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**PROBLEMS ASSOCIATED WITH THE USE OF
UREA-FORMALDEHYDE FOAM FOR
RESIDENTIAL INSULATION**

**Part I: The Effects of Temperature and Humidity on
Formaldehyde Release from Urea-Formaldehyde
Foam Insulation**

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PART OF
THE NATIONAL PROGRAM
FOR
BUILDING THERMAL ENVELOPE SYSTEMS
AND INSULATING MATERIALS

OAK RIDGE NATIONAL LABORATORY
OPERATED BY UNION CARBIDE CORPORATION • FOR THE DEPARTMENT OF ENERGY

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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.

The first annual National Program Plan developed by a team of DOE, NBS, ORNL, and LBL staff was published in January 1979 as DOE/CS-0059, available from the National Technical Information Service (NTIS), U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161. The price is \$6.50.

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Purpose: This study is concerned primarily with those properties related to formaldehyde and its application as an ingredient in urea-formaldehyde resins. In particular the effects of temperature and humidity on urea-formaldehyde foam are discussed.

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. These foams are used primarily as thermal insulation materials.

Although urea-formaldehyde based foams have been commercially available in the United States since the 1950's, they have not been widely used. However, with recent emphasis on energy conservation, its use as an insulation material has increased. These foams are particularly useful as a retrofit insulation in existing buildings.

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 (2). This reactivity is reflected in the fact that formaldehyde is not found, generally, in simple monomeric form, thus complicating the chemistry of formaldehyde.

Walker (3) 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 (4). 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 (5). 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 (8). 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 (9).

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 (6). Because of these effects OSHA has set the threshold limit value (TLV) at 3 parts per million of formaldehyde vapor by volume in air (7).

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 (10). 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 (11). 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 (12).

The structure of the resin beyond the first stages of condensation is not known in great detail (13). 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 (14) 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 (15).

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 (16). 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 (17). Further descriptions of the various spectral characteristics of this polymer can be found in Walker (18) and Urbanski (19).

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 (20, 21, 22).

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

FIGURE 1
TYPES OF COMBINED FORMALDEHYDE

Methylol End Group

Methylene Bridge

Dimethylene Ether Bridge

FIGURE 2
POSSIBLE RESIN STRUCTURE

(foaming agent) which contains an acid catalyst or hardening agent and air. The resin and surfactant-catalyst are both water solutions. Naphthalene sulfonic acid (23), and dodecyl benzene sulfonic acid (24) have been used as foaming agents and phosphoric (25), oxalic (26), citric, malic, and tartaric acids (27) have been used as the acid catalyst.

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 (28).

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 (29).

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 (30). 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 (31).

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 Yagoda (33) 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 (34, 35). 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 (36). Boyd and Bambach (37) were in agreement with Jahoda'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 (38). Some recent methods of electrochemical detection of formaldehyde have used alternating current polarography (39), twin cell sweep voltammetry (40), argentimetric potentiometric titration using an iodide ion sensitive electrode (41), and short circuit argentimetric/amperometric titration using a rotating platinum micro-electrode (42). 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 (43) 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 (44, 45).

The determination of trace concentrations of formaldehyde in air using Schiff's reagent was adapted by Rayner and Jephcott (46). 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 (47) in 1965. The reagent, a mixture of dichlorosulfitomercurate (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 (48). 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 (49). Determination of formaldehyde in air using chromotropic acid was developed by MacDonald (50) in the form in which it is commonly used today (51). Altshuller, Miller, and Sleva (52) proposed a modification of the method which was 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. Cares (53) 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., (54) 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 (55) 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., (55) 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 660 nm. 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 (57) 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 (58, 59). Spectrofluorometric determination of formaldehyde with J-acid follows Beer's Law in the range of 0.001 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 (60).

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

FIGURE 3
GENERAL EXPERIMENTAL SET-UP

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.

Relative humidity was varied within each small chamber. Air from the compressor flowed 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 DESIGN

PROCEDURES

Formaldehyde Emissions. Foam samples used for the emission study were foamed and allowed to cure for twelve 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% (63). Sampling was performed for 20 to 30 minutes with calibration of pumps before and after a day of sampling. After 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 and was 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 ($\epsilon = 1.57 \times 10^4$). 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 a ten-thousandfold excess without interference (61). Phenols result in a 10-20% negative interference (62). 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 (ref. 22). 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 dilute to one liter). The liberated sulfite was then titrated with 0.01N iodine using a microburet to a faint blue end-point.

