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TEXTILE TREATMENT WITH NOVEL AQUEOUS DISPERSIONS TO ACHIEVE FLAME-RESISTANT AND WATER-REPELLANT FINISHES

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The present invention relates to novel aqueous dispersions, their application to materials and the resulting fire-resistant and water-repellent articles. These dispersions have particular application to textile materials containing cellulose fibers.

A wide variety of treatments have been proposed for imparting flame-resistant characteristics to various combustible materials and many others have been suggested for the purpose of rendering porous textile materials water repellent while still retaining a considerable degree of porosity. Although considerable advances have been made, these agents leave much to be desired, particularly in maintaining the effectiveness of finish when subjected to dry cleaning or laundering. Cloth treated with many finishes must be retreated after a single washing or dry cleaning. Further, many of the fire-retardant and water-repellent compositions are not compatible when with one another; and even if compatible, greatly reduce or destroy the effect of the other agent in a combination. Some of the prior art materials must be applied in solution in an expensive or hazardous organic solvent and some release obnoxious or highly poisonous gases while being dried or cured on a textile material. Many combination treatments are complicated by the necessity of using two or more treating baths. Accordingly, there is a continuing demand for better flame-retardant and water-repellent finishes for textiles and especially those which can be applied by means of a single aqueous dispersion to provide a finish durable to at least mild washing or dry cleaning.

An object of the invention is to provide improved compositions for imparting fire-retardant and water-repellent effects.

Another object of the invention is to provide improved durable flame-retardant water-repellent agents for textile materials of a combustible and porous nature.

A further object of the invention is to provide an improved composition for imparting a flame-retardant water-repellent finish to textile fabrics containing cellulose fibers.

Still another object of the invention is to provide an improved method for imparting a flame-resistant water-repellent finish which is durable to laundering.

A still further object of the invention is to provide flame-resistant water-repellent textile fabrics containing cellulose fibers which retain their desired characteristics after washing and dry cleaning.

Other objects and advantages of the invention will be apparent to those skilled in the art, especially upon consideration of the detailed disclosure hereinbelow.

The present invention concerns compositions of matter which comprise aqueous dispersions of a wax-like compound with a melting point above about 100° F. which contains one or more hydroxylated aliphatic acyl groups of at least 12 carbon atoms; a hydrophilic protective colloid; a dispersing agent of the group consisting of an aliphatic chain of at least 8 carbon atoms, sulfonated lignin, condensation products of polyalkylene polyamines with fatty acids containing at least 8 carbon atoms, dialkyl

alkylol alkylamide quaternary ammonium salts and water-dispersible reaction products of an aliphatic amine containing at least 12 carbon atoms with epichlorohydrin; monomethylol dicyandiamide, and a phosphoric acid. The application of these dispersions to materials containing cellulosic fibers and the resulting treated articles are also a part of the invention. Narrower aspects involve the addition of waxes, the incorporation of a long chain fatty alcohol, the employment of aminotriazine resins to improve the permanence of the finish, the preferred constituents and the proportions of the various components.

The hydrophobic component of the novel oil-in-water dispersions is, of course, in the dispersed phase. This water-insoluble wax-like material contains a compound with a melting point above 100° F. and preferably above 150° F. which has a hydroxylated saturated fatty acyl radical of at least 12 carbon atoms and preferably between 16 and 30 carbon atoms. In these substances, one or more hydroxy groups are attached to one or more carbon atoms in the alkyl chain other than the acyl or carboxylic carbon atoms. Thus this component may be a hydroxylated saturated higher fatty acid or an ester thereof with a monohydric or polyhydric alcohol including glycerol. Among the suitable compounds are hydrogenated castor oil which appears to produce the optimum results, hydrogenated ricinoleic mono- and di-glycerides, 9,10-dihydroxystearic acid, methyl, butyl, cetyl and other alkyl esters of hydrogenated ricinoleic acid, lauryl-9,10-dihydroxy stearate, and mixtures thereof.

A certain percentage of one or more hydrocarbon or ester waxes melting above about 100° F. may be blended with the hydroxylated waxy material with excellent results. In the hydrocarbon category are included various grades of paraffin, ozokerite, scale wax, microcrystalline waxes, and so forth. A few examples of suitable ester waxes of natural or synthetic origin are carnauba, japan, montan, candelilla, beeswax, and other insect waxes. Refined paraffin wax is preferred when the dispersion is intended for the treatment of light colored textiles and grades melting above about 120° F. are recommended for best results. Mineral waxes are cheaper than hydroxylated fatty acyl compounds; hence, a blend of the two reduces the cost of the textile treatment. In addition, it has been found that within proper limits a hydrocarbon wax actually enhances the water-repellent characteristics of the textile finish and somewhat improves its durability to dry cleaning and laundering. Blends of equal parts of the two waxy materials seem to appear to be the optimum. However, the hydrocarbon or ester wax may desirably constitute from about 5% up to about 80% of the weight of the hydrophobic component; beyond that, the dry cleaning durability of the textile finish suffers.

