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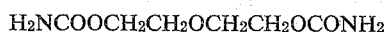
TREATED TEXTILE MATERIAL AND METHOD OF PRODUCING THE SAME

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No Drawing. Application December 17, 1954, Serial No. 476,068

23 Claims. (Cl. 117—138.8)

This invention concerns the treatment of textile materials, such as fibers, filaments, yarns or fabrics, with aqueous dispersions or solutions of certain resin-forming reaction products of the dicarbamate (or biscarbamate) of diethylene glycol, having the formula



with formaldehyde and either with or without methanol. This treatment may be effected for various purposes for imparting a variety of properties to the textile materials as will appear hereinafter. One particularly important aspect of the invention is the treatment of plastic textile materials, especially those comprising thermoplastic fibers or yarns, to impart improved qualities in respect to stiffness, appearance, drape and feel.

The primary object of the present invention is to provide novel textile materials. An ancillary object is to provide textile fabrics which are improved in respect to various properties such as stiffness and hand and particularly in respect to resistance to change in such properties on washing under conventional conditions. Another object is to provide processes for treating textile materials to impart improved properties thereto. Other objects and advantages will be apparent from the description thereof hereinafter.

In general, textile materials are improved in accordance with the present invention by the application of certain novel resin-forming reaction products of formaldehyde with the dicarbamate of diethylene glycol and subsequently drying and curing the reaction product to convert it to an insoluble condition by means of heat and catalyst. The purposes and the properties obtained may be various and depend on various factors, such as the amount of the resin added to a fabric, whether reaction occurs between the resin and fabric, and the manner or extent of distribution on the textile material as well as others as will be explained in more detail hereinafter.

The composition applied to the textile material in accordance with the invention is a special film-forming condensate of the dicarbamate of diethylene glycol with formaldehyde and with or without methanol in an aqueous solution or dispersion. These special condensates, which are hereinafter generally referred to simply as dicarbamate condensates, are obtainable only under certain reaction conditions and are the subject matter of co-pending application Serial No. 437,268, filed June 16, 1954, and now Patent No. 2,774,746. The required conditions include the use of a narrow pH range of 2.3 to 3.5 during the reaction of the formaldehyde with the dicarbamate in aqueous medium. The concentration of the formaldehyde and dicarbamate in the initial reaction medium should be between 50% and 85% by weight of the total weight of the reaction medium. The molar ratio between the formaldehyde and the dicarbamate in the reaction medium at the start of the reaction must be between 2:1 and 3.5:1. The preferred mole ratio of formaldehyde to dicarbamate is between 2.5 and 3 moles of formaldehyde to one of the carbamate. The temperature may vary from 70° C. to the boiling point of the reaction medium which may be as high as 105° to 110° C. at normal atmospheric pressure, or higher when the

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reaction is carried out under pressures above normal atmospheric pressure or in the presence of other solvents which are inert to the reaction, for example, dimethylformamide.

Under the conditions just outlined, the reaction is carried out until the condensation product has a viscosity, as determined in a solution in water of a 60% "solids" concentration at 25° C., of at least 2 poises but not over 25 poises. Preferably the condensate when tested under these conditions has a viscosity between 6 and 20 poises. The "solids" referred to is determined by diluting a sample of the aqueous condensate with an equal weight of water, weighing the residue of a portion (0.6 to 0.8 gram) after heating 90 minutes at 125° C. to determine the percentage of solids in said portion and multiplying by a factor of 2 to compensate for the dilution. The time required to attain the required viscosity depends upon the several conditions of pH, concentration, temperature and ratio of formaldehyde to dicarbamate within the ranges set out above. Depending upon the several conditions just stated, the desired molecular weight of the condensation may be attained within a period of from ten minutes to eight hours or more reaction time.

The condensation may also take place in the presence of methyl alcohol which is believed to combine with the reactants to form methylated derivatives. The proportion of methyl alcohol when used may be from 1 to 2.5 moles per mole of dicarbamate and is preferably from 1.5 to 2 moles per mole of dicarbamate. When the condensation is effected in the presence of methyl alcohol, it is preferred to carry out the reaction in the lower portion of the pH range, that is from 2.3 to about 2.8. When the condensation is effected in water in the absence of methyl alcohol, the preferred pH is within the range of 2.5 to 3. Ethanol or high alcohols cannot be used since condensates with them have practically no water-compatibility or are completely water-insoluble, have poor film-forming quality unless they are dissolved in organic solvents, and washing or cleaning of equipment used for making or applying them would require the use of organic solvents.

The temperature of the reaction medium is preferably that which corresponds to the reflux or boiling temperature thereof which is generally lower when methyl alcohol is present than when the reaction medium is simply water. The preferred temperature when water alone is used as the solvent medium is from 90° to 100° C., but as pointed out hereinabove, higher temperatures may be employed when superatmospheric pressure is employed, whether the reaction medium contains methyl alcohol or not.

