United States Patent Office

3,558,263

Patented Jan. 26, 1971

3,558,263

POTASSIUM IODIDE CROSS-LINKING INHIBITOR FOR N-METHYLOLACRYLAMIDE

William Frederick Baitinger, Jr., Hillsborough Township, Somerset County, N.J., assignor to American Cyanamid Company, Stamford, Conn., a corporation of Maine

No Drawing. Filed Oct. 1, 1968, Ser. No. 764,347

Int. Cl. C08g *51/56;* **D06m** *13/40*

U.S. Cl. 8—116.3 **10 Claims**

ABSTRACT OF THE DISCLOSURE

A method for inhibiting cross-linking of cellulose when N-methylolacrylamide is reacted with cellulosic textile materials in the presence of acid-acting catalysts, which comprises the use of potassium iodide with or without cupric chloride. An aqueous textile finishing composition for permanent press cellulosic textiles containing N-methylolacrylamide, an acid-acting catalyst and potassium iodide, with or without cupric chloride.

This invention relates to permanent press finishes for cellulosic textile materials. More particularly, it relates to a method for inhibiting the cross-linking of cellulose when N-methylolacrylamide is reacted with cellulosic textile materials in the presence of an acid-acting catalyst. It also relates to an aqueous textile finish containing N-methylolacrylamide, zinc nitrate and potassium iodide, and optionally cupric chloride.

At least three methods have been suggested for the reaction of cellulosic textile materials with N-methylolacrylamide to obtain cross-linking of the cellulose and a durable press finish. Each of the methods is a 2-step operation, the first step in each case specifying the reaction of the cellulosic textile material with N-methylolacrylamide by heating in the presence of an acid-acting catalyst. The methylol groups react with hydroxyl groups of cellulose to form an ether (Formula I).

FORMULA I

$$CH_2=CH\underset{\underset{O}{\|}}{C}NHCH_2O-Cell$$

In the second step, further reaction of the cellulose ether (Formula I) is carried out in the presence of (1) a base (U.S. Pat. 2,837,511), (2) a free radical initiator (U.S. Pat. 3,125,405), or (3) high energy radiation [Tex. Res. J. 35, 648 (1965)]. Two types of reactions are reported, both causing cross-linking of the cellulose, and the fabric acquires permanent press properties. In one type of reaction, the double bond of the acrylamide moiety reacts with a cellulose hydroxyl group to give a product of Formula II:

FORMULA II

$$Cell\ OCH_2CH_2\underset{\underset{O}{\|}}{C}NHCH_2O-Cell$$

In the other type of reaction, homopolymerization occurs at the double bonds to form a polymer in the fiber and attached thereto by multiple ether linkages. In either case, cross-linking of cellulose occurs and the fabric acquires permanent press properties.

For some purposes, such as deferred cure processes for durable press, it is desirable to keep the two steps separate and distinct; that is, when the reaction of the methylol group of N-methylolacrylamide with cellulose is being carried out, reactions of the double bond of N-methylolacrylamide must be prevented. The use of a free radical inhibitor has been suggested to prevent, or at least minimize, the reactions at the acrylamide double

bond. In the absence of a free radical inhibitor, at least some cross-linking may occur during the acid-catalyzed reaction. This is particularly true when the catalyst is zinc nitrate.

Hydroquinone has been suggested and used as a free radical inhibitor in the reaction of cellulose with N-methylolacrylamide in the presence of an acid-acting catalyst. But, hydroquinone causes severe discoloration of white fabrics and shade changes of dyed fabrics when the fabrics are heated in the presence of an acid-acting catalyst, such as zinc nitrate. Other phenolic compounds, such as mono-methyl ether of hydroquinone and p-tertiary-butylcatechol, do not prevent the cross-linking of cellulose.

Therefore, an object of this invention is to provide a method, using an inhibitor which (1) will prevent or minimize cross-linking by reaction of cellulose with the double bond, or homopolymerization at the double bond, of N-methylolacrylamide when the latter is heated on the fabric in the presence of an acid-acting catalyst, such as zinc nitrate, and (2) will not cause discoloration of white goods or color change of dyed goods.

