TECHNICAL BULLETIN

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FORMALDEHYDE IN TEXTILES

I. INTRODUCTION

Although formaldehyde is a gas it in its purest form, it is seldom processed in that state. One exception is the vapor phase reaction process of formaldehyde with cellulose-containing textiles. Formaldehyde is usually handled as an aqueous solution, as paraformaldehyde (a homopolymer of formaldehyde) or as a reaction product in a resin. Aqueous formaldehyde is most frequently 37% active and contains 0.05% to 15% methanol, to prevent polymerization to paraformaldehyde. In water, an equilibrium exists between formaldehyde and dihydroxymethane. Aqueous formaldehyde and most reaction products tend to emit some free formaldehyde.

A number of unique properties are offered by formaldehyde. Foremost, it is cheap, readily available, reactive, easily handled, and efficient. The end products made with formaldehyde are durable and non-yellowing as compared to those made with other aldehydes. Without formaldehyde as the building block, the performance and value of a broad array of products that benefit from its chemistry would suffer. Home buyers would likely face increased costs or reduced performance from construction materials such as plywood, particleboard and fiberboard used in housing and furniture. In a like manner, many textile products would also suffer in performance. Other affected sectors would include automotive materials and personal care products.

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. These resins included urea-formaldehyde, phenol-formaldehyde, polyacetal, and melamine-formaldehyde. Textile chemicals amounted only to a few percent of the world consumption.

In the early years of the twentieth century, French chemists studied the reaction of formaldehyde with cotton to improve wrinkle resistance and to control shrinkage. Derivatives of formaldehyde are now preferred in order to obtain a better balance of physical properties and to reduce environmental impacts. Today, a large percentage of cellulose-containing textiles are processed with such products.

II. RELEVANCE OF 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 we eat and in our blood as part of our normal metabolism. The concentration ranges from approximately 6 parts per million (ppm) in tomatoes to 20 ppm in apples. In fact, the average person produces about 1.5 ounces of formaldehyde each day as part of normal metabolic processes. Formaldehyde is normally present in human blood at a low steady-state concentration of approximately 1 to 2 ppm. [Note: Formaldehyde is also reported in “micrograms per gram (µg/g) which is equivalent to ppm.]
Since free formaldehyde can be generated by formaldehyde-containing resins, it can be expected to be found in the vicinity of, and within, the following items:

- Construction materials
- Home fabrics

- Permanent press apparel fabrics
- Cosmetics
- Glues and adhesives
- Paints and coatings
- Slow-release fertilizers

Formaldehyde may also be generated by combustion of various materials. Typical sources include

- Tobacco smoke
- Kerosene space heaters
- Automobile exhaust
- Open fires

All of these sources combine to create a typical person's exposure.

III. TOXICITY OF FORMALDEHYDE

As with practically all reactive compounds, formaldehyde is toxic at certain levels. Although formaldehyde is less toxic than most reactive compounds, certain factors make formaldehyde a particular problem. Firstly, it is a gas that can spread throughout the work and living space. Secondly, most of the formaldehyde resins and their end-use products tend to liberate free formaldehyde. For humans, the routes of exposure that cause concern are skin contact and inhalation. Fortunately, 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. The risk of an adverse reaction to formaldehyde will depend on the sensitivity of the individual, the time of exposure, and the type of contact (skin or lungs) and on the toxicity.

Formaldehyde can be irritating to the eyes, nose, and throat, but, for most people, the irritation is temporary and reversible. Other reported symptoms include fatigue, nausea, vomiting, nosebleeds, headaches, and dizziness. At some levels of exposure, some of these symptoms can be felt immediately. Exposure to large amounts of formaldehyde may cause fluid build-up in the lungs as well as damage to the liver, the kidneys, and the central nervous system.

Dermatitis, especially in the textile industries, is well documented. Formaldehyde is a well-known sensitizer. In fact, in Title 16 Code of Federal Regulations Part 1500.13(d), 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.

High levels of formaldehyde (6-15 ppm) were shown to cause nasal cancer in laboratory rats whereas low levels (at or below 2 ppm) did not cause nasal cancer. It was later demonstrated that the level of formaldehyde must be high enough to kill cells before cancer is expected to occur. After reviewing epidemiological studies of funeral home workers, the International Agency for Research on Cancer, a World Health Organization panel of 26 scientists from 10 countries, has concluded that formaldehyde is a human carcinogen.

IV. REGULATING ENVIRONMENTAL EXPOSURE TO FORMALDEHYDE

For environmental, safety, and health reasons, formaldehyde is regulated by various federal and state agencies. These requirements allow for the safe production, storage, handling and use of this important chemical.

In order to protect the environment, the U.S. Environmental Protection Agency (EPA) governs the emission of formaldehyde into the air from manufacturing exhaust through the Clean Air Act. (Some manufacturers reduce the emission of formaldehyde through the use of a thermal oxidizer.) One state, California, lists gaseous formaldehyde as a substance known to the state to cause cancer in the Safe Drinking Water and Toxic Enforcement Act of 1986 ("California Proposition 65"). Additionally, the California Air Resources Board (CARB) has released an indoor air pollution report that includes numerous references to formaldehyde. CARB has enacted regulations to reduce formaldehyde exposure due to wood products.

