TECHNICAL BULLETIN

Environment +

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Formaldehyde in Textiles

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INTRODUCTION

The reaction of formaldehyde with cotton to improve wrinkle resistance and to control shrinkage was first used in the early 20th century. Derivatives of formaldehyde are now preferred for textile processing, in order to obtain a better balance of physical properties and to reduce environmental impacts. Today, a large percentage of performance-enhanced cellulose-containing apparel is finished with resins containing formaldehyde derivatives. Less commonly, formaldehyde gas also is used in a vapor-phase reaction with cellulose-containing textiles.

Although formaldehyde in its pure form exists as a gas, it is seldom processed in that state. Formaldehyde is usually handled as an aqueous solution (formalin) or a solid homopolymer (paraformaldehyde), and it occurs as a reaction product remaining within other compounds, such as reactants or resins. Aqueous formaldehyde solutions most commonly contain 37% formaldehyde and 0.05% to 15% methanol as a stabilizer to prevent polymerization to paraformaldehyde. In water, formaldehyde and dihydroxymethane are in equilibrium. Aqueous formaldehyde and most formaldehyde reaction products tend to emit some free formaldehyde gas.

In addition to its use in textile processing, formaldehyde is used in the manufacture of a wide variety of products, ranging from plywood, particleboard, and fiberboard used in housing and furniture to personal-care products, such as cosmetics. Formaldehyde offers a number of unique properties for industrial use. It is inexpensive, readily available, reactive, easily handled, and efficient, and the end products made with formaldehyde are durable and non-yellowing. Without formaldehyde as a building block, the performance and value of a broad array of products that benefit from its chemistry would suffer.

World consumption of 37% formaldehyde solution was about 28 million metric tons in 2006, up from 24 million metric tons in 2003. Between 2003 and 2006, world capacity grew at an average annual rate of 3.9%, while world consumption grew at an average rate of 5.4%. Most of the production went into resins for building materials, including urea-formaldehyde, phenol-formaldehyde, polyacetal, and melamine-formaldehyde. Textile chemicals accounted for only a small percentage of world consumption.

FORMALDEHYDE IN THE ENVIRONMENT

Formaldehyde gas occurs in the environment from both natural and manmade sources. In nature, formaldehyde occurs in small quantities in some foods, at concentrations ranging from about 6 ppm in tomatoes to 20 ppm in apples. People also naturally produce formaldehyde through their normal metabolic processes. The average person produces about 1.5 oz of formaldehyde each day, and formaldehyde normally is present in human blood at a low steady-state concentration of about 1 to 2 ppm. (Formaldehyde concentration is also reported in units of micrograms per gram, which is equivalent to parts per million.)

Because free formaldehyde can be released by formaldehyde-containing resins and preservatives, it can be expected to be found within (or in the air around) such items as construction materials, finished apparel and home fabrics, cosmetics and other personal-care products, household cleaning agents, glues and adhesives, paints and coatings, and slow-release fertilizers. Formaldehyde may also be generated by incomplete combustion of organic materials, from such sources as cigarettes, wood stoves, kerosene space heaters, automobile and other internal combustion engines, refineries, power plants, incinerators, and forest fires.

TOXICITY OF FORMALDEHYDE

Like nearly all reactive compounds, formaldehyde is hazardous at certain levels. Although formaldehyde is less toxic than most reactive compounds, certain characteristics may increase the risks associated with exposure: (1) it exists as a gas that can spread throughout workplaces and living spaces, and (2) most formaldehyde resins and their end-use products tend to liberate free formaldehyde gas. For humans, the routes of exposure that cause concern are skin contact and inhalation. Formaldehyde does not accumulate in the environment, because it is broken down within a few hours by sunlight or by bacteria present in the soil or water. Humans metabolize formaldehyde quickly, so it does not accumulate in the body (although it is continually produced by normal metabolism). The risk of an adverse reaction to formaldehyde depends on the sensitivity of the individual and the form, level, duration, and route of exposure.

Formaldehyde can be irritating to the eyes, nose, and throat; for most people, the irritation is temporary and reversible. Other reported symptoms include fatigue, nausea, vomiting, nosebleeds, headaches, and dizziness. At higher exposure levels, some of these symptoms can be felt immediately. Inhalation exposure to formaldehyde at very high concentrations can cause pulmonary edema (accumulation of fluid in the lungs).

Dermatitis in reaction to formaldehyde is well documented, especially in the textile industries. The U.S. Consumer Product Safety Commission has defined formaldehyde and products containing at least 1% formaldehyde as “strong sensitizers.” Once sensitized, a person may continue to react to small concentrations of formaldehyde for years.

In laboratory rats, inhalation exposure to formaldehyde caused nasal cancer at high concentrations (6 to 15 ppm), but not at low concentrations (2 ppm or less). Nasal cancer has been linked to genetic damage in the cells of the respiratory tract, resulting from proliferation of the cells in response to the toxic effects of formaldehyde. In 1981, the U.S. Department of Health and Human Services listed formaldehyde as “reasonably anticipated to be a human carcinogen,” and in 2006, the World Health Organization’s International Agency for Research on Cancer concluded that formaldehyde was a human carcinogen, based on increased risk of nasopharyngeal cancer in epidemiological studies of workers exposed to formaldehyde, as well as the results of studies on experimental animals.

REGULATING EXPOSURE TO FORMALDEHYDE

For environmental, health, and safety reasons, formaldehyde is regulated by various federal and state agencies, to ensure its safe production, storage, handling, and use.

Environmental Releases

Under the Clean Air Act, the U.S. Environmental Protection Agency regulates the emission of formaldehyde into air from manufacturing exhaust, as well as from automobile exhaust. Some textile manufacturers reduce stack emissions of formaldehyde through the use of a thermal oxidizer. Other methods for reducing formaldehyde emissions are discussed below, under “Reducing the Free Formaldehyde Released by Textiles.”