The treating agent also contains a small quantity of one or more hydrophilic protective colloids which serve to stabilize the suspension or dispersion. Polyvinyl alcohol appears to provide the best results and the lower viscosity grades are especially recommended; however, a variety of other materials can be used including carboxymethyl cellulose, gum ghatti, gum arabic, gelatin, polyacrylamide, polymethylolacrylamide, polymethacrylamide, polymethylolmethacrylamide, and the like. In general, any hydrophilic protective colloid that is free of rewetting tendencies after drying is suitable in the present invention. Based on the total weight of waxy ingredients, the protective colloids are desirably present in quantities ranging from about 0.5% to about 20% or more on a dry basis.

A higher fatty alcohol containing from about 12 up to 30 or more carbon atoms is an optional but often highly desirable component of the mixture, especially where a hydrocarbon wax is present. This alcohol is thought to act as a coupling agent which improves the

miscibility of the hydroxylated waxy material and the mineral wax. More importantly, it is a stabilizer which provides long shelf life for the wax dispersion. This obviates any necessity for preparing the wax dispersion at the place it is to be used, a feature which is often important, inasmuch as textile finishing plants, etc., are seldom equipped with good emulsification equipment, such as homogenizers. Thus it is possible to sell the ingredients for preparing the novel dispersions as three items as having a prolonged storage life, namely, monomethylol dicyandiamide, a phosphoric acid, and an aqueous dispersion of the waxy material. In addition, it appears that the fatty alcohol facilitates the preparation of wax dispersions on a large scale and it is well known that large quantities of wax emulsions are often less stable than smaller laboratory batches. Cetyl alcohol is preferred for the purpose but one or more other saturated and unsaturated fatty alcohols may be employed, including lauryl, myristyl, stearyl, palmitoleyl, cetoleyl alcohols and the like may be substituted, if desired. The recommended quantities are from about 1 to 6 parts for each 100 parts of total waxy components.

Many emulsifiers or dispersing agents are unsuitable for the present compositions by reason of incompatibility, a tendency toward rewetting after drying, etc. However, certain classes of wetting or dispersing agents have been discovered which produce good results when 1 or more are present. Among these are sulfonated or sulfated higher fatty acids, alcohols and esters containing an aliphatic chain of at least 8 but seldom over about 30 carbon atoms. Sulfated fatty alcohols are especially desirable for the purpose and this expression is used herein to include the alkali metal salts, usually sodium or potassium salts, of such materials since this is the form in which they are commonly available in the market. The many suitable materials encompass esters which term is used herein to include the esters of polyhydric alcohols, such as ethylene glycol, glycerine, etc., as well as monohydric alcohols. Moreover, the aliphatic chains of these materials may be either saturated or unsaturated prior to the sulfonation or sulfation treatment. Among those suitable are caprylyl, capryl, lauryl, myristyl, cetyl, and stearyl alcohol sulfates, sulfonated ricinoleyl alcohol, etc., and their alkali salts; methyl, butyl and other alkyl esters of the aforementioned alcohols; sulfated caprylic, lauric, palmitic, stearic, oleic, linoleic, and linolenic acids, as well as sulfonated ricinoleic acid and the corresponding mono-, di- and triglyceride derivatives. For example, good results are also obtainable with sodium glyceryl monolaurate sulfate and sulfonated castor oil. Sodium lignin sulfonate has been used with success. Also polyalkylene polyamine condensates of higher fatty acids like the products of reacting diethylene triamine, hexamethylene tetramine, tetraethylene pentamine, hexaethylene septamine, and the like with from about 10% up to a full stoichiometric proportion of a long chain fatty acid (8 to 30 carbon atoms), such as capric, lauric, and stearic acids, frequently accompanied by a lower aliphatic acid, such as formic or propionic acid in minor proportion; dialkyl alkylol alkylamide quaternary ammonium salts, as exemplified by palmitamidoethyl diethyl gammahydroxypropyl ammonium chloride, and similar compounds containing two lower alkyl groups of about 1 to 4 carbon atoms, a 1 to 4 carbon alkylol radical, a halogen atom and a radical containing a higher alkylamide of about 8 to 30 carbons combined with a 1 to 4 carbon alkyl group; and the water-dispersible reaction products of long chain aliphatic amines containing from 8 to about 22 carbon atoms, like dodecylamine and eicosylamine, with epichlorohydrin can be employed for the purpose. Suitable amine-epichlorohydrin reaction products and their preparation are disclosed in detail in Lundberg application Serial No. 393,246 filed November 19, 1953 (Patent No. 2,753,372) and these may be neutralized with acetic or another lower carboxylic acid for greater stability. The amine-epichlorohydrin molar ratios may range from about 1:2 to 2:1 and this particular group of compounds is preferred for use under acid conditions, as for instance, where the resinous component is in the acid colloid form. The quantity of dispersing agent should be ample to disperse the hydrophobic component but not so great as to produce any rewetting effect after curing which would seriously impair the water repellency of the finish. Based on the total weight of waxy materials, the dispersing agents described may be present in amounts ranging from about 0.5 to 15%, and for most purposes, between about 1 and about 4% is recommended.