The concentration in the reaction medium when methyl alcohol is present may vary from 50% to 85%. When no methyl alcohol is present, the concentration of formaldehyde and dicarbamate within the aqueous medium is from 50% to 75% and is preferably between 60% and 70%.

After the reaction has been effected to the viscosity within the range specified hereinabove, the reaction medium or mass is cooled to 30° C. or lower. Preferably the cooled mass is then neutralized by the addition of a suitable alkaline material such as a soluble oxide, hydroxide, or carbonate, and preferably with the hydroxide of ammonium or an alkali metal such as sodium or potassium. After neutralization with sodium or potassium hydroxide, the reaction mass still shows infinite water tolerance. When neutralized with ammonium hydroxide, however, those reaction masses, in which the higher viscosity is attained within the range specified, sometimes have less than infinite water tolerance, but in all cases the composition will stand a considerable amount of water. Generally, 10 grams of a reaction mass containing 50% resin solids and neutralized with ammonium

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hydroxide can be diluted with from 30 to 70 cc. of water at normal room temperature without forming distinct layers. However, even in those cases where neutralization reduces the water-compatibility or tolerance, the material recovers infinite tolerance to water upon re-acidification.

The reaction between the dicarbamate and formaldehyde may be carried out generally as follows: The dicarbamate is introduced into aqueous 37% formaldehyde producing various concentrations depending upon the ratio of formaldehyde to the carbamate, the initial concentration being about 64% when the mole ratio of formaldehyde to dicarbamate is 3.0:1. The dispersion on heating becomes a clear solution and it is preferred to strip water by distillation to bring the concentration to about 60% reaction product at which time sulfuric acid or other catalysts are added to reduce the pH to a value from 2.3 to 3.5, preferably from 2.3 to 2.8 if methanol is present or from 2.5 to 3.0 if methanol is absent. At this point, the viscosity of the reaction medium is generally about $\frac{1}{2}$ to 1 poise (at 65% concentration). It should be understood that the acid may be added before stripping, but this is not preferred. The reaction mass is heated to condense the formaldehyde dicarbamate reaction product to a viscosity of at least 2 poises at 60% concentration in water at 25° C. The reaction mass at this time has infinite water tolerance and retains it on partial or complete neutralization with sodium hydroxide or potassium hydroxide to a pH of 5 to 7.5.

The resulting reaction mass may have a concentration of the condensate of 50% to 70% or more and it may be used directly for coating or film-forming purposes. When so used reasonably promptly, neutralization may be omitted. Thus the unneutralized condensate formed without methanol can be used within about 12 to 24 hours whereas those formed with methanol can be used within one week to several months depending on the degree of condensation without encountering troublesome gelling.

If reasonably prompt use is not desired, the reaction mass should be treated with an alkaline material to raise the pH to a value of 5 to 7, preferably 6.0 to 6.5. It is preferred to avoid raising the pH above 6.5 because of the tendency for too much salt to be formed so that the salt tends to crystallize out of the reaction mass on standing. The partially or completely neutralized reaction mass may be stored indefinitely without dilution and transported to the point of application where an acid catalyst may be introduced just before it is applied for the formation of coatings or films on the textile materials. A strong acid catalyst such as sulfuric acid, toluenesulfonic acids, ethanesulfonic acid, ammonium phosphate, ammonium thiocyanate, hydrochloric or other acid salts of a hydroxy aliphatic amine including 2-methyl-2-amino-1-propanol, 2-methyl-2-amino-1,3-propanediol, tris(hydroxymethyl)-aminomethane, 2-phenyl-2-amino-1-propanol, 2-methyl-2-amino-1-pentanol, 2-aminobutanol, triethanolamine, 2-amino-2-ethyl-1-butanol, ammonium chloride, pyridine hydrochloride, and benzyldimethylamine oxalate may be used. The amine salts are watersoluble latent catalysts substantially neutral at ordinary temperature which dissociate into volatile components one of which is acidic at the elevated temperatures used for baking and curing, so that the catalyst after exerting its accelerating effect is automatically discharged from the mass during the heating stage. The amount of catalyst used may be from 0.2% to 6% or more by weight based on the total weight of the dispersion, and is preferably about $\frac{1}{2}$ % to 1%.

Because of the water-compatibility of the reaction mass, it may be diluted to any desired extent before application merely by the addition of water.

Besides the introduction of an acid catalyst to accelerate the insolubilization of coatings, films or other products obtained from the condensate, various materials may be added for other purposes. For example, surface-active

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agents of anionic, non-ionic, or cationic type may be introduced to improve the flow and make the coating or film more uniform especially when the compositions are used for making continuous coatings on textile materials.