Workplace exposures are limited 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 exposures should not exceed 2 ppm during any 15-minute work period. The standard also lists requirements for monitoring employee exposures; protective measures; medical surveillance; and communication and training about the hazards. In addition to the OSHA regulation, the National Institute of Occupational Safety and Health (NIOSH), part of the Centers for Disease Control, recommends that 0.1 ppm as a ceiling limit that should not be exceeded for more than 15 minutes at any time. Also to prevent possible health effects over a working lifetime, NIOSH has recommended that workers not be exposed to more that 0.016 ppm averaged over a 10-hour workday. All of these limits are much lower than the odor threshold, which is the minimum amount that can be smelled. The odor of formaldehyde is generally first sensed at 1 ppm, but some individuals can smell it a 0.05 ppm.

Formaldehyde is usually present in concentrations less than 0.03 ppm in both outdoor and indoor air. The U. S. Consumer Product Safety Commission (CPSC) and the U.S. Department of Housing and Urban Development (HUD) have addressed indoor air exposure to formaldehyde. Since industry voluntarily adopted product emission standards and low-emitting resins were developed, indoor formaldehyde emissions have declined significantly. CPSC determined that mandatory regulation was unnecessary given the voluntary actions and low levels of formaldehyde. HUD set standards that limit formaldehyde emissions from wood products that are used in manufactured housing. In homes with many new pressed-wood products, levels can be greater than 0.3 ppm. This level could cause a problem since formaldehyde is a carcinogen, and there are no known safe levels of exposure to carcinogens. The World Health Organization recommends that exposure should not exceed 0.05 ppm.

In the United States, the only regulation of formaldehyde in consumer products is found in the Federal Hazardous Substances Act (FHSA), which states that products with levels greater than 1% must be labeled in a specific manner 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 the limit on the amount of formaldehyde to accept. This limit is determined, in part, by how the level on the fabric will affect the ability of the textile mill to meet the legal limitations for formaldehyde in the air, as described above, and by the consumers' demands for performance.

However, the formaldehyde content of textiles has been legally limited in a few countries. For instance, Finland and Japan introduced strict limits for textile formaldehyde content. In order to sell the same finish to a variety of customers, the 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.

V. MEASURING THE CONTENT OF FREE FORMALDEHYDE IN TEXTILES

Measuring the content of free formaldehyde in textiles has been a subject of research for a number of years. The formaldehyde released from a treated fabric will depend on a number of factors including the following:

- The type of formaldehyde resin used
- The quantity of the formaldehyde resin used
- Temperature
- Relative humidity
- Time that the fabric is exposed to the air
- The area of the fabric exposed
- The degree that the formaldehyde resin had been cured, which is affected by the initial preparation of the fabric, as well as the curing conditions used for the reaction
- Whether the treated fabric had been after-washed or further processed before testing

There are presently two generally accepted methods of measuring the formaldehyde content of textiles. In the AATCC Method 112, the test specimen is suspended over an aqueous solution in a sealed jar at a given temperature for a specific period of time. The formaldehyde gas that is given off by the specimen is adsorbed 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. The margin for error in low-level samples is about 75 ppm. Both free and releasable formaldehyde may be captured in the incubation procedure. In contrast, the Japanese Law Method 112 procedure requires the free formaldehyde from the test specimen to be extracted into a cold aqueous solution of sodium sulfite, which is then derivatized and measured as stated above. This procedure does not necessarily capture releasable formaldehyde. The limit of detection for the Japanese method is 20 ppm. Not surprisingly, the two methods yield different values. Thus, the method to be used must be specified. For example, an AATCC Method 112 reading of 300 ppm (meeting many United States retailer requirements) may give a Japanese Law Method 112 value of 75 ppm. But, an exact correlation between the two methods is not possible.

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. A “fish bowl” type arrangement where the relative humidity of the environment containing the specimen may be varied can be used to collect air samples from around a textile sample. Although these methods have merits, drawbacks include a lack of convenience, longer times, and a need for specialized equipment.

VI. REDUCING THE FREE FORMALDEHYDE PRODUCED BY TEXTILES

The air concentration of the formaldehyde that is evolved when treating textiles (i.e., stack emissions) may be reduced by a number of methods including:

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

Reduction of the free formaldehyde on the fabric is one of the most effective methods for reducing the free formaldehyde in the surrounding air. Some of the options that may be utilized for reducing free formaldehyde on the fabric are outlined below:

- Use resins containing low free formaldehyde
- Use dimethyloldihydroxyethyleneurea (DMDHEU)-type resins
- Use DMDHEU that was 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
- Use a non-formaldehyde-containing durable press resin
- Prepare fabric to obtain a neutral pH with low fabric alkalinity

The use of a non-formaldehyde containing resin would be the desirable choice if other properties would remain acceptable. Many effective non-formaldehyde crosslinking resins are more toxic than formaldehyde-containing resins. Two candidates that have generated some interest and limited usage include selected polycarboxylic-acid derivatives (such as butanetetracarboxylic acid) and dimethylurea glyoxal (DMUG). Both of these products are significantly more expensive than the etherified DMDHEU. To obtain efficiency, the polycarboxylic acid derivatives require a reductive catalyst that can adversely affect the shade of a number of dyes. DMUG alone in most cases does not impart adequate durable press and shrinkage resistance.

VII. CONCLUSIONS

Formaldehyde is a vital chemical for products that we utilize everyday. It has a long history of relatively safe usage. Much research has been conducted on the toxicity, prevalence in the environment, and control of the substance. It is imperative that formaldehyde be used in accordance with the current safety rules and regulations.

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- 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.

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