To make the stable dispersion mentioned above of the wax-like substances, the hydroxylated waxy material may be melted and thoroughly blended with any hydrocarbon wax or fatty alcohol which may be added at a temperature of 235° F. for example. Meanwhile, the protective colloid may be stirred into about 70 parts by weight of water with heating until it is dissolved; then the dispersing agent may be added and the aqueous phase heated to about 180–195° F. Next about 30 parts of the molten waxy mixture may be combined with the aqueous phase with vigorous agitation followed by passing the crude emulsion through a homogenizer at 3,000 pounds per square inch. After this, the suspension of wax-like material is cooled rapidly to a temperature below 120° F.

Another essential ingredient of the novel compositions is monomethylol dicyandiamide in combination with a phosphoric acid which is desirably orthophosphoric acid but may also be metaphosphoric or pyrophosphoric acid. Monomethylol dicyandiamide is known and appears to have no equivalent for the present purposes. It is prepared by reacting formaldehyde with dicyandiamide and for the present purposes, molar ratios between about 0.7 and about 1.5 mols of formaldehyde per mole of the nitrogen compound are contemplated inasmuch as the term monomethylol is used somewhat loosely herein and because condensates of this type need not be pure compounds and there is an equilibrium in solution between the combined and free formaldehyde present. The comparatively insoluble condensate is dissolved in an aqueous phosphoric acid with gentle heating which must be carefully controlled and followed by cooling to avoid any substantial polymerization of the amide compound prior to being cured on a cellulosic material in the presence of the other constituents of the novel formulations. Although it has been established with certainty, it is believed that the monomethylol dicyandiamide forms a complex with the phosphoric acid. This agent imparts not only a flame-resistant finish on cellulosic materials, surprisingly enough even in combination with the above-described fatty and waxy materials which are quite combustible per se, but also serves to bind the wax-like compounds to the treated cellulose. Thus it renders the waxy materials fairly durable against washing off of the treated material in mild laundering as is apparent from the spray ratings hereinbelow whereas in its absence, the waxy matter is rapidly removed from a treated fabric by a single mild washing with soap. Suitable amounts of monomethylol dicyandiamide may range from about 200 to about 1,200%, and preferably between about 400 and 900%, based on the weight of wax-like solids. Calculated as H_3PO_4, the phosphoric acid may be between about 50 and 500% on the same basis. For optimum results the phosphoric acid desirably amounts to between about 15 and about 60% of the weight of monomethylol dicyandiamide.

An optional but highly desirable component of the present compositions is an aminotriazine resin which produces durability to dry cleaning as well as greatly enhancing the durability of the finish to mild laundering operations. Any aminotriazinealdehyde condensate or mixture of such compounds may be utilized which is capable of forming either a true solution in water or a