Examples of non-ionic surface-active agents include polyethylene oxide derivatives of phenol, of alkyl phenols having 6 to 18 carbon atoms in the alkyl substituent, of higher fatty acids having from 8 to 18 carbon atoms, of higher fatty alcohols or mercaptans having from 8 to 18 carbon atoms, of long chain aliphatic amides having from 8 to 18 carbon atoms, of long chain fatty amines having from 8 to 18 carbon atoms, such derivatives containing from 10 to 50 or more oxyethylene units per molecule. Besides the non-ionic surface-active agents just mentioned, anionic types such as lauryl alcohol sulfate, sodium dioctyl sulfosuccinate, the sodium salt of isopropyl naphthalenesulfonic acid, or cationic agents such as lauryl pyridinium chloride may be employed. The proportion of surface-active agent may be from 0.01 to 3% of the weight of the condensate therein.

If desired, a volatile non-aqueous solvent may be added. Preferably, any such additional solvent is water-soluble, such as ethanol, propanol, isopropanol, and t-butanol.

The coatings may be clear and colorless when formed without the addition of dyes or pigments, or they may be colored by the introduction of pigments or dyes, such as titanium oxide, lithopone, carbon black, ultramarine blue or the like.

After the films or coatings are formed from the aqueous condensate containing the catalysts with or without other materials, they are dried and hardened by heating at temperatures of about 180° F. to 350° F. or higher.

The aqueous compositions comprising the resin-forming dicarbamate condensate have the advantage during their application of not requiring special precautions to avoid the danger of fire or toxic effects on the operators. They require no equipment for solvent recovery and water is all that is needed to wash off residue left on the equipment. They are also dilutable to lower concentrations so that they may be shipped as a highly concentrated aqueous composition and then diluted, especially for such textile applications as sizing, dressing and/or stiffening various fabrics, such as nylon, rayon, Orlon, Dacron, and the like. Those compositions which are derived from reaction media comprising methanol have the additional advantages of being substantially free from odor and producing somewhat greater flexibility in the final water-insolubilizing film or coating.

Depending upon the results desired, the aqueous dispersions of the resin-forming dicarbamate condensates may be applied at a concentration of 1% to 90% of the resin-forming condensate in the dispersion. Generally, the pick-up on the textile material may be between 25% and 50% and most commonly about 30% of the concentration in the aqueous dispersion when applied to hydrophobic materials. On hydrophilic materials, such as of cellulosic types, the pick-up may be as high as 100% to 120%. The application of about $\frac{1}{2}$ to 1% by weight on the weight of a textile fabric such as a woven or knitted fabric provides a slight modification of hand and anti-slip properties; that is, there is imparted to the fabric a resistance to relative displacements of the yarns with respect to each other during handling or wear. The application of 1% to 35% on the weight of the fabric imparts a stiffness thereto in proportion to the amount deposited. This is desirable in the modification of fabrics of many materials and especially of polyamides, such as nylon, polyesters such as Dacron (polyethylene terephthalate), cellulose esters such as cellulose acetate (or the primary or triacetate type and also of the secondary acetone-soluble type), and polyvinyl resin yarns such as Orlon and other polyacrylonitrile fabrics comprising fibers or filaments formed of acrylonitrile polymers or copolymers containing at least 80% by weight of acrylonitrile polymerized in the molecule. Such plastic fabric materials

frequently have excessive softness and sleaziness which is overcome by the application of the condensates of the present invention. Generally, 4% to 5% by weight on the weight of the textile material of the dicarbamate condensate is preferred for the stiffening of dress materials, such as women's summer dresses and men's shirting materials and especially open weave summer shirts. Somewhat higher proportions, preferably 8% to 10%, may be used for the stiffening of foraminous or netted shoe cloths of netted or woven character comprising fibers, filaments or yarns of the above-mentioned plastic materials. Other materials that may be improved by the stiffening action imparted by the resins of the present invention include ladies' undergarments and petticoats, netting (either knitted or woven), such as materials used in making ornaments or decorations for evening gowns and so on. It has been found also that the application of the dicarbamate condensates to certain plastic materials and particularly nylon renders such treated materials more resistant to heat. Thus, fabrics of nylon which are subjected to heat during their use, such as ironing board covers, quickly lose their strength. However, nylon fabrics treated with resins of the present invention maintain their strength even after prolonged use under heat even under such severe conditions as are encountered during ironing.

The dicarbamate condensates are applicable to yarns as a loom finish. The application of 3% to 10% of the condensate based on the weight of the yarn renders the yarn more amenable to weaving and serves as a permanent finish on the woven fabric. For this purpose, yarns of any type of fiber may be treated including cotton, silk, wool, rayons, cellulose esters, nylons, Dacron, and vinyl polymers such as those of polyacrylonitrile mentioned above.

