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Formaldehyde Release from Durable Press Fabrics

By THEODORE F. COOKE

ABSTRACT

The treatment of cellulosic fabrics with formaldehyde reactants to give durable press fabrics and the release of formaldehyde from these fabrics has been reviewed historically. The toxicity of formaldehyde and the results of recent epidemiological studies are summarized. Also presented are the results of recent studies sponsored by the Consumer Product Safety Commission of formaldehyde released by consumer products including durable press fabrics and of formaldehyde transfer from patches of cotton fabric treated with dimethyloldihydroxyethyleneurea (DMDHEU) to shaven rabbits wearing these patches next to their skin. The mechanism of formaldehyde release is discussed, including recent data obtained from an ongoing study at Textile Research Institute. This work shows that surprisingly large amounts of free formaldehyde are sorbed by cellulosic fabric. It also shows that the rate of cleavage of C-O bonds in crosslinks of DMDHEU with cellulose is high under acid conditions and very low under neutral and alkaline conditions, whereas the rate of cleavage of the C-N bond is relatively low under acid and neutral conditions and high under alkaline conditions. The important factors in the control of formaldehyde release from durable press fabrics are summarized.

KEY TERMS

Cellulose
Crosslinking
Durable Press
Formaldehyde Reactant
Formaldehyde Release
Olney Medal Address: 1983

DURABLE press fabrics treated with formaldehyde reactants have the potential to release small quantities of formaldehyde, particularly at elevated temperature and high relative humidity. Since formaldehyde is a toxic chemical and since recent studies have shown that it is carcinogenic to rats and mice, a great deal of effort has been expended to decrease the amount of formaldehyde released from the treated fabrics. This paper will discuss work that has been carried out in the past as well as research currently underway which is beginning to provide a reasonably clear picture of the important factors involved in formaldehyde release from durable press fabrics.

Durable press properties are imparted to fabrics containing cellulosic fibers mainly by treatment with formaldehyde reactants. To be sure, some degree of durable press properties can be imparted by (1) blending the cellulose fibers with other fibers, such as polyester, having greater recovery from deformation; (2) surface treatments which may reduce fiber and yarn friction, such as polyethylene emulsion treatment, and/or which may provide an elastic fiber-to-fiber or yarn-to-yarn bond, such as a polyurethane emulsion treatment; and (3) treatment with a swelling agent such as liquid ammonia.

In many cases, one or more of the above are combined with formaldehyde reactant treatments to give optimum durable press properties. These formaldehyde reactants, which are small enough in size to diffuse into the cellulosic fiber, have ranged historically from urea-formaldehyde through triazine-formaldehyde, triazone-formaldehyde, uron-formaldehyde, ethylene urea-formaldehyde, propylene urea-formaldehyde, methylol carbamates and others. Today the most commonly used commercial formaldehyde reactant is dimethyloldihydroxyethyleneurea (DMDHEU) or its methylated derivatives (1). Of course, formaldehyde itself can be used to obtain durable press properties with cellulosic fabrics, but decrease in strength of the treated fabric

and lack of uniformity of treatment have prevented the use of this product from becoming important commercially.

Reactions of Formaldehyde Reactants With Cellulose

Although it was postulated initially that durable press properties were imparted to the cellulosic fabrics by polymerization of the formaldehyde reactant within the fiber, it is well accepted now that crosslinking of cellulose with the formaldehyde reactant is the mechanism that provides the durable press properties (1). Fig. 1 shows (a) the crosslink with an *N*-methylol compound along with other possible reactions, including (b) where free formaldehyde in the reactant solution or formaldehyde from the hydrolysis of the *N*-methylol compound gives a methylene bridge crosslink, (c) a one-sided reaction with cellulose leaving a pendant *N*-methylol group, and (d) polymerization of the formaldehyde reactant producing an inclusion of resin.

It is also well accepted today that the durable press properties obtained by crosslinking adjacent cellulose chains with a formaldehyde reactant are produced by increasing the recovery from deformation of the cellulosic fiber and reducing the permanent set (1). Without the treatment, breakage of hydrogen bonds or other weak forces permits slippage between cellulose chains when a deforming load is applied. With crosslinking, this slippage is reduced and there is increased recovery from deformation. This property imparted to the cellulose fiber is transferred through the yarn to the fabric (2).