colloidal solution exhibiting the characteristic Tyndall haze. These condensates may be either etherified or alkylated with a suitable alcohol like methanol or simple unetherified condensates of an aldehyde and an aminotriazine. A wide variety of the unalkylated and alkylated aminotriazine-aldehyde condensates and their preparation are disclosed in Widmer et al. Patents Nos. 2,197,357 and 2,191,362; and hence need not be reiterated here. The triamino- and diaminotriazine derivatives are most readily available, especially melamine and the guanamines such as acetoguanamine and propioguanamine. Of these, the methyl ethers of methylol melamines are greatly preferred as providing outstanding results; and such ethers may contain from 1 to 6 mols of combined formaldehyde and 1 to 6 mols of combined methanol per mol of melamine. The combined methanol content does, of course, not exceed the combined formaldehyde content on a molar basis. For each 100 parts total of the waxy materials described hereinafter, between about 30 and about 600 parts of the aminotriazine resin may be employed and the preferred amount is between about 50 and about 200 parts. The aminotriazine-aldehyde condensate may be employed either in essentially monomeric form or in the partially polymerized colloidal state in acid solution as described in Patents Nos. 2,345,543 and 2,609,307. Textile finishing resins of the urea-formaldehyde type are compatible with but not equivalents of the aminotriazine resins in the novel compositions because the finish imparted thereby to textiles has no permanence or durability whatsoever to dry cleaning and laundering.

Optionally, one or more additional textile finishing agents derived from urea may be employed along with the aminotriazine resin for the purpose of reducing the yellowing which occurs to some extent due to the retention of chlorine by a melamine resin finish on a textile fabric. This is accomplished without any improvement or decrease in the durability or spray rating of textile fabrics finished according to the present invention. Among the suitable agents for decreasing yellowing are essentially monomeric methylated methylol ureas and their water-soluble lower polymers, and the unalkylated and alkylated formaldehyde condensates of alkylene ureas like dimethylol ethylene urea, dimethylol propylene urea, dimethylol trimethylene urea, and their methyl ethers. These substances and their preparation are well understood and they may contain from 1 to 4 mols of combined formaldehyde per mol of urea or urea derivative as well as a combined methanol content ranging from about 20% up to but not exceeding the formaldehyde content on a molar basis. The water-soluble lower polymers of methylated methylol urea may be easily obtained by refluxing with heating about 2.5 mols of paraformaldehyde per mol of urea in a methanol medium for several hours at an alkaline pH, cooling, adding methanol in stoichiometric excess, adjusting the mixture to a moderately acid pH, refluxing for a short period, then stopping the reaction by cooling and adjusting the pH to a moderately alkaline value. These substances may be employed in quantities ranging up to but not exceeding the weight of aminotriazine resin, and it is generally recommended that at least about 6.7 and preferably about 30 to about 100% (based on the weight of aminotriazine resin) be used when chlorine retention is a significant problem. It is seldom, if ever, desirable to have more than a total of 600 parts of urea derivative and aminotriazine-aldehyde condensate in a dispersion containing 100 parts of waxy material or materials.

The novel compositions may be used in a variety of applications in the textile, leather, paper, and pulp board carton fields. They are especially intended for rendering porous combustible materials containing a substantial amount of cellulose fibers both water-repellent and fire-resistant. This is accomplished by impregnating the cellulose material with the aqueous dispersion followed by drying and curing to convert the finish to the substantially water-insoluble state. This curing is accomplished in about 2 to 15 minutes at elevated temperatures of preferably about 200 to 350° F. or even higher if smoking due to vaporizing a portion of the waxy matter from the impregnated material during curing is not objectionable. In compositions containing a colloidal partially polymerized aminotriazine resin, heating is not required to cure the finish but is usually preferred in commercial operations in order to expedite the drying of the impregnated material.

The present compositions are particularly adaptable to the finishing of textile fabrics including woven and non-woven, knitted and felted materials containing cellulose fibers like cotton, linen, flax, viscose and cuprammonium rayons, ramie, jute, and blends thereof. Such treatments are also applicable to blends of any of the aforesaid fibers with any other of the great variety of known textile fibers, but it should be borne in mind that only cellulose fibers are rendered flame retardant by the present treatment; hence, the treatment is effective from a standpoint of flame resistance only to an extent commensurate with the proportion of total fibers in the fabric.

