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N-METHYLOLACRYLAMIDE TEXTILE FINISH CONTAINING CITRIC ACID OR DICYANDIAMIDE

Robert George Weyker, North Plainfield, William Frederick Baitinger, Jr., Hillsborough Township, Somerset County, and John Gregory de Marco, Somerville, N.J., assignors to American Cyanamid Company, Stamford, Conn.

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ABSTRACT OF THE DISCLOSURE

This invention relates to textile finishes employing N-methylolacrylamide. More particularly, it relates to (1) aqueous solutions of N-methylolacrylamide containing citric acid or dicyandiamide (2) the method of treating cellulose-containing textile materials with the solutions and (3) the textile materials thus treated.

N-methylolacrylamide has been used as a wash-and-wear or permanent press finish on textile materials containing cellulosic fibers. However, the finish suffers from a serious defiency, namely, yellowing of the treated textile material, particularly after commercial laundering in alkaline (high pH) wash liquors. The yellowing effect is especially severe when the preferred curing catalyst, zinc nitrate, is employed. Furthermore, concentrated solutions of N-methylolacrylamide on standing have a tendency to polymerize, particularly under conditions of elevated temperature or in the presence of contaminants such as iron. A storage problem, therefore, exists for N-methylolacrylamide.

Cupferron, which is C_6H_5—N(NO)—ONH_4, is a contional stabilizing agent used during the preparation of N-methylolacrylamide. Whereas cupferron is presumably helpful in reducing polymerization during the preparation step. It is not adequate to prevent polymerization during the storage of solutions of N-methylolacrylamide.

It has now been discovered that when citric acid or dicyandiamide is added to the N-methylolacrylamide finish, the yellowing of cellulosic fibers is greatly decreased. The improvement is particularly apparent when zinc nitrate is employed as the curing catalyst in a heat curing procedure. Solutions of N-methylolacrylamide are also stabilized against polymerization by the addition of citric acid or dicyandiamide.

In copending, commonly assigned application Ser. No. 665,966, filed Sept. 7, 1967, now Pat. 3,561,916 is disclosed a method for imparting a durable press finish by applying N-methylolacrylamide and zinc nitrate, and heating the fabric to effect cross-linking of cellulosic fibers.

The textile finishes of this invention comprise aqueous solutions of N-methylolacrylamide containing citric acid or dicyandiamide.

The concentrated solutions of N-methylolacrylamide as normally prepared, stored, shipped and sold contain between 30% and 85%, preferably between 50% and

80%, of N-methylolacrylamide. The amount of citric acid monohydrate or dicyandiamide added to the concentrated solution to prevent polymerization is between 0.01% and 12%, preferably between 0.1% and 8%, based on weight of the solution. For maximum stability of the solution, the pH of the solution should be adjusted to between 3.5 and 5.5, preferably between 4 and 5.

N-methylolacrylamide is normally applied to textile material from aqueous solution using any conventional method such as by padding, dipping, spraying and the like, as well known in the art. Before application, the concentrated solution of N-methylolacrylamide is diluted with water to a desired strength, of between 2% and 30%, preferably between 5% and 20%, depending on the type of fabric and the method used for applying the finish. The amount of N-methylolacrylamide deposited on the textile material is between 2% and 10%, preferably between 3% and 7%.

The application solutions of N-methylolacrylamide contain between 0.2% and 2%, preferably between 0.6% and 1.6%, of citric acid monohydrate or dicyandiamide. The amount of citric acid or dicyandiamide is dependent on the amount of catalyst employed. It is generally from about 3 to 4 times the amount of catalyst. For example, when 1%, 2% or 3% of zinc nitrate is used, the recommended amounts of citric acid monohydrate or dicyandiamide are 3% to 4%, 6% to 8% and 10% to 12%, respectively. The pH of the finish containing citric acid as it is to be applied to textiles should be between 3.5 and 5.5, preferably between 4 and 5, for maximum effectiveness of the citric acid. Since the pH of the solution after addition of the required amount of citric acid is normally between 2.0 and 2.5, it will require adjustment to obtain the desired pH for applying to textiles. Sodium hydroxide or other alkaline material can be used to effect the pH adjustment. The same pH range for applying to textiles is also recommended for the solution when using dicyandiamide, but adjustment may not be necessary with this solution.

The finish containing N - methylolacrylamide and citric acid or dicyandiamide can be applied to cellulosic textile materials and cured thereon by any of the methods described above. The reduction in discoloration of the textile material is particularly noticeable when heat curing in the presence of zinc nitrate is at least one step in the cross-linking procedure.

The preferred catalyst is zinc nitrate. However, other catalysts may be used if desired, for example, the well-known acid-acting catalysts, such as magnesium chloride, ammonium nitrate, ammonium chloride, ammonium sulfate, diammonium acid phosphate, 2-amino-2-methyl-1-propanol hydrochloride, and the like. The amount of catalyst applied to the fabric is between 0.1% and 5% on the weight of the fabric, preferably between 0.5% and 3% on the weight of the fabric.

The textile materials treated by the process of this invention should contain at least 25% of cellulosic fibers. These cellulosic fibers include cotton, viscose, linen, ramie, hemp, sisal, etc., and mixtures thereof. Blends of cellulose fibers with non-cellulosic fibers, including polyester fibers such as Dacron, polyamide fibers such as nylon, acrylic fibers such as Orlon and Creslan may be used.

The textile materials can be in the form of woven or nonwoven fabrics, also yarns, threads, webbing, batting, etc.

After application of N-methylolacrylamide, catalyst and citric acid or dicyandiamide, the textile material is normally dried to remove the water present. This can be done in any conventional manner, as by oven drying at 200° F.–225° F. The dried material can then be treated in a number of ways as suggested above. The cross-linking can be accomplished in one or two steps. The heat cure method in the presence of a catalyst requires a temperature between 300 and 375° F., preferably between 340° F. and 370° F. Of course, the drying and heat curing steps may be combined in one operation. The time required for curing depends on the temperature used and is easily determined. At 350° F. about 1.5 minutes are required.

The following examples are given to illustrate the invention and are not intended to be limitative. In the examples fabrics treated with N-methylolacrylamide to render them crease resistant as described above, were submitted to tests to determine the degree of discoloration during laundering.

A commercially used, accelerated test for discoloration of fabrics treated with N-methylolacrylamide during alkaline laundry operations consists of placing swatches of the treated fabric in a boiling aqueous 0.5% sodium hydroxide solution. Fabrics which show little or no discoloration under these two tests are considered to be satisfactory for withstanding normal alkaline commercial laundering. This test was used in the examples.

EXAMPLE 1

Preparation of N-methylolacrylamide solution

A mixture of 560 g. (8.0 moles) of acrylamide, 734 g. (8.8 moles) of 36% aqueous formaldehyde, 2 g. of 50% aqueous sodium hydroxide and 0.06 g. of cupferron was stirred at 20–25° C. for several hours. The cupferron, which is nitrosophenyl hydroxylamine, was used as a stabilizing agent during the preparation of the N-methylolacrylamide. The resulting solution of N-methylolacrylamide contained 60% solids and 4% free formaldehyde (89% complete methylolation of the acrylamide). The pH was adjusted to 5.2 with hydrochloric acid.

EXAMPLE 2

Preparation of N-methylolacrylamide solution containing citric acid

A mixture of 280 g. (4.0 moles) of acrylamide, 367 g. (4.4 moles) of 36% aqueous formaldehyde, 2 g. of 50% aqueous sodium hydroxide and 0.06 g. cupferron was stirred at 20–25° C. for several hours. The resulting solution of N-methylolacrylamide contained 58.8% solids and 3.4% free formaldehyde (92.5% complete methylolation of the acrylamide). The pH was 10.0. After adding 22.6 g. of citric acid monohydrate, the pH was 3.2. The pH was adjusted to 5.2 with 50% aqueous sodium hydroxide.

EXAMPLE 3

In this example four aqueous pad baths of the following composition were prepared:

	A	B	C	D
Product of Example 1 (60%)	12.2	12.2	16.7	16.7
Zinc nitrate hexahydrate	1.22	1.22	1.67	1.67
Citric acid monohydrate		0.41		0.57
Water to	100	100	100	100
pH	5.5	*5.5	5.5	*5.5

*Adjusted from pH 2.3 to pH 5.5 with sodium hydroxide.

Pad Baths A and B were applied to white 80 x 80 cotton percale and Pad Baths C and D were applied to white 65%/35% Dacron/cotton poplin by standard padding procedures obtaining 82% and 60% wet pickups, respectively. The fabrics containing 6% on weight of fabric of N-methylolacrylamide solids and 1% on weight of fabric and zinc nitrate hexahydrate, were dried at 225° F. for 2 minutes, and then were heated at 350° F. for 1.5 minutes. Fabrics A, B, C, and D correspond to Pad Baths A, B, C, and D respectively.

Swatches of the four fabric samples were placed in boiling 0.5% aqueous sodium hydroxide for one hour. Fabrics B and D were less yellow than Fabrics A and C, thus demonstrating the effectiveness of citric acid in reducing the yellowness caused by N-methylolacrylamide. This represents an accelerated test for yellowing under alkaline laundering conditions.

EXAMPLE 4

In this example three aqueous pad baths of the following composition were prepared:

	A	B	C
Product of Example 1 (60%)	16.7		
Product of Example 2 (58.8%)		17.0	17.0
Zinc nitrate hexahydrate	1.67	1.67	1.67
Water to	100	100	100
pH	4.7	2.7	*4.7

*pH adjusted with sodium hydroxide.

The pad baths were applied to white 65%/35% Dacron/cotton poplin by standard padding procedure obtaining a 69% wet pickup. The fabrics, containing 6% on weight of fabric N-methylolacrylamide solids and 1% on weight of fabric of zinc nitrate hexahydrate, were dried at 225° F. for 2 minutes, and then heated at 350° F. for 1.5 minutes. Fabrics A, B and C correspond with Pad Baths A, B and C.

The fabrics were examined for yellowing compared to the original untreated fabric. Fabric C showed very little yellowing, while Fabrics A and B showed a greater degree of yellowing.

Swatches of the fabric were placed in boiling 0.5% aqueous sodium hydroxide for one hour as described in Example 3. Fabric C showed very little increase in yellowness, while Fabrics A and B showed a considerable increase in yellowness when compared with the initial Fabrics A, B and C respectively.

This example demonstrates the effectiveness of citric acid, when used in a pad bath of pH 4–5, in reducing the discoloration caused by N-methylolacrylamide.

EXAMPLE 5

In this example, the following solutions were prepared:

Solution I: Dicyandiamide (1.5 parts) was added to 100 parts of the product of Example 1.

Solution II: Dicyandiamide (3.7 parts) was added to 100 parts of the product of Example 1.

Two aqueous pad baths of the following compositions were prepared:

	A	B
Solution I (60%)	16.7	
Solution II (60%)		16.7
Zinc nitrate hexahydrate	1.67	1.67
Water to	100	100
pH	5.5	5.5

Pad Baths A and B were applied to white 65%/35% Dacron/cotton poplin by standard padding procedure obtaining a 60% wet pickup. The fabrics containing 6% O.W.F. of N-methylolacrylamide solids and 1% zinc nitrate hexahydrate, were dried at 225° F. for 2 minutes and then heated at 350° F. for 1.5 minutes. Fabrics A and B correspond to Pad Baths A and B, respectively.

Swatches of the fabrics were placed in boiling 0.5% aqueous sodium hydroxide for one hour. Fabrics A and B were less yellow than a similar fabric treated in the same manner with the product of Example 1 with no dicyandiamide added, thus demonstrating the effectiveness of dicyandiamide in reducing yellowness caused by N-methylolacrylamide.

EXAMPLE 6

In this example, two pad baths of the following composition were prepared:

	A	B
Product of Example 1 (60%)	16.7	16.7
Zinc nitrate hexahydrate	1.67	3.33
Citric acid	0.62	0.62
Water to	100	100
pH	*4.9	*4.9

*pH adjusted from 2.5 with sodium hydroxide.

The pad baths were applied to white 65%/35% Dacron/cotton poplin by standard padding procedure obtaining a 60% wet pickup. The fabrics containing 6% O.W.F. of N-methylolacrylamide solids and 1% of zinc nitrate hexahydrate, were dried at 225° F. for 2 minutes and then heated at 350° F. for 1.5 minutes. Fabrics A and B correspond to Pad Baths A and B, respectively.

Fabric B was yellower than Fabric A indicating the necessity for using increased amounts of citric acid when the amount of zinc nitrate is increased.

EXAMPLE 7

In this example solutions (a) to (d) were prepared by adding the amounts of citric acid or dicyandiamide shown below to 100 parts of the product of Example 1.

(a) 3.7 parts citric acid monohydrate
(b) 7.4 parts citric acid monohydrate
(c) 3.7 parts dicyandiamide
(d) 7.4 parts dicyandiamide

Five Pad Baths (A–E) of the following composition were prepared:

	A	B	C	D	E
Solution (a)	16.7				
Solution (b)		16.7			
Solution (c)			16.7		
Solution (d)				16.7	
Product of Example 1					16.7
Zinc nitrate hexahydrate	3.33	3.33	3.33	3.33	3.33
Water to	100	100	100	100	100
pH*	4.5	4.5	4.5	4.5	4.5

*The pH's were adjusted with hydrochloric acid or sodium hydroxide as required.

The pad baths were applied to white 60%/35% Dacron/cotton poplin by a standard padding procedure obtaining a 60% wet pickup. The fabrics, containing 6% O.W.F. of N-methylolacrylamide solids and 2% zinc nitrate hexahydrate, were dried at 225° F. for 2 minutes and then heated at 350° F. for 1.5 minutes. Fabrics A–E correspond to Pad Baths A–E, respectively.

Swatches of the fabrics were placed in boiling 0.5% aqueous sodium hydroxide solution for 0.5 hour. Fabrics F and H were less yellow than Fabrics E and G, demonstrating the benefit of using increased amounts of citric acid or dicyandiamide when the amount of zinc nitrate is increased over the amounts used in Examples 3 and 5.

EXAMPLE 8

(A) A glass reaction vessel was charged with 47.6 g. (0.698 mole) of 44% aqueous formaldehyde, 14.4 g. of water, 0.004 g. cupferron, 47 g. (0.662 mole) of acrylamide and sufficient 50% aqueous sodium hydroxide to provide a pH of 9.5–10.0. The mixture was stirred at 25–30° C. for 3.5 hours. The resulting clear solution contained 2.2% free formaldehyde, indicating 93.5% complete methylolation of the acrylamide, and 58.2% solids.

(B) A 45 g. portion of Solution A was removed and 2.3 g. of dicyandiamide was added.

Each solution was adjusted to pH 5 with hydrochloric acid. Samples of each solution were stored in closed containers at room temperature (about 22°), 39° and 50° C. The time for polymerization was noted and is shown in Table I.

TABLE I

	Polymerization time		
	22°	39°	50°
A	4 days	<3 days	<3 days
B	>14 days	>14 days	>14 days

This example demonstrates the effectiveness of dicyandiamide as a stabilizing agent for aqueous solutions of N-methylolacrylamide.

EXAMPLE 9

(A) The procedure of Example 8–A was followed with the exception that 0.5 g. of steel wool was introduced into the reaction mixture before the acrylamide. The resulting clear solution contained 2.0% free formaldehyde, indicating 94.6% complete methylolation of the acrylamide, and 58% solids.

(B) A 45 g. portion of Solution A was removed and 2.3 g. of dicyandiamide was added.

Samples of each solution, after pH adjustment to 5, were tested for stability by the method of Example 8. The results are shown in Table II.

TABLE II

	Polymerization time		
	22°	39°	50°
A	<3 days	<3 days	<3 days
B	>14 days	>14 days	>14 days

EXAMPLE 10

(A) The procedure of Example 8–A was followed with a 3-hour reaction period. The resulting clear solution contained 2.5% free formaldehyde, indicating 92.5% complete methylolation of the acrylamide.

(B) The procedure of Example 9–A was followed. The clear solution contained 3.0% free formaldehyde.

Citric acid monohydrate (2.9 g.) was added to each of the above solutions and the pH was adjusted to 5 with 50% aqeuous sodium hydroxide. Samples of each solution were tested for stability by the method of Example 8. The results are shown in Table III.

TABLE III

	Polymerization time		
	22°	39°	50°
A	>18 days	>18 days	>18 days
B	>18 days	>18 days	>18 days

The effectiveness of citric acid as a stabilizing agent for aqueous solutions of N-methylolacrylamide is demonstrated when solutions of A and B are compared with Solution A of Example 8 and Solution A of Example 9, respectively.

We claim:

1. In the process of imparting wash-and-wear and permanent press properties to a cellulosic textile material wherein (1) the material is impregnated with a solution of N-methylolacrylamide, (2) zinc nitrate is employed as a catalyst and (3) the fabric is heated to effect cross-linking of cellulose fibers, the improvement comprising using a solution of N-methylol acrylamide which includes dicyandiamide or citric acid monohydrate as a stabilizer.

2. An aqueous textile treating composition containing between 2% and 75% of N-methylolacrylamide, between

1% and 12% of citric acid monohydrate or dicyandiamide as a stabilizer and zinc nitrate.

3. A cellulosic textile material produced by the process of claim 1.

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GEORGE F. LESMES, Primary Examiner

J. CANNON, Assistant Examiner

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