Indoor Emissions

Formaldehyde usually is present in both outdoor and indoor air at concentrations of less than 0.03 ppm. However, in homes with many new pressed-wood products, and especially in manufactured housing, levels can exceed 0.3 ppm. The U.S. Consumer Product Safety Commission (CPSC) and the U.S. Department of Housing and Urban Development (HUD) have addressed exposure to formaldehyde in indoor air. Since industry voluntarily adopted product formaldehyde emission standards, and since low-emitting resins were developed, indoor formaldehyde emissions have declined significantly. Given these voluntary actions and the low levels of formaldehyde observed, the CPSC determined that mandatory regulation was unnecessary. HUD has set standards that limit formaldehyde emissions from wood products that are used in manufactured housing. The World Health Organization recommends that non-workplace indoor air levels should not exceed 0.05 ppm.

The California Air Resources Board published a report on indoor emissions of formaldehyde from building materials and consumer products and has enacted regulations to reduce formaldehyde emissions from composite wood products. In addition, California’s Safe Drinking Water and Toxic Enforcement Act of 1986 (known as “Proposition 65”) lists gaseous formaldehyde as a substance believed to cause cancer. However, no fabrics have been found to emit formaldehyde gas at levels above the threshhold specified by the regulation as being thought to increase the risk of cancer.

Workplace Exposure

Workplace exposure to formaldehyde is regulated by the U.S. Department of Labor’s Occupational Safety and Health Administration (OSHA) under a chemical-specific standard. The legal permissible exposure limit for workplaces covered by OSHA is 0.75 ppm averaged over an 8-hour work shift. In addition, OSHA requires that short-term exposure not exceed 2 ppm (assessed as a 15-minute average). The standard also lists requirements for monitoring of employee exposure, protective measures, medical surveillance, and communication and training about the hazards. The National Institute for Occupational Safety and Health (within the Centers for Disease Control and Prevention) recommends more stringent guidelines of 0.016 ppm averaged over a 10-hour work day and 0.1 ppm as a ceiling limit that should not be exceeded at any time during the work day (assessed as a 15-minute average). All of these limits and guidelines are near or below the odor threshold, which is the lowest concentration at which formaldehyde can be smelled. The odor of formaldehyde generally is first sensed at 1 ppm, but some individuals can smell it at 0.05 ppm.

Consumer Products

In the United States, formaldehyde in consumer products is regulated only by the Federal Hazardous Substances Act, which states that products containing formaldehyde at concentrations of greater than 1% must be labeled to warn of the hazards. There is no legal limit on the formaldehyde content of textiles. It is up to the commercial buyer (or retailer) to set a limit, which is determined, in part, by how the formaldehyde level of fabric will affect the ability of the textile mill to comply with legal limits on the concentration of formaldehyde in workplace air (discussed above) and by consumers' demands for textile performance. However, a few countries place legal limits on the formaldehyde content of textiles. For example, Finland and Japan have strict limits on textile formaldehyde content. In order to sell the same finish to a variety of customers, mills find it expedient to use finishes that meet the strictest requirements. Many mills, apparel companies, and retailers have adopted Restricted Substances Lists to guide suppliers in this regard.

MEASURING THE FREE FORMALDEHYDE CONTENT OF TEXTILES

Various methods have been used to measure the formaldehyde released from a treated fabric. The measured levels depend both on fabric characteristics and on the specific test method used. Therefore, the results obtained by different test methods are not comparable. The following fabric-related factors affect the release of formaldehyde during testing:

- The type and quantity of formaldehyde resin used.
- How long the fabric is exposed to air.
- The degree to which the formaldehyde resin had been cured, which is affected by both the initial preparation of the fabric and the curing conditions used for the reaction.
- Whether the treated fabric had been after-washed or further processed before testing.

The two generally accepted methods for measuring the release of formaldehyde from textiles are the American Association of Textile Chemists and Colorists (AATCC) Method 112 (Determination of Formaldehyde Release from Fabric: Sealed Jar Method) and the International Organization for Standardization (ISO) Standard 14184-1 (Textiles — Determination of Formaldehyde — Part I: Free and Hydrolyzed Formaldehyde, Water Extraction Method).

AATCC Method 112. The test specimen is suspended over an aqueous solution in a sealed jar at an elevated temperature for an extended period, and the formaldehyde gas given off by the specimen is absorbed into the aqueous solution. The formaldehyde in the solution is derivatized, and the color of the resulting complex is measured with a visible spectrophotometer. The amount of formaldehyde is expressed as micrograms of formaldehyde per gram of fabric. For a single fabric with low levels of formaldehyde, the critical difference (i.e., the difference between measured levels that is considered to be significant) is about 75 ppm. One study estimated the background level (i.e., the level measured for a non-formaldehyde-treated fabric) in the AATCC test to be 25 ppm. The AATCC method can capture both free and releasable formaldehyde.

ISO 14184-1 Method. This method is essentially the same as the Japanese Industrial Standard JIS L 1041, Part 1, Method 2-B procedure (also referred to as "Japanese Law 112 Method"). The test specimen is immersed in water and incubated at near body temperature (40°C) for a short time, so that the free formaldehyde is extracted into the water; it is then derivatized and measured as described for the AATCC method. The limit of detection is 20 ppm. The ISO method does not necessarily capture releasable formaldehyde.

Not surprisingly, the AATCC and ISO methods yield different values. For example, a fabric measured at 300 ppm by AATCC Method 112 (meeting the requirements of many U.S. retailers) may be measured at 75 ppm by the ISO 14184-1 method. However, no exact correlation can be made between the results of the two methods. Therefore, it is essential to specify the test method used.

Other methods for measuring free formaldehyde on fabrics have been described in the literature. One technique uses a headspace gas chromatograph, and another uses derivatization and analysis by high-performance liquid chromatography. Electrochemical analysis has also been employed. To measure formaldehyde released into air, air samples from around a textile sample can be collected in a "fish bowl" arrangement, in which the relative humidity of the environment containing the specimen can be varied. Although these methods have merits, drawbacks include a lack of convenience, longer testing times, and the need for specialized equipment.

