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Problems Associated with the Use of Urea-Formaldehyde Foam for Residential Insulation

**Part II: The Effects of Temperature and Humidity
on Free Formaldehyde, Extractable
Formaldehyde, Formaldehyde Emission, and Physical
Characteristics of the Foam**

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Part of
The National Program
for
Building Thermal Envelope Systems
and Insulating Materials

Prepared for the
U.S. Department of Energy
Conservation and Solar Energy
Office of Buildings and Community Systems
Buildings Division

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DEPARTMENT OF ENERGY**

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FOAM FOR RESIDENTIAL INSULATION

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FOREWORD

This is one of a series of reports to be published describing research, development, and demonstration activities in support of the National Program for Building Thermal Envelope Systems and Insulating Materials. The National Program involves several federal agencies and many other organizations in the public and private sectors who are addressing the national objective of decreasing energy wastes in the heating and cooling of buildings. Results described in this report are part of the National Program through delegation of management responsibilities for the DOE lead role to the Oak Ridge National Laboratory.

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21. ORNL/Sub-7715/1: Operating Temperatures for a Convectively Cooled Recessed Incandescent Light Fixture (December 1980).
22. ORNL/TM-7481: Analysis of Heat Transfer in Building Thermal Insulations (December 1980).
23. ORNL/tr-4679: Roofing Felt on Polystyrene (December 1980).

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Purpose: This study is a continuation of earlier work related to the effects of temperature and humidity on urea-formaldehyde foam insulation with special reference to the off-gassing of formaldehyde.

INTRODUCTION

The condensation reaction between urea and formaldehyde was first reported in Europe in the late 1800's. Extensive studies on the nature of the reaction were published by Dixon (1) as early as 1918. Urea-formaldehyde based foam has been known since 1933 when it was developed at the I.G. Farbenindustrie in Germany. A comprehensive review of urea-formaldehyde resins by Meyer (2) has recently been published.

Although urea-formaldehyde based foams have been commercially available in the United States since the 1950's, they were not widely used. With the advent of recent emphasis on energy conservation there has been an increasingly greater use of these materials for residential insulation and in particular as retrofit applications in existing structures.

Earlier work described in Oak Ridge National Laboratory report number ORNL/SUB-7559/1 published in 1979 entitled "Properties Associated with the use of Urea-formaldehyde foam for Residential Insulation. Part 1: The Effects of Temperature and Humidity on Formaldehyde Release from Urea-Formaldehyde Foam Insulation" concluded that: (1) Temperature and humidity affect the levels of formaldehyde off-gassing from urea-formaldehyde foam insulation; (2) There appear to be two emission phenomena, one involving a short term release of formaldehyde and one involving a lower level long term release and (3) Products tested reflected the same general release pattern but there are product related characteristic differences in the amounts of formaldehyde released.

This report describes the results of testing with two additional products and describes additional intrinsic and extrinsic characteristics now recognized.

Formaldehyde. Formaldehyde is a colorless gas with a pungent, irritating odor. The chemistry of formaldehyde is characterized by its extreme reactivity due, in most part, to its two hydrogen atoms (3). This reactivity is reflected in the fact that formaldehyde is not found, generally, in simple monomeric form, thus complicating the chemistry of formaldehyde.

Walker (4) has divided formaldehyde compounds into two basic groups. The first deals with compounds of the general formula $(CH_2O)_n$. These include the monomer, trioxane, tetraoxane, and high molecular weight polyoxymethylenes. The second group includes addition compounds and solvates whose formula is $HO(CH_2O)_nH$. Methylene glycol and low

molecular weight polyoxymethylene glycols are the most common of this type in solution.

Formaldehyde is usually handled as an aqueous solution, ranging in concentration from 37 to 56 percent by weight (5). As the concentration is increased the percentage of methylene glycol decreases, and the polymer length of the polyoxymethylene glycols increase as dictated by:

With increased chain length the polymer is less soluble and has a tendency to precipitate unless the temperature is increased or a stabilizer such as methanol is added (6). Commercial solutions may contain up to 7 percent methanol for this purpose.

Formaldehyde is used mainly as an intermediate in the preparation of explosives, dyes, synthetic lacquers, and resins (9). Large volumes of formaldehyde solutions are used in the preparation of urea-formaldehyde, phenol-formaldehyde, and melamine-formaldehyde resins. Of the six billion (6×10^9) pounds of formaldehyde solution (37%) produced in 1974, approximately 30% was utilized in the production of urea-formaldehyde resins (10).

The reported toxicity indices of formaldehyde are generally related to the olfactory properties of the vapor. Both solutions and vapors act as irritants to the mucous membranes of the nose and eyes on contact, and the upper respiratory tract upon inhalation (7). Because of these effects OSHA has set the threshold limit value (TLV) at 3 parts per million of formaldehyde vapor by volume in air (8).

Urea-Formaldehyde Resins. Urea formaldehyde resins have many commercial uses, including thermosetting materials for moulding compositions laminating, protective coatings, and for treating paper and textiles (11). In addition they can serve as adhesives for particle board, plywood, and other wood products.

Urea-formaldehyde resins are a mixture of products from the condensation reaction between urea and formaldehyde. The first stage of condensation is carried out at 70° to 100° C, with a urea to formaldehyde ratio of approximately 1.5 and a pH of 4 to 8 (12). This results in a mixture of mono- and di-methylolurea. The products of this first stage of condensation take on a variety of forms which are dependent on reaction conditions such as pH, temperature and the mole ratio of urea to formaldehyde. They can be prepared as syrupy aqueous solutions, water soluble fine grained powders or water insoluble materials which precipitate from the reaction solution. (13).

The structure of the resin beyond the first stages of condensation is not known in great detail (14). Depending on the conditions of the reaction, formaldehyde is present in the complex polymer in a variety of forms. Three types of combined formaldehyde are dimethylene ether bridges ($-\text{CH}_2\text{OCH}_2-$), methylene bridges ($-\text{CH}_2-$), and methylol end groups as shown in Figure 1. In addition to combined formaldehyde, these resins always contain variable amounts of free formaldehyde. One possible structure for the resin was given by I.M. Mayofis (15) and is shown in Figure 2.

Methylol groups ($-\text{CH}_2\text{OH}$) are considered the most reactive of the combined forms of formaldehyde in the resin. The dimethylene ether bridges are less reactive. All these forms are hydrolyzed when treated with base to yield free formaldehyde even at room temperature. Methylene bridges are the most stable and are split only when heated with strong mineral acids (16).

Cross-linking in the resin appears to be related to the urea-formaldehyde stoichiometry used in the original preparation of the resin. Infrared spectrometric studies suggest a possible mechanism for cross-linking (17). The IR spectrum is not generally affected by cross-linking except for the $9.9\text{ }\mu\text{m}$ and $3.0\text{ }\mu\text{m}$ hydroxyl absorption bands. The appearance of a shoulder at $9.5\text{ }\mu\text{m}$ suggests that the hydroxyl groups are replaced by dimethylene ether bridges. Since this feature is not well defined it is believed that dimethylene ether bridges decompose with the subsequent loss of formaldehyde (18). Further descriptions of the various spectral characteristics of this polymer can be found in Walker (19) and Urbanski (20).

Urea-Formaldehyde Foam Insulation. The urea-formaldehyde resin mixture described is used for the production of urea-formaldehyde foam insulation. The foam resulting from a resin of just urea and formaldehyde is brittle, thus plasticizers are added to the resin mixture to reduce the brittleness. The chemical formulations used in the production of foam insulation varies among manufacturers. Recent patents have been described for the production of the foam (21, 22, 23).

Three major components are necessary for the production of the final product which is generated on site using portable equipment. The components are a partially polymerized urea-formaldehyde resin, a surfactant (foaming agent) which contains an acid catalyst or hardening agent and air. The resin and surfactant-catalyst are both water solutions. Naphthalene sulfonic acid (24), and dodecyl benzene sulfonic acid (25) have been used as foaming agents and phosphoric (26), oxalic (27), citric, malic, and tartaric acids (28) have been used as the acid catalyst.

FIGURE 1

TYPES OF COMBINED FORMALDEHYDE

Methylol End Group

Methylene Bridge

Dimethylene Ether Bridge

FIGURE 2

RESIN STRUCTURE

In general, generation of the foam insulation in the United States requires the use of an air compressor and a mixing or foaming gun. The process involves two events which consecutively take place in the gun. The foaming agent-catalyst mixture is pumped into the gun where compressed air mixes with it to form a foam of small detergent bubbles. Subsequently, the bubbles are coated in the nozzle of the gun by urea-formaldehyde resin which is supplied from a separate line. The resin coated bubbles are forced out of the gun under pressure which results in a white foam which resembles shaving cream. The resin, after mixing with the catalyst at the surface of the bubbles, begins to polymerize (cure) and within less than a minute the resin has partially cured into a stiff, self-supporting foam.

The rate of chemical curing is dependent upon factors such as temperature, humidity, and foam formulation. The water present dissipates at a rate which is dependent upon temperature, humidity, and type of construction to which foam is applied (29).