The dispersions may be applied to either fibers or fabrics by an suitable means such as padding, spraying, immersion, roll coating, etc. A typical treatment involves passing a fabric through a dispersion containing from about 8 to about 65% solids, and preferably between about 15 and about 50%, with the squeeze rolls adjusted to provide a dry pick up of between about 11 and about 60% solids, about 15 to about 50% being usually recommended, based on the weight of dry cellulose fibers; followed by curing as described above. For good durability of the finish, the dry pick up should amount to at least about 1% of the aminotriazine resin, at least about 8% of monomethylol dicyandiamide and at least about 2% of the wax-like component. However, it is also contemplated that the invention may find utility in connection with a lighter treatment of children's dolls and other toys and accessories. Such a finish would not possess the durability desired herein for most purposes, but nevertheless would be suitable as a nonpermanent finish. It is contemplated that the light treatment would still be desirable for reducing the flammability of highly combustible cottons having a long nap without changing the hand of the material an unacceptable degree. The amount of free phosphoric acid in the dispersions of the present invention will generally be adequate to catalyze the curing of the finish in a short enough time for commercial purposes. However, the addition of other conventional catalysts for aminotriazine and urea derivative resins of the type disclosed is also contemplated especially where the quantity of such resins is large and the amount of phosphoric acid small. These accelerators may be used in amounts of 0.5% or more based on the weight of resin, and suitable examples thereof include oxalic, tartaric or other mild organic acid; diammonium hydrogen phosphates and other ammonium salts; acid salts of organic amines such as the hydrochloride salts of isopropanolamine and butanolamine; magnesium chloride and the like.

Textile fabrics treated according to the invention may be employed as tarpaulins, tents, boat covers, awnings, stage scenery, upholstery fabrics, slip covers, draperies, batting, insulation, padding, rope, string, twine, and wearing apparel for welders, foundrymen, military personnel and the like, as well as fabrics for covering the wings and fuselages of airplanes. In the textile industry, any material of appreciable cellulose fiber content (e.g., 5% or more) including raw fibers, carded stock, rovings, threads, yarns and felts may be treated as well as the knitted, woven and unwoven fabrics which appear to provide the largest field of utility.

For a better understanding of the nature and objects of this invention, reference should be had to the following illustrative examples in which all proportions are

stated in terms of weight unless otherwise indicated therein. In addition, all testing of fabrics is carried out by standard methods adopted by the American Association of Textile Chemists and Colorists (AATCC) unless otherwise stated.

Following the procedure outlined above, a series of aqueous wax dispersions is prepared from the following constituents. A water-dispersible product of the reaction of 1 mol of octadecylamine with 2 mols of epichlorohydrin is designated in the table as OAE product.

	Wax Dispersions				
	A	B	C	D	E
Refined paraffin wax (133-135° F., M.P.)	14.10	14.10	9.3	18.7	14.0
Hydrogenated castor oil	14.10	14.10	18.7	9.3	14.0
Polyvinyl alcohol	1.25	1.25	0.3	0.3	3.0
Sodium lauryl sulfate	0.50		0.5	0.5	0.5
OAE product		0.50			
Cetyl alcohol	0.90	0.80			
H_3PO_4		0.10			
Water	69.15	69.15	71.2	71.2	68.5

These are finely divided suspensions of the waxy materials in water which are stable indefinitely. In the textile finishing operations described hereinbelow, they are employed in more dilute form in combination with monomethylol dicyandiamide, phosphoric acid and optionally, also with an aminotriazine resin or suitable mixture containing such a resin.

In preparing a suitable pad bath, the monomethylol dicyandiamide may be slurried in about one-half the total quantity of water and then the phosphoric acid added. Upon heating the aqueous mixture to about 130° F., a clear solution is formed which is desirably cooled to about 80° F. in order to forestall any exothermic reactions. A concentrated wax dispersion as exemplified in the above table is diluted with the balance of the water. Then the diluted wax dispersion is stirred into the solution of dicyandiamide derivative. If an aminotriazine-aldehyde resin is employed alone or in admixture with other resins, the water may be divided into three approximately equal proportions and one of the proportions used to dissolve this resin-forming material for addition to the solution of the dicyandiamide derivative either before or simultaneously with the wax suspension.

Examples 1–6

Samples of 5.5 ounce white mercerized cotton poplin are padded through pad baths of the composition set forth in the table below using 2 dips and 2 nips with the squeeze rolls adjusted for a wet pick up of about 85% based on the weight of dry untreated poplin. The impregnated fabrics are dried and cured in a single operation requiring 6 minutes in a ventilated oven maintained at 290° F. After cooling, the cured fabrics are subjected to two 5-minute rinses using water at 100° F. in a reversing type laundry wash wheel to remove any loose and water-soluble materials in the finish followed by drying relaxed for 10 minutes at 220° F. in a circulating hot air oven.

