsed, is hydroextracted and treated with the bath on the apparatus for 30–40 minutes at 40° C, then again hydroextracted and dried. It may be used for the manufacture of umbrella silk.

The treatment on the yarn dyeing apparatus involves a further advantage of the emulsions according to the present invention in that they are much less foaming than emulsions containing protective colloids, such as glue.

ADALBERT MÜLLER.