The quality of the resulting product is dependent upon a number of parameters including the quality of the ingredients, the ratio of ingredients, the mixing of ingredients, the viscosities of ingredients, the age or shelf-life of the ingredients and the temperature at which the foaming takes place. The foam is easy to install, however, there are also a number of disadvantages. Some material and performance properties have yet to be established and examined. These include effect of foams on other building materials, the resistance of foams to freezing and thawing, water vapor transmission, effect of absorbed water on the thermal conductivity, shrinkage, maximum service temperature, and the effect of high temperature and high humidity (30).

Determination of Formaldehyde. The monitoring of formaldehyde emission requires a method which can be applied to the determination of the aldehyde in air. Detection and quantitative determination of formaldehyde can be accomplished by numerous methods. Titrimetric methods for the determination of formaldehyde are reviewed extensively by Walker (31). Two of the methods used for the determination of large amounts of formaldehyde have been the sodium sulfite and iodometric method. The sulfite method is based on the quantitative liberation of sodium hydroxide when formaldehyde reacts with sodium sulfite to form the formaldehyde bisulfite addition product.

The sodium hydroxide is then titrated with standard sulfuric or hydrochloric acid using thymophthalein indicator. The endpoint can also be determined potentiometrically. (32).

The iodometric method is dependent upon the oxidation of formaldehyde by hypoiodite formed when potassium hydroxide is added to a solution of formaldehyde to which a known amount of a standard iodine solution has been added. The iodine consumed is measured by back titration of the liberated iodine upon acidification. Liberated iodine is titrated with standard thiosulfate solution. The reactions involve:

1. Formation of hypoiodate:

2. Oxidation of formaldehyde in alkaline solution:

3. Formation of iodate from excess hypoiodite:

4. Liberation of iodine upon acidification:

5. Titration of iodine with thiosulfate:

Another titrimetric procedure which is not described by Walker is that of Goldman and Yogoda (34) who applied the procedure to the determination of aldehydes in air. Formaldehyde reacts with sodium bisulfite to form the formaldehyde-bisulfite addition complex. Analysis is performed by destroying the excess bisulfite at neutral pH, after which the solution is made alkaline, liberating the sulfite complexed with formaldehyde. The liberated sulfite is then titrated with a standard iodine solution to give an indirect measure of formaldehyde.

Volumetric methods are not sensitive nor specific enough for the detection of formaldehyde in air. Numerous analytical methods for the quantitation of small amounts of formaldehyde have been developed. Spectrophotometric, fluorescence, and polarographic methods have been developed for the determination of trace amounts of the aldehyde. The polarographic measurement of small quantities of formaldehyde was first reported by Jahoda in 1935 (35, 36). The height of the current wave in the polarogram is directly proportional to the formaldehyde concentration. The temperature and pH was controlled because the height of the wave changed with these parameters. Jahoda claimed that 0.07 parts per million formaldehyde could be determined with a precision of 10%.

Reduction of the aldehyde occurred at -1.63 volts in a neutral or weakly alkaline media (37). Boyd and Bambach (38) were in agreement with Johoda's findings. The temperature dependence of the current was also examined and found to change 6.5% for each 1°C change in temperature. Formaldehyde in the atmosphere has been determined by bubbling air through supporting electrolyte followed by polarographic detection (39). Some recent methods of electrochemical detection of formaldehyde have used alternating current polarography (40), twin cell sweep voltammetry (41), argentimetric potentiometric titration using an iodide ion sensitive electrode (42), and short circuit argentimetric/amperometric titration using a rotating platinum micro-electrode (43). The only method applied to trace determinations of the above was that of using twin cell sweep voltammetry. The semicarbazide derivative of formaldehyde was prepared before the determination. A detection limit at the part per billion level was reported. This method was applied to the detection of total carbonyl content in natural waters and industrial effluents.

Fluorescence and spectrophotometric detection are the most popular methods of determination of formaldehyde. Sawicki (44) has prepared an extensive review on the photometric determination of aldehydes with a chapter devoted to the determination of formaldehyde. A large number of methods are available for the detection of formaldehyde. Of these, the most popular methods use Schiff's reagent (pararosaniline and sulfite), chromotropic acid (1,8-dihydroxy-3,6-disulfonic acid), MBTH (3-methyl-2-benzothiazoline hydrazone), J-acid (7-anilino-4-hydroxy-2-naphthalenesulfonic acid), phenyl J-acid (6-anilino-1-naphthol-3-sulfonic acid) and 2,4-pentanedione and an ammonium salt as color forming reagents (45, 46).

The determination of trace concentrations of formaldehyde in air using Schiff's reagent was adapted by Rayner and Jephcott (47). Formaldehyde was collected in impingers containing 0.005N hydrochloric acid solution. The solutions then were reacted with Schiff's reagent (pararosaniline and sulfite) and the absorbances measured at 560 nanometers. Color development took up to twenty-four hours. A modified Schiff's reagent was developed by Lyles (48) in 1965. The reagent, a mixture of di-chlorosulfitomercurate (II) complex and acid-bleached pararosaniline hydrochloride, was collected in water using a midjet impinger. Sodium tetrachloromercurate (II) solution sodium sulfate, and pararosaniline hydrochloride was added and mixed. After the solution was allowed to stand for an hour, the absorbance was determined at 560 nm. Both methods were reported to be sensitive to 0.05 ppm with application to Beer's Law from 0.05 to 9 ppm.

The method which is recommended by the National Institute for Occupational Safety and Health and the official method for the analysis of formaldehyde for the American Association of Analytical Chemists uses chromotropic acid (1,8-dihydroxy-3, 6-disulfonic acid) as the color developing reagent (49). The method relies upon the production of a purple chromogen which absorbs at 560 nm by the reaction between formaldehyde, chromotropic acid, and sulfuric acid. The reagent was first

proposed as a specific reagent for formaldehyde in 1937 by Eegriwe (50). Determination of formaldehyde in air using chromotropic acid was developed by MacDonald (51) in the form in which it is commonly used today (52). Altshuleer, Miller, and Sleva (53) proposed a modification of the method which is said to improve sensitivity, stability, and freedom from interferences. The proposed sampling method used chromotropic acid in sulfuric acid as the collection media. However, use of such an absorbing solution required special care and handling. Care (54) recommended that samples be collected in a sodium bisulfite solution. More stable solutions result and the interference from NO_2 is removed.

Sawicki, et. al., (55) introduced the MBTH (3-methyl-2-benzothiazoline hydrazone) test for formaldehyde. The authors found increased sensitivity and more accuracy from drawing the air sample directly into the reagent for air analysis. Modification of MBTH analysis by Cummins and Hauser (56) resulted in an increased sensitivity which easily permits determination of formaldehyde in the part per billion (ppb) range for ambient air. Determination is accomplished by sampling into a dilute aqueous solution of MBTH. The sample is allowed to sit at room temperature for an hour after collection to allow for the MBTH to completely react with formaldehyde. Then the sample is oxidized with 1.6% sulfamic acid and 1% ferric chloride. The absorbance of the blue dye is measured at 628 nm. Beer's Law applies from 0.05 to 0.92 ppm.

Sawicki, et al., (57) compared the chromotropic acid method with the J-acid (7-anilino-4-hydroxy-2-naphthalenesulfonic acid) and phenyl J-acid (6-anilino-1-naphthol-3-sulfonic acid) methods. They established that J-acid and phenyl J-acid are extremely sensitive and selective reagents. The J-acid chromogen absorbs at 612 nm while the phenyl J-acid chromogen absorbs at 660nm. Beer's Law applies from 0.6 to 13 ppm for phenyl J-acid. One great disadvantage with using these reagents is that long periods of time are required for color development.

Nash (58) introduced 2,4-pentanedione (acetylacetone) as a reagent for formaldehyde. This reagent is highly specific for formaldehyde. The method is based on the Hantzsch reaction of formaldehyde with 2,4-pentanedione and an ammonium salt to give diacetyldihydrotoluidine. This lutidine derivative is yellow with a molar extinction coefficient of 8000 at 412 nm.

Two of the reagents described for spectrophotometric determinations are also fluorescent when reacted with formaldehyde. J-acid and 2,4-pentanedione fluorescence methods have been developed (59, 60). Spectrofluorometric determination of formaldehyde with J-acid follows Beer's Law in the range of 0.0001 ppm to 0.2 ppm. The excitation wavelength is 470 nm and the emission wavelength, 520 nm. The presence of bisulfite inhibits the coupling of formaldehyde with 2,4-pentanedione and ammonium.

The interference of bisulfite results from the reaction of the bisulfite addition complex and ammonia, making formaldehyde unavailable for reaction with 2,4-pentanedione:

Interference from bisulfite is removed by addition of a dilute solution of iodine in acetone prior to the addition of the other reagents (61).

In addition to the wet chemical methods just described above for measurement of formaldehyde concentrations, there are several instrumental methods of analysis available including the CEA Model 555 analyzer and the Wilkes Infrared Analyzer. The most promising of these is the Foxboro Wilkes Infrared Analyzer available from Foxboro Wilkes, Inc. The instrument is simple to operate and provides for real time concentration data. It has a detection capability of about 100 ppb.