The application of from 5% to 12% on the weight of final fabric of the dicarbamate condensate to fibers, filaments, yarns or fabrics of certain materials, such as rayon, cotton, proteinaceous fibers such as of casein and the like tends to reduce shrinkage on subsequent washing and thereby imparts dimensional stability.

The dicarbamate resin condensate may also be incorporated in fibrous structures of matted character, such as felt-like mats or bats comprising fibers of any type whatsoever including mineral fibers such as those formed of glass or siliceous material known as mineral wools. For this purpose, the fibers may be dispersed into an air stream and the dispersion of resin-forming condensate may be sprayed on to the fibers as they are conveyed in such stream to a point of deposition where they are laid in haphazard disposition and subsequently heated to effect drying and curing of the condensate deposit and thereby binding the fibers together. For producing this type of product when glass fibers or mineral fibers are involved, the condensate spray may be directed against the fibers in close proximity to their point of initial formation by the impingement of a gaseous stream, such as of air or steam, against a stream of molten glass or the like.

As mentioned above, the aqueous dispersion of the resin-forming dicarbamate condensate may contain from 1% to 90% by weight of the condensate, depending upon the particular purpose for which the condensate is to be applied and the amount that is to be deposited on the textile material. A concentration approaching 90% is generally necessary to obtain a heavy deposit of 30% to 35% on the weight of the textile material, whereas a concentration of 1% is adequate to apply about $\frac{1}{3}$ % to $\frac{1}{2}$ % of the condensate on the textile material. Intermediate concentrations are used to provide intermediate deposit weights on the textile material. The condensate dispersion may be applied to the textile material by spraying, padding, by rolls, brush or any other conventional device. Generally application is made at room temperature though somewhat elevated temperatures or lower temperatures may be employed if desired in certain cases,

The dispersion of condensate should contain a catalyst such as ammonium chloride, an amine salt or any other of the catalysts mentioned hereinabove. As pointed out hereinbefore, the catalyst is preferably added shortly before the dispersion is to be used.

After the dispersion of condensate is applied to the textile material, it is dried. This may be merely drying in air or it may be effected at elevated temperatures, such as from 180° F. to 240° F. or even higher.

The condensate may then be converted to an insoluble condition by prolonging the drying at temperatures of 180° F. to 240° F. or preferably by heating for a short period at elevated temperatures. For example, insolubilization may be effected at temperatures of 300° F. to 450° F. or higher for periods of time whose length varies inversely with the degree of temperature from about ten minutes at the lower temperatures to about five seconds at the higher temperature mentioned. In all cases, the temperature should not be so high or the time prolonged to such an extent as to cause decomposition of the material composing the fabric or other textile.

As compared to such resin-forming condensates as those of urea-formaldehyde and melamine-formaldehyde which have heretofore been used for the stiffening of plastic materials, such as nylon, the dicarbamate condensates have several advantages. Generally, they produce a fuller hand than can be obtained from a urea-formaldehyde condensate used at corresponding concentrations. This is apparently the result of better wetting of the fiber by the dicarbamate condensates or improved adherence of the dicarbamate condensates to the fiber in the final product. Another important characteristic of the fabrics treated with the dicarbamate condensates as compared with those treated with condensates of urea-formaldehyde and melamine-formaldehyde is the lower tendency of the former treated fabrics to propagate flame. The dicarbamate condensates also show less loss after washing particularly on such materials as Orlon and Dacron. Whereas a urea-formaldehyde resin heretofore used for stiffening Orlon and Dacron shows only 55% and 67% retention on those respective fabrics after washing for one hour at the boil in water containing 0.1% of sodium tetraphosphate and 0.2% of Ivory soap and Orlon and Dacron fabrics carrying melamine-formaldehyde show only 60% and 56% respectively after washing. Orlon and Dacron fabrics carrying dicarbamate condensates show a retention of 70% and 86% respectively after such a wash.

In the following examples, which are illustrative of the present invention, the glass electrode (G. E.) pH was always determined on a 5.0 g. sample of the batch which had been diluted to about 10% solids with 25.0 ml. of distilled water. In the following examples where stiffness is determined, a Gurley stiffness tester was employed and the values given represent milligrams required to bend a standard sample of 1" by 3" dimension.