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 the 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:

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

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 foam 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.

Extractable Formaldehyde. Approximately 0.5g of foam, weighed on an analytical balance, was required for extractable formaldehyde determination. Samples were extracted with 50 ml distilled deionized water by placing the sample containers in a rotorack shaker for fourteen hours. This time period was chosen for convenience. The samples were then filtered, rinsed with two 50 ml portions of distilled deionized water, and the filtrate diluted to 250.0 ml. All samples were determined in duplicate.

The aqueous solutions containing extractable formaldehyde were then diluted to an appropriate concentration (0.1 to 2 ppm) and determined colorimetrically by NIOSH method number P&CAM125.

To determine the reproducibility of the procedure, ten samples were cut from the foam block, extracted as described previously, and determined. Samples were cut from the exterior of the foam block as for regular samples. The results are shown in Table 1. The poor reproducibility originated from the following possible sources of error:

1. Nonhomogenous foam.
2. Inconsistent sampling of the foam.
3. Experimental errors such as weighing, dilutions, temperature of extraction, and time of extraction.

A very large dilution was required to bring formaldehyde concentrations to the working range of the method. Repetitive determinations of the filtrate after extraction provided information on dilution reproducibility. Results within $\pm 1\%$ were obtained which represented errors from dilutions and the chromotropic acid determination itself. Thus, it was concluded that the majority of error originated from the sample taken or the extraction procedure. To differentiate between these sources of error, another reproducibility study was performed. Foam samples were obtained using a modified sampling method. The exterior sides of the foam block were cut away and the remaining interior portion was separated into five samples. These samples were analysed for extractable formaldehyde using normal procedures. The conditions and results are listed in Table 2.

The reduction in error led to the conclusion that most of the problems with respect to reproducibility came from inhomogenous sampling of the foam. It was assumed that the foam block was essentially homogenous. The error of $\pm 4\%$ in this study was mainly attributed to extraction conditions even though the samples were extracted for the same time in

Table 1. Reproducibility of Extractable
Formaldehyde Method - Normal
Sampling Procedure

Sample	Mass (g)	CH ₂ O mg/g sample
1	.4019	13.2
2	.4887	17.9
3	.4392	16.7
4	.6206	22.5
5	.5329	20.5
6	.6205	12.5
7	.5758	14.2
8	.6847	24.5
9	.3450	17.2
10	.7239	19.5

Average CH₂O : 17.9

Average Deviation: ±3

% Error: ±17%

Table 2. Reproducibility of Extractable
Formaldehyde Method - Modified Sampling
Procedure

Sample	Mass (g)	CH ₂ O mg/g sample
1	.5286	24.4
2	.4956	25.1
3	.5257	23.3
4	.5632	21.4
5	.7089	23.7

Average CH₂O: 23.6

Average Deviation: ±1

% Error ±4%

the same shaker.

A study of the extraction procedure provided information on the recovery of formaldehyde as a function of time. "Identical" samples were subjected to different extraction times and analyzed for extractable formaldehyde as previously described. The results are illustrated in Figure 5. It can be seen that an extraction time of 14 hours (as used in the described procedure) represents a practical recovery mechanism for formaldehyde. Beyond 14 hours, levels increase very gradually.

The effect of extraction temperature on results was also evident from Figure 5. As the rotorack shaker heated up from continuous use, samples also heated up. Depending on the number of samples and their position on the shaker, temperature varied as much as $\pm 3^{\circ}\text{C}$. This obviously affected the results and led to deviations from the general curve. In particular, note the increase in recovery between 48 and 72 hours resulting from a 2°C increase in temperature. At constant temperature a small, linear increase in recovery was expected beyond approximately 10 hours of extraction due to hydrolysis of the foam.

Free Formaldehyde. Three foam samples (3-4 g) were weighed and placed in 400 ml beakers. One hundred milliliters of formaldehyde-free distilled water and 100 ml reagent grade methanol were added. The solution was mixed and allowed to sit for two hours.