As samples are exposed to air, some formaldehyde is released from the treated fabric, and measured formaldehyde levels decrease. Cotton Incorporated conducted an experiment to determine how much formaldehyde was released over time when treated fabrics were hung in air under ambient conditions. A standard 100% cotton 3/1 twill fabric (7.5 oz/yd^2) was treated with two different resin formulations — an uncapped (non-etherified) buffered dimethyloldihydroxyethyleneurea (DMDHEU) reactant and a capped (glycolated) DMDHEU resin from the same manufacturer. Samples were then hung in an office environment for periods ranging from 4 hours to 14 days. Both the ISO and AATCC formaldehyde tests were performed, and the concentration of formaldehyde released from the fabric at each time point was compared with that of samples that were bagged and tested immediately. The results are shown in Figures 1 through 4.

As shown in Figures 1 and 3, fabric tested by the ISO method showed a dramatic decrease in free and hydrolyzed formaldehyde during the first two days of exposure to air, after which the concentration appeared to level off. As shown in Figures 2 and 4, fabric tested by the AATCC method showed a slower decrease to less than half of the original value after two weeks of exposure. The trends observed for the AATCC method suggest that the amounts of formaldehyde released would continue to decrease slowly during exposure continuing for longer than 14 days.

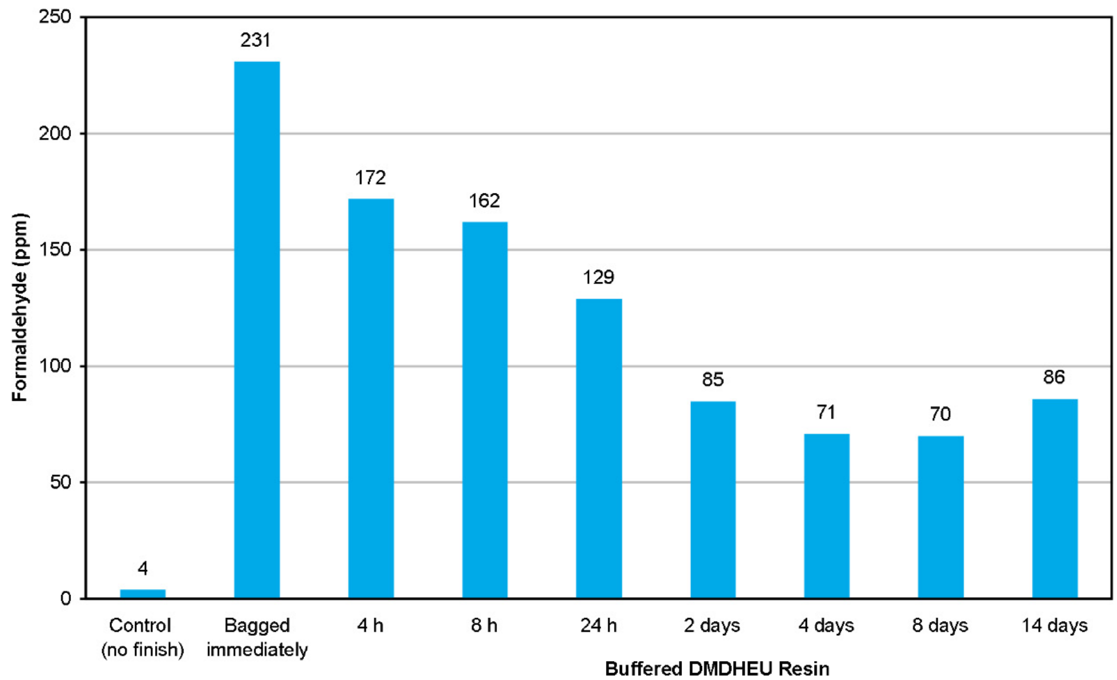

Figure 1. ISO 14184-1 test results for samples finished with buffered DMDHEU resin.

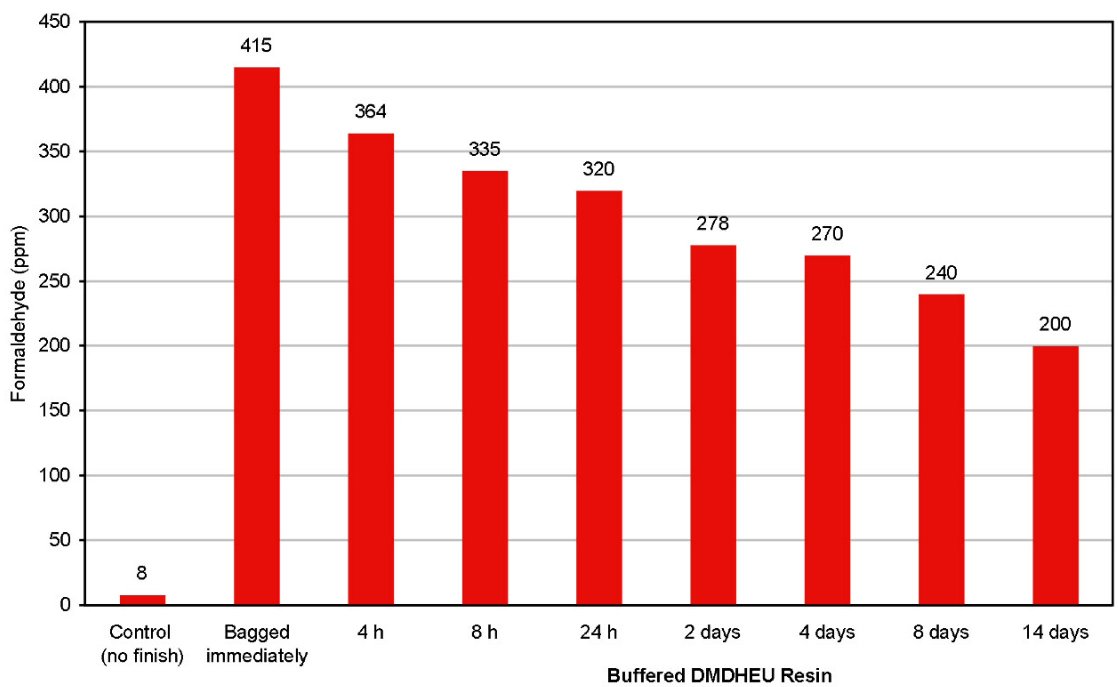

Figure 2. AATCC 112 test results for samples finished with buffered DMDHEU resin.