EXAMPLE 1

Dithylene glycol dicarbamate (480 grams or 2.5 moles) was charged to a one liter flask containing 613 grams of aqueous 36.7% formaldehyde (7.5 moles HCHO). The mixture was heated and when it cleared at about 80° C. sulfuric acid was added to lower the pH to about 3.3. Heating continued to reflux (starting about 102° C.). Refluxing was continued until a Gardner-Holdt viscosity of T+ was attained at a solids concentration of 68%. At this point the dispersion had water tolerance and had a pH of 2.8. Caustic soda was added to adjust the pH to about 6 to 7 and about 9.2 grams of a polyethylene oxide derivative of an octyl phenol containing about 10 oxyethylene units was added. The dispersion was then diluted with water to a 12.5% resin-solid concentration and $\frac{1}{2}$ % (on the total weight of dispersion) of ammonium chloride was added. In a

EXAMPLE 4

pad arranged for two dips and two nips in squeeze rolls, the above 12.5% aqueous dispersion of the resin-condensate was applied to a nylon taffeta, a Dacron shirting fabric, an Orlon shirting fabric and a cellulose acetate satin. After drying the treated fabrics in air, the condensate was insolubilized by heating at 300° F. for ten minutes. The fabrics were then conditioned at 70° F. and 65% relative humidity. The fabrics were tested for stiffness and then all except the acetate were subjected to a wash at the boil for one hour in an aqueous solution of 0.1% sodium tetraphosphate, 0.2% of Ivory soap. After the wash the stiffness was again tested. The following table gives the results of the stiffness tests.

Table I

Nylon		Orlon		Dacron		Acetate
Un-washed	Washed	Un-washed	Washed	Un-washed	Washed	Un-washed
10	9	37	31	29	22	43

EXAMPLE 2

A nylon taffeta was padded as before with a series of resin condensates prepared as in Example 1 except that each dispersion was finally diluted to solids concentrations of 5%, 10%, 15%, 20%; and 25% respectively. To each dispersion, there was added ½% of ammonium chloride based on the total weight of the dispersion.

The fabrics after drying, curing and conditioning as in Example 1 were tested for stiffness, then washed as in Example 1 and again tested for stiffness. Table II summarizes the results obtained after application of the different concentrations of resin-dispersion and comparing it with a control using water.

Table II

	Unwashed	Washed
H ₂ O	2	4
5%	7	7
10%	9	8
15%	12	11
20%	15	15
25%	18	13

EXAMPLE 3

Samples of a Dacron fabric were treated with the several catalyzed dispersions of condensate prepared as in Example 2 having 5%, 10%, 15%, 20%, and 25% concentrations respectively. Similarly catalyzed urea-formaldehyde and melamine-formaldehyde condensates having corresponding concentrations were also applied to similar samples of the Dacron fabric. The treated samples were dried, cured and conditioned as in Example 1. They were then tested for stiffness, washed as in Example 1 and again tested for stiffness. Table III summarizes the results of these tests. The symbols "DGC-F" refers to the condensates of the present invention; "U-F" to the urea-formaldehyde; and "M-F" to the melamine-formaldehyde condensates. "Unw." refers to unwashed and "W." refers to washed.

Table III

Disp. Con.	DGC-F		U-F		M-F	
	Unw.	W.	Unw.	W.	Unw.	W.
H ₂ O	9	4	9	4	9	4
5	22	19	23	16	28	23
10	21	25	26	19	38	22
15	35	28	31	17	43	17
20	49	35	33	22	45	21
25	58	40	38	20	47	23

Dispersions of the diethylene glycol dicarbamate-formaldehyde condensate prepared as in Example 1 and of urea-formaldehyde and melamine-formaldehyde were applied, at solids concentrations of 5% and 15% respectively and in each case containing 0.5% ammonium chloride on the weight of the dispersion, to nylon taffetas in the manner described in Example 1. The treated fabrics were air-dried, cured and conditioned as in Example 1. Strips 1" wide by 8" in length were then subjected to burning tests. Other portions of the fabric were washed as in the manner described in Example 1 and again after drying were tested for flammability. The results are tabulated in Table IV, wherein the values define the inches burned before the samples extinguished themselves. Infinity (∞) indicates that the sample burned beyond a 6" mark.

Table IV

	Unwashed, inches	Washed, inches
5% U-F	2	4
5% M-F	5	∞
5% DGC-F	1½	3
15% U-F	∞	3
15% M-F	∞	∞
15% DGC-F	3	2

EXAMPLE 5

There are charged into a reaction vessel 1,152 grams of diethylene glycol dicarbamate (6 moles) and 983 grams of an aqueous solution containing 55% of formaldehyde, 35% of methanol and 10% of water. This provides 18 moles of formaldehyde and approximately 10.6 moles of methanol. The mixture is heated and when it clears at about 70° C. 100 grams of 85% phosphoric acid is added to adjust the pH to about 2.6. The mixture is then refluxed. After several hours, 200 grams of water is added to reduce the viscosity and 70 grams of a 40% solution of paratoluenesulfonic acid in isopropyl alcohol is added to reduce the pH to a value of 2.6. After additional refluxing the viscosity increased to U (Gardner-Holdt) and 200 grams of water were added to reduce it. Refluxing continued until a viscosity of U was attained. This completed the reaction and 400 grams of water were added to reduce the viscosity to G. A 50% solution of sodium hydroxide was added until the pH was raised to about 6½. Then water was added to reduce the dispersion to a 10% solids content and ½% of ammonium chloride was added (based on the weight of the dispersion).