Five drops of thymolphthalein indicator were added and sodium hydroxide (0.1 N) was added dropwise to a blue endpoint. The solution was backtitrated with sulfuric acid (0.1 N) until the solution was clear.

Ten grams of cracked ice prepared from distilled water was added to one of the beakers and mixed. To this, 50 ml of 1 M sodium sulfite solution was added, and titrated at once with standard sulfuric acid (0.1 N) to a colorless endpoint. The volume of sulfuric acid required was recorded. The procedure beginning with the addition of ice was then repeated for the remaining samples.

A blank was determined by adding ten grams of ice and sodium sulfite solution to the methanol-water mixture and subsequently titrating the solution. The volume of standard sulfuric acid required was recorded. Results were reported as the percentage of free aldehydes in the sample as formaldehyde.

FIGURE 5

RECOVERY OF FORMALDEHYDE AS A FUNCTION OF EXTRACTION TIME

The sodium sulfite procedure is the Canadian standard test method for free formaldehyde. It was found that the method was not well suited for the low levels of free formaldehyde found in the foam samples. The gradual slope in the titration curve resulted in very poor endpoint detection. Reagent grade methanol was employed in the procedure containing less than .001% aldehydes. Blank titrations obtained still approached sample titration values.

Because of these problems, the method was modified to an automatic titration system. Titrant was delivered via syringe with an associated drive mechanism. The titration curve was recorded by following the pH with respect to titration volume. Reproducibility was still poor due to high blank values. Results could be obtained within an order of magnitude.

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.

RESULTS AND DISCUSSION

General. Emission of formaldehyde from urea-formaldehyde foams was measured using four different environmental conditions. A high temperature environment, 33°C , coupled with high and low humidity, was used. The other environment was maintained at low temperature, 7°C , coupled with high and low humidity. Samples were taken simultaneously from the high and low humidity chambers of the same temperature to compare the effects of humidity on the emission. The effect of high and low temperature was also examined.

Samples were foamed at room temperature into a wood container with dimensions of approximately 90 cm by 40 cm by 8.9 cm. Before filling the sample container, simulated wall panels were foamed to assure the quality of the foam with respect to component ratios and density. This also resulted in a more homogeneous sample. Component ratios (resin mixture to foaming agent-catalyst mixture) and density of foam samples that resulted were within the recommended values; these being 10 to 7.5 (resin to detergent) for the component ratio and about 0.04 gm/cm^3 for the wet density (64). The initial foam contained about 75% by weight of water so that changes in density were presumed to have resulted from loss of water. The suggested range of dry density values is 0.01 gm/cm^3 . The initial densities of the foam samples used for the study were 0.032 gm/cm^3 for both low and high humidity chambers in the high temperature chamber and 0.044 gm/cm^3 for the low and high humidity chambers, respectively, for the low temperature chambers (65). These densities were measured twelve hours after foaming to allow for partial curing and ease of manipulation. After twelve hours, the sample container was dismantled leaving the rectangular volume of foam intact. The sample then was sliced into six equal volumes. The samples also had approximately equal exposed surface areas. The foam samples were placed in the respective chambers and the aforementioned parameters were measured as a function of time, temperature and humidity.

Product A

Formaldehyde Emission. Results of the emission study are tabulated in Tables 3, 4, 5, and 6, and in Figures 6 and 7. The concentrations listed are in micrograms per cubic meter and parts per million, by volume

Table 3. Emission of Formaldehyde From the High Temperature*, Low Humidity** Environment

Time (days)	$\frac{[\text{HCHO}] \times 10^3}{***(\mu\text{g}/\text{m}^3 \times 10^3)}$	$\frac{[\text{HCHO}]}{****(\text{ppm}, \mu\text{l}/\text{l})}$
1.3	16.80	13.69
2.5	9.83	8.01
6.2	0.73	0.60
9.4	0.27	0.23
10.1	0.25	0.20
13.3	0.21	0.17
15.5	0.19	0.15
19.4	0.23	0.18
20.1	0.32	0.26
22.2	0.49	0.40
24.0	0.66	0.54
27.2	1.22	0.99
32.2	1.50	1.22
34.2	1.19	0.97
37.2	1.93	1.57
39.4	1.83	1.49
41.9	1.49	1.22
43.3	1.61	1.31

*330 C.