Reaction with cellulose can occur with DMDHEU (Fig. 2) through either the OH groups on the ring or the N-CH₂OH groups. With *N,N'*-dimethyloldihydroxyethyleneurea (DMdHEU) (Fig. 2), reaction can occur only with the ring OH groups since they are the only reactive groups; thus cellulose crosslinking can occur without the use of a formaldehyde reactant. This product produces durable

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press properties in cellulosic fabrics with no formaldehyde release; however, the durable press properties are not quite equal to those obtained with DMDHEU, and also the cost of this product is considerably higher. In addition it has been reported that DMedHEU often produces off-white goods and sometimes does not provide satisfactory stabilization to shrinkage (3). As a result, the commercial success of this product has been limited. Other nonformaldehyde cellulose cross-linking agents have been synthesized and applied to cellulosic fabrics, but none to date has been commercially successful.

Formaldehyde Toxicity

Formaldehyde is a toxic chemical, being a severe eye irritant, a mucous membrane irritant, a skin irritant/sensitizer and toxic if ingested. It does not appear to be a teratogen, but it or its metabolites in the living cell have been shown to be mutagenic. Recent animal inhalation tests, carried out at the Chemical Industry Institute of Toxicology (CIIT) (4) and at the New York University Medical Center (5), have shown that formaldehyde is a nasal carcinogen to rats and mice. This finding of animal carcinogenicity has been responsible for intensified studies of the mechanism of formaldehyde release from durable press fabrics and of methods for reducing formaldehyde release. Also, government regulatory agencies have been studying the possibility of imposing new regulations to control formaldehyde.

Several epidemiological studies have been made recently of workers exposed to formaldehyde, and the results of these studies have shown no statistical overall increase in the cancer rate of these exposed workers compared with similar cohorts not exposed to formaldehyde, and no nasal cancers were found. The studies of selected populations included New

Table I. Ranking Based on Formaldehyde Release (13)

Sample Type	Formaldehyde, Average Offgassing ($\mu\text{g}/\text{m}^2/\text{Day}$)
Plywood Paneling	34,000
Particle Board	2,000-25,000
Plywood	55-14,000
Paneling	5,400- 7,300
Ladies' Dresses	570
Men's Shirts	470
Drapery Fabric, 100% Cotton	100-340
Girls' Dresses, PET/Cotton	130
Drapery Fabric, 77% Rayon/23% Cotton	50
Child's Clothes, 65% PET/35% Cotton	35

York State morticians by the National Cancer Institute (6), workers in Monsanto's Springfield/Indian Orchard, Mass., plant by the University of Pittsburgh (7), workers in an industrial plant manufacturing formaldehyde (8) by Environmental Health Associates Inc., morticians in West Virginia (9) and Ontario by CIIT (10) and workers at eight Du Pont plants using formaldehyde (11) by Du Pont.

Although in the NCI study of New York State morticians there was no significant overall increase in death due to cancer, there were slight increases in death due to cancer of the kidney, brain and central nervous system, and to leukemia, and a significant increase in death from skin cancer.

A much more extensive epidemiological study than any of those carried out to date is planned by NCI in co-operation with the Formaldehyde Institute. This study may include up to 25,000 workers exposed to formaldehyde. It is hoped that the results of this study will be definitive as to whether or not formaldehyde is a human carcinogen.

There is considerable pressure on both EPA and OSHA to propose new regulations concerning formaldehyde control. At the present time, OSHA has a 3 ppm exposure limit averaged over an eight-hour day for workers exposed to formaldehyde. NIOSH recommended to OSHA in 1976 that this limit be reduced to 1 ppm of

formaldehyde. In a study for OSHA, Clement Associates Inc. (12) concluded that "maximum likelihood estimates" based on CIIT animal carcinogenicity data show a risk of 620 excess cancers per 100,000 workers exposed in their jobs over a lifetime at the current OSHA limit of 3 ppm average daily exposure. This study also showed that reduction in exposure from 3 ppm to 1 ppm would reduce the risk of cancer by "almost 27 fold." It is my understanding that most plants producing durable press fabrics today control the concentration of formaldehyde to under 1 ppm.