The 10% dispersion of condensate thereby obtained was applied to a nylon taffeta, which was then dried, cured and conditioned all as in Example 1. The tensile strength in pounds (at break) was measured by a Scott testing machine on a strip 6" long in the warp direction which was frayed in conventional manner to a 1" width to assure that the same number of warp yarns extended through the entire length of the strip. Similar strips of nylon taffeta were prepared except that they were treated with 10% dispersions of urea-formaldehyde and melamine-formaldehyde condensates respectively each containing ½% of an acidic catalyst; ammonium chloride being used in the case of urea-formaldehyde and a diammonium phosphate being the catalyst used in the case of the melamine-formaldehyde. The dried and cured strips thus obtained were tested for tensile strength as in the case of the strip treated with the diethylene glycol

dicarbamate-formaldehyde condensate. Another set of similarly treated nylon taffeta strips, which had been cured in the same manner, was subjected to a heat treatment for ten minutes at 400° F. and the tensile strength measured thereafter. Table V summarizes the results of these tensile tests before and after the heat treatment.

Table V

	Cured Only 10 Min. at 300° F.	Cured plus 10 Min. at 400° F.
H ₂ O-----	83±5	41±5
U-F-----	57±6	47±7
M-5-----	49±6	21±2
DGO-5-----	78±5	73±3

EXAMPLE 6

(a) Diethylene glycol dicarbamate (480 grams or 2.5 moles) was charged to a one-liter flask containing 613.0 grams of aqueous 36.7% formaldehyde (7.5 moles HCHO). The mixture was heated with stirring to reflux (102° C.) and held at this temperature for 15 minutes in order to allow time for some reaction to take place between formaldehyde and the carbamate before starting to strip the batch. Then the heat was shut off while the apparatus was arranged for distillation (ca 10 min.) after which heating was resumed and 63.0 grams of aqueous distillate was distilled from the reaction mixture (batch temp. was 104° C. at this point). Heat was again shut off while the apparatus was arranged for total reflux (about 15 minutes). When heating was then resumed, the batch temperature was 90° C. and the pH of the batch was adjusted to 3.0 (G. E.) with 2.4 ml. of 50% aqueous H₂SO₄ and the batch (having about 60% solids content) was sampled for viscosity. The viscosity at this point was "A—" on the Gardner-Holdt scale at 25° C. or slightly less than ½ poise at 25° C.

Further polymerization of the batch was effected by continuing to heat at reflux until the viscosity reached a value of D on the Gardner-Holdt scale. At this point, about ⅓ of the batch was removed providing a dispersion hereinafter referred to as dispersion A having a solids concentration of about 60%. Refluxing of the original batch continued until the viscosity reached a value of O+. At this point, about one-half of the remaining batch was removed and it is hereinafter referred to as resin dispersion B. It had a solids concentration of about 56.3%. The remainder was refluxed further until it reached a viscosity of M at about 52% solids. This will be referred to as resin dispersion C.

(b) A mixture of 1,080 grams of aqueous 36.5% formaldehyde, 1,920 grams (10 moles) of diethylene glycol dicarbamate, 915 grams of a solution containing 55% of formaldehyde, 35% methanol and 10% water, and 475 grams of water was charged into a reaction vessel and heated. When the temperature reached about 70° C., the reaction mass cleared and 10 grams of a 50% aqueous sulfuric acid was added to lower the pH to 3.3 and heat was continued to reflux (starting at about 88° C.). After about 8 hours reflux the reaction mass had a solids concentration of about 55.5% and a Gardner-Holdt viscosity of about C. Twelve hundred grams of the reaction mass was removed and this removed portion will hereinafter be referred to as resin dispersion D. About one gram of 50% sulfuric acid was added to the remaining reaction mass and refluxing thereof was continued until the viscosity reached M+ at a 56% solids concentration. At this time, 1,200 grams of the reaction mass were removed and will hereinafter be referred to

as resin dispersion E. The remaining reaction mass was further refluxed until a viscosity of V— was attained at a 60% solids concentration and this remaining portion will hereinafter be referred to as resin dispersion F.

(c) A mixture of 1,920 grams (10 moles) of diethylene glycol dicarbamate, 1,640 grams of an aqueous solution containing 55% formaldehyde (30 moles), 35% methanol and 10% water, 67 grams of additional methanol (providing a total of 20 moles of methanol), and 760 grams of additional water were mixed in a reaction vessel and heated. The mass cleared at about 75° C. at which point 6 grams of 50% sulfuric acid was added to lower the pH to 3.3. Heating was continued to bring the mass to reflux which started at about 95° C., and at this stage an additional one gram of the 50% sulfuric acid was added to maintain the pH at 3.3. Refluxing was continued until the mass attained a viscosity of C+ at a concentration of 59.2% solids. At this point, 1,200 grams of the dispersion was removed and will be hereinafter referred to as resin dispersion G. About eight grams of 50% sulfuric acid was added to the remainder to lower its pH to 3.3 and refluxing continued. The refluxing temperature lowered to about 85° C. during the process until a viscosity of M is attained at a solids concentration of 57.7%. A 1,200 gram portion of the mass was removed and this portion will be hereinafter referred to as resin dispersion H.