**<20% relative humidity.

*** $\mu\text{g}/\text{m}^3$: micrograms per cubic meter.

****ppm, $\mu\text{l}/\text{l}$: part per million by volume, microliters per liter.

Table 4. Emission of Formaldehyde From the High Temperature*, High Humidity** Environment

Time (days)	$\frac{[\text{HCHO}] \times 10^3}{(\mu\text{g}/\text{m}^3 \times 10^3)}$	$\frac{[\text{HCHO}]}{(\text{ppm}, \mu\text{l}/\text{l})}$
1.3	8.93	7.27
2.5	7.32	5.96
6.2	4.88	3.98
9.4	2.05	1.67
10.1	1.61	1.31
13.3	2.76	2.25
15.5	1.61	1.32
19.4	2.84	2.31
20.1	2.72	2.22
22.2	3.27	2.67
24.0	2.10	1.71
27.2	3.05	2.48
32.2	2.11	1.72
34.2	2.10	1.71
37.2	3.13	2.55
39.4	2.02	1.65
41.9	1.20	0.98
43.3	1.15	0.94

*33° C.

**>80% R.H.

Table 5. Emission of Formaldehyde From the Low Temperature*, Low Humidity Environment

Time (days)	$[\text{HCHO}] \times 10^3$ ($\mu\text{g}/\text{m}^3 \times 10^3$)	$[\text{HCHO}]$ (ppm, $\mu\text{l}/\text{l}$)	Conditions (R.H. - relative humidity)
1.1	7.69	6.27	7°C, 75% R.H.
3.1	18.16	14.80	7°C, 70% R.H.
5.4	13.62	11.10	7°C, 70% R.H.
8.0	12.98	10.57	7°C, 75% R.H.
9.4	9.54	7.77	7°C, 75% R.H.
13.8	6.64	5.41	7.5°C, 65% R.H.
16.3	7.03	5.73	7°C, 63% R.H.
20.2	6.86	5.69	7°C, 53% R.H.
23.4	1.21	0.98	7°C, 50% R.H.
26.3	3.45	2.81	6.5°C, 52% R.H.
29.2	5.80	4.73	6.6°C, 52% R.H.

*7° C.

Table 6. Emission of Formaldehyde From the Low Temperature*, High Humidity Environment

Time (days)	$[\text{HCHO}] \times 10^3$ ($\mu\text{g}/\text{m}^3 \times 10^3$)	$[\text{HCHO}]$ (ppm, $\mu\text{l}/\text{l}$)	Conditions (R.H. - relative humidity)
1.1	6.83	5.56	7°C, 91% R.H.
3.1	16.88	13.75	7°C, 91% R.H.
5.4	10.67	8.69	7°C, 91% R.H.
8.0	7.71	6.28	7°C, 94% R.H.
9.4	5.98	4.88	7°C, 93% R.H.
13.8	5.05	4.11	7.5°C, 85% R.H.
16.3	5.29	4.31	7°C, 86% R.H.
20.2	4.19	3.41	7°C, 91% R.H.
23.4	5.70	4.65	7°C, 91% R.H.
26.3	4.31	3.51	6.5°C, 91% R.H.
29.2	5.63	4.59	6.6°C, 92% R.H.

*7°C.

FIGURE 6
EMISSION OF FORMALDEHYDE VERSUS TIME FOR
PRODUCT A AT HIGH TEMPERATURE
(33°)

Figure 7

EMISSION OF FORMALDEHYDE VERSUS TIME
FOR PRODUCT A AT LOW TEMPERATURE (7°C)

(microliter per liter). The humidity of the dry chambers varied during the period of examination due to the large amount of water in the foam samples.

Concentrations of formaldehyde released from the foam samples ranged from 14 to 0.15 parts per million for the hot, dry chamber, 7 to 0.9 parts per million for the hot, humid chamber, 15 to 3 parts per million for the cold, dry chamber and 14 to 3 parts per million for the cold, humid chamber. Solutions of known concentration used for quality assurance resulted in precisions of 10 to 15%. The concentrations reported in Tables 3 and 4 would then have an error of about $\pm 20\%$ assuming the pumps used to sample the air maintained a flow rate to $\pm 5\%$.