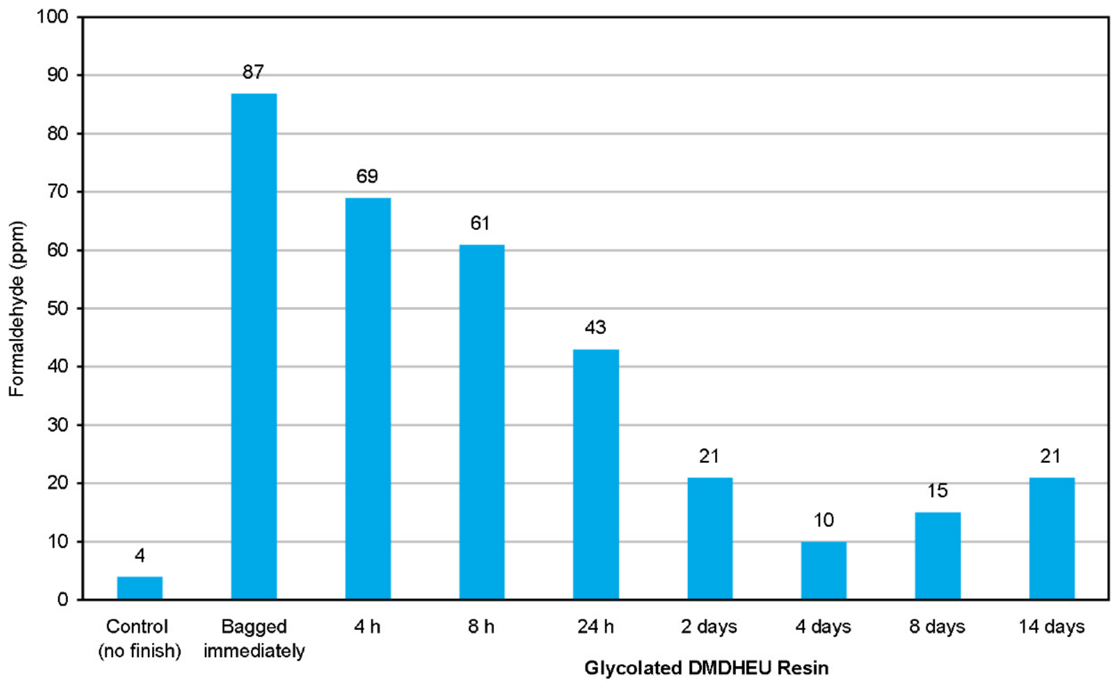

Figure 3. ISO 14184-1 test results for samples finished with glycolated DMDHEU resin.

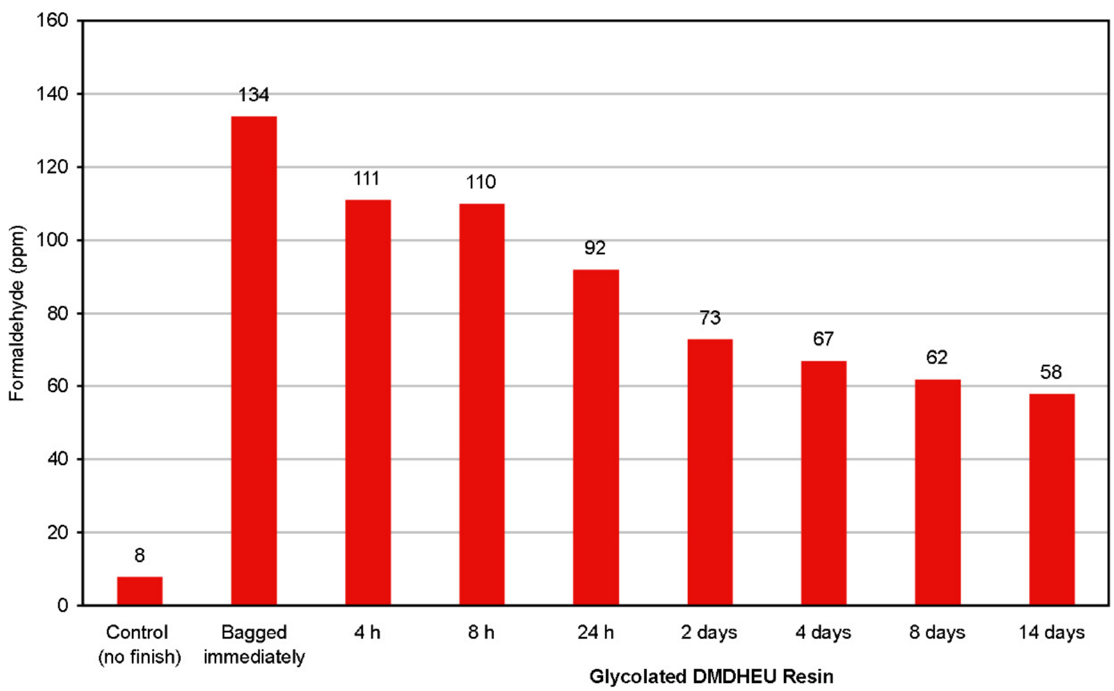

Figure 4. AATCC 112 test results for samples finished with glycolated DMDHEU resin.

REDUCING THE FREE FORMALDEHYDE RELEASED BY TEXTILES

The concentration of the formaldehyde that is evolved during treatment of textiles (which contributes to both workplace exposure levels and environmental emissions) may be reduced by a number of methods, including the following:

- Dilution with fresh air.
- Air filtration (with charcoal or other media).
- Reduction of the curing temperature.
- Reduction of the relative humidity of air exiting the dryer.
- Effective use of hoods.
- Thermal oxidation of exhaust gases.
- Reduction of the free formaldehyde level on the fabric.