Release Of Formaldehyde From Consumer Products

The Consumer Product Safety Commission has sponsored a study of the release of formaldehyde from consumer products including durable press fabrics by the Lovelace Biomedical & Environmental Research Institute of Albuquerque, N. M. (13). Consumer products purchased at random were subjected to a flow of humidified air in a chamber, and the amount of formaldehyde offgassed from the products was measured using a modified pararosaniline procedure and reported as micrograms per square meter of product surface/day. Comparative values of release of formaldehyde from durable press fabrics with those from pressed wood products are given in Table I. Although it is unfortunate that more information is not available on the treatment of the samples shown in Table I, it is

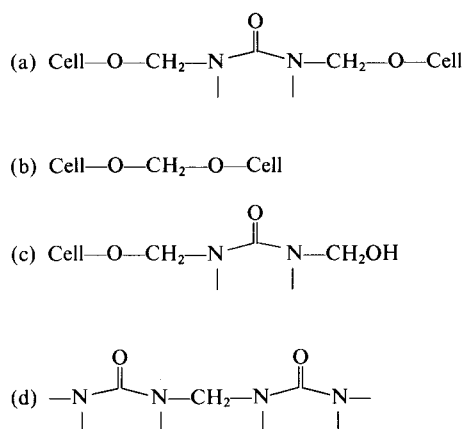


Fig. 1. Results of reactions of formaldehyde and its reactants.

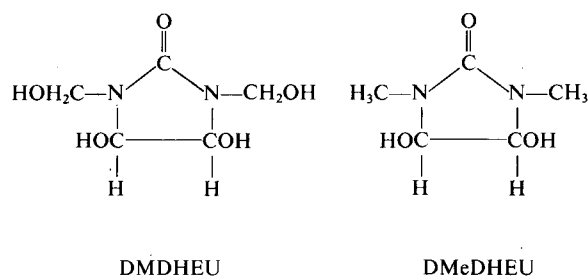


Fig. 2. Structure of DMDHEU and DMedHEU.

obvious that the amounts of formaldehyde released from durable press fabrics purchased at random are much less under the conditions of test than those from the pressed wood products also purchased at random.

Transfer Of Formaldehyde From Durable Press Fabric

In an effort to estimate the amount of formaldehyde that might migrate from a durable press garment to the skin and into the body of the wearer, a study was sponsored by the CPSC with the U.S. Department of Agriculture using rabbits as the

test subjects. Cotton and cotton/polyester blended fabrics were treated at USDA's Southern Regional Research Center at New Orleans, with DMDHEU containing ¹⁴C-labeled formaldehyde. In studies at the Richard B. Russell Agricultural Research Center at Athens, Ga., patches of the treated fabrics were applied to the shaven skin of rabbits with medical adhesive tape along the four sides of the patches (14). In some cases the cloth patches were moistened with artificial perspiration prior to being applied to the skin of the rabbits, and in others the patches were covered with a layer of latex. The rabbits were housed for 48 hours in

metabolism cages with CO₂ collectors. Measurement of the radioactive carbon permitted the determination of the formaldehyde, formaldehyde reactant or their metabolites in the various organs of the rabbit after sacrifice.

The total amount of radioactive carbon transferred from the cloth to the rabbit in 48 hours was less than 3% of the amount in the patch, even under the most severe conditions (with added perspiration and with the patch covered with latex). Most of the radioactive carbon transferred to the rabbit was found in the skin directly under the cloth patch. In those experiments in which the patches were not cov-

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About this year's Olney Medalist . . .

THEODORE F. Cooke, one of the world's leading authorities on resin reactions with cellulosic fibers, is the 1983 recipient of The Olney Medal for achievement in textile chemistry.

Cooke, who holds a BS in chemistry from the University of Massachusetts (1934) and a doctorate in physical chemistry from Yale University (1937), has spent almost his entire professional career in textile chemistry. After receiving his doctorate, he joined Standard Oil Development Co. as a research chemist. He began his textile career in 1940 when he joined American Cyanamid Co. as a research chemist. With the exception of military service in World War II—he was director of the materials laboratory for the Army Corps of Engineers at Fort Belvoir, Va., from 1942 to 1945—Cooke was with Cyanamid 38 years.

