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TEXTILE MATERIALS

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This invention relates to the improvement of textile materials by treating them with condensates of formaldehyde and amides of malonic acid having at least one N-aminoalkyl substituent, the hydrocarbon portion of which may be interrupted by —NH— to form alkylene chains of at least two carbon atoms each between nitrogen atoms. In the preferred form this invention deals with altering the susceptibility of textile fibers to dyes by treating fibers with said condensates.

Resins have heretofore been used in finishing textile fabrics to impart increased resilience or stiffness, or to improve the wearing qualities of dyed fabrics by protecting the dye with a deposit of resin. Prior methods of resin finishing have not, however, markedly changed the affinity between fiber and dye. Nor have such methods permitted the dyeing of different types of fiber with the same dye or the effective dyeing of cellulose with acid dyes. In this last respect, attempts have been made to increase the affinity of cellulose for acid dyes by chemical treatments which, while often attacking cellulose fibers severely, have not been particularly effective. In general such methods have been too complicated and uneconomical to gain acceptance.

It has been found that valuable improvements in textile materials are obtained by treating and heating them with the reaction product of formaldehyde and an N-aminoalkyl malonamide of the type set forth. The treating is accomplished by coating or impregnating the textile material with the said reaction product or with a solution thereof in water or organic solvent. The treated material is heated at a temperature generally above about 100° C. but below the decomposition temperature of the material being treated.

Textile materials so processed have an increased affinity for acid dyes and acquire full, deep shades when treated therewith. Other dyes ordinarily effective only on wool or silk are tenaciously held by thus treated fibers without regard to the original type of fiber. On the other hand, this treatment of textile materials or fibers renders them resistant to various basic dyes. The process may also be used for local effects and patterns on cloth or sheets. At the same time that the affinity of textile fibers, yarns, or fabrics is altered toward dyes, increased resilience is imparted without development of a harsh or unpleasant handle of the textile material so that cellulose fibers truly become more wool-like in both dyeing properties and physical properties.

The condensates which are useful in the proc-

ess of improving textile fibers are obtainable by reacting a mixture of formaldehyde and an aminoalkyl malonamide having a reactive methylene group in juxtaposition to the amide carbonyl group in the presence or absence of a solvent while the temperature of the reacting mixture is held below about 100° C. The aminoalkyl amides are obtained by reaction between a malonic ester and an alkylene polyamine, such as ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, N,N'-bis(aminopropyl) ethylene diamine, tripropylene tetramine, tris(trimethylene) tetramine, etc. or mixtures of polyalkylene polyamines. This reaction leads to mono- and di-amides which are soluble in aqueous systems. Typical of the aminoamides which result are N-aminoethylaminoethyl ethyl malonamide, N,N'-bis(aminoethyl) malonamide, N,N'-bis(aminoethylaminoethyl) malonamide, N-aminoethylaminoethylaminoethyl propyl malonamide, N,N'-bis(aminoethylaminoethylaminoethylaminoethyl) malonamide, etc. These amides react with aqueous or solvent solutions of formaldehyde or with formaldehyde from a solid polymer to yield condensates which resinify on further heating. To prevent premature gelation of these condensates it is often desirable to condense the aminoamide and formaldehyde in the presence of a primary or secondary amine such as ethylene diamine, methylamine, dimethylamine, diethylamine, caprylmethylamine, etc. Details of the preparation and nature of the aminoamides and their condensates are given in applications having Serial Nos. 387,679, 387,680, 387,681 (now Patent No. 2,325,567), filed on even date.