Then about 1 gram of the 50% sulfuric acid was added to the remaining reaction mass amounting to approximately 1,200 grams which was refluxed for a further period of time until the viscosity reached a value of T+ at a concentration of 57.9% solids. This remaining portion is hereinafter referred to as resin dispersion I.

(d) The several resin dispersions of parts (a), (b), and (c) hereof represent three diethylene glycol dicarbamate-formaldehyde condensate types; that in part (a) containing no methanol and being divided into dispersions containing condensates carried to different degrees of condensation; that in part (b) obtained from a mixture containing about 1 mole of methanol per mole of dicarbamate divided into dispersions containing condensates of different degrees of condensation; and that in part (c) being a condensate obtained from a mixture containing about two moles of methanol per mole of dicarbamate and being divided into three portions, each having a different degree of condensation.

Each of the resin dispersions thus obtained is neutralized to a pH between about 5 and 6.5 with a 50% aqueous solution of sodium hydroxide. To portions of each of the dispersions water is added to reduce the solids concentration to 25% and to other portions water is added to reduce the solids concentration to 7.5%. Then there is added to each of the resulting dispersions, 0.5% of ammonium chloride (on the weight of dispersion).

Condensates of urea-formaldehyde and melamine-formaldehyde were also prepared in concentrations of 25% and 7.5% in aqueous dispersions and provided with ½% of ammonium chloride as a catalyst (based on the total weight of dispersion).

(e) The 18 dispersion of dicarbamate-formaldehyde condensates, the 2 dispersions of urea-formaldehyde condensates and the 2 of melamine-formaldehyde were then applied to nylon, Orlon and Dacron fabrics in a pad by the procedure of Example 1. After drying, curing and conditioning as in Example 1, the samples of the several treated fabrics were tested for stiffness. Additional samples were subjected to the wash as in Example 1 and then again tested for stiffness. Table VI summarizes the results of these tests. Under each fabric designation the third column with the "percent" sign at the top represents percentage retention of stiffness after washing.

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Table VI

	Nylon			Orlon			Dacron		
	UN	W	Per-cent	UN	W	Per-cent	UN	W	Per-cent
7.5% Concentration Resin Dispersion:									
U-F	12	11	91	32	8	25	25	13	52
M-F	13	10	77	34	13	38	29	12	42
A	8	7	87	32	28	87	23	21	91
B	9	7	78	34	29	85	25	19	76
C	9	8	89	34	26	76	25	22	88
D	10	9	90	32	26	84	22	16	73
E	11	9	81	36	26	72	25	21	84
F	9	7	78	33	25	76	24	18	75
G	7	7	100	28	25	89	19	17	90
H	11	9	81	32	22	69	19	17	90
I	8	9	110	32	26	81	20	18	90
25% Concentration Resin Dispersion:									
U-F	15	12	80	48	17	35	36	20	56
M-F	16	12	75	50	18	36	42	21	50
A	15	12	80	48	37	77	35	30	86
B	14	13	93	46	38	79	38	27	71
C	16	15	94	52	36	69	39	20	51
D	14	14	100	44	33	75	41	32	78
E	14	14	100	46	31	67	41	30	73
F	14	13	93	48	33	69	36	30	84
G	14	12	86	43	33	77	38	36	95
H	15	13	87	44	36	82	36	33	92
I	10	9	90	44	35	80	38	32	84

The stiffness test on untreated samples run approximately 3 for nylon, 8 for Orlon, and 15 for Dacron.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined in the appended claims.

We claim:

1. A method of modifying a textile material comprising treating it with an aqueous dispersion containing dispersed therein 1% to 90% of a water-soluble high molecular weight condensate obtained by reacting at a pH between 2.3 and 3.5 a mixture comprising the dicarbamate of diethylene glycol and formaldehyde, in which the molar ratio of formaldehyde to the dicarbamate is from 2.5:1 to 3.0:1, said condensate having a viscosity, at a concentration of 60% in water at 25° C., of 2 to 25 poises, said composition containing 1% to 6% by weight of an acid catalyst, drying and heating the treated material at a temperature of at least 180° F. to 350° F.

2. An article of manufacture comprising a woven textile fabric carrying thereon 3% to 10%, based on the weight of the material, of an insoluble deposit of a condensate of the dicarbamate of diethylene glycol and formaldehyde, said article being the product of the method defined in claim 1.