Following the war he returned to Cyanamid as assistant director for physical chemical research in the company's organic chemicals division. In 1952 he was named manager of the division's textile chemicals laboratory, commercial development manager in 1958, director of chemical research in 1960 and assistant director of research and development in 1962. In 1972 he was named director of the scientific services department of the chemical research division, a post he held until his retirement from the company in 1978.

Following retirement from Cyanamid, Cooke joined Textile Research Institute at Princeton, N.J., as a research associate and director of the institute's newly established Regulatory Technical Information Center. He also is currently serving as industry liaison for the Office of Co-Operative Research at Yale University.

Broadly Based R&D

During his career at Cyanamid, Cooke

played a key role in developing broadly based research and development activities that led to the commercialization of minimum care consumer products. He made significant contributions to new developments in dyeing, antimicrobial finishing, soil resistant finishing and abrasion resistance.

At Textile Research Institute, he has developed the Regulatory Technical Information Center into an important source of information pertaining to government regulations covering products, processes and the environment.

Professional Contributions

In addition to his work at TRI and Cyanamid, Cooke has provided considerable personal and professional service to a number of other organizations. He was presented a Certificate of Appreciation by the Department of the Army for his work in the development of protective clothing against combat surveillance and against chemical warfare agents. And he was

presented an Honor Scroll Award by the New Jersey Institute of Chemists for his contributions to the advancement of chemistry.

He has served as chairman of the National Research Council's advisory committee serving the Army's research and development laboratories at Natick, Mass., and was for six years a consultant to the Department of Agriculture. He is a past chairman of the TRI research advisory committee and was for five years a member of the institute's board of trustees. He also is a past chairman of the Gordon Research Conference on Fiber Science and a past chairman of the New Jersey Institute of Chemists.

Cooke holds membership in the American Chemical Society, American Institute of Chemists, Association of Research Directors and the Yale Alumni Association.

Listed in AMERICAN MEN & WOMEN OF SCIENCE and in WHO KNOWS AND WHAT, he is the holder of 20 U.S. patents and an author of some 40 publications published in technical and scientific journals. He and TRI co-worker Hans-Dietrich Weigmann were presented AATCC's Paper of the Year award for 1982 for their literature review on the chemistry of formaldehyde release from durable press fabrics. The two-part series was published in the May and June 1982 issues of TEXTILE CHEMIST AND COLORIST.

The Olney Medal

Established in 1944 in honor of Dr. Louis Atwell Olney, the founder and first president of AATCC, The Olney Medal is presented in recognition of technical and scientific contributions to the advancement of textile chemistry. The award consists of a gold medal, a scroll and an honorarium. Its presentation each year is a highlight of AATCC conferences. ☺



THEODORE F. COOKE: Fortieth recipient of The Olney Medal for outstanding achievement in textile chemistry.

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ered with latex (which should more closely reflect conditions under which clothing is worn), the radioactivity transferred to the rabbit was approximately one-tenth that of the experiments with latex-covered patches. The amount of radioactivity found at various sites expressed as the percentage of the amount in the cloth patch is given in Table II.

As can be seen, very little radioactivity was found at any site other than the skin. If the amount of formaldehyde or one of its metabolites, as determined by the quantity of radioactive carbon transferring from a treated durable press patch to a shaven rabbit during a 48 hour period, corresponds to the amount of formaldehyde transferred from a durable press garment worn by a human being during the same period, then the amount is very small; also the amount is concentrated in the skin next to the garment and extremely small amounts enter the body.

Mechanism Of Formaldehyde Release

A research project sponsored by industry currently being carried out at Textile Research Institute is designed to learn more about the underlying mechanisms of formaldehyde release from durable press fabrics. The study has produced some very interesting findings so far. There are several sources of released formaldehyde. Free formaldehyde sorbed by durable press fabrics is one source. This formaldehyde may have been present in the treating solution or hydrolyzed from the formaldehyde reactant during the treatment.