Reducing the free formaldehyde on the fabric is one of the most effective methods for reducing the free formaldehyde in the workplace air (and thus in stack emissions). The following are some options for reducing free formaldehyde on the fabric:

- Prepare the fabric to attain a neutral pH with low fabric alkali content.
- Use resins containing low levels of free formaldehyde.
- Use DMDHEU-type resins.
- Use DMDHEU etherified with diethylene glycol or another alcohol.
- Cure the treated fabric properly.
- Use selective formaldehyde scavenging agents in the finish, or post-treat with a scavenging agent after curing.
- After-wash the cured fabric or garment at the appropriate pH.
- Use a non-formaldehyde-containing durable-press resin.

The use of a non-formaldehyde-containing resin is the desirable choice if other properties remain acceptable. However, many effective non-formaldehyde crosslinking resins are more toxic than formaldehyde-containing resins. Two candidates that have generated some interest and limited use include selected polycarboxylic-acid derivatives (such as butanetetracarboxylic acid) and dimethylurea glyoxal (DMUG). Both of these products are significantly more expensive than etherified DMDHEU. For efficiency, use of the polycarboxylic acid derivatives requires the use of a reductive catalyst, which can adversely affect the shade of a number of dyes, and the acid itself causes yellowing of white fabrics. DMUG alone generally does not impart adequate durable-press performance or shrinkage resistance.

STUDIES ON THE REDUCTION OF FORMALDEHYDE RELEASE FROM FABRIC

Cotton Incorporated has conducted studies to determine whether economical means could be used to reduce or eliminate the release of formaldehyde from durable-press cotton fabrics or garments. Two methods of reducing formaldehyde release were evaluated, including after-washing and adding a formaldehyde scavenger to the finish bath.

After-Washing Studies

In laboratory trials, the following specifications for the ISO and AATCC test methods were used as benchmarks to evaluate experimental data:

- ISO 14148-1:
  - Oeko-Tex Standard 100 limit value (in direct contact with skin) = 75 ppm (Oeko-Tex 2010).
  - < 20 ppm was considered "not detectable" (ISO 1989).
- AATCC 112:
  - Typical retailer's specification = 250 ppm.
  - < 25 ppm was considered to be a background level (Pasad *et al.* 1989).

For the after-washing studies, a cotton twill fabric was padded with the two resin formulations described above, dried and cured at 177°C (350°F) for 90 seconds, and immediately placed into reclosable plastic bags. The fabric was then washed in a Mathis Labomat at a liquor ratio of 15:1 to simulate a garment wash, dried, and immediately placed in a plastic bag to await testing. The Labomat was used because it has a controlled wash procedure and does not require ballast, which could add formaldehyde or interfere with the results. The washes were conducted with AATCC Standard Reference Liquid Detergent (scaled to the liquor ratio), a nonionic/anionic scour, or a nonionic scour.

The results are shown in Figures 5 and 6. In both the AATCC and ISO tests, all of the after-washed samples had significantly lower formaldehyde values than did the unwashed control samples. The results were similar for the various scours. All after-washed samples had formaldehyde levels significantly below the 75-ppm limit value in the ISO test and the 250-ppm typical retailers' specification in the AATCC test.

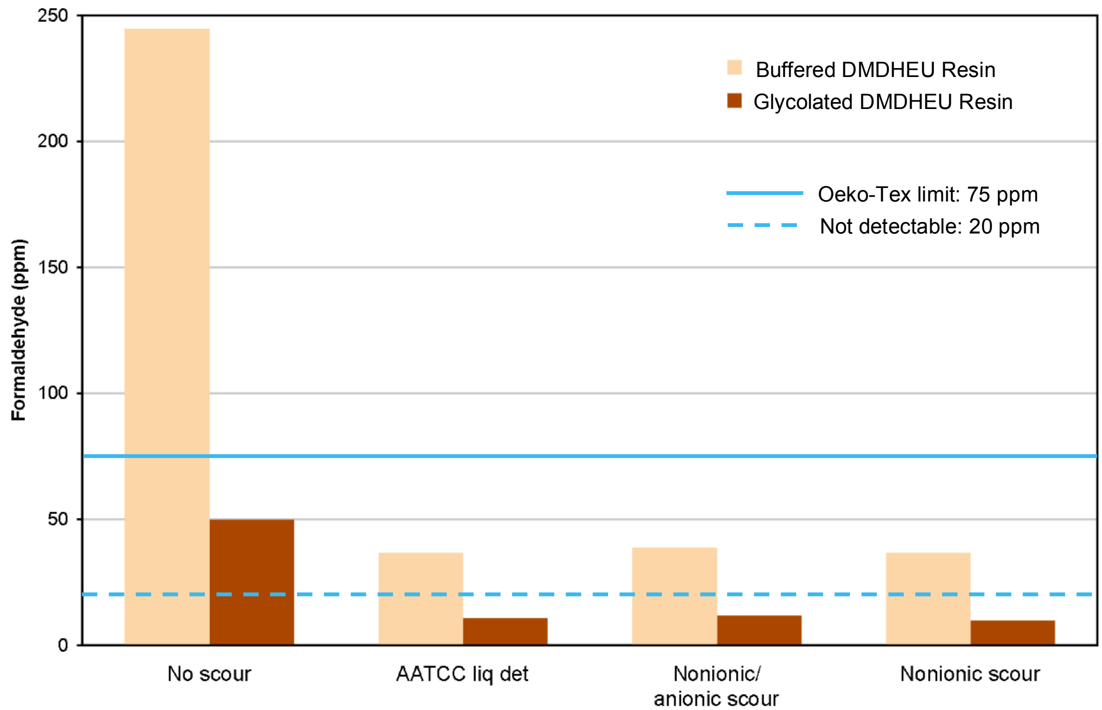

Figure 5. ISO 14184-1 test results for after-washed samples treated with buffered DMDHEU resin or glycolated DMDHEU resin.