The treated fabrics are tested according to the standard procedures of the American Association of Textile Chemists and Colorists (AATCC) and the flame tests are performed on fabrics hanging vertically. The initial tests are made after the fabrics are processed, rinsed, and dried as indicated above and the other tests are made after being subjected to one or more laundering or dry cleaning operations as listed in the table below. Each washing consists of washing in a 1% soap solution at 100° F. for 45 minutes then rinsing for 5 minutes in 100° F. water and drying under no tension for 10 minutes at 220° F. in an oven. The dry cleaning is carried out in a hydrocarbon solvent known as Varsol II for 60 minutes followed by a similar drying operation. The tensile strength ratios are determined by the Suter method and represent the total tensile strength (sum of warp tensile and fill tensile strengths) of the treated sample divided by the total tensile strength of the same untreated poplin. In Examples 1, 2 and 6, tensile determinations are made after the initial rinsing while those in Examples 3 and 4 are made after four washes and in Example 5 after 5 hours of washing.

In the table MD represents monomethylol dicyandiamide, MMM stands for methylated trimethylol melamine—67% methylated and prepared similarly to the procedure disclosed in Example 2 of British Patent No. 556,347, and wax A and wax B denote the corresponding wax dispersions in the table above. The proportions of the ingredients of the aqueous baths are set forth as the percentages by weight of the constituents on an anhydrous basis.

Example	Bath Composition	Flame Tests—Char Height, Inches					Spray Ratings						Tensile Strength Ratio—Warp+Fill Control
		Initial	After Washes 1	After Washes 3	After Washes 5	5+Dry Cleaning	Initial	After Washes 1	After Washes 3	After Washes 5	5+Dry Cleaning	Dry Cleaning	
1	30 MD, 10 H_3PO_4, 5 Wax A	3.1	3.2				90	80+				0	132/144
2	25 MD, 10 H_3PO_4, 5 Wax A, 5 MMM	2.8	3.5				80+	80				70−	122/144
3	30 MD, 10 H_3PO_4, 5 Wax B	2.7	3.4	6.1	Burned		90+	90	70				120/147
4	30 MD, 10 H_3PO_4, 7.5 Wax B	2.8	3.6	5.5	Burned		70+	70+	70+				123/147
5	30 MD, 10 H_3PO_4, 10 Wax B	2.7	3.6	6.0	Burned		80−	80	80				121/147
6	25 MD, 10 H_3PO_4, 5 Wax B, 5 MMM	2.7	3.0	3.8	4.4	4.7	90+	90	80	80	80−		122/144

From the above data, it is apparent that the finishes of the present invention achieve a high degree of flame resistance combined with good water-repellent qualities with only a minor and acceptable impairment of the tensile strength of the fabric. It is further apparent that the incorporation of an aminotriazine resin in the treating baths provides a finish with good durability to dry cleaning and a considerably greater durability to washing than is obtainable without the resin.

A small section of a cellulose wallboard was soaked for 1 minute in the bath of Example 6; then dried and cured for 6 minutes at 290° F. The surface of the treated board was considerably harder, quite flame resistant and moderately water repellent.

Examples 7–18

A series of pad baths is prepared in the manner indicated in Example 1 and a viscose rayon upholstery fabric of heavy weight, a cuprammonium rayon gabardine, and an 80 x 80 cotton percale are impregnated in each of the pad baths and processed according to the procedure described above unless otherwise indicated. All samples are found to have flame-retardant and water-repellent finishes of good durability to mild laundering and fair resistance to dry cleaning.

Example 7:

Monomethylol dicyandiamide	20
Orthophosphoric acid	7
Wax dispersion C—solids basis	10
Dimethylol melamine	10
Water	53

Example 8:

Monomethylol dicyandiamide	30
Orthophosphoric acid	10
Wax dispersion D—solids basis	5
Dimethylol beta-cyanopropioguanamine	10
Water	45

Example 9:

Monomethylol dicyandiamide	25
Orthophosphoric acid	5
Wax dispersion E—solids basis	5
Colloidal methylated trimethylol melamine	5
Water	60

The partially polymerized colloidal melamine resin above is prepared as a 20% aqueous solution exhibiting the characteristic blue Tyndall haze of cationic water-dispersible melamine resin aged in acetic acid as described in Patent No. 2,609,307. The reaction product of this mixture is converted to the water-insoluble state by drying for 15 minutes at 225° F.