A further object is to obtain permanent pressed white and colored cellulose goods of good color.

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

It has now been discovered that potassium iodide, used either alone or in combination with cupric chloride, acts as a free radical inhibitor in the reaction of cellulosic textile materials with N-methylolacrylamide. Essentially no cross-linking of cellulose takes place when N-methylolacrylamide is heated on a cellulosic textile material in the presence of an acid-acting catalyst and the inhibitor. Also, there is little or no discoloration of white goods or color change of dyed goods.

Since N-methylolacrylamide and the acid-acting catalyst are normally applied to cellulosic textile materials from an aqueous pad bath, it is convenient to add the inhibitor to the pad bath. The pad bath can be applied to the textile material by conventional procedures, such as padding, dipping, spraying, etc. The materials are then dried and heated at an elevated temperature to effect reaction of the methylol group of N-methylolacrylamide with cellulose.

The quantities of N-methylolacrylamide, catalyst and inhibitor deposited on the textile material can be determined from the quantities in the pad bath and amount of pad bath solution applied to the textile material.

The amount of N-methylolacrylamide applied to the textile material should be between 2% and 20%, preferably between 5% and 10%, based on the weight of the material.

Although various acid-acting catalysts well known in the art can be used, the preferred catalyst is zinc nitrate. The amount of zinc nitrate, calculated as the hexahydrate, should be at least 0.5%, preferably between 1% and 2%, based on the weight of the textile material.

The amount of inhibitor used depends on whether the potassium iodide is used alone or in combination with cupric chloride. When used alone, the amount of potassium iodide should be between 0.2% and 2%, preferably between 0.5% and 1%, based on the weight of the bath. When used in combination with cupric chloride, the amount of potassium iodide is between 0.1% and 1.0%, preferably between 0.1% and 0.5%, and the amount of cupric chloride is between 0.1% and 1.0%, preferably between 0.1% and 0.5%, based on the weight of the bath.

After the methylolacrylamide, acid-acting catalyst and inhibitor have been applied to the textile material, the material is normally dried and heated at an elevated temperature to cause reaction of the methylol group with

cellulose. Optionally, the drying and heating operations can be performed at the same time.

If performed separately, the fabric can be dried at any convenient temperature, but short drying periods at 200–230° F. are preferred.

For the heating operation, a temperature of between 250 and 375° F., preferably between 300 and 350° F., is employed. A curing oven is normally used, but any conventional method for heating the textile material at the required temperature can be employed. The time required can be determined as well known in the art, about 1.5 minutes at 350° F., for example.

The fabrics, after the heating step, should be rinsed in water to remove unreacted N-methylolacrylamide, catalyst and inhibitor. The fabrics are then normally dried.

The cellulosic textile materials on which the finish can be applied include all the cellulosic fibers, such as cotton, viscose rayon, linen, ramie, etc., and mixtures thereof. Blends of cellulosic fibers with noncellulosic fibers, such as polyesters (Dacron), polyamides (nylon) and so forth may be used. The textile material can be in the form of woven or nonwoven fabrics, also as yarns, threads, webbing, batting, etc.

The cellulosic textile material obtained by the process of this invention can be used in conventional postcuring operations to obtain very good durable press finishes. Such operations normally include a pressing step to impart creases where creases are desired and smoothness where creases and wrinkles are not desired. The fabric is then further processed (1) by heating in the presence of a suitable catalyst, such as a basic material or a free radical initiator, or (2) by radiation methods, to effect cross-linking and to impart durable press characteristics, including permanence of creases and resistance of flat surface to wrinkling. These procedures are known to those skilled in the art.

Furthermore, it has been discovered that the post-curing operation can be accomplished by heating the fabric obtained by the process of this invention in the presence of zinc nitrate, which of all the acid-acting catalysts is believed to be uniquely suitable for effecting cross-linking of cellulose with N-methylolacrylamide.