The formaldehyde-aminomalonamide condensates are applied to textile materials from neutral, acidic, or alkaline solutions by spraying, dipping, padding, printing, or other method of treatment. Excess solution is then desirably removed by a suitable means, such as a centrifugal extractor, vacuum slot extractor, or squeeze roll. The impregnated material is dried at room or higher temperature as a separate step or as part of the baking step. It is then baked above 100° C. Temperatures of 120° up to 130° C. for 5 to 30 minutes are particularly effective in fixing the condensate in the fibers, although temperatures as high as 150–160° C. may be used in some cases. If desired, after this curing step the materials may be washed or scoured in a bath of a natural or synthetic soap or other detergent. The materials may now be dyed with wool and silk dyes with highly satisfactory results. The process is

applicable to all types of textile materials, including cotton, linen, regenerated cellulose fibers, paper, straw, silk, fibers or superlinear polymers, and even wool. Its greatest advantage is obtained with cellulosic materials. The materials may be in the form of fibers, films, yarns, braids, woven or knit goods, mats, felts, battings, etc.

The following examples are illustrative of the process of treating textile materials with the formaldehyde-aminomalonamide condensates.

Example 1

Ten parts of the reaction product obtained by heating together one mol of N,N'-bis(aminoethylaminoethyl)malonamide, three mols of formaldehyde, and 3.5 mols of dimethylamine was taken up in water. Hydrochloric acid was added thereto until a pH of 6.8 was attained. The solution was then diluted with water to 100 parts. Bundles of rayon fiber (3 denier, 19/16" staple) were immersed in the solution, which was kept at the boil for five minutes. The bundles were removed from the treating solution and squeezed to remove excess liquor. They were then dried and heated for 30 minutes in an oven at 125° C. The fibers showed a definite increase in stiffness and were light tan in color. The bundles of fibers were accordingly washed in warm soap solution, which removed most of the tan color. They were then placed for one-half hour in a simmering solution containing 1% Pontacyl Carmine 6B (Color Index No. 57) and ½% of acetic acid. The fibers were dyed a deep purple color which was fast to washing and reasonably fast to light.

Example 2

A 20% solution of the reaction product obtained by reacting one mol of N-aminoethylaminoethyl cyanoacetamide and one mol of formaldehyde was approximately neutralized with acetic acid. Rayon taffeta was soaked for five minutes in this solution while it was maintained at 70° C. and stirred from time to time. The taffeta was run through squeeze rolls to remove excess solution and dried. It was then baked for one-half hour in an oven at 130° C. and washed in a soap solution. The fabric was dyed in a bath of Acid Brown EW #3 (Color Index No. 234) to a medium brown shade, which was fast.

Example 3

A 10% solution of the reaction product of one mol of N,N'-bis(aminoethylaminoethylaminoethyl) malonamide and 1.5 mols of formaldehyde was made slightly acid with hydrochloric acid. The solution was then used for the impregnation of bundles of viscose fibers at room temperature. Excess solution was squeezed from the bundles which were dried. They were heated for three-quarters of an hour in an oven at 125° C. and washed in soap solution. They were then dyed in a bath of Amarant W (Color Index No. 184). The resulting color was a medium rose, which was fast to washing and to light.

Example 4

Cotton cloth was soaked at 70° C. for five minutes in a 20% solution of the reaction product from one mol of N,N'-bis(aminoethyl) malonamide, two mols of ethylene diamine, and one mol of formaldehyde. The cloth was removed from the solution and immediately placed in an oven at 130° C. for a 40 minute period. It

was then washed in soap solution and dyed in a bath of Pontacyl Carmine 6B to give a medium purple shade.

Example 5

Spun rayon fabric was impregnated by repeated padding through a hot solution containing 20% of the reaction product from one mol of N,N'-bis(aminoethylaminoethyl)malonamide and two mols of formaldehyde. The fabric was dried, heated in an oven at 125° C. for one-half hour, and washed in soap solution. It was dyed in a bath of Brilliant Wool Blue (Prototype 40). The fabric was deep blue and retained this color. It was noticeably fuller and more resilient than untreated fabric and did not change dimensions appreciably on being laundered.

Example 6

A 10% aqueous solution of the reaction product, obtained by heating at 70-80° C. a mixture of 27.4 parts of N,N'-bis(aminoethylaminoethyl)malonamide, 60 parts of dimethylamine, and 30 parts of 30% formaldehyde solution, was heated to 50° C. A hank of nylon yarn was immersed in this solution for fifteen minutes and squeezed free of excess solution. It was then dried and heated for 20 minutes in an oven at 130° C. The yarn was dyed in a bath of Pontacyl Carmine 6B. It retained a bright red color. Untreated nylon retained only a pale color.