The work at TRI has shown that surprisingly large amounts of formaldehyde can be held by untreated cellulosic fabric. This is shown in Table III (15) where V_m is the maximum sorbable volume of formaldehyde calculated from a Langmuir isotherm:

$$V_m = V(1 + bp)/bp$$

where V is the volume sorbed, p is the partial pressure and b is the sorption coefficient.

In addition to free formaldehyde sorbed on the fabric, formaldehyde may be formed by the hydrolysis of the N—CH₂OH groups from unreacted DMDHEU or from pendant N—CH₂OH groups of DMDHEU molecules that have reacted with cellulose through only one N—CH₂OH group. Of course, breaking of the C—O bond of any crosslink of DMDHEU with cellulose will provide an additional N—CH₂OH group, which in turn can hydrolyze to release formaldehyde.

The rate of formaldehyde release

Table II. Distribution of Radioactivity in Rabbits Exposed for 48 Hours to DMDHEU Treated Fabric (14)

Site of Measurement	Radioactivity (% of Amount in Patch)
Skin	0.09-2.6
Kidney	0.001
Liver	0.001-0.005
Blood	0.001-0.004
Urine	0.003-0.102
Expired CO ₂	0.001-0.018
Back Muscle	<0.0005
Thigh Muscle	<0.0005
Fat	<0.0005
Gonads	<0.0005
Brain	<0.0005
Feces	<0.0005

depends on the relative stability of the C—O and C—N bonds. If the rate of cleavage of the C—O bond is faster than that of the C—N bond, the latter still determines the rate of formaldehyde release. Petersen (16), using model dimethoxymethyl compounds, showed that the rate of cleavage of the C—O bond was much faster under acidic conditions than that of the C—N bond. Reinhardt et al. (17) studied the effect on formaldehyde release of varying the pH with buffers while washing fabrics treated for durable press with various formaldehyde reactants. They found the lowest release values in the pH range of 5 to 7. With DMDHEU they found the lowest values in the 3 to 7 range, the highest release values at very low pH, and medium values of release at high pH.

The TRI study determined the rates of cleavage of both the C—O and the C—N bonds in DMDHEU treated cellulosic fabric. It was found that the rate of cleavage of the C—O bond was high under acidic conditions and very low under neutral and alkaline conditions, whereas the rate of cleavage of the C—N bond was relatively low under acid and neutral conditions and high under alkaline conditions. Since the C—N bonds cleave at a high rate under alkaline conditions, an afterwash of DMDHEU treated fabric under alkaline conditions should hydrolyze pendant N—CH₂OH groups and therefore reduce the amount of formaldehyde released from the finished durable press fabric.

In the work at TRI, the rates of release

Table III. Sorption Characteristics of Formaldehyde on Cellulosic Fabrics (15)

Fabric	T(C)	V_m	
		ppm	cm ³ STP/g
Cotton	40	77,000	58
	65	80,000	60
Rayon	65	94,000	70

of formaldehyde from DMDHEU treated cotton fabric were determined at 40 and 60C by placing one-gram samples of fabric in 100 milliliters of distilled water with stirring at a controlled temperature and analyzing the formaldehyde released into the water spectrophotometrically using 3-methyl-2-benzothiazolinone hydrazone as the reagent. The results of this study are plotted in Fig. 3. As can be seen, the rate of formaldehyde release is much faster at 60C than at 40C. The initial steep slope of the curves at very low times can be explained by the release of free formaldehyde from the fabric. The second less steep slope at intermediate times appears to result from the hydrolysis of pendant N—CH₂OH groups. The leveling off at longer times can be explained by hydrolysis of N—CH₂OH groups formed by breakage of C—O bonds of crosslinks.

Control Of Formaldehyde Release

The literature shows that the amount of formaldehyde released from durable press fabrics treated with formaldehyde reactants can be reduced with the optimum choice of reactant composition, leaving group of the reactant, catalyst and time and temperature of cure, purity of the reactant, condition of the fabric prior to treatment, additives to the impregnating bath, concentration of reactant, afterwash and aftertreatment.