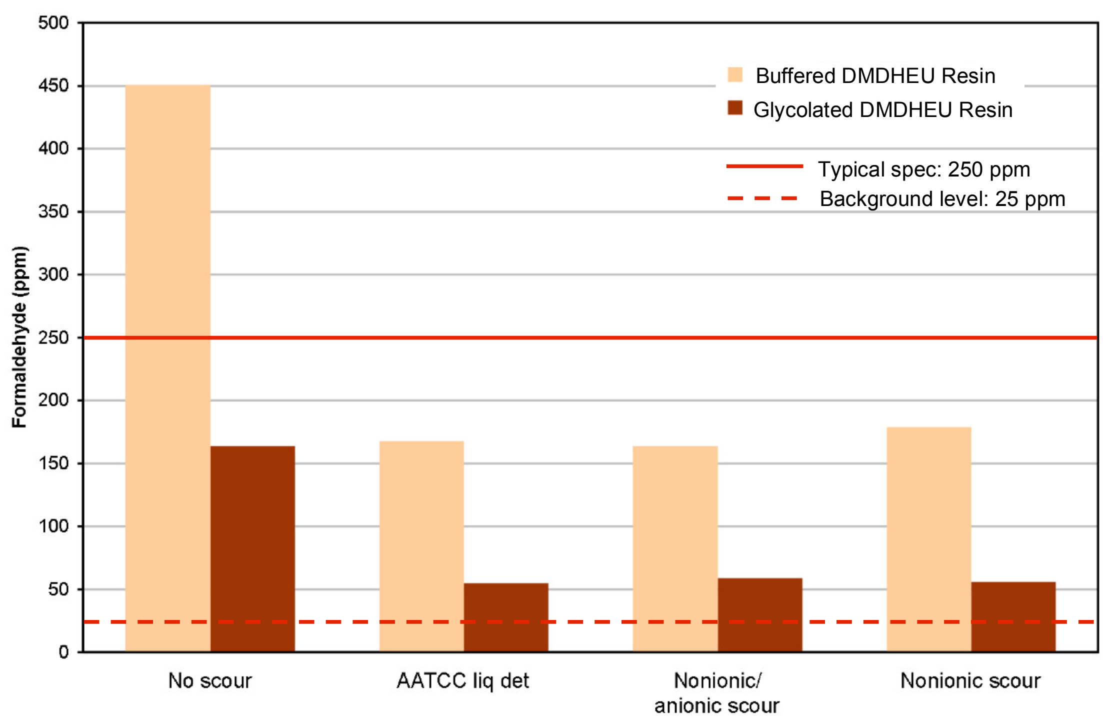

Figure 6. AATCC 112 test results for after-washed samples treated with buffered DMDHEU resin or glycolated DMDHEU resin.

Scavenger Studies

Adding a formaldehyde scavenger to a resin finish can adversely affect durable-press performance and the physical properties of fabric. Therefore, specific scavengers should be evaluated for their effects on wrinkle-resistance performance before use. In this study, durable-press performance was evaluated by the crease recovery angle test, using a Fangyuan Instrument Co. Fully Automatic Crease Recovery Tester, model YG541D.

A commercially available proprietary formaldehyde scavenger was added directly into the finish formulations at concentrations ranging from 1% to 5%. The finishes were pad-applied, dried and cured at 177°C (350°F) for 90 seconds, and immediately bagged to await testing.

The results are shown in Figures 7 and 8. The scavenger significantly reduced the formaldehyde levels in both AATCC and ISO tests, to well below the desired specifications, and had little effect on crease recovery angles.

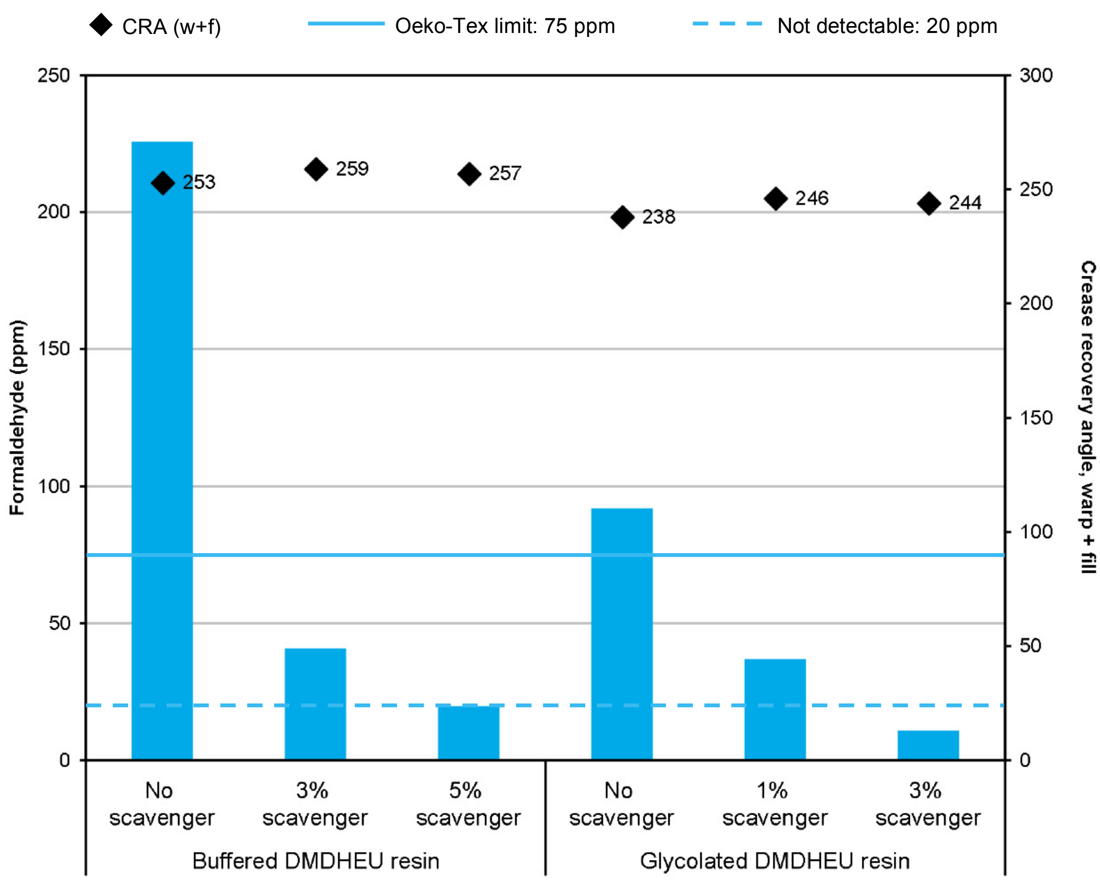

Figure 7. ISO 14184-1 test results and crease recovery angles for samples with a formaldehyde scavenger in the bath.