EXPERIMENTAL DESIGN

Environmental Chambers. Temperature and relative humidity were controlled using a combination of two metal environmental chambers. The general experimental set-up is illustrated in Figure 3. The larger of the two chambers was used for temperature control. Three chambers were constructed, two capable of operating at high temperature ($\sim 30^{\circ}\text{C}$) and the third designed to maintain low temperature ($\sim 7^{\circ}\text{C}$). Inside each large unit were placed four smaller chambers for humidity control. Two operated at high relative humidity ($\sim 80\%$) and the remaining two were maintained at a low level ($<20\%$).

The three large chambers were constructed of 22 gauge galvanized sheet metal using a supporting wooden frame. Inside dimensions were $2.4 \times 1.1 \times 1.8$ meters, representing a volume of 4.75 cubic meters. With the door closed, the chambers were essentially air tight.

The small chambers were constructed of 26 gauge galvanized sheet metal and were self supporting. Dimensions were $91 \times 61 \times 77$ centimeters, representing a volume of 0.425 cubic meters. An opening, covered by a metal plate, provided access to the foam samples. Humidity probes could be inserted through a $1\frac{1}{2}$ " diameter pipe which was connected to the side of the chamber. These pipes extended outside the large chamber and were sealed when not in use. A metal baffle on the inlet side of the chamber prevented air channeling. The air inlet was sealed with a $\frac{1}{4}$ " Swagelock fitting, the outlet was a $\frac{1}{2}$ " pipe to prevent pressurization of the chamber.

Air was pumped through the system by a compressor equipped with two air line filters. The air was passed through a drying column, Lector dryer Model LAB-B available from the McGraw-Edison Company. Before entering the environmental chambers, air flow to the small chambers was controlled with Matheson #604 flowmeters. Flow calibration curves, supplied by the manufacturer, were used to obtain desired flow rates.

All tubing was $\frac{1}{4}$ " o.d. polyethylene with Swagelock fittings. Compressor air pressure was maintained at 15 p.s.i. and the flowmeters adjusted to deliver 3 liters per minute to give an air exchange in each small chamber every 142 minutes.

The high temperature chambers were equipped with resistance wire heaters and fans for air circulation. Powerstat[®] variable transformers controlled the current through the resistance wire heaters. Temperature was monitored continuously with a Y.S.I. Model 47 Scanning Tele-Thermometer equipped with Y.S.I. Series 400 probes. The large chambers were insulated with fiberglass and temperature control to $\pm 1^{\circ}\text{C}$ was obtained. The low temperature chamber was cooled with a modified conventional air conditioner.

FIGURE 3

Relative humidity was varied within each small chamber. Air from the compressor was allowed to flow directly into the two "dry" chambers resulting in a low relative humidity. "Humid" conditions were generated by bubbling the air through water before it entered the other two chambers. The humidifier used for this purpose is illustrated in Figure 4.

The relative humidity of the air could be increased by heating the water in the humidifier. This was accomplished by wrapping the cylinder with heating tape obtained from the Brisco Manufacturing Company. Powerstat® variable transformers controlled the current through the tape. Humidifiers were constructed of steel pipes (3" x 24"), with $\frac{1}{4}$ " o.d. copper tubing and Swagelock fittings. Relative humidity was monitored with an Electro-Hygrometer made by Lab Line Instruments, Inc.

FIGURE 4
HUMIDIFIER

PROCEDURES

Formaldehyde Emissions. Foam samples used for the emission study were foamed and allowed to cure for 12 - 27 hours before placing them in the two small chambers. Emission studies were initiated upon placement of the samples in the chambers. The samples remained in the chambers for the duration of the observations.

Collection of air samples was performed using two graduated midjet impingers (Ace Glass, Inc.) connected in series to a vacuum pump (E.I. Dupont De Nemours & Co., Inc., personal air sampling pump, Model P4000 A) calibrated at one liter per minute. A glass tube was placed in the outlet of the chamber so that collection of air was taken from the middle of the chamber. With the impingers connected in series, the reported collection efficiency is 95% (64). Sampling was performed for 20 to 30 minutes with calibration of pumps before and after a day of sampling. After the sampling, the volume of the absorbing solution (1% sodium bisulfite solution) was measured and transferred to a sample bottle for transport to the laboratory for formaldehyde determination.

Air samples were collected three times a week. Each collection from the chambers consisted of three to four collections per chamber. The resulting calculated formaldehyde concentrations were averaged and reported as an average value.

Formaldehyde was determined using the chromotropic acid method, chosen because it is the recommended method of the National Institute of Occupational Safety and Health. A large number of samples were to be analyzed and the chromotropic acid method required the least time per sample per analysis while having good sensitivity and reproducibility.

The reaction of formaldehyde in solution with chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid, reagent grade, J. T. Baker Chemical Co.) and concentrated sulfuric acid (95%, analytical reagent, Mallinckrodt Chemical Works) forms a purple chromogen which absorbs at 580 nanometers ($\epsilon = 1.57 \times 10^3$). From 0.1 to 2.0 parts per million can be measured in the ten milliliter final volume of solution. This procedure has few interferences. Saturated aldehydes give less than a 0.01% positive interference and the unsaturated aldehyde acrolein results in a few percent positive interference. Ethanol and higher molecular weight alcohols and olefins are negative interferences. Methanol can be tolerated up to ten-thousandfold excess without interference (62). Phenols result in a 10 - 20% negative interference (63). However, all these interferences mentioned were not likely to be encountered in the sample atmosphere.

Standards of formaldehyde for the calibration curve were prepared from a formaldehyde stock solution (approx. 1 part per thousand) in deionized, distilled water. This stock solution was prepared by diluting 2.7 mL of 37% formaldehyde solution (A.C.S. reagent grade, 10- 15% methanol added as preservative, Matheson Coleman and Bell) to one liter with deionized, distilled water. This solution was standardized using the method of Godman and Yagoda (23). One milliliter of formaldehyde solution, ten milliliters of 1% sodium bisulfite and one milliliter of 1% starch indicator solution were mixed and titrated with 0.1N iodine (standardized with arsenic trioxide) to a dark blue color. The excess iodine was destroyed using 0.05N sodium thiosulfate and 0.01N iodine was added until a faint blue end-point was reached. The excess bisulfite was completely oxidized to sulfate. The bisulfite from the formaldehyde addition complex was liberated by the addition of 25% chilled sodium carbonate buffer (80 gm of anhydrous sodium carbonate in 500 mL water, 20 mL of glacial acetic acid and diluted to one liter). The liberated sulfite was then titrated with 0.01N iodine to a faint blue end-point using a microburet.

From this solution, the standards for the calibration curve were prepared. Aliquots of the second solution (0.0, 0.1, 0.3, 0.5, 0.7, 1.0 and 2.0 mLs.) were taken and diluted to 4 mLs with 1% sodium bisulfite. The color was developed by adding 0.1 mL of 1% chromotropic acid solution and slow addition of 6 mLs concentrated sulfuric acid solution. The solutions were allowed to cool to room temperature and the absorbance was measured at 580 nm.

Sample solutions were developed in the same manner. A 4 mL aliquot of sample solution was used. If the concentration of formaldehyde was above linear range (0.1 to 2.0 ppm), a smaller aliquot was used and then diluted to 4 mLs with 1% sodium bisulfite. Dilutions in this case were such that absorbances were in the range of 0.15 to 0.5.

The amount of formaldehyde in the sample solution was determined from a calibration curve. A linear regression fit of the calibration data was used in the calculation of the amount of formaldehyde.

To calculate the concentration of formaldehyde in air, the volume of air collected was converted to volume at standard conditions (760 mm Hg, 25°C). The temperature of the air sampled was that of the environmental chamber. The atmospheric pressure was assumed to be at one atmosphere. The effect of pressure on the volume conversion was found to be negligible compared to the effect of temperature. The total amount of formaldehyde present in the two sample impingers in series (A and B) was calculated using the following equation:

$$C_t = C_A \times F_A \times C_B \times F_B$$

C_t = total micrograms of formaldehyde in solution,

C_A, C_B = respective formaldehyde concentration (μg) in sample:
aliquots taken from impingers A and B as determined from
calibration curve,

F_A, F_B = respective aliquot factor; $\frac{\text{sample solution volume (mL)}}{\text{mL aliquot used}}$

The concentration of formaldehyde in the air sampled was calculated as micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) and parts per million, by volume (microliter per liter, $\mu\text{L}/\text{L}$). The following equation was used to calculate the concentration in parts per million, by volume (ppm):

$$\text{ppm}(\text{volume}, \mu\text{L}/\text{L}) = \frac{(C_t) (24.47)}{(V_s) (\text{M.W.})}$$

C_t = total micrograms formaldehyde,

V_s = liters of air sampled at standard conditions,

M.W. = molecular weight of formaldehyde, 30.03 $\mu\text{g}/\mu\text{mole}$,

24.47 = microliters of formaldehyde in one micromole at standard conditions.