Example 10:

Monomethylol dicyandiamide	25.00
Metaphosphoric acid	10.00
Methylated pentamethylol melamine—50% methylated	7.50
Hydrogenated castor oil	2.50
Candelilla wax	2.50
Polyvinyl alcohol	0.22
Cetyl alcohol	0.16
Sodium lauryl sulfate	0.09
Water	52.03

Example 11:

Monomethylol dicyandiamide	25.00
Orthophosphoric acid	10.00
Methylated pentamethylol melamine—50% methylated	4.20
Partially polymerized methylated dimethylol urea—80% methylated	2.10
Hydrogenated castor oil	3.15
Refined paraffin wax	3.15
Polyvinyl alcohol	0.28
Cetyl alcohol	0.20
Sulfonated castor oil	0.11
Water	51.81

Example 12:

Monomethylol dicyandiamide	25.00
Orthophosphoric acid	10.00
Methylated trimethylol melamine	6.00
Dimethylol ethylene urea	3.00
Hydrogenated castor oil	2.50
Refined paraffin wax	2.50
Gum ghatti	0.27
Sodium ligninsulfonate	0.16
Water	50.57

Example 13:

Monomethylol dicyandiamide	12.00
Pyrophosphoric acid	4.00
Methylated trimethylol melamine	2.50
Methylated dimethylol trimethylene urea	1.25
Hydrogenated castor oil	5.00
Polyacrylamide	0.22
Sodium ligninsulfonate	0.16
Water	74.87

Example 14:

Monomethylol dicyandiamide	30.00
Orthophosphoric acid	10.00
Methylated trimethylol melamine	6.00
Monomeric methylated dimethylol urea	3.00
Hydrogenated castor oil	1.50
Montan wax	1.50
Carboxymethyl cellulose	0.15
Sodium ligninsulfonate	0.10
Water	47.75

Example 15:

Monomethylol dicyandiamide	25.00
Orthophosphoric acid	10.00
Methylated pentamethylol melamine—50% methylated	10.00
Hydrogenated castor oil	2.50
Beeswax	2.50
Polyvinyl alcohol	0.22
Cetyl alcohol	0.16
Stearamidopropyl dimethyl beta-hydroxyethyl ammonium chloride	0.09
Water	49.53

Example 16:

Monomethylol dicyandiamide	25.00
Orthophosphoric acid	5.00
Dimethylol melamine	10.00
Hydrogenated castor oil	2.50
Carnauba wax	2.50
Polyvinyl alcohol	0.23
Reaction product of 2.9 mols of technical stearic acid per mol of tetraethylenepentamine plus 1.5% acetic acid	0.56
Water	54.21

Example 17:

Monomethylol dicyandiamide	15.00
Orthophosphoric acid	7.50
Methylated trimethylol melamine	5.00
9,10-dihydroxy stearic acid	2.50
Refined paraffin wax	2.50
Polyvinyl alcohol	0.22
Cetyl alcohol	0.16
Sodium lauryl sulfate	0.09
Water	67.03

Example 18:

Monomethylol dicyandiamide	25.00
Orthophosphoric acid	10.00
Methylated trimethylol melamine	5.00
Hydrogenated castor oil	2.50
Refined paraffin wax	2.50
Polyvinyl alcohol	0.22
Cetyl alcohol	0.14
Acetic acid neutralized reaction product of 1 mol of octadecylamine with 1.4 mols of epichlorohydrin	0.09
Water	54.55

From the above description, it is apparent that many benefits are obtained by the present invention in providing a simple one-bath treatment to provide a durable finish which is not only flame resistant but also water repellent. This is accomplished without the foaming and odor difficulties which plague certain prior art treat-

ments, and the ingredients of the present composition are of lower cost than many used heretofore.

An important feature of the invention is that treated cellulose textiles lose only an insignificant part of their original tensile strength whereas individual treatments with textile resins, water-repellent agents and especially flame-retardant agents of the prior art have frequently produced considerable losses in tensile strength, often so great as to restrict the utility of the particular agent in the textile finishing field.

My concurrently filed application Serial No. 586,357 relates to treatments employing some but not all of the components described herein, which treatments produce water-repellent effects with no increase in flame resistance.

While there are disclosed herein only a limited number of embodiments of the composition, process and product of the invention, it is possible to produce still other embodiments without departing from the inventive concept set forth, and it is desired, therefore, that only such limitations be imposed upon the appended claims as are stated therein or required by the prior art.