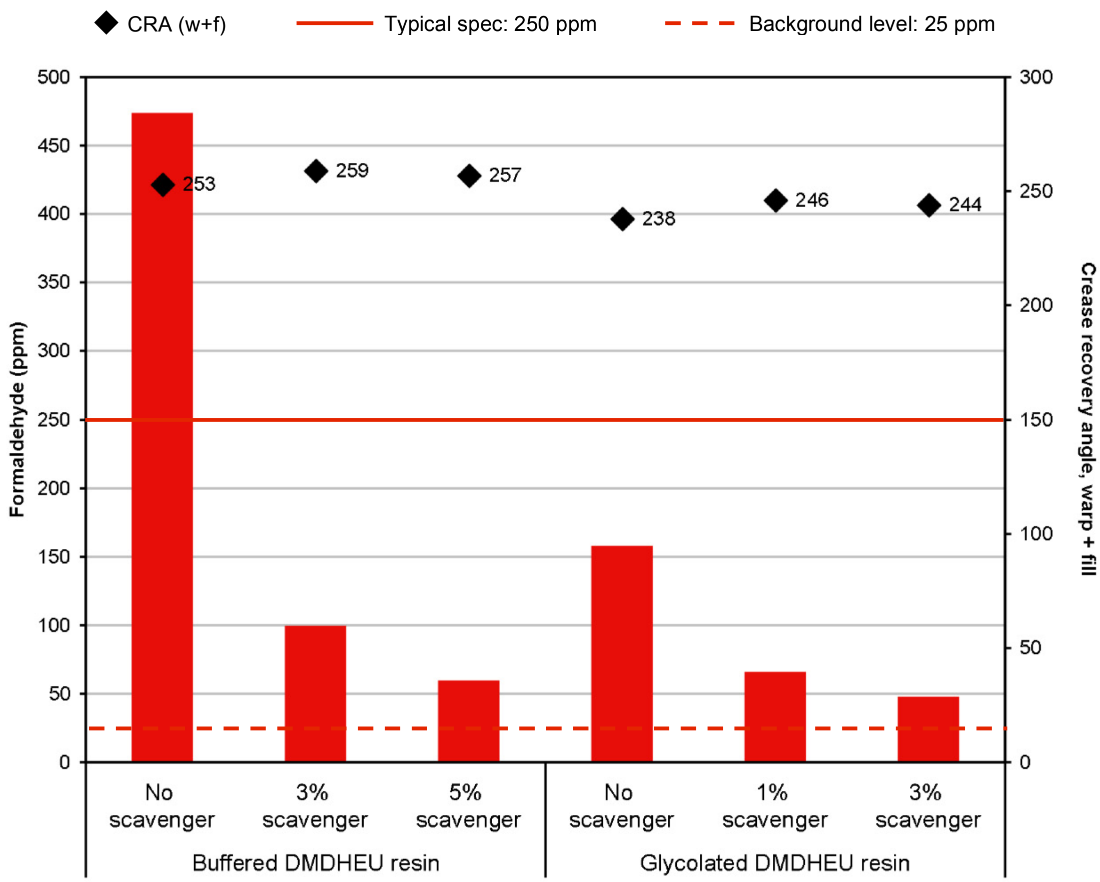

Figure 8. AATCC 112 test results and crease recovery angles for samples with a formaldehyde scavenger in the bath.

Studies Combining After-Washing and a Scavenger

Prior experience indicated that scavengers sometimes washed off, and that the formaldehyde levels increased after laundering. Therefore, samples in the scavenger studies were also tested after one wash in the Labomat, as described above, with the AATCC liquid detergent. In these studies, formaldehyde in the final fabric was reduced to below the background levels of 25 ppm in the AATCC test and 20 ppm in the ISO test, meaning that no detectable free formaldehyde was present. The results are shown in Figures 9 and 10. However, formaldehyde levels after washing may vary depending on the type of scavenger used.

