

United States Patent

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[54] FIRE-RETARDANT FINISH FOR NYLON
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2,795,513	6/1957	Rossin.....	117/138.8 X
2,922,726	1/1960	Moretti et al.	117/138.8 X
3,317,345	5/1967	Fluck et al.	117/138.5
3,335,113	8/1967	Dundon	117/139.5 X

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[56] References Cited

UNITED STATES PATENTS

2,415,112	2/1947	Seymour et al.	117/137
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[57] ABSTRACT

A composition for imparting fire retardancy to nylon textiles, comprising highly methylolated urea, thiourea and ammonium chloride; the method of imparting fire retardancy to nylon textiles; and a nylon textile having fire-retardant properties.

3 Claims, No Drawings

FIRE-RETARDANT FINISH FOR NYLON

This invention relates to a fire-retardant finish for nylon textile materials. More particularly, it relates to (1) a fire-retardant finish comprising highly methylolated urea, thiourea and ammonium chloride, (2) the method of applying the finish to nylon textile materials and (3) to be treated nylon materials.

The importance of imparting fire-retardant properties to nylon textile materials is well known. Textile fabrics have been treated with a wide variety of thermosetting resins to produce a diversity of resin finishes on the cloth. Among the many objects have been resistance to shrinking, resistance to wrinkling, the stiffening of limp fabrics and reducing the combustibility of the material. The commoner varieties of textile resins include water-soluble condensation products of formaldehyde with urea or melamine and the ethers obtained by treating the aforesaid condensation products with methanol. Water-soluble unalkylated thiourea-formaldehyde resins have also been proposed for flameproofing nylon. As might be expected, the resin finishes used to produce or improve one desirable effect on a textile fabric occasionally have an undesirable effect on other qualities of the material. In addition, the various resins have peculiarities which in one manner or another limit their use.

In spite of the many patents on fire-retardant finishes for nylon, the need is still present for an economical, easily applied, and effective fire-retardant finish for textile materials containing a principal amount of nylon fibers.

It is therefore an object to provide a composition and process for imparting flame retardance to nylon textiles.

It is a further object to provide a flame-retardant finish for nylon textiles which is economical, easily applied, and highly effective.

Another object is to provide a flameproof nylon textile.

These and other objects of my invention will become apparent as the description thereof proceeds.

Such a finish has now been discovered which meets the above requirements. The finish of the present invention comprises an aqueous solution of highly methylolated urea, thiourea, and ammonium chloride.

The methylolated urea contains at least 3.0 moles of combined formaldehyde, preferably at least 3.3 moles, per mole of urea. The preparation of the highly methylolated urea is described in U.S. Pat No. 3,335,113, and is as follows:

The process for preparing a water-soluble stable urea formaldehyde condensation product comprises reacting relative amounts of 1 mol of urea with from between 4 and 5 mols of formaldehyde at a pH above 10 and in the presence of an amount of alkali that does not exceed 0.1 mol of sodium hydroxide per mol of urea and at a temperature of between 40° and 100° C. This reaction is carried out until the mols of combined formaldehyde per mol of urea are from about 3.4 to about 3.8 and the formaldehyde content of the reaction mixture is below 4 percent.

In preparing the highly methylolated urea composition, relative amounts of 1 mol of urea are reacted with between 4 and 5 mols of formaldehyde and preferably with from between from about 4.2 and about 4.6 mols of formaldehyde. Amounts of formaldehyde in excess of 4.6 mols are undesirable because of the resulting large amounts of unreacted formaldehyde remaining in the composition.

The reaction is preferably carried out in water as a solvent, and the formaldehyde may be used as the commercial 37 percent or 44 percent formaldehyde solutions or as paraformaldehyde.