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

EXAMPLE I

Seven aqueous pad baths were prepared, each bath containing 15.3% of N-methylolacrylamide, 1.18% of zinc nitrate hexahydrate and the amount of additive shown in Table I.

TABLE I

	Additive	Amount of additive percent
Pad bath:		
A	None	
B	Hydroquinone	0.5
C	Hydroquinone, methyl ether	0.1
D	p-tert.-Butylcatechol	0.1
E	Potassium iodide	1.0
F	Potassium iodide	0.1
G	Potassium iodide and cupric chloride, dihydrate.	{0.1 / 0.1}

The pad baths were applied to 80 x 80 cotton percale by a standard padding procedure. The wet pickup was 85%, indicating the treated fabrics contained 13% of N-methylolacrylamide and 0.95% of zinc nitrate hexahydrate. The fabrics were dried at 225° F. for 2 minutes and were then heated at 350° F. for 1.5 minutes.

The wrinkle recoveries of the fabrics were measured by AATCC Tentative Test Method 66–1959T. Wrinkle recovery values below 240° indicate that minimal cross-linking had occurred.

The results are shown in Table II, Fabrics A–G corresponding to Pad Baths A–G, respectively.

TABLE II

	Wrinkle recovery, W+F degrees	Color
Fabric:		
A	272	Pale yellow.
B	234	Light brown.
C	266	Yellow.
D	277	Green/yellow.
E	237	Off white.
F	274	Pale yellow.
G	236	Off white.

This example demonstrates the effectivenes of potassium iodide, and the combination of potassium iodide and cupric chloride, as a cross-linking inhibitor, i.e., an inhibitor with respect to the reaction of the double bonds of N-methylolacrylamide.

Although hydroquinone acts as an inhibitor, accompanied by discoloration of the fabric, the related phenolics, hydroquinone mono-methylether and p-tertiary-butylcatechol, showed no inhibitive action.

While certain specific embodiments and preferred modes of practice 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 without departing from the spirit of the disclosure or the scope of the appended claims.

I claim:

1. A method for reacting N-methylolacrylamide with a cellulosic textile material comprising impregnating the textile material with N-methylolacrylamide, an acid-acting catalyst and .5% to 2% based on the weight of the impregnating solution potassium iodide and heating the material at a temperature of between 250° and 375° F.

2. The method of claim **1** where the acid-acting catalyst is zinc nitrate.

3. The method of claim **1** wherein said textile material is shaped and creased prior to said heating.

4. A method for reacting N-methylolacrylamide with a cellulosic textile material as in claim **1** comprising impregnating the textile material with N-methylolacrylamide, an acid-acting catalyst, .1% to 1% based on the weight of the impregnating solution potassium iodide and .1% to 1% based on the weight of the impregnating solution cupric chloride and heating the material at a temperature of between 250° and 375° F.

5. The method of claim **4** where the acid-acting catalyst is zinc nitrate.

6. An aqueous textile finish containing N-methylolacrylamide, an acid-acting catalyst and .5% to 2% by weight potassium iodide.

7. A finish as in claim **6** where the acid-acting catalyst is zinc nitrate.

8. An aqueous textile finish containing N-methylolacrylamide, an acid-acting catalyst, .1% to 1% by weight potassium iodide and .1% to 1% by weight cupric chloride.

9. A finish as in claim **8** where the acid-acting catalyst is zinc nitrate.

10. A cellulosic textile material having permanent press properties as obtained by the method of claim **1**.

References Cited

UNITED STATES PATENTS

3,434,161 3/1969 Walsh ..... 8—116.3X

FOREIGN PATENTS

1,383,268 11/1964 France ..... 8—116.3

GEORGE F. LESMES, Primary Examiner

J. CANNON, Assistant Examiner

U.S. Cl. X.R.

8—115.7, 120, 243; 38—144; 117—93.31; 252—397; 260—666.5, 681.5, 29.4