I claim:

1. A composition of matter which comprises an aqueous dispersion of (1) 100 parts of a hydrophobic component selected from the group consisting of a wax-like compound melting above 100° F. containing an hydroxylated aliphatic acyl radical of between 12 and about 30 carbon atoms and a composition comprising such a wax-like compound melting above 100° F. and a wax melting above 100° F., said wax in said compositions being present in an amount not exceeding about four times the weight of said wax-like compound; (2) between about 0.5 and about 20 parts of a hydrophilic protective colloid free from rewetting tendencies after drying; (3) between about 0.5 and about 15 parts of an emulsifying agent of the group consisting of sulfonated and sulfated fatty acids, alcohols and esters containing an aliphatic chain of between 8 and about 30 carbon atoms, sulfonated lignin, condensation products of polyalkylene polyamines with fatty acids containing between 8 and about 30 carbon atoms, dialkyl alkylol alkylamide quaternary ammonium salts containing two lower alkyl groups of from about 1 to 4 carbon atoms, a 1 to 4 carbon alkylol radical, a halogen radical containing a higher alkylamide of about 8 to 30 carbon atoms combined with a 1 to 4 carbon atoms alkyl group, and water-dispersible reaction products of an aliphatic amine containing from about 8 to about 22 carbon atoms with epichlorohydrin; (4) between about 200 to about 1200 parts of monomethylol dicyandiamide and 50 to 500 parts of a phosphoric acid.

2. A composition according to claim 1 containing from between about 1 and about 6 parts of an aliphatic alcohol having between 12 and about 30 carbon atoms.

3. A composition according to claim 1 containing between about 30 and about 600 parts of an aminotriazine-aldehyde resin selected from the group consisting of water-soluble aminotriazine-aldehyde resin and colloidal aminotriazine-aldehyde resins.

4. A composition of matter which comprises a stable aqueous dispersion of (1) between about 30 and about 600 parts by weight of a water-soluble methylated methylol melamine; (2) 100 parts of wax-like substances comprising paraffin wax melting above 100° F. and hydrogenated castor oil melting above 100° F. in a weight ratio not exceeding about 4:1, said paraffin wax to said hydrogenated castor oil respectively; (3) between about 0.5 and about 20 parts of a hydrophilic protective colloid free from rewetting tendencies after drying; (4) between about 1 and about 6 parts of an aliphatic alcohol containing between about 12 and about 30 carbon atoms; (5) between about 1 and about 4 parts of a sulfated alcohol containing between about 8 and about 30 carbon atoms; (6) between about 200 and about 1200 parts of monomethylol dicyandiamide and (7) between about 50 and 500 parts of a phosphoric acid.

5. A composition of matter which comprises a stable aqueous dispersion of (1) between about 32 and about 600 parts by weight of a mixture comprising a minor portion of a substance of the group consisting of water-soluble methylated methylol urea, methylol alkylene urea, and methylated methylol ureas together with a major proportion amounting to at least 30 parts of a methylated methylol melamine selected from the group consisting of water-soluble methylated methylol melamines and colloidal methylated methylol melamines; (2) 100 parts of a hydrophobic component selected from the group consisting of a wax-like compound melting above 100° F. containing a hydroxylated aliphatic acyl radical of between 12 and about 30 carbon atoms and a composition comprising such a wax-like compound and a wax melting above 100° F. said wax in such compositions being present in an amount not exceeding about four times the weight of said wax-like compound; (3) between about 0.5 and about 20 parts of a hydrophilic protective colloid free from rewetting tendencies after drying; (4) between about 1 and about 6 parts of an aliphatic alcohol containing from between 12 and about 30 carbon atoms; (5) between about 1 and about 4 parts of a sulfated fatty alcohol containing between 8 and about 30 carbon atoms; (6) between about 200 and about 1200 parts of monomethylol dicyandiamide and (7) between about 50 and 500 parts of a phosphoric acid.

6. A process which comprises treating material containing cellulose fibers with a composition according to claim 1 and heating the treated material to impart a fire-retardant, water-repellent finish.

7. A process which comprises treating a textile material containing cellulose fibers with a composition according to claim 4 in sufficient amount to deposit thereon quantities of at least about 1% of the methylated methylol melamine, 2% of said wax-like substance and 8% of monomethylol dicyandiamide based on the dry weight of cellulose fibers and heating the treated material to impart a fire-retardant, water-repellent finish which is durable to laundering.

8. An article which comprises a material containing cellulose fibers and having as a flame-retardant, water-repellent finish the heat cured product of a composition according to claim 1.

9. An article which comprises a textile material containing cellulose fibers and having as a fire-retardant, water-repellent finish the heat cured product of a composition according to claim 4 containing at least about 1% of methylated methylol melamine, 2% of said wax-like substance and 8% of monomethylol dicyandiamide based on the dry weight of cellulose fibers.

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UNITED STATES PATENT OFFICE
CERTIFICATION OF CORRECTION

Patent No. 2,971,931 February 14, 1961

Nathaniel J. Glade

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, line 48, after "has" insert -- not --.

Signed and sealed this 1st day of August 1961.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents