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REMOVAL OF FREE FORMALDEHYDE FROM SOLUTIONS OF METHYLOLATED CARBAMATE FINISHING AGENTS AND TEXTILES TREATED THEREWITH

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ABSTRACT OF THE DISCLOSURE

The free formaldehyde content of a solution of methylolated carbamate finishing agent is reduced by removal of free formaldehyde through reaction with phthalimide to give an insoluble phthalimide-formaldehyde adduct that is readily separated from the solution. Fabric sensitized by treatment with the so-modified solution has a low level of formaldehyde release. When the sensitized fabric is cured, the resultant fabric is wrinkle resistant and exhibits all the other properties characteristic of the carbamate finish.

FIELD TO WHICH INVENTION RELATES

This invention relates to a process for removing and thereby decreasing the amount of free formaldehyde in solutions of carbamate finishing agents. The so-modified solutions are suitable for use in finishing treatments to impart wrinkle resistance to textile materials. More specifically, the invention relates to a method of reducing the amount of free formaldehyde in solutions of carbamate finishing agents by reaction of free formaldehyde with phthalimide. This reaction gives an insoluble adduct that is readily separated from the solution of the finishing agent to reduce the free formaldehyde content thereof. The invention also relates to the use of the so-modified solutions of carbamate finishing agents to give sensitized fabrics with greatly decreased levels of formaldehyde release that are suitable for use in post-cure processing but without adverse effect on the wrinkle resistance, chlorine resistance, and hydrolysis resistance of the subsequently cured fabric.

DEFINITIONS

By free formaldehyde we mean the formaldehyde that is present but not bound and is therefore free to volatilize from solutions of agents and from sensitized fabric. Free formaldehyde can be quantitatively determined conveniently by a titration method. Details of a procedure for the determination of free formaldehyde are given by Reid, Kullman, and Reinhardt in American Dyestuff Reporter, vol. 59, No. 6, pp. 26–34, 1970.

The amount of formaldehyde release from a fabric is determined by a test method of the American Association of Textile Chemists and Colorists (AATCC Test Method 112–1968, Formaldehyde Odor in Resin Treated Fabric, Determination of: Sealed Jar Method, Technical Manual of the AATCC, vol. 47, pp. 85–86, 1971). The standardized conditions of this test provide the means of obtaining comparative values of formaldehyde release from fabrics finished by various treatments.

The term sensitized fabric is used in the textile finishing and garment fabrication industries to denote the material at an intermediate stage of the post-cure finishing process. A sensitized fabric is one that (a) has been impregnated with a finishing agent, usually a methylol-amide type crosslinking agent that is capable of producing durable press properties in cotton or cellulose-containing fabrics, and a catalyst for the reaction between the finishing agent and the textile material, and (b) has been dried under conditions that do not cause any appreciable reaction between the finishing agent and the textile material. The sensitized fabric is then ready for use in the post-cure durable press process. The sensitized fabric is packaged and may be stored for prolonged periods before garment manufacture in which it is cut to pattern, sewn, trimmed, then shaped by pressing to introduce creases, pleats, etc., and to smooth the garment in its final configuration. The sensitized fabric in the form of the shaped garment is then cured, usually in an oven, to bring about the reaction of the finishing agent and the cellulosic component of the textile material of the garment and thus make the shaped configuration durable to wearing and laundering.

Post-cure processing refers to that class of finishing treatments which impart durable press properties to the textile product through a postponed cure of the sensitized fabric after the textile product has been made up into a garment or other apparel or household item. The term post-cure processing is widely used in the textile industry; however, the terms deferred cure and delayed cure also have been applied to this type of durable press process.

THE PROBLEM

In the manufacture of post-cure durable press garments, a serious problem is the odor of formaldehyde from sensitized fabric which causes discomfort and sometimes is an actual health hazard to those who cut, sew, trim, and press the garment. This odor is due to the release of free formaldehyde from the fabric which can cause objectionable response—lachrymatory and sometimes allergenic—from those who come into proximity of the fabric. The same is true for those in the finishing plant who must handle solutions of the finishing agent that contain excessive amounts of free formaldehyde.

When packages of sensitized fabric are opened at the garment cutting plant, the free formaldehyde therein is slowly released to create unpleasant and potentially unsafe working conditions. The presence of a recirculation air-conditioning system can intensify this problem. The free formaldehyde in the sensitized fabric is due to (a) residual or unreacted formaldehyde that was present in the finishing solution when it was applied and has dried on the fabric; and (b) formaldehyde that has been produced due to de-methylolation (reversal of the chemical reaction by which the agent was prepared) of the methylolated amide compound used in finishing. In the industry today, the problem of free formaldehyde has restricted post-cure finishing mainly to one agent, dimethylol dihydroxyethyleneurea, which is available in solutions of low free formaldehyde content and which yield sensitized fabrics with moderate levels of formaldehyde release. The industry, however, would like to use other agents which may be more suitable, less expensive, or have other desirable qualities but which at present are unusable because of formaldehyde release problems.

Among those agents that could be utilized advantageously in the post-cure process, if formaldehyde release could be eliminated or reduced to an unobjectionable level, are the methylol carbamates. The primary source of free formaldehyde in fabric sensitized with carbamate agents is the excess formaldehyde which must be used in preparation of the finishing agent to maximize conversion of the carbamate to the dimethylol derivative. Stability of the methylolated carbamate agent in the sensitized fabric to de-methylolation during storage has been demonstrated to be excellent.

THE PRIOR ART

In the prior art various means have been proposed for reducing the free formaldehyde content of finishing agents. Albeit many proposed methods are successful in decreasing the amount of free formaldehyde, elimination of some desirable characteristic of the finish or the introduction of an undesirable effect is often a consequence of the action.

For example, it has been suggested by Frich and Reinhardt, American Dyestuff Reporter, vol. 56, No. 9, p. 41, Apr. 24, 1967, that by use of lower molar ratios of formaldehyde to carbamate in synthesis, agents can be prepared which release less formaldehyde fumes in durable press processing. However, this improvement is achieved at the expense of a lower level of chlorine resistance in the finished fabrics.

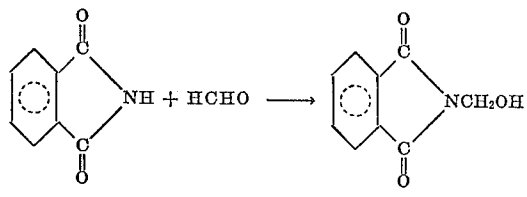
Another approach to decreased free formaldehyde has been the treatment of the solution of the methylolated finishing agent with a chemical reactant that combines with the free formaldehyde and thus binds it from release during fabric processing. Although successful in controlling free formaldehyde, undesirable collateral effects on the finished fabrics have been produced by this chemical technique, principally decreased durability and substantially decreased chlorine resistance of the finish upon hydrolysis and severe laundering. Chemical methods of this type have been disclosed by Reid, Kullman, and Reinhardt in American Dyestuff Reporter, vol. 59, No. 6, pp. 26–28, 32, and 34, 1970, by Weiland in U.S. Pat. 3,590,-100, and by Bertini and Edmondson in U.S. Pat. 3,597,-380. The principal fault with these chemical methods lies in the fact that the free formaldehyde is bound through some chemical reaction but remains in the solution of finishing agent. In this type of modification, extraneous materials are thus applied to the textile substrate along with the desired finishing agent and become bound in the finish. These extraneous materials impart properties and susceptibilities that are different than those of the finish produced by the finishing agent being used.

OBJECTS OF THE PRESENT INVENTION

It is an object of this invention to provide a method for decreasing the amount of free formaldehyde in solutions of methylolated carbamate finishing agents by removal of the free formaldehyde from the solution. It is a further object to produce sensitized fabrics with reduced levels of formaldehyde release. Another object is to produce a wrinkle resistant fabric from said sensitized fabric without undesirable side effects that impair the utility, aesthetics, value, or durability of the resulting wrinkle resistant product.

HOW THE OBJECTIVES ARE ACHIEVED

The objects of the present invention are achieved by removing free formaldehyde from solutions of methylolated carbamate finishing agents by reaction of the free formaldehyde with phthalimide. The chemical reaction may be represented by the following equation:



The product of the reaction, the phthalimide-formaldehyde adduct (also called N-methylol phthalimide and N-hydroxymethyl phthalimide), is insoluble and readily separated from the solution. After separation, the adduct can be dissociated so that the phthalimide can be recovered for subsequent reuse which, of course, is advantageous from an economic viewpoint.

Separation of the adduct from the methylol carbamate solution completely and irreversably removes the free formaldehyde. This is unlike those methods in which the free formaldehyde is bound through formation of a soluble adduct which remains in the solution and is thus subject to reversion to regenerate the free formaldehyde. Furthermore, with a soluble adduct in a solution of finishing agent, a foreign material is present that can react with the cellulose during the textile finishing treatment. Such reaction introduces other, often undesirable, properties and susceptibilities along with those desired from the finishing agent employed. In the process of the present invention, separation of the insoluble phthalimide-formaldehyde adduct from the solution of the finishing agent precludes the introduction of such extraneous effects in the finishing treatment.

Textile materials sensitized by treatment with carbamate finishing agents with free formaldehyde removed by the process of the instant invention have greatly diminished formaldehyde release values. The sensitized fabrics when cured yield wrinkle resistant fabrics with the excellent chlorine resistance and hydrolysis resistance that are characteristic of carbamate finishes. There are no undesirable collateral properties introduced as no extraneous material is present along with the carbamate finishing agent.

Use of solutions of methylolated carbamates with free formaldehyde removed by the process of this invention eliminates the need for extra care in handling, expensive safety equipment, and special processing methods to avoid pollution of the surrounding atomsphere by the noxious fumes of formaldehyde during preparation of treatment baths and subsequent finishing of fabric. The necessity is minimized for extra precautions to protect workers from inhalation of noxious formaldehyde fumes during application of finishing solutions to textile materials, during drying operations in sensitization, during handling of the sensitized fabric in warehousing and in garment fabrication, and in curing operations to accomplish final finishing of the fabric.

SCOPE OF THE INVENTION

Textile materials which can be treated with finishing agents modified by the process of this invention include cellulose fibers, yarns, fabrics, and the like. The fabrics can be woven, knitted, or nonwoven. The cellulose may be natural, such as cotton, linen, ramie, and the like, or regenerated, such as viscose and other types of rayon. In addition to textile materials consisting wholly of cellulose, those in which cellulose fibers are blended with synthetic fibers can be treated. Among these, particularly amenable are blends that contain cotton and polyester fibers.

Treatment of the textile materials with finishing agents modified by the process of this invention may be carried out by any of those methods inw hich methylolated agents are employed to impart wrinkle resistance and durable press properties. No changes in treatments are necessary to accommodate use of these finishing agents in which free formaldehyde has been removed. The finishing agents of this invention are particularly suited to post-cure processing because of the low formaldehyde release from sensitized fabrics so-treated. The amount and type of finishing agents, catalyst, chemical auxiliaries, and the treatment conditions, and other variables of chemical finishing processes for producing wrinkle resistant cellulosic textiles known to those skilled in the art are not affected by use of agents from which free formaldehyde has been removed by the process of this invention.

Free formaldehyde is removed from the solution of finishing agent by addition of phthalimide to the solution. A reaction between the free formaldehyde and phthalimide

occurs to give an insoluble adducts as shown in the above cited chemical equation. The pH of the solution must be below about 8. Preferably, the pH should be below 7. Other imides that yield insoluble formaldehyde adducts can be employed similarly in the process of this invention. The insoluble adduct is separated from the solution of finishing agent by filtering, decanting, or any other convenient technique. Removal of the adduct from the solution of finishing agent removes the free formaldehyde which has reacted with the phthalimide to produce the adduct. By adjustment of the amount of phthalimide added to the solution of finishing agent, the amount of free formaldehyde removed can be adjusted. That is, ideally, one mole of phthalimide is needed for complete removal of each mole of free formaldehyde present in the solution of finishing agent. In actual practice, as is the case in most reactions of organic chemistry, a slight excess of phthalimide is necessary to react with all the free formaldehyde. However, if complete removal of free formaldehyde is not needed but merely reduction of the amount to a specified level, less phthalimide than that chemically euqivalent to the free formaldehyde can be employed. Thus, the operator has the means of decreasing the level of free formaldehyde as desired.

This invention is directed particularly at removal of free formaldehyde from solutions of methylolated carbamate finishing agents. Among such agents are the methylol derivatives of alkyl carbamates such as methyl, ethyl, propyl, butyl, and the like, methylolated derivatives of hydroxyalkyl carbamates such as hydroxyethyl, hydroxypropyl and the like, and methylolated derivatives of alkoxyalkyl carbamates such as methoxyethyl, methoxypropyl and the like. In principle, the invention is applicable to other methylol type finishing agents such as the methylol derivatives or ureas, modified ureas including ethyleneureas, dihydroxyethyleneureas, propyleneureas, urons, triazones, and the like, and triazines.

SUMMARY OF THE INVENTION

In summary, this invention makes available a method whereby free formaldehyde is removed from a solution of finishing agent. The solution is treated with phthalimide which reacts with the free formaldehyde to produce an insoluble phthalimide-formaldehyde adduct that can be separated from the solution and thus remove the free formaldehyde. Not only does separation of the phthalimide-formaldehyde adduct remove free formaldehyde but it assures that there are no undesirable side effects of subsequently finished fabrics from such removal as are often experienced when other chemical methods are employed for decreasing the level of free formaldehyde in the finishing agent solution. Sensitized fabrics produced by use of the finishing agents of this invention have low formaldehyde release values and upon post-curing yield wrinkle resistant fabrics without impairment of the other properties characteristically produced by the finishing agent. The invention provides a route to the production of methylolated carbamate finishing agents with low free formaldehyde content which makes these agents attractive and practical for greater utilization in the important post-cure process for durable press finishing.

The following examples must not be construed as limiting the scope of the invention but are given to illustrate its teachings. Numerous modifications within the spirit of the invention will become apparent to those skilled in the art.

EXAMPLE 1

To 30 parts of a 50% (wt./wt.) aqueous solution of dimethylol methyl carbamate (Solution A) that had a strong odor of formaldehyde was added 8.8 parts of phthalimide. The mixture was heated to 167° F. with stirring until solubilization of the phthalimide occurred, then held at 158–167° F. for five minutes. On cooling to room temperature, precipitation of the phthalimide-formaldehyde adduct occurred. The solution was filtered; no strong odor of formaldehyde was evident in the filtrate (Solution B).

EXAMPLE 2

Portions of Solutions A and B of Example 1 were analyzed for free formaldehyde content by the aforementioned procedure of Reid, Kullman, and Reinhardt. The results were:

Solution:	Percent free formaldehyde
A	5.0
B	0.4

The efficacy of removal of free formaldehyde through formation of the insoluble phthalimide-formaldehyde adduct is readily apparent from these figures. Of the free formaldehyde originally present, 92% was removed in this embodiment of the process of this invention.

EXAMPLE 3

Two solutions were prepared for the treatment of fabric consisting of:

Solution C

20 parts of Solution A (Ex. 1)
0.6 part of $Zn(NO_3)_2 \cdot 6H_2O$
79.4 parts of water

Solution D

20 parts of Solution B (Ex. 1)
0.6 part of $Zn(NO_3)_2 \cdot 6H_2O$
79.4 parts of water

Samples of cotton printcloth were impregnated with these solutions and the excess squeezed off, and the process was repeated to ensure thorough impregnation. The wet, impregnated fabrics were sensitized by drying in an oven at 140° F. for 7 minutes. Immediately after sensitization a weighed portion of each fabric was suspended above 50 ml. of distilled water in a glass jar and the jar sealed. The jars were placed in an oven at 120° F. (49° C.) for 20 hours as specified in AATCC Test Method 112–1968 and the formaldehyde release subsequently determined. Fabric sensitized with Solution C released 5800 p.p.m. of formaldehyde and fabric sensitized with Solution D released only 2200 p.p.m.

It can be readily noted that sensitization treatment with Solution D resulted in a substantially lower formaldehyde release value than that of sensitization treatment with Solution C. This illustrates that removal of free formaldehyde from the dimethylol methyl carbamate solution through formation and separation of the phthalimide-formaldehyde adduct gives a solution with lowered free formaldehyde content and use of this solution for sensitization gives a sensitized fabric with a substantially lowered level of formaldehyde release.

EXAMPLE 4

Portions of the sensitized fabrics of Example 3 were cured in an oven for 3 minutes at 320° F., then washed and dried. To determine resistance to acid hydrolysis of the finished fabrics, portions of each were treated with a solution buffered to pH 3.2 for 30 minutes at 104° F., then washed and dried. It is known that hydrolysis of this type does not affect a carbamate finish but causes susceptibility to chlorine damage in a finish produced by treatment with a carbamate agent modified with ethyleneurea for decreased free formaldehyde content (cf. Table IV and related discussion in the previously cited paper by Reid, Kullman and Reinhardt).

Properties of the fabrics of the present example before and after hydrolysis are given in Table I. Conditioned wrinkle recovery (WRA) was determined by the procedure of AATCC Test Method 66–1968; wet wrinkle recovery was determined following the same procedure on wet specimens that had been blotted to remove excess moisture. Resistance to chlorine damage was determined by AATCC Test Method 92–1967.

TABLE I

Treatment	WRA, (W+F), deg. Cond.	Wet	Str. retention in chlor.-scorch test, percent
Solution C:			
Cured (before hydrolysis)---	281	271	100
Cured (after hydrolysis)----	274	270	100
Solution D:			
Cured (before hydrolysis)---	274	266	100
Cured (after hydrolysis)----	270	273	94

The properties of fabric finished with Solution D are as good as those of fabric finished with Solution C. This shows that phthalimide treatment of dimethylol methyl carbamate solution to reduce the free formaldehyde content and to lower formaldehyde release from the sensitized fabric has no adverse effect on the properties of the cured fabric.

We claim:

1. A process for the treatment of cellulose containing textiles to give wrinkle-, acid-, and chlorination-scorch resistance properties which comprises:

(a) preparing a treatment bath consisting of:

(i) about from 0.3 to 1.0 part of zinc nitrate hexahydrate;

(ii) about from 8 to 20 parts of the solution resulting after separation of the insoluble adduct produced by reaction of about 8.8 parts of phthalimide with the free formaldehyde present in about 30 parts of a 50% (wt./wt.) aqueous dimethylol methyl carbamate, and;

(iii) sufficient water to make 100 parts

(b) impregnating a cellulosic containing textile with the solution of step (a);

(c) sensitizing the impregnated fabrics by heating at 140° F. for 7 minutes; and

(d) curing the sensitized fabric of step (c) by heating at 320° F. for 3 minutes.

2. The sensitized cellulose containing textile product prepared by the process which comprises:

(a) preparing a treatment bath consisting of:

(i) about from 0.3 to 1.0 part of zinc nitrate hexahydrate;

(ii) about from 8 to 20 parts of the solution resulting after the separation of the insoluble adduct produced by reaction of about 8.8 parts of phthalimide with the free formaldehyde present in about 30 parts of a 50% (wt./wt.) aqueous dimethylol methyl carbamate; and

(iii) sufficient water to make 100 parts;

(b) impregnating a cellulosic containing textile with the solution of step (a); and

(c) sensitizing the impregnated fabric by heating at 140° F. for 7 minutes.

3. The textile product prepared by the process of claim 1.

References Cited

UNITED STATES PATENTS

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8—115.5, 115.7, Dig.; 38—144; 260—29.4 R, 482 C, 701