Samples, Other Studies. Two blocks were required for each small "humid" and "dry" chamber. One remained intact and was used for density determinations. Foam samples for extractable and free formaldehyde determinations were cut from the other foam block and placed in wide mouth containers. Each sample was labeled and transported to the laboratory for subsequent analysis.

Free Formaldehyde. The small chambers containing the foam samples for measurement of formaldehyde, both free and extractable, density and shrinkage were opened twice weekly for less than 5 minutes each time. Each time the same foam sample was removed and about 1.5 cm cut from the same end. The main sample was then returned to the chamber, and the small piece was cut into two approximately 0.5 gm samples, one for determination of free formaldehyde and the other for extractable formaldehyde. Each was weighed on an analytical balance.

Free formaldehyde was determined by placing the sample in 50 mL distilled water at room temperature and blending in a mechanical blender for 10 seconds. The sample was immediately filtered by suction and the filtrate diluted to 100 mL with distilled water. Formaldehyde was then determined by the chromotropic acid method as previously described. This procedure proved to be quite satisfactory.

Extractable Formaldehyde. The sample taken for extractable formaldehyde was taken as described above under free formaldehyde, except that extractable formaldehyde was determined by compressing the small sample of foam into the bottom of an 8 ounce jar to which 50 mL of distilled water at room temperature was added. The jar was capped and shaken over night (18 hours) on a mechanical shaker. The solution was filtered by suction and the filtrate diluted to 100 mL with distilled water. Formaldehyde was determined by the chromotropic acid method. The value obtained for formaldehyde represents the combined total of free and extractable hydrolyzable formaldehyde in the foam sample.

Density. After initial foaming, the sample was allowed to "set" for approximately twelve hours. The foam was then cut into blocks (approximately 15 cm x 10 cm x 30 cm) as precisely as possible. The block's dimensions and mass were measured and recorded before placing it into the environmental chamber. A triple beam balance, accurate to within 0.03 g, was used for all mass determinations.

At regular intervals (two to three days) the block was removed from the chamber, weighed, and its dimensions recorded. From this data the density of the foam was calculated.

The method results in the determination of foam density to within $\pm 5\%$. This error results from the inaccuracy of measuring the foam block. In order to minimize this measurement error, the foam blocks in the high temperature chambers were shaved to remove rough edges.

PRODUCT D

Formaldehyde Emission: The results of the emission study for Product D are tabulated in Tables 1, 2, 3, and 4 and are graphically represented in Figures 5 and 6. The concentrations listed are in both micrograms of formaldehyde per cubic meter and in parts per million, ($\mu\text{L/L}$).

Samples were observed in the chambers for approximately 29 days and the concentrations of formaldehyde in the air were measured during that period.

The amounts of formaldehyde released from the foam samples ranged from 18 to 0.21 ppm in the high temperature-low humidity chamber, 2.05 to 0.51 ppm in the high temperature-high humidity chamber, 2.96 to 0.24 ppm in the low temperature-low humidity chamber and 3.10 to 0.22 ppm in the low temperature-high humidity chamber.

After 29 days, the samples from the low humidity and high humidity chambers were reversed, that is the sample from the high humidity chamber was placed in the low humidity chamber and the sample from the low humidity chamber was placed in the high humidity chamber. Subsequent emissions were measured and are listed at the bottoms of Tables 1, 2, 3, and 4. The emission of formaldehyde increased for the cold dry sample switched to humid conditions while the humid sample remained relatively stable when placed in the dry chamber.

Extractable Formaldehyde - High Temperature Condition:

Figures 7 and 8 are plots of $\mu\text{g}/\text{cm}^3$ vs age of foam. The results of extractable formaldehyde concentrations under high temperature conditions (33°C) are listed in Table 5 and summarized in Figure 7. The levels of extractable formaldehyde are similar for humid and dry conditions. There is a definite decrease in extractable formaldehyde as the foam ages.

Extractable Formaldehyde - Low Temperature Condition:

The low temperature was maintained at 10°C . In the dry chamber the relative humidity dropped from 43% to below 30% after ten days and remained below 30% for the length of the study, while the relative humidity in the humid chamber was fairly constant at 80%.

The extractable formaldehyde concentrations are listed in Table 6 and presented graphically in Figure 8. After a rapid decrease, concentrations of extractable formaldehyde level off and fluctuate around the mean value of about 65 ppm by volume.

A comparison of the mean extractable formaldehyde concentrations for the two different temperature conditions reveals that the extractable formaldehyde concentration in the foam maintained in the cold chamber is higher than that in the foam maintained in the warm chamber.

TABLE 1
EMISSION OF FORMALDEHYDE FROM PRODUCT D
IN A HIGH TEMPERATURE, LOW HUMIDITY ENVIRONMENT.^a

<u>Time</u> (days)	<u>Formaldehyde Concentration</u> ($\mu\text{g}/\text{m}^3$)	<u>Formaldehyde Concentration</u> ($\mu\text{L}/\text{L}$, ppm)
2.1	22,140	18.0
4.1	1,320	1.07
6.0	1,560	1.27
12.1	1,290	1.05
13.9	1,100	0.90
18.2	260	0.21
20.1	580	0.47
22.0	810	0.66
26.2	1,030	0.84
29.0	650	0.53
Change to High Humidity Chamber		
36	650	0.53

^a 33°C, 20% relative humidity

TABLE 2
EMISSION OF FORMALDEHYDE FROM PRODUCT D IN A HIGH TEMPERATURE,
HIGH HUMIDITY ENVIRONMENT.^a

<u>Time</u> (days)	<u>Formaldehyde Concentration</u> ($\mu\text{g}/\text{m}^3$)	<u>Formaldehyde Concentration</u> ($\mu\text{L}/\text{L}$, ppm)
2.1	2,520	2.05
4.1	1,920	1.56
6.0	970	0.79
12.1	1,180	0.96
13.9	1,530	1.24
18.2	1,020	0.83
20.1	630	0.51
22.0	950	0.77
26.2	1,330	1.08
29.0	730	0.59
Change to Low Humidity Chamber		
36	360	0.29
42	260	0.21
48	260	0.21

^a 33°C, 75 % relative humidity

TABLE 3
EMISSION OF FORMALDEHYDE FROM PRODUCT D
IN A LOW TEMPERATURE, HIGH HUMIDITY ENVIRONMENT.^a

<u>Time</u> (days)	<u>Formaldehyde Concentration</u> $\mu\text{g}/\text{m}^3$	<u>Formaldehyde Concentration</u> ($\mu\text{L}/\text{L}$, ppm)
2.0	1,220	0.99
4.0	3,810	3.10 ^b
5.9	1,750	1.42 ^b
12.1	1,570	1.28
14.0	340	0.28
18.1	900	0.73
20.0	310	0.25
21.9	270	0.22
26.1	320	0.26
28.9	710	0.58
Change to Low Humidity Chamber		
42	320	0.27
48	380	0.31

^a 10°C, 75% relative humidity

^b humidity ~ 55%

TABLE 4
EMISSION OF FORMALDEHYDE FROM PRODUCT D
IN A LOW TEMPERATURE, LOW HUMIDITY ENVIRONMENT.^a

<u>Time</u> (days)	<u>Formaldehyde Concentration</u> ($\mu\text{g}/\text{m}^3$)	<u>Formaldehyde Concentration</u> ($\mu\text{L}/\text{L}$, ppm)
2.0	2,180	1.77 ^b
4.0	1,270	1.03 ^b
5.9	3,640	2.96 ^b
12.1	1,650	1.34
14.0	450	0.37
18.1	290	0.24
20.0	480	0.39
21.9	540	0.44
26.1	1,080	0.88
28.9	700	0.57
Change to High Humidity Chamber		
36	900	0.73
42	980	0.80
48	1,400	1.14

^a 10°C, < 30% relative humidity

^b Humidity $\approx$ 40%

FIGURE 5
EMISSION OF FORMALDEHYDE ($\mu\text{L/L}$) AT HIGH TEMPERATURE
FOR PRODUCT D

FIGURE 6
EMISSION OF FORMALDEHYDE ($\mu\text{L/L}$) AT LOW TEMPERATURE
FOR PRODUCT D

FIGURE 7

EXTRACTABLE FORMALDEHYDE ($\mu\text{g}/\text{cm}^3$) AT HIGH
TEMPERATURE FOR PRODUCT D

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FIGURE 8
EXTRACTABLE FORMALDEHYDE ($\mu\text{g}/\text{cm}^3$) AT LOW TEMPERATURE
FOR PRODUCT D

TABLE 5
EXTRACTABLE FORMALDEHYDE FROM PRODUCT D
IN A HIGH TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration ($\mu\text{g/g}$ sample)		Formaldehyde Concentration ($\mu\text{g/cm}^3$ sample)	
	Dry (20%)	Humid (80%)	Dry (20%)	Humid (80%)
4	9900	5820	123	125
12	1240	7020	15.6	87.8
18	5210	7520	65.8	94.8
21	6420	4060	82.2	52.0
27	7600	7680	98.0	99.8
32	1570	2100	20.1	28.1

Foam reversed in chambers

	Humid	Dry	Humid	Dry
42	3970	4130	51.2	52.9
49	4140	5420	53.4	72.6

TABLE 6
EXTRACTABLE FORMALDEHYDE FROM PRODUCT D
IN A LOW TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration ($\mu\text{g/g}$ sample)		Formaldehyde Concentration ($\mu\text{g/cm}^3$ sample)	
	Dry (20%)	Humid (80%)	Dry (20%)	Humid (80%)
4	1180	5410	360	209
12	5400	2400	74.0	47.3
18	4990	5450	65.4	81.8
21	6450	6380	85.8	90.0
27	7310	5380	99.4	73.4
32	2240	950	29.8	13.2
Foam Reversed in Chambers				
Reverse Foam	Humid	Dry	Humid	Dry
42	5810	4530	79.6	62.1
49	4460	3080	63.3	41.9

Free Formaldehyde - High Temperature Condition:

The results of the free formaldehyde study are listed in Table 7 and graphically represented in Figure 9. It was observed that the initial free formaldehyde concentration was higher in the foam maintained in the hot humid conditions after the 16th day of this study. The free formaldehyde levels of the foam in the humid and dry chambers approached a constant value between $4.1 \mu\text{g}/\text{cm}^3$ and $2 \mu\text{g}/\text{cm}^3$.