The principal reaction between urea and formaldehyde in an aqueous medium is carried out at a pH above 10 and in the presence of an amount of alkali that does not exceed the equivalent of 0.1 mol of sodium hydroxide per mol of urea. As examples of strong alkalis, sodium hydroxide, potassium hydroxide, lithium hydroxide, and suitable alkaline earth metal hydroxides, such as barium hydroxide, may be cited. These alkaline materials or their equivalents are employed in amounts that are equivalent to an alkalinity of about pH 10 and above, but should not be employed in an amount that ex-

ceeds 0.1 mol of sodium hydroxide or its equivalent per mol of urea. At pH's appreciable below 10, the rate of reaction between urea and formaldehyde is slow and the desired degree of methylation to be discussed more fully hereinafter is not obtainable. In addition, because of the well-known Cannizzaro's reaction; that is, the reaction between sodium hydroxide and formaldehyde, in which caustic soda is consumed and sodium formate is formed, it is necessary to add to the caustic soda throughout the reaction period in order to maintain the pH at a value of at least 10, while employing the caustic soda or its equivalent in an amount not exceeding 0.1 mol of sodium hydroxide or its equivalent per mol of urea. It should be noted that if amounts of caustic soda or its equivalent significantly in excess of 0.1 mol per mol of urea are employed in the preparation of a highly methylolated urea, undesirably large amounts of sodium formate are found to be present in the finished product which interfere with the textile-finishing properties of the resulting product. The sodium formate appears to buffer the acidic catalyst normally employed to cure aminoplasts by the textile-finishing industry.

The reaction between urea and formaldehyde is carried out until the mols of combined formaldehyde per mol of urea ratio is at least 3.4:1 and preferably is a value of between 3.6 and 3.8:1 as determined by analyses of unreacted formaldehyde.

In the carrying out of the process it has been found convenient to carry out the reaction in two stages. In the first stage urea and formaldehyde are reacted until the amount of free formaldehyde constitutes from 4 to about 8 percent of the reaction mixture while this excess free formaldehyde may be removed by distillation, in accordance with the important and preferred aspect of this invention the pH of the reaction mixture is adjusted to a value of below 8.5 but above 7 and urea in an amount of from between 0.2 mol and 1 mol per mol of initial urea is added to the reaction mixture. Methylation of the additional urea is then carried out until the unreacted or free formaldehyde content of the reaction mixture is less than 4 percent and preferably less than 3 percent by weight of the reaction mixture.

If the pH is not adjusted to a value of below 8.5 but above 7, prior to the second addition of urea, undesirable side reactions occur which appear to result in the formation of polymeric materials which are detrimental to the stability of the final product. As indicated above the amount of additional urea is from about 0.2 to about 1 mol relative to the initial mol of urea but is added in an amount sufficient to reduce the free formaldehyde content to a value of less than 4 percent and preferably less than 3 percent based on the total weight of the reaction mixture.

In accordance with the process, the methylation is carried out at a temperature of from between 40° and 100° C. and preferably at a temperature from between 60° and 80° C. In accordance with the above-described two-stage methylation in which the pH is adjusted downwardly prior to the second addition of urea, this adjustment can be conveniently accomplished in accordance with the present invention by raising the temperature of the reaction mixture to a value of about 90° C., which accelerates the Cannizzaro reaction between the formaldehyde and caustic soda resulting in a lowering of the pH to a value of between 7 and about 8.5.

Typical compositions of methylated urea products may be characterized as containing 1 mol of a polymethylol urea, having between 3.6 and 3.8 mols of combined formaldehyde, about 0.1 to about 0.3 percent of dimethylol urea and about 0.2 to about 0.4 mols of free formaldehyde.

A typical final methylated urea product may be characterized as containing 1 mol of a polymethylol urea having between 3.6 and 3.8 mols of combined formaldehyde, about 0.2 mols of dimethylol urea and about 0.3 mols of free formaldehyde plus water and minor amounts of dissolved salts.

The typical products will be water-white liquids having a pH of between 7 and 8.5. As stated above, the formaldehyde should be less than 4 percent and preferably less than 3 percent of the weight of the product.