The high temperature, low and high humidity samples were in the chambers for 43.3 days and the concentration of formaldehyde in the air was measured during that period. The low temperature, low and high humidity sample run lasted 29.2 days. Although concentrations of formaldehyde are reported for the high temperature chamber over a 43 day period, values after 30 days are suspect because a breakdown in the temperature control unit occurred at this time.

After 43 days, the samples from the high and low humidity chambers (high temperature) were reversed. The sample from the high humidity chamber was placed in the low humidity environment and the low humidity sample was placed in the high humidity environment. The subsequent emissions were measured and are listed in Table 7. It can be observed that the emission of formaldehyde increased for the dry sample switched to humid conditions while a decrease was observed for the humid sample switched to the low humidity environment.

Extractable Formaldehyde -- High Temperature Condition. The results of extractable formaldehyde under high temperature conditions are summarized in Figures 8 and 9, and illustrate is the difference in formaldehyde content at high and low humidity conditions at high temperature. The difference between results reported in mg/cm^3 sample versus mg/g sample can be seen by comparing Figures 8 and 9. During the first few days after foaming, most of the weight of the samples was due to water. Hence, extractable formaldehyde results reported in mg/g sample are somewhat misleading. Table 8 presents a summary of mass and volume changes for the foam as a function of time.

Table 7. Emission of Formaldehyde From Samples Reversed in Humidity Conditions

Sample Age (days)	Time after change of conditions (days)	$\frac{[\text{HCHO}] \times 10^3}{(\mu\text{g}/\text{m}^3 \times 10^3)}$	$\frac{[\text{HCHO}]}{(\text{ppm}, \mu\text{l}/\text{l})}$
Sample previously in high humidity switched to low humidity environment. Last measured concentration was 0.94 ppm before the switch.			
47.7	1.7	0.43	0.35
50.2	4.2	0.48	0.39
53.1	7.1	0.25	0.21
56.2	10.2	0.09	0.08
59.2	13.2	0.29	0.23
62.0	16.0	0.46	0.38
Sample previously in low humidity switched to high humidity environment. Last measured concentration before switch was 1.31 ppm.			
47.7	1.7	2.88	2.35
50.2	4.2	3.23	2.63
53.1	7.1	2.93	2.39
56.2	10.2	3.67	2.99
59.2	13.2	3.74	3.05
62.0	16.0	4.12	3.36

FIGURE 8

EXTRACTABLE FORMALDEHYDE OF PRODUCT A
AT HIGH TEMPERATURE (33°C)
MG/GM

FIGURE 9

EXTRACTABLE FORMALDEHYDE OF PRODUCT A
AT HIGH TEMPERATURE (33°)
MG/CM³

Table 8. Mass and Volume Changes Under High Temperature Conditions As a Function of Time

Days	DRY CHAMBER (20%)		HUMID CHAMBER (80%)	
	Mass (g)	Volume (cm ³)	Mass (g)	Volume (cm ³)
0.46	121.35	3849	122.10	3855
1.3	89.10	3569	106.40	3599
3.3 ^a	36.80	3005	81.60	3132
6.3	34.90	2892	72.60	2930
8.4	34.64	2881	69.90	2897
10.0	34.60	2881	65.80	2886
13.3	34.81	2845	61.18	2886
15.0	34.80	2881	57.45	2875
17.0	34.69	2835	57.20	2843
19.0	34.88	2835	57.20	2843
22.0	34.87	2845	59.23	2854
24.2	34.87	2845	59.20	2819
27.3	35.04	2845	59.75	2854

^aSamples were solid enough at this point to be cut exactly square for better accuracy in density determinations.

A definite difference in extractable formaldehyde was observed between high and low humidity samples. After large initial decreases, levels of extractable formaldehyde seem to decrease at the same rate. Results show that decreases were greater under humid conditions, considering both samples initially were identical. The fact that initial levels were identical was not shown in Figures 8 and 9, presumably due to the rapid decreases during the first day.

After the foam samples had been subjected to the high temperature condition for approximately 50 days, the high and low humidity samples were reversed. The purpose of exchanging the samples was to determine if levels of extractable formaldehyde would follow a characteristic pattern. The sample which was originally in the humid chamber exhibited increased extractable formaldehyde levels when subjected to low humidity conditions. This is attributed to the associated loss in weight, and/or volume.