3. A method of modifying a textile material comprising treating it with an aqueous dispersion containing dispersed therein 1% to 90% of a water-soluble high molecular weight condensate obtained by reacting at a pH between 2.3 and 3.5 a mixture comprising methanol, the dicarbamate of diethylene glycol and formaldehyde in which the molar ratio of formaldehyde to the dicarbamate is from 2:1 to 3.5:1 and that of the methanol to the dicarbamate is from 1:1 to 2.5:1, said condensate having a viscosity, at a concentration of 60% in water at 25° C., of 2 to 25 poises, said composition containing 1% to 6% by weight of an acid catalyst, drying and heating the treated material at a temperature of at least 180° F. to 350° F.

4. An article of manufacture comprising a textile material carrying thereon ½% to 35%, based on the weight of the material, of an insoluble deposit formed from a condensate obtained by reacting at a pH between 2.3 and 3.5 a mixture comprising the dicarbamate of diethylene glycol, formaldehyde, and methanol, in which the molar ratio of formaldehyde to dicarbamate is from 2:1 to 3.5:1 and that of the methanol to the dicarbamate is 1:1 to 2.5:1, said article being the product of the method defined in claim 3.

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5. An article as defined in claim 4 in which the material is a fiber.

6. An article as defined in claim 4 in which the material is a yarn.

7. An article as defined in claim 4 in which the material is a textile fabric.

8. An article as defined in claim 4 in which the material is a textile fabric comprising yarns of polyethylene terephthalate.

9. An article as defined in claim 4 in which the material is a textile fabric comprising yarns of nylon.

10. An article as defined in claim 4 in which the material is a textile fabric comprising yarns of a polymer of acrylonitrile comprising at least 80% acrylonitrile polymerized therein.

11. An article as defined in claim 4 in which the material is a textile fabric comprising yarns of a cellulosic material.

12. An article as defined in claim 3 in which the material is a textile fabric comprising yarns of cellulose acetate.

13. An article as defined in claim 4 in which the material is a textile fabric comprising yarns of rayon.

14. A method of modifying a textile material comprising treating it with an aqueous dispersion containing dispersed therein 1% to 90% of a water-soluble high molecular weight condensate obtained by reacting at a pH between 2.3 and 3.5 a mixture comprising the dicarbamate of diethylene glycol and formaldehyde, in which the molar ratio of formaldehyde to the dicarbamate is from 2:1 to 3.5:1, said condensate having a viscosity, at a concentration of 60% in water at 25° C., of 2 to 25 poises, said composition containing 1% and 6% by weight of an acid catalyst, drying and heating the treated material at a temperature of at least 180° F. to 350° F.

15. A method as defined in claim 14 in which the material is a woven textile fabric comprising fibers or filaments of polyethylene terephthalate.

16. A method as defined in claim 14 in which the material is a woven textile fabric comprising fibers or filaments of nylon.

17. A method as defined in claim 14 in which the material is a woven textile fabric comprising fibers or filaments of cellulosic material.

18. A method as defined in claim 14 in which the material is a woven textile fabric comprising fibers or filaments of cellulose acetate.

19. A method as defined in claim 14 in which the material is a woven textile fabric comprising fibers or filaments of rayon.

20. A method as defined in claim 14 in which the material is a woven textile fabric comprising fibers or filaments of a polymer of acrylonitrile comprising at least 80% acrylonitrile polymerized therein.

21. An article of manufacture comprising a textile material carrying thereon ½% to 35%, based on the weight of the material, of an insoluble deposit of a condensate of the dicarbamate of diethylene glycol and formaldehyde, said article being the product of the method defined in claim 14.

22. A method of modifying a textile material comprising treating it with an aqueous dispersion containing dispersed therein 1% to 90% of a water-soluble high molecular weight condensate obtained by reacting at a pH between 2.3 and 3.5 a mixture comprising methanol, the dicarbamate of diethylene glycol and formaldehyde, in which the molar ratio of formaldehyde to the dicarbamate is from 2.5:1 to 3:1 and that of the methanol to the dicarbamate is from 1.5:1 to 2:1, said condensate having a viscosity, at a concentration of 60% in water at 25° C., of 2 to 25 poises, said composition containing 1% to 6% by weight of an acid catalyst, drying and heating the treated material at a temperature of at least 180° F. to 350° F.

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23. An article of manufacture comprising a woven textile fabric carrying thereon 3% to 10%, based on the weight of the fabric, of an insoluble deposit formed from a condensate obtained by reacting at a pH between 2.3 and 3.5 a mixture comprising the dicarbamate of diethylene glycol, formaldehyde, and methanol, in which the molar ratio of formaldehyde to dicarbamate is from 2.5:1 to 3:1 and that of the methanol to the dicarbamate is 1.5:1 to 2:1, said article being the product of the method defined in claim 22.

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