The amount of highly methylolated urea applied to the fabric should be between 1 percent and 15 percent, preferably between 3 percent and 10 percent, based on the weight of the fabric (o.w.f.). The amount of thiourea should be between 0.5 percent and 15 percent o.w.f., preferably between 1 percent and 8 percent o.w.f. The amount of ammonium chloride should be between 0.035 percent and 0.55 percent o.w.f., preferably between 0.10 percent and 0.35 percent o.w.f.

The aqueous finish is applied to the nylon material by standard procedures such as by padding, dipping, spraying, etc.

After the nylon is dried (for example in an air dryer at 225° F.), it is heated at an elevated temperature. A temperature between 300° F. and 375° F., preferably between 325° F. and 350° F., is normally used. The heating period is of sufficient duration to essentially insolubilize the urea and thiourea components on the fabric.

The nylon textile materials may contain other fibers, both natural and synthetic, such as silk, cotton, wool, viscose, Dacron, Orlon, acetate, etc., but will comprise at least 80 percent nylon. The textile materials may be fibers, threads, woven or knit fabrics, or nonwoven materials, etc.

The following specific examples are provided to illustrate the invention and are not intended to be limitative.

EXAMPLE I

Two pad baths were prepared of the composition shown in table 1.

Resin A—methylolated urea containing 2.8 moles of combined formaldehyde.

Resin B—methylolated urea containing 3.5 moles of combined formaldehyde.

Table 1

Pad Bath	1	2
Resin A	13.0%	—
Resin B	—	13.0%
Thiourea	6.5	6.5
Ammonium Chloride	0.45	0.45

The above pad baths were applied to swatches of 5-ounce, white nylon filament (tarpaulin) fabric by a padding procedure using two dips and two nips at 2 tons pressure. The wet pickup was 31 percent. The treated fabrics contained the percentage amounts of active ingredients shown in table 2. The fabrics were dried at 225° F. and then heated at 350° F. for 1.5 minutes.

Fire retardancies of the treated fabrics were tested by hold-

ing a flame for 12 seconds at the lower edge of swatches of each fabric held vertically. The results are shown in table 2. Fabrics 1 and 2 correspond to pad baths 1 and 2, respectively.

Table 2

Fabric	1	2
Resin A, % o.w.f.	4.0	—
Resin B, % o.w.f.	—	4.0
Thiourea, % o.w.f.	2.0	2.0
Ammonium Chloride, % o.w.f.	0.14	0.14
Fabric Burned	Yes	No
After Flame	1 sec.	

For comparison, a swatch of the untreated nylon fabric melted.

This example demonstrates the effectiveness of the finish of this invention. It also demonstrates the superior fire-retardant properties imparted by a finish containing a methylolated urea having more than 3.0 moles of combined formaldehyde per mole of urea as compared with a finish containing a methylolated urea having less than 3.0 moles of combined formaldehyde per mole of urea.

While certain specific embodiments and preferred modes of practice of the invention have been set forth, it will be understood that this is solely for the purpose of illustration, and that various changes and modifications may be made in the invention without departing from the spirit of the disclosure or the scope of the appended claims.

I claim:

1. A fire-retardant composition for nylon containing textiles consisting essentially of an aqueous solution of methylolated urea, having at least 3.5 moles of combined formaldehyde per mol of urea, thiourea, and ammonium chloride, present in sufficient quantities to deposit by weight of said textile on said textile: from about 1 to 15 percent of methylolated urea; from about 0.5 to 15 percent of thiourea; and from about 0.035 to 0.55 percent by weight of ammonium chloride.

2. The composition of claim 1 wherein the amount of methylolated urea is from about 3 to 10 percent; said thiourea is from about 1 to 8 percent; and said ammonium chloride is from about 0.10 to 0.35 percent.

3. A nylon textile material having a fire retardant finish thereon, comprising a deposit by weight of from about 1 to 15 percent of methylolated urea, having at least 3.5 mols of combined formaldehyde per mol of urea; from about 0.5 to 15 percent of thiourea; and from about 0.035 to 0.55 percent by weight of ammonium chloride.

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