Reactant Composition

The rates of reaction of formaldehyde reactants with cellulose vary over a wide range. Reactivity with cellulose shows a direct relationship to ease of hydrolysis of the reactant from the cellulose: the higher the reactivity, the greater the release of formaldehyde. Petersen (18) has classified some formaldehyde reactants into three classes of compounds according to reactivity and rates of hydrolysis. The ureas and ethyleneureas have high reactivity and poor hydrolysis stability; 5,5-dimethyl- and 5-hydroxy-propyleneureas have medium reactivity and hydrolysis stability; while glyoxal diureine and dihydroxyethyleneurea have low reactivity and good resistance to hydrolysis. Formaldehyde reactants produced from the last two compounds should therefore provide durable press fabrics with low formaldehyde release.

Leaving Group

As has been pointed out earlier, the methyl ethers of DMDHEU release less formaldehyde than DMDHEU. Petersen (19) has studied the effect of leaving groups in a series of ethyleneureas. He found that the methyl leaving group showed the lowest reactivity, the isopropyl group the

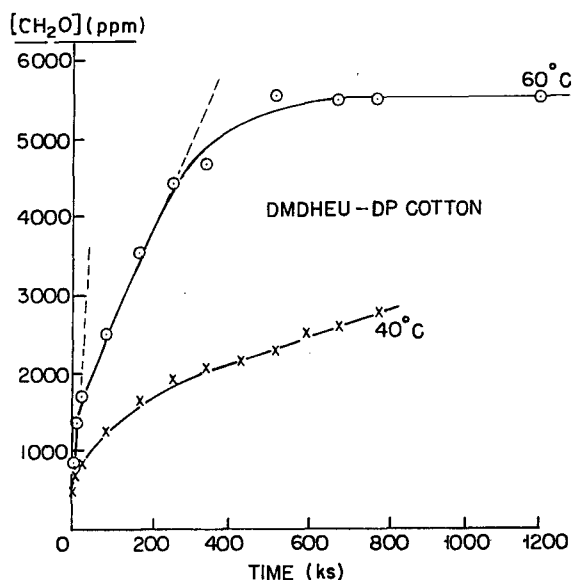


Fig. 3. Rate of release of formaldehyde from DMDHEU-treated cotton fabric into water at 40 and 60°C (15).

highest; the leaving groups methoxyethyl, ethyl and hydrogen were intermediate in reactivity. Since the rate of hydrolysis of the formaldehyde reactants is directly related to the reaction rate, the methoxymethyl compounds are preferred to the methylol compounds for low formaldehyde release from treated fabrics.

Catalyst And Time And Temperature Of Cure

The amount of catalyst used depends on the reactivity of the formaldehyde reactant and the time and temperature of cure. With formaldehyde reactants having a low rate of reaction with cellulose, strong catalysts and/or long times and high temperatures of cure may be required. Weaker catalysts and/or shorter times and lower temperatures of cure may be used with reactants that have a high rate of reaction with cellulose. Generally, optimum curing conditions to produce the minimum unreacted N—CH₂OH groups and the maximum crosslinks will result in the minimum formaldehyde release.

Recently, Andrews et al. (20) studied the effect of the catalyst on formaldehyde release with buffered and unbuffered DMDHEU. They came to the conclusion that "catalysts of predominantly Lewis acid activity (zinc nitrate, magnesium chloride, aluminum hydroxychloride) produce fabrics with lower formaldehyde release than do those of predominantly Brønsted activity (aluminum sulfate, magnesium chloride-citric acid, sodium hydrogen sulfate, magnesium hydrogen phosphate); catalyst concentration must be sufficiently high to catalyze the amount of agent present and to overcome the effects of buffering if a buffered agent is used."

Impurities In The Reactant

Impurities present in commercial reactants can, of course, have an effect on the properties of a durable press fabric. These impurities can include additives such as buffering agents that have been added purposely, intermediates from the reaction mixtures and materials that have been added inadvertently.

Buffering agents require greater amounts of catalyst. An example of an intermediate from a reaction mixture is urea present in DMDHEU. In the glyoxal-urea reaction to form the dihydroxyethyleneurea, some unreacted urea may be present, which during the subsequent reaction with formaldehyde will produce urea-formaldehyde. Since this latter product releases more formaldehyde than does DMDHEU, the durable press fabric treated with it will give a higher formaldehyde release value than one treated with pure DMDHEU. Examples of other chemicals that might be present in DMDHEU are glyoxal, formaldehyde and alkali. Materials that are inadvertently added could include any number of chemicals.