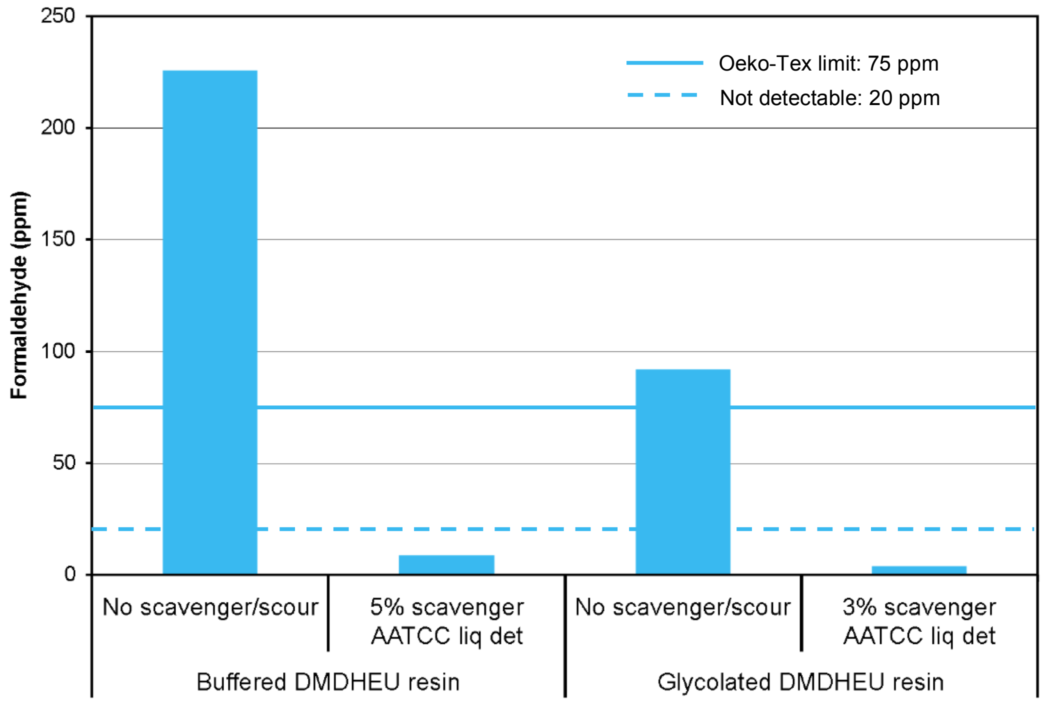

Figure 9. ISO 14184-1 test results for after-washed samples with a formaldehyde scavenger in the bath.

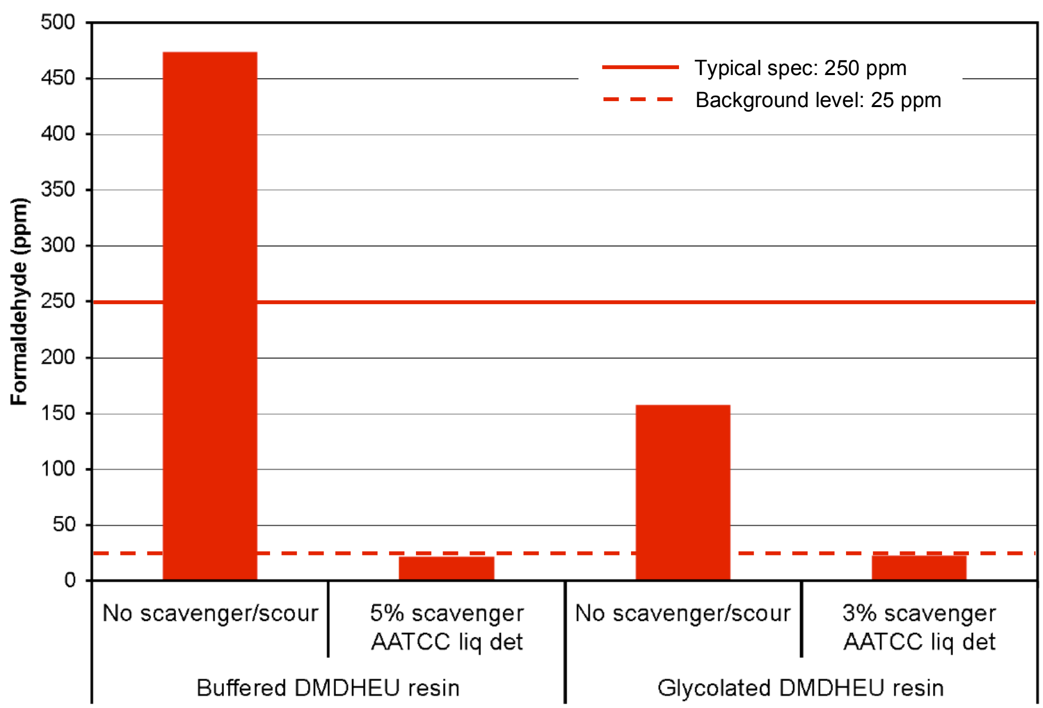

Figure 10. AATCC test results for after-washed samples with a formaldehyde scavenger in the bath.

SUMMARY

Formaldehyde is widely used to improve the performance and physical properties of cellulose-containing textile products. Like other reactive chemicals, formaldehyde can be irritating or toxic to humans exposed by inhalation or skin contact, and occupational exposure has been linked with increased risk of nasopharyngeal cancer. It is therefore imperative that formaldehyde be used in accordance with regulations that limit formaldehyde emissions in the workplace and to the environment. The release of free formaldehyde during textile processing can be reduced by a number of methods. Among the most effective methods are reduction of free formaldehyde on the fabric through the use of a low-formaldehyde resin, proper preparation and curing methods, the use of a formaldehyde scavenger in the finish, and/or after-washing of the fabric.

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RESEARCH AND TECHNICAL SERVICES

Cotton Incorporated is a research and promotion company representing cotton worldwide. Through research and technical services, the company has the capability to develop, evaluate, and then commercialize the latest technology to benefit cotton.

- Agricultural research leads to improved agronomic practices, pest control, and fiber variants with properties required by the most modern textile processes and consumer preferences. Ginning development provides efficient and effective machines for preservation of fiber characteristics. Cottonseed value is enhanced with biotechnology research to improve nutritional qualities and expand the animal-food market.
- Research in fiber quality leads to improved fiber testing methodology and seasonal fiber analyses to bring better value both to growers and to mill customers.
- Computerized fiber management techniques result from in-depth fiber processing research.
- Product Development and Implementation operates programs leading to the commercialization of new finishes and improved energy- and water-conserving dyeing and finishing systems. New cotton fabrics are engineered — wovens, circular knits, warp knits, and nonwovens — that meet today's standards for performance.
- Technology Implementation provides comprehensive and customized professional assistance to the cotton industry and its customers — textile mills and manufacturers.
- A fiber-to-yarn pilot spinning center allows full exploration of alternative methods of producing yarn for various products from cotton with specific fiber profiles.
- The company operates its own dyeing and finishing laboratory, knitting laboratory, and laboratory for physical testing of yarn, fabric, and fiber properties, including high volume instrument testing capable of measuring micronaire, staple length, strength, uniformity, color, and trash content.

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