Free Formaldehyde - Low Temperature Condition:

The concentrations of the free formaldehyde in the foam at 10°C in the dry and humid chambers are listed in Table 8 and represented graphically in Figure 10. The initial concentrations were above 50 ppm and decreased rapidly to a concentration between 5 and 10 ppm. It appears that in the dry environment the free formaldehyde concentration was less than in the humid environment after 12 days.

Comparison of Free Formaldehyde Concentration:

The order of the mean free formaldehyde concentrations is $\bar{x}$ cold humid > $\bar{x}$ cold dry > $\bar{x}$ hot humid > $\bar{x}$ hot dry. However, the order from the 12th day to the end of the study is $\bar{x}'$ cold humid > $\bar{x}'$ cold dry > $\bar{x}'$ hot humid.

Density - High Temperature Condition:

The mass, volume, and densities of the foam samples under high and low relative humidity conditions at 33°C are listed in Table 9 and density vs time is plotted in Figure 11. The density of the low humidity sample decreased rapidly in 4 days and subsequently became constant. The high humidity sample required 6 days to approach the same constant value.

Density - Low Temperature Condition:

The mass, volume and density of the foam samples under high and low relative humidities at 10°C are listed in Table 10 and the dynamic density plot is presented by Figure 12. At 10°C the loss of water was not as fast as the water loss in the 33°C chamber. In fact, the time required for a constant density was approximately 18 days for the humid chamber and 12 days for the dry chamber. In the cold chamber the rate of water loss from the foam samples is significantly less than the warm chambers.

Shrinkage - High Temperature Condition:

Shrinkage data for the foam sample in the high temperature chamber are listed in Table 11 as percent volume shrinkage and percent linear shrinkage and graphically are presented in Figure 13. Percent volume shrinkage was determined by measuring the decrease in length, width, and height of sample and percent linear shrinkage was determined from the length measurements.

It is observed that the foam in both chambers approaches a constant percent linear shrinkage. However, the foam in the dry hot chamber approached the constant value of 8% at a faster rate than did the foam in the humid hot chamber.

TABLE 7
FREE FORMALDEHYDE FOR PRODUCT D
IN A HIGH TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration ($\mu\text{g/g}$ sample)		Formaldehyde Concentration ($\mu\text{g/cm}^3$ sample)	
	Dry (20%)	Humid (80%)	Dry (20%)	Humid (80%)
4	519	1386	6.44	29.9
12	225	940	2.84	11.8
18	289	226	6.06	2.85
21	450	235	5.76	3.01
27	328	127	4.23	1.65
32	147	92.7	1.88	1.24
			$\bar{x} = 4.54$	$\bar{x} = 8.41$
			$S = 1.87$	$S = 11.23$
			$\bar{x}' = 4.15$	$\bar{x}' = 4.11$
			$S = 1.81$	$S = 4.37$
Foam Reversed in Chambers				
	Humid	Dry	Humid	Dry
43	364	250	4.70	3.20
49	537	259	6.93	3.47

$\bar{x}$ = mean concentration from 4th day to 32nd day

$\bar{x}'$ = mean concentration from 12th day to 32nd day

FIGURE 9

FREE FORMALDEHYDE ($\mu\text{g}/\text{cm}^3$) at HIGH TEMPERATURE
FOR PRODUCT D

TABLE 8
FREE FORMALDEHYDE FOR PRODUCT D IN A LOW TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration		Formaldehyde Concentration	
	Dry	Humid	Dry	Humid
4	1,820	2,160	55.5	60.3
12	368	747	5.04	14.7
18	507	509	6.64	7.64
21	683	680	9.08	9.59
27	283	964	3.84	13.40
32	172	690	2.29	9.59
			$\bar{x} = 13.73$	$\bar{x} = 19.20$
			$S = 20.6$	$S = 20.30$
			$\bar{x}' = 5.38$	$\bar{x}' = 10.98$
			$S = 2.61$	$S = 2.95$
Foam Reversed in Chambers				
	Humid	Dry	Humid	Dry
43	316	295	4.32	4.04
49	492	523	6.99	7.11

$\bar{x}$ = mean concentration from 4th day to 32nd day

$\bar{x}'$ = mean concentration from 12th day to 32nd day

FIGURE 10
FREE FORMALDEHYDE ($\mu\text{g}/\text{cm}^3$) AT LOW TEMPERATURE
FOR PRODUCT D

TABLE 9

MASS, VOLUME, AND DENSITY RELATIONSHIPS UNDER
HIGH TEMPERATURE CONDITIONS FOR PRODUCT D

Time (days)	Low Humidity Chamber (20%)			High Humidity Chamber (80%)		
	Mass (g)	Volume (cm ³)	Density (g/cm ³)	Mass (g)	Volume (cm ³)	Density (g/cm ³)
1	155.2	5034	0.0308	152.5	4891	0.0312
4	51.0	4119	0.0124	98.0	4541	0.0216
6	48.8	3920	0.0125	56.2	4310	0.0130
12	48.2	3835	0.0126	48.8	3900	0.0125
18	47.8	3844	0.0124	48.8	3862	0.0126
21	47.8	3728	0.0128	48.2	3755	0.0128
27	47.7	3693	0.0129	47.9	3697	0.0130
32	47.4	3705	0.0128	47.7	3555	0.0134

TABLE 10

MASS, VOLUME, AND DENSITY RELATIONSHIPS UNDER LOW TEMPERATURE CONDITIONS FOR PRODUCT D

Time (days)	Low Humidity Chamber			High Humidity Chamber		
	Mass (g)	Volume (cm ³)	Density (g/cm ³)	Mass (g)	Volume (cm ³)	Density (g/cm ³)
1	151.0	4,619	0.0327	94.75	2,853	0.0332
4	139.2	4,571	0.0305	78.1	2,801	0.0279
6	114.7	4,475	0.0256	72.4	2,746	0.0264
12	60.0	4,366	0.0137	57.0	2,639	0.0197
18	49.6	3,792	0.0131	39.9	2,661	0.0150
21	50.9	3,829	0.0133	36.0	2,561	0.0141
27	50.9	3,710	0.0136	35.8	2,574	0.0139
32	49.9	3,745	0.0133	35.5	2,553	0.0139

FIGURE 11

FOAM DENSITY AS A FUNCTION OF TIME AT HIGH TEMPERATURE
FOR PRODUCT D

FIGURE 12
FOAM DENSITY AS A FUNCTION OF TIME AT LOW TEMPERATURE
FOR PRODUCT D

TABLE 11
SHRINKAGE OF PRODUCT D UNDER
HIGH TEMPERATURE CONDITIONS

Time (days)	Shrinkage Low Humidity		Shrinkage High Humidity	
	(% Volume)	(% Linear)	(% Volume)	(% Linear)
1	0	0	0	0
4	18.2	5.9	7.2	2.2
6	22.1	7.2	11.9	4.3
12	23.8	7.5	20.3	7.4
18	23.4	7.8	21	7.7
21	25.9	7.8	23.2	8.0
27	26.6	8.1	24.4	7.7
32	26.4	7.8	27.3	8.3

Foam reversed in chambers				
	High Humidity		Low Humidity	
42	24.8	7.5	25.9	8.9
49	25.0	7.2	28.7	8.9

FIGURE 13

LINEAR SHRINKAGE AT HIGH TEMPERATURE CONDITIONS
FOR PRODUCT D

Shrinkage - Low Temperature Condition:

The results of the shrinkage study at low temperature conditions are listed in Table 12 and graphically are represented in Figure 14. At 10°C a significant difference in shrinkage between humid and dry conditions was observed. The shrinkage in the humid chamber approached a constant value of 3% whereas the shrinkage in the dry chamber approached a value of 6.5%.