Example 7

The solution used in Example 6 was similarly applied to silk yarn, which was likewise dyed with Pontacyl Carmine 6B. A full red color was obtained. Yarn dyed directly without processing was pink.

The aminomalonamide condensates described above are unusually effective in "animalizing" textile fibers, probably because of the multiplicity of nitrogen atoms therein. Not only are these condensates unusually effective in altering the dyeing properties of fibers, but they also impart resilience and increased fullness to yarns and fabrics and stabilize fabrics against changes in dimensions. These improvements appear due partly to resinous deposits and partly to actual combination between fiber and condensate or resin. The formaldehyde-aminoalkyl malonamides may be applied to fibers as the sole finishing agent or they may be applied in conjunction with other resin-forming materials such as urea-formaldehyde, acrylic resins, etc. or in conjunction with finishing agents such as sulfonated oils, long-chained quaternary ammonium salts, etc.

We claim:

1. The process of improving textile materials which comprises treating said materials with the reaction product of formaldehyde and a malonamide having at least one N-aminoalkyl substituent, the hydrocarbon portion of which may be interrupted by —NH— to form alkylene chains of at least two carbon atoms each between nitrogen atoms, and heating the treated materials above about 100° C. but below the decomposition temperature of said materials.

2. The process of improving the affinity of cellulosic textile fibers to acid dyes which comprises impregnating said fibers with an aqueous solution containing the reaction product of formaldehyde and a malonamide, having at least one N-poly-amino polyalkylene substituent in which the alkylene chains consist of at least two carbon

atoms each, and heating the impregnated fibers above about 100° C. but below the decomposition temperature of said fibers.

3. The process of improving textile fibers, yarns, and fabrics which comprises impregnating said textile materials with a solution containing the reaction product of formaldehyde and an N,N'-bis(polyaminopolyalkylene) malonamide, the alkylene chains of which contain at least two carbon atoms each, and heating the treated materials above about 100° C. but below the decomposition temperature of said materials.

4. The process of improving textile fibers, yarns, and fabrics which comprises impregnating said textile materials with a solution containing the reaction product of formaldehyde and a malonamide, having at least one N-aminoethylaminoethylaminoethylaminoethyl group, and heating the impregnated materials between about 100° C. and about 150° C.

5. The process of improving textile fibers, yarns, and fabrics which comprises impregnating said textile materials with a solution containing the reaction product of formaldehyde and N,N'-bis(aminoethylaminoethylaminoethyl) malonamide, and heating the impregnated materials between about 100° C. and about 150° C.

6. The process of improving textile fibers which comprises impregnating said fibers with an aqueous solution of the reaction product of formaldehyde and N,N'-bis(aminoethylaminoethyl) malonamide and heating the impregnated fibers between about 100° C. and about 150° C.

7. A textile material carrying the insolubilized reaction product of formaldehyde and a malonamide having at least one N-amioalkyl substituent, the hydrocarbon portion of which may be interrupted by —NH— to form alkylene chains of at least two carbon atoms each between nitrogen atoms.

8. A textile fabric carrying insolubilized thereon the reaction product of formaldehyde and an N,N'-bis(polyaminopolyalkylene) malonamide, the alkylene chains of which contain at least two carbon atoms each.

9. A textile material carrying insolubilized thereon the reaction product of formaldehyde and a malonamide having at least one N-aminoethylaminoethylaminoethylaminoethyl group.

10. A textile fabric carrying insolubilized thereon the reaction product of formaldehyde and N,N'-bis(aminoethylaminoethylaminoethylaminoethyl) malonamide.

11. A textile fabric carrying insolubilized thereon the reaction product of formaldehyde and N,N'-bis(aminoethylaminoethylaminoethyl) malonamide.

12. A textile fabric carrying insolubilized thereon the reaction product of formaldehyde and N,N'-bis(aminoethylaminoethyl) malonamide.

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