Levels for the dry sample placed in the humid chamber rapidly decreased then remained fairly constant. These results are attributed to mass and volume increases.

Extractable Formaldehyde -- Low Temperature Condition. The low temperature chamber was maintained at 7°C. In the dry chamber the relative humidity decreased very slowly. During the 30 day study, the relative humidity dropped from 76% to ~50% at a constant rate. The relative humidity of the high humidity chamber was fairly constant at ~90%.

The extractable formaldehyde results for the low temperature condition are summarized in Figures 10 and 11. After a rapid decrease, concentrations of extractable formaldehyde leveled. The increase in extractable formaldehyde (mg/g sample) observed after 15 days may have been due to the decrease in relative humidity from 75% to 63% between 13 and 15 days. There was little variation between high and low relative humidity results in mg/cm³ sample at low temperature beyond 20 days.

Free Formaldehyde. Determinations of free formaldehyde were performed on low temperature samples. Results for these samples ranged from 0.6% to 0.5% over the first 20 days. No correlation with respect to relative humidity was possible. Concentrations of free formaldehyde did fall within the 0.6% limit recommended by the U.S. Department of

FIGURE 10

EXTRACTABLE FORMALDEHYDE OF PRODUCT A
AT LOW TEMPERATURE (7°C)
MG/GM

FIGURE 11

EXTRACTABLE FORMALDEHYDE OF PRODUCT A
AT LOW TEMPERATURE (7°C)
mg/cm³

Housing and Urban Development in Use of Materials Bulletin, No. 74.

The urea-formaldehyde resin used in foaming samples for the low temperature studies was also analyzed for free formaldehyde. The result of $0.8 \pm .1\%$ aldehydes was within the recommended 1% limit.

Density -- High Temperature Condition. The mass, volume, and density of the foam samples under high and low relative humidity conditions are shown in Table 9 and Figure 12. The density of the low humidity sample decreased rapidly and subsequently became constant after approximately three days. The humid sample decreased in density very gradually and leveled at a value nearly twice that of the dry sample. The volume changes between high and low humidity samples were nearly identical. Hence, decreasing densities were entirely a function of water loss.

Water could also be absorbed by foam samples as indicated by reversing high and low relative humidity samples. The results of this study are shown in Table 10. A complete reversal of mass, volume, and density values was observed. The increase in volume of the dry sample when placed in the humid chamber should be noted.

Since the amount of foam originally placed in the two chambers was almost equivalent, additional information could be obtained on reversal of the samples. It should be noted that the mass of the original dry sample at the time of exchange was approximately equal to that of the humid sample after 17 days in the dry chamber. The volumes and resulting densities of the same two foam samples were far from identical.

To explain these discrepancies, a qualitative description of the foam samples is useful. The foam subjected to low relative humidity conditions was white and fairly rigid. When squeezed, the foam remained collapsed. After placing this sample in the humid chamber for 17 days it became slightly spongy and less rigid. The sample from the humid chamber was white nonrigid and very compressable. After exposure to dry conditions for 17 days the sample became yellowed, developed deep cracks, and disintegrated into dust when handled. A collapse of foam porosity was evident.

These qualitative descriptions and the fact that the shrinkage was much greater under humid conditions, suggests a possible degradation of the foam. Whether this can be attributed to a breakdown of the tertiary

Table 9. Mass, Volume, and Density Relationships Under High Temperature Conditions (33°C)

Days	DRY CHAMBER (20%)			HUMID CHAMBER (80%)		
	Mass ^a	Volume ^b	Density ^c	Mass	Volume	Density
0.46	121.35	3849	.032	122.10	3855	.032
1.3	89.10	3569	.025	106.40	3599	.030
3.3 ^d	36.80	3005	.0122	81.60	3132	.0260
6.3	34.90	2892	.0121	72.60	2930	.0248
8.4	34.64	2881	.0120	69.90	2897	.0241
10.0	34.60	2881	.0120	65.80	2886	.0228
13.3	34.81	2845	.0122	61.18	2886	.0212
15.0	34.80	2881	.0121	57.45	2875	.0200
17.0	34.69	2835	.0122	57.20	2843	.0201
19.0	34.88	2835	.0123	57.20	2843	.0201
22.0	34.87	2845	.0123	59.23	2854	.0207
24.2	34.87	2845	.0123	59.20	2819	.0207
27.3	35.04	2845	.0123	59.75	2854	.0209

^aMass in grams.