Product D in Control Panel:

A control panel was foamed by the company representative for general observation and to insure that the foam used in this study was of high quality. The control panel was constructed to simulate a wall in a home and consisted of 6 spaces to be foamed with inside dimensions of 3 ½" x 14 ½" x 92". The outside dimensions were 4" x 96" x 96". One side of the panel consisted of 4 mil polyethylene covered with sheets of ½" x 4' x 8' sheet rock. The other side was covered with sheets of ½" fiber board. The panels were foamed through a 2" hole.

The 8' x 8' control panel was opened at the end of the study. One of the six small panels was not completely filled. The average horizontal shrinkage was 7.2% and the average vertical shrinkage was 6.5%.

Toward the bottom of panels, a green mold, identified as Penicillium notatum, was present on the foam insulation and on the two by four studs.

TABLE 12

SHRINKAGE OF PRODUCT D UNDER LOW TEMPERATURE CONDITIONS

Time (3 Days)	Shrinkage Low Humidity		Shrinkage High Humidity	
	(% Volume)	(% Linear)	(% Volume)	(% Linear)
1	0	0	0	0
4	0	0	1.8	1
6	3.1	0.9	3.8	1.4
12	5.5	2.2	7.5	2.4
18	17.9	6.8	6.7	2.4
21	17.1	6.5	10.2	2.7
27	19.7	6.5	9.8	3.1
32	29.9	6.8	10.5	3.1
Foam Reversed in Chambers				
	High Humidity		Low Humidity	
42	16.8	5.6	21.5	7.5
49	20.2	6.5	21.7	7.8

FIGURE 14

LINEAR SHRINKAGE AT LOW TEMPERATURE CONDITIONS
FOR PRODUCT D

PRODUCT E

Formaldehyde Emission: The results of the emission study are tabulated in Tables 13, 14, 15, and 16 and data for the first 24 days are graphically represented in Figures 15 and 16. The concentrations listed are in micrograms of formaldehyde per cubic meter and in parts per million.

Samples were monitored in the chambers for approximately 60 days and the concentrations of formaldehyde in the air were measured during that period.

Concentrations of formaldehyde released from the foam samples ranged from 24 to 0.48 ppm in the high temperature-low humidity chamber, 14.7 to 1.04 ppm in the high temperature-high humidity chamber, 6.80 to 0.45 ppm in the low temperature-high humidity chamber and 6.37 to 1.06 ppm in the low temperature-low humidity chamber.

After 55 days, the samples in the low temperature chamber were subjected to ambient temperatures (24-25°C). Subsequent emissions were measured and are listed at the bottom of Tables 15 and 16. The emission of formaldehyde increased with the increase in temperature.

Extractable Formaldehyde-High Temperature Condition:

The results of extractable formaldehyde concentration under high temperature conditions (33°C) are listed in Table 17 and the first 24 days are summarized in Figure 17. The level of extractable formaldehyde in the dry chamber is higher than the humid chamber. There is a definite decrease in extractable formaldehyde as the foam ages.

Extractable Formaldehyde-Low Temperature Condition:

The extractable formaldehyde concentrations of the foam samples exposed to 10°C are listed in Table 18 and data for the first 24 days are represented graphically in Figure 18. After a rapid decrease, concentrations of extractable leveled and fluctuated around a mean value of about 220 µg/cm³. The extractable formaldehyde concentration decreased significantly when the chamber temperature was increased to ambient conditions.

A comparison of the mean formaldehyde concentration for the two different temperature conditions reveals that the extractable formaldehyde concentration in the foam maintained in the cold chamber was higher than the extractable formaldehyde concentration in the foam maintained in the warm chamber.

Free Formaldehyde-High Temperature Condition:

The results of the free formaldehyde study at 33°C are listed in Table 19 and the first 24 days are graphically represented in Figure 19. It was observed that a high free formaldehyde concentration was maintained for at least 3 days in the humid chamber and for only one day in the dry chamber. However, it appears that a constant free formaldehyde level was approached more rapidly in the humid chambers.

TABLE 13
EMISSION OF FORMALDEHYDE FROM PRODUCT E IN A HIGH TEMPERATURE,
LOW HUMIDITY ENVIRONMENT.^a

Time (days)	Formaldehyde Concentration ($\mu\text{g}/\text{m}^3$) ^b	Formaldehyde Concentration ($\mu\text{L}/\text{L}$, ppm) ^c
1	30,480	24.7
2	24,900	20.2
3	14,100	11.5
4	4,430	3.60
7	10,300	8.38
8	4,900	3.98
9	1,690	1.37
10	1,700	1.38
11	1,750	1.42
14	1,810	1.47
16	1,450	1.18
18	1,430	1.16
21	1,300	1.06
24	ND	ND
43	1,860	1.51
46	1,700	1.38
56	1,410	1.15
60	1,830	1.49
64	4,070	3.31
81	1,030	0.84

^a 33°C, 20% Relative Humidity

^b $\mu\text{g}/\text{m}^3$: μg of formaldehyde per cubic meter of air

^c (ppm). $\mu\text{L}/\text{L}$: parts per million microliters of formaldehyde per liter of air.

TABLE 14
EMISSION OF FORMALDEHYDE FROM PRODUCT E
IN A HIGH TEMPERATURE, HIGH HUMIDITY ENVIRONMENT.^a

Time (days)	Formaldehyde Concentration ($\mu\text{g}/\text{m}^3$)	Formaldehyde Concentration ($\mu\text{L}/\text{L}, \text{ppm}$)
1	18,080	14.7
2	9,630	7.83
3	5,570	4.53
4	5,830	4.74
7	6,420	5.22
8	4,720	3.84
9	6,350	5.16
10	4,820	3.92
11	2,850	2.32
14	2,560	2.08
16	2,610	2.12
18	2,950	2.40
21	2,730	2.22
24	2,920	2.37
43	1,600	1.30
46	1,650	1.34
56	1,380	1.12
60	1,570	1.28
64	1,720	1.40
81	1,280	1.04

^a 33°C, < 75% Relative Humidity.

TABLE 15
EMISSION OF FORMALDEHYDE FROM PRODUCT E IN A
LOW TEMPERATURE, HIGH HUMIDITY ENVIRONMENT.^a

Time (days)	Formaldehyde Concentration ($\mu\text{g}/\text{m}^3$)	Formaldehyde Concentration ($\mu\text{L}/\text{L}$, ppm)
1	2880	2.34
2	3280	2.67
3	2560	2.08
4	8360	6.80
7	4130	3.36
8	4420	3.59
9	1750	1.42
10	3300	2.68
11	2930	2.38
14	2640	2.15
16	3120	2.54
18	3600	2.93
21	1050	0.85
24	550	0.45
43	890	0.72
46	1250	1.02
Change to ambient conditions		
56		3.08
60		3.41
64		5.69

^a 10°C, 75% Relative Humidity

TABLE 16
EMISSION OF FORMALDEHYDE FROM PRODUCT E IN A
LOW TEMPERATURE, LOW HUMIDITY ENVIRONMENT.^a

Time (days)	Formaldehyde Concentration ($\mu\text{g}/\text{m}^3$)	Formaldehyde Concentration ($\mu\text{L}/\text{L}$, ppm)
1	7840	6.37
2	4920	4.00
3	5980	4.86
4	9040	7.35
7	6250	5.08
8	8980	7.30
9	1930	1.57
10	4230	3.44
11	2140	1.74
14	1700	1.38
16	1910	1.55
18	1460	1.19
21	1300	1.06
24	----	----
43	1560	1.27
46	2820	2.29
Change to ambient conditions		
56	2070	1.68
60	4620	3.76
64	6330	5.15

^a 10°C, <30% Relative Humidity

FIGURE 15

EMISSION OF FORMALDEHYDE ($\mu\text{L/L}$)
AT HIGH TEMPERATURE FOR
PRODUCT E

FIGURE 16

EMISSION OF FORMALDEHYDE ($\mu\text{L/L}$)
AT LOW TEMPERATURE FOR
PRODUCT E

TABLE 17
EXTRACTABLE FORMALDEHYDE FROM PRODUCT E IN A HIGH TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration ($\mu\text{g/g}$ sample)		Formaldehyde Concentration ($\mu\text{g/cm}^3$ sample)	
	dry(20%)	Humid(80%)	dry(20%)	Humid(80%)
1	26,100	12,900	673	498
2	11,700	11,900	192	334
3	15,400	19,100	248	359
7	10,900	5,740	177	85.5
8	10,400	9,940	169	151
10	14,300	8,550	227	131
15	13,400	6,610	218	99.8
17	12,100	5,650	195	87.6
21	12,500	4,960	198	72.9
24	11,900	6,480	188	95.9
45	47,700	10,960	749	16.0
57	10,600	5,670	170	83.4
59	12,000	5,450	207	79.0
66	11,400	4,130	181	59.9