Condition Of The Fabric

Just as impurities may be present in the formaldehyde reactant, so impurities may be present in the fabric being treated. An example of an impurity that would have an important bearing on durable press properties is alkali. Any residual alkali on the fabric from scouring treatments could have a deleterious effect on the degree of cure of the formaldehyde reactant, thereby increasing the formaldehyde release potential. The moisture content of the fabric is an important factor as well, since

it will have an effect on the concentrations of the formaldehyde reactant and catalyst involved in treating the fabric.

Additives To The Impregnating Bath

Any additives to the impregnating bath containing the formaldehyde reactant should be carefully controlled and tested to determine their effect on formaldehyde release. Examples of additives are hand builders, softeners and soil repellents.

Additives to control the formaldehyde odor of treated fabrics—such as urea, dicyandiamide and ethyleneurea—were used in the early days of finishing fabrics with formaldehyde reactants. These materials, called formaldehyde scavengers, were added to the pad bath to react with any free formaldehyde. With the use of these products, however, the durable press properties of the treated fabric may be decreased. If the additive is effective, it will form a formaldehyde reaction product which may react with cellulose to give an inferior fabric finish. For example, urea added to a DMDHEU bath can form urea-formaldehyde which may react with the cellulosic fabric to give a finish inferior to that obtained when DMDHEU is used alone. It is expected that a formaldehyde scavenger reacts with free formaldehyde on the fabric during the curing step. It might also react with any pendant N—CH₂OH groups. In this latter case, the effect might be a capping similar to that of using a methylated N—CH₂OH reactant, which therefore might reduce formaldehyde release from the treated fabric.

The addition of polyhydroxy alcohols to the pad bath to reduce formaldehyde release from durable press fabrics has been recently proposed by Andrews et al. (21). By adding 1-4% of polyhydroxy alcohols—such as ethylene glycol, diethylene glycol, 1,2-propanediol and sorbitol—Andrews et al. have been able to lower the formaldehyde release values of durable press fabrics by one to two-thirds. They postulate that the polyhydroxy alcohols modify methylolamide reactants by capping them in a manner similar to etherification with primary alcohols.

Concentration Of Reactant

If the concentration of formaldehyde reactant on the fabric is decreased, formaldehyde release is decreased, as would be expected since the total amount of formaldehyde available for release is reduced. Of course, as the amount of formaldehyde reactant is reduced, so are the durable press properties.

Afterwashing

Afterwashing the treated fabric usually

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decreases the amount of formaldehyde released by the fabric. It removes free formaldehyde and catalysts that may have an effect on the hydrolysis of the finish to produce formaldehyde during storage. If the afterwash is on the alkaline side, pendant N—CH₂OH groups on DMDHEU treated fabric will be removed and therefore the formaldehyde released should also be reduced.

Aftertreatment

Aftertreatment of a durable press fabric with a chemical that reacts with free

formaldehyde or unreacted *N*-methylol groups on the fabric reduces the formaldehyde released from the fabric. The same compounds proposed as additives to the pad bath as formaldehyde scavengers may also be effective as aftertreating agents.

Historical HCHO Reduction

Industry has made great strides in reducing the amount of formaldehyde released from durable press fabrics. In the 1960s it was not uncommon for treated fabrics to have formaldehyde release values in the precursor of the accelerated AATCC test method (22) as high as 3000 ppm (23). With the introduction of DMDHEU, these values were reduced to 1500-2000 ppm, and in the early 1970s, values of 800-1000 ppm were achieved with

improved DMDHEU products. Late in the 1970s, the introduction of the partially methylated DMDHEU products enabled values of 250-500 to be obtained. With a higher degree of methylation, formaldehyde release values were lowered still further. In May 1983, a manufacturer of a modified DMDHEU product (23) claimed that values of 100 ppm can be obtained consistently. Certainly great strides have been made in reducing formaldehyde release from durable press fabrics, and with improved knowledge of mechanisms and kinetics, still further improvements should be made in the future. ∞∞

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