TABLE 18
EXTRACTABLE FORMALDEHYDE FOR PRODUCT E IN A LOW TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration ($\mu\text{g/g}$ sample)		Formaldehyde Concentration ($\mu\text{g/g}$ sample)	
	Dry (45%)	Humid (80%)	Dry (45%)	Humid (80%)
1	22,300	18,200	970	766
2	17,300	13,200	716	529
3	15,100	13,400	607	508
7	20,680	11,500	531	421
8	21,800	12,800	532	445
10	20,200	14,000	351	445
15	15,000	12,900	246	357
17	14,300	13,400	233	335
21	11,800	8,990	204	209
24	13,400	10,500	227	233
45	10,500	8,420	188	162
Changed to Ambient Conditions				
57	9,900	10,300	157	173
59	8,900	9,160	142	147
66	9,600	7,260	151	107

FIGURE 18

TABLE 19
FREE FORMALDEHYDE FOR PRODUCT E IN A HIGH TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration ($\mu\text{g/g}$ sample)		Formaldehyde Concentration ($\mu\text{g/cm}^3$ sample)	
	Dry (20%)	Humid (80%)	Dry (20%)	Humid (80%)
1	20,400	6,750	526	261
2	3,560	11,000	58	309
3	-----		---	199
7	1,670	730	27	11
10	1,580	160	25	2
15	4,840	800	79	12
21	8,920	290	141	4
24	1,440	350	23	5
45	----	840	---	12
53	3,200	210	51	3
57	740	820	12	12
59	130	86	2	1

$\bar{x} = 94$ $s = 157$ $\bar{x} = 69$ $s = 115$

$\bar{x} = 51$ $s = 52$ $\bar{x} = 7$ $s = 5$

FIGURE 19

FREE FORMALDEHYDE ($\mu\text{g}/\text{cm}^3$) AT HIGH TEMPERATURE FOR PRODUCT E

Free Formaldehyde-Low Temperature Conditions:

The concentrations of the free formaldehyde in the foam at 10°C in the low and high relative humidity chambers are listed in Table 20 and data for the first 24 days are represented graphically in Figure 20. The initial concentrations were about 300 µg/cm³ and decreased to a constant level after 15 days. It appears that in the low relative humidity environment the free formaldehyde concentration was less than in the high relative humidity environment. The free formaldehyde concentration appeared to decrease slightly when the chamber temperature was increased to ambient conditions.

Comparison of Free Formaldehyde Concentration:

The order of the mean free formaldehyde concentrations is $\bar{x}$ cold humid > $\bar{x}$ cold dry > $\bar{x}$ hot dry > $\bar{x}$ hot humid. However, the order of the means from the 15th day to the end of the study is $\bar{x}$ cold humid > $\bar{x}$ hot dry > $\bar{x}$ cold dry > $\bar{x}$ hot humid.

Density - High Temperature Condition:

The mass, volume, and densities of the foam samples exposed to high and low relative humidity conditions at 33°C are listed in Table 21. Density vs the first 24 days is plotted in Figure 21. The density of the low humidity sample decreased rapidly for 3 days and subsequently became constant. The high humidity sample required 7 days to approach a constant value.

Density - Low Temperature Condition:

The mass, volume and density of the foam samples under high and low relative humidity conditions at 10°C are listed in Table 21 and the density plot for the first 24 days is represented in Figure 21. At 10°C (Figure 22, Table 22), the loss of water was not as fast as the water loss in the 33°C chamber. The time required to allow a constant density in the 10°C chamber was approximately 21 days in the high relative humidity and 10 days in the low relative humidity.

After the temperature in the cold chamber was allowed to approach ambient temperature (24 - 25°C) the density decreased by approximately 10%.

Shrinkage - High Temperature Condition:

Shrinkage data for the high temperature chamber are listed in Table 23 as percent volume shrinkage and percent linear shrinkage. Percent linear shrinkage vs time is graphically represented in Figure 23. Percent volume shrinkage was determined by measuring the decrease in the volume of the sample and percent linear shrinkage was determined from the length measurements.

It is observed that the foam in the low relative humidity chamber approaches a constant percent linear shrinkage of 6.4% and the foam in the high relative humidity chamber approaches a constant value of about 4%.

TABLE 20

FREE FORMALDEHYDE FOR PRODUCT E IN A LOW TEMPERATURE ENVIRONMENT

Time (days)	Formaldehyde Concentration ($\mu\text{g/g}$ sample)		Formaldehyde Concentration ($\mu\text{g/cm}^3$ sample)	
	Dry (40%)	Humid (80%)	Dry (45%)	Humid (80%)
1	5980	7730	260	328
2	8550	9530	358	382
3	8530	9460	334	359
7	10,300	6920	266	253
10	11,300	6910	197	220
15	1200	7170	20	179
21	1780	4370	31	101
24	1540	3900	28	87
45	2950	4440	53	85
53	----	4150	----	74
$\bar{x} = 172 \quad s = 140 \quad \bar{x} = 207 \quad s = 120$ $\bar{x}' = 33 \quad s = 14 \quad \bar{x}' = 105 \quad s = 42$				
Change to Ambient Condition				
57	1410	3310	22	56
59	2700	4240	43	68

FIGURE 20

FREE FORMALDEHYDE ($\mu\text{g}/\text{cm}^3$) AT LOW TEMPERATURE FOR PRODUCT E

TABLE 21

MASS, VOLUME, AND DENSITY RELATIONSHIPS UNDER HIGH TEMPERATURE CONDITIONS FOR PRODUCT E

Time (days)	Low Humidity Chamber			High Humidity Chamber		
	Mass (g)	Volume (cm ³)	Density (g/cm ³)	Mass (g)	Volume (cm ³)	Density (g/cm ³)
0.3	134.1	2970	.0452	129.5	2879	.0450
1	69.6	2696	.0258	109.7	2842	.0386
2	41.5	2528	.0164	76.7	2732	.0281
3	40.4	2512	.0161	51.1	2723	.0188
4	40.2	2479	.0162	43.7	2723	.0161
7	39.9	2462	.0162	38.9	2617	.0149
8	39.8	2462	.0162	40.3	2640	.0153
10	39.7	2494	.0159	40.6	2640	.0154
15	39.6	2432	.0163	40.1	2658	.0151
17	39.5	2453	.0161	41.7	2690	.0155
21	39.5	2494	.0158	38.1	2584	.0147
24	39.5	2492	.0158	38.5	2607	.0148
45	39.4	2524	.0156	39.3	2691	.0146
53	39.2	2472	.0159	38.5	2681	.0144
57	39.1	2440	.0160	38.4	2616	.0147
59	39.2	2462	.0159	38.5	2658	.0145
66	39.1	2462	.0159	37.6	2617	.0144

FIGURE 21

FOAM DENSITY AS A FUNCTION OF TIME
AT HIGH TEMPERATURE FOR PRODUCT E

TABLE 22

MASS, VOLUME, AND DENSITY RELATIONSHIPS UNDER LOW TEMPERATURE CONDITION FOR PRODUCT E

Time (days)	Low Humidity Chamber			High Humidity Chamber		
	Mass (g)	Volume (cm ³)	Density (g/cm ³)	Mass (g)	Volume (cm ³)	Density (g/cm ³)
.3	130	2784	0.0467	133.6	2987	0.0447
1	119.7	2753	0.0435	125.9	2989	0.0421
2	114.4	2766	0.0414	121.3	3023	0.0401
3	109.3	2721	0.0402	118.3	3014	0.0393
4	91.3	2672	0.0342	113.9	2953	0.0386
7	67.6	2618	0.0258	105.7	2886	0.0366
8	63.4	2597	0.0244	101.3	2923	0.0348
10	46.5	2672	0.0174	92.3	2899	0.0318
15	42.7	2606	0.0164	78.4	2830	0.0277
17	42.2	2597	0.0163	70.9	2830	0.0250
21	45.3	2615	0.0173	66.6	2866	0.0232
24	44.2	2615	0.0169	62.6	2830	0.0221
45	48.1	2681	0.0179	55.8	2909	0.0192
Changed to ambient conditions						
53	42.4	2650	0.0159	51.8	2909	0.0178
57	41.3	2606	0.0159	48.6	2885	0.0168
59	41.3	2584	0.0160	47.5	2943	0.0161
66	41.2	2619	0.0157	42.4	2886	0.0147

TABLE 23
SHRINKAGE OF PRODUCT E UNDER HIGH TEMPERATURE CONDITIONS

Time (days)	Shrinkage Low Humidity		Shrinkage High Humidity	
	(% Volume)	(% Linear)	(% Volume)	(% Linear)
1	7.0	3.0	1.3	1.7
2	12.8	4.7	5.1	2.7
3	13.4	5.7	5.4	3.1
4	14.5	5.7	5.4	3.1
7	15.1	6.4	9.1	4.4
8	15.1	6.4	8.3	3.7
10	14.0	6.4	8.3	3.7
15	16.2	6.7	7.7	3.7
17	15.4	6.7	6.6	3.4
21	14.0	6.4	10.2	4.4
24	14.1	6.0	9.5	4.4
45	13.0	6.0	6.5	3.7
53	14.8	6.4	6.9	3.7
57	15.9	6.4	9.1	4.1
59	15.1	6.4	7.7	3.7
66	15.1	6.4	9.1	4.4

FIGURE 23

LINEAR SHRINKAGE AT
HIGH TEMPERATURE CONDITIONS
FOR PRODUCT E

Shrinkage - Low Temperature Conditions:

The results of the shrinkage study at low temperature conditions are listed in Table 24 and graphically are represented in Figure 24. The percent linear shrinkage in the humid chamber fluctuates between 1.7 and 1% while the shrinkage in the low humidity chamber approaches a constant value of 2.0%.

Product E in Control Panel:

A control panel was foamed by the foam representative, for general observations and to insure that the foam used in this study was of high quality. The control panel was constructed to simulate a wall in a home and consisted of 6 spaces to be foamed with inside dimensions of $3\frac{1}{2}$ " x $14\frac{1}{2}$ " x 92". The outside dimensions were 4" x 96" x 96". One side of the panel consisted of 4 mil polyethylene covered with two sheets of $\frac{1}{2}$ " sheet rock and the other side was covered with sheets of $\frac{1}{4}$ " fiber board. The panels were foamed through a 2" hole.

The 8 x 8' control panel was opened at the end of the study. The average horizontal shrinkage was less than .1% and the average vertical shrinkage was less than 0.2%.

TABLE 24
SHRINKAGE OF PRODUCT E AT LOW TEMPERATURE CONDITIONS

Time (days)	Shrinkage Low Humidity		Shrinkage High Humidity	
	(% Volume)	(% Linear)	(% Volume)	(% Linear)
1	1.1	0.4	-0.08	.3
2	.7	0.7	-1.2	0
3	2.3	1.7	-0.09	.3
4	4.0	2.4	1.1	.3
7	6.0	2.4	3.4	1.0
8	6.7	1.7	2.1	1.4
10	4.0	2.0	2.9	1.4
15	6.4	2.0	5.2	1.7
17	6.7	2.4	5.2	1.7
21	6.1	1.7	4.1	1.7
24	6.1	1.7	5.2	1.7
45	3.7	1.3	2.6	1.0
Changed to ambient conditions				
53	4.8	1.7	2.6	1.0
57	6.4	2.0	3.4	1.0
59	6.4	2.0	1.5	.7
66	5.9	2.0	3.4	1.0

FIGURE 24
LINEAR SHRINKAGE AT
LOW TEMPERATURE CONDITIONS (10°C)
FOR PRODUCT E

SUMMARY AND CONCLUSIONS

The mechanism of formaldehyde release from foamed urea-formaldehyde polymer is very complex and off-gassing formaldehyde may arise from a variety of sources (2). Sources of formaldehyde emission include the free unreacted formaldehyde in the resin, formaldehyde dissolved in surface moisture or water of condensation and formaldehyde resulting from hydrolysis of methylol and methylene urea linkages.

In general, in this work and work reported earlier, temperature and humidity have a marked effect on the magnitude of formaldehyde emission.

All urea-formaldehyde resin mixtures used in the production of foam insulation contain a certain amount of unreacted formaldehyde. Some of this unreacted formaldehyde reacts when mixed with the foaming agent/catalyst mixture while some of it remains uncombined and is incorporated into the foam. From the results reported here free formaldehyde in the foam samples tested was shown to be present in appreciable amounts.

Another source of formaldehyde is the combined formaldehyde that manifests itself as a result of chemical reaction. The final structure of the polymerized resin contains terminal methylol groups ($-\text{CH}_2\text{OH}$), methylene ($-\text{NHCH}_2\text{NH}-$) and (bis)methylene ether linkages ($-\text{CH}_2-\text{O}-\text{CH}_2-$). Formaldehyde can result from the hydrolysis of the terminal methylol groups and by further condensation of the bismethylene linkage to a methylene linkage with subsequent release of formaldehyde. The ester linkage could also hydrolyze yielding two methylol groups. In addition, a long term formaldehyde source, paraformaldehyde, can be formed from the polymerization of formaldehyde vapor.

The initial differences in emission between the high and low humidity conditions may be explained by the differences in humidity. Formaldehyde emission could be lower due to the solubility of formaldehyde in water. Levels of formaldehyde emission remain higher over time for the high humidity condition. Also, the area under the curve or total formaldehyde emitted was greater than the low humidity environment which is consistent with slow polymer hydrolysis. The lower humidity would explain the lower levels because less moisture in the foam reduces the degree to which hydrolysis occurs. Additional evidence explaining the emission due to hydrolysis was found after the sample Product D in the low humidity chamber was placed in the high humidity environment where increased formaldehyde emission levels were observed.

Emissions of formaldehyde from the low temperature chambers were similar to that of the high temperature condition. The difference between the emission from the low humidity and high humidity chambers

was not as pronounced as in the high temperature situation. Evaporation (water and HCHO), attainment of equilibrium and hydrolysis would occur at a slower rate. Since the temperature was low, differences in emission due to hydrolysis would not be seen until the free formaldehyde had disappeared. Both types of emission from free and hydrolyzed formaldehyde would be indistinguishable if the emission is prolonged due to lower temperatures.

The patterns of emission of formaldehyde for both low and high temperature conditions are similar for all products tested (A, B, C, D, and E). The magnitude of this difference is directly influenced by humidity levels. This recognition is suggested by the observation of the alteration in emission values when the foam sample from the dry chamber is placed in the humid chamber.

Extractable formaldehyde values are intrinsically related to changes in density of the foam polymer and are therefore obviously related to the presence of water. The fluctuation in levels of extractable formaldehyde from product to product is probably heavily influenced by the presence of proprietary additives in the samples. The values for extractable formaldehyde are consistently lower at high temperature than at lower temperature. These values are correlated with the slow decrease in density which reflects the degree of water retention by the sample at low temperature. These observations strongly support the need for a better understanding of the role of water and water vapor in relationship to formaldehyde in UF foam insulation.

The free formaldehyde values for the products observed fluctuate rather widely; however, the behavior of all the samples is consistent with regard to rather large amounts being released for a period of 10-12 days after which the products appear to stabilize at a lower value for free formaldehyde. In essence all plots of free formaldehyde are similar in shape to the plots for emission of formaldehyde. It appears from observations made of the products during testing that additives i.e., phenolic derivatives, influence the formation of free formaldehyde and may have a bearing on the magnitude of extractable formaldehyde that may be present.

Recently there has been an awakening as to the possible role of methylol, particularly in regard to free formaldehyde in the resin and eventual out-gassing from foam formed from it. Methylol groups serve a necessary function as a basis for crosslinking in the formation of the polymer. Undoubtedly some of the methylol undergoes hydrolysis to form formaldehyde. In seeking a source for free formaldehyde in fresh foam, one must ask the following question: "Does free formaldehyde in freshly formed foam have free formaldehyde in the resin as its only precursor?" The answer to this question is "probably not". Based upon some of the early research data from the Iowa group on behavior of formaldehyde emission, it was attractive to speculate that free formaldehyde in resin was the principal precursor of free formaldehyde in foam

that provided for an initial out-gassing lasting from 4 to 8 days while decaying rapidly to only a few parts per million dependent upon temperature and humidity. Recent findings provide for the following observations. The release of formaldehyde from U-F foam is intimately related to the water content and the removal of that water through the drying process. This earlier assumption is not entirely without support since Neusser and Zentner (65), after reviewing several studies on urea-formaldehyde resins, expressed the opinion that formaldehyde release is proportional to the free formaldehyde content of the resin and that changes in temperature and humidity influenced the release of formaldehyde.

There is no doubt that the release of formaldehyde from U-F foam is intimately related to the water content and the removal of that water through the curing process. Based upon present information one may speculate on the sequence of events that may take place during the drying process. Freshly made foam contains a high percentage of closed cell structures and is approximately 70 percent water. Curing foam at ambient conditions of temperature and humidity results in a product with largely open cell structure. Rupture of the polymer membrane most probably results from pressure exerted on the membrane by water vapor and other gases trapped within the closed cell structure, by shrinkage resulting from both cell collapse and cross polymerization of the resin-formaldehyde polymer, hydrolysis of the membrane or possibly by thermal softening of the polymer. The release of formaldehyde is influenced by these phenomena and is associated with this loss of water. Research has shown that there is a more rapid release of formaldehyde at high temperature and low humidity. As the temperature is lowered and the humidity is increased there is less out-gassing of formaldehyde which is accompanied by a corresponding increase in extractable formaldehyde. Extractable formaldehyde is defined as being a combination of free formaldehyde and formaldehyde resulting from the hydrolysis of methylol and methylene urea groups with perhaps some methylene ether linkages being involved. While there is no data to support the following assumption, it would appear that a formaldehyde-water-temperature gradient exists with respect to cell rupture, extractable formaldehyde and formaldehyde out-gassing. Recent studies at Iowa support this idea in that findings on studies of one foam product indicate that shrinkage is considerably less if the foam is cured at low temperature and moderately elevated humidity. Concurrently, formaldehyde out-gassing is lowered while extractable formaldehyde is increased. The gradient alluded to above is probably heavily influenced by pH and the type of building components in which the foam is placed.

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