^bVolume in cm³.

^cDensity in gms/cm³.

^dSamples were solid enough at this point to be cut exactly square for better accuracy in density determinations. See shrinkage discussion.

FIGURE 12

FOAM DENSITY AS A FUNCTION OF TIME OF PRODUCT A
AT HIGH TEMPERATURE (33°C)

Table 10. Change in Density After Reversing High and Low Humidity Samples

Days ^a	DRY CHAMBER (20%)			HUMID CHAMBER (80%)		
	Mass ^b	Volume ^c	Density ^d	Mass	Volume	Density
0	63.59	2840	.0224	35.12	2870	.0122
3	35.03	2473	.0142	53.27	3058	.0174
5	35.10	2463	.0142	58.00	3026	.0192
8	34.50	2482	.0139	61.28	2989	.0205
10	34.79	2450	.0142	62.79	2989	.0210
12	34.14	2422	.0141	63.71	3010	.0212
15	34.90	2460	.0142	65.16	3010	.0216
17	34.79	2482	.0140	65.52	3010	.0218

^aDays after switching samples.

^bMass in grams.

^cVolume in cm³.

^dDensity in grams/cm³.

structure of the resin or actually a decrease in cross-linking was not determined.

Density -- Low Temperature Condition. Results for high and low relative humidity samples at low temperature are reported in Table 11 and Figure 13. The density decreased at a faster rate under dry conditions than with humid conditions. This decrease at high relative humidity was very slow and almost linear. The decrease in volume for the two samples was nearly identical after the 27 day period. Again results indicate that density decreases were a function of water loss.

Foam samples from the dry and humid chambers had the same general appearance. They were white with a spongy consistency, returning to their original shape after being compressed.

Shrinkage. As previously noted, volume data for the high temperature chamber should be disregarded prior to 3.3 days. By extrapolating back to initial volumes, however, shrinkage results could be determined. Table 12 lists linear shrinkage resulting from the various conditions. These values were obtained by subtracting final volumes from initial volumes and calculating the percent change. Volume changes were converted to linear shrinkage.

Product B

General. The conditions of "foaming" for this material were very similar to that of Product A. The temperature of the resin and detergent on application was 76°C. and the resin to detergent ratio was approximately 10:1. The ambient conditions reflected a low relative humidity (10%) and temperature (66°F.) were observed during the application. The initial foam density was 0.043g/cm².

Eight foot studded panels containing a dry wall and a vapor barrier seal were foamed for quality assurance of the sample. The shrinkage over the period of observation was less than 5%.

Formaldehyde Emission. Results of the formaldehyde emission study for Product B are presented in Figures 14 and 15. As can be observed, the profiles of the emission dynamics are similar to those of Product A.

Concentrations of formaldehyde varied the greatest with the high temperature, low humidity condition (25.01 to 1.17 ppm) over the 31 days of observation. Attainment of stable formaldehyde rates occurred more rapidly at high temperature than at low temperatures. The data for

Table 11. Mass, Volume, and Density Relationships Under Low Temperature Conditions (7°C)

Days	DRY CHAMBER (50%)			HUMID CHAMBER (90%)		
	Mass ^a	Volume ^b	Density ^c	Mass	Volume	Density
0.3	133.80	3005	.0445	133.70	3070	.0435
1.3	124.39	2960	.0420	125.07	2950	.0424
3.2	116.21	2940	.0395	121.20	2950	.0411
5.4	106.06	2920	.0363	116.89	2960	.0395
7.4	92.35	2852	.0324	109.89	2924	.0377
9.4	84.09	2799	.0300	106.39	2871	.0371
12.2	73.34	2852	.0257	102.00	2915	.0350
14.9	63.46	2852	.0222	97.65	2842	.0344
17.2	56.70	2852	.0199	94.88	2856	.0332
20.1	52.59	2852	.0184	91.43	2823	.0324
22.0	47.71	2842	.0168	89.05	2813	.0316
24.0	42.47	2794	.0152	86.81	2813	.0309
27.3	43.32	2804	.0154	83.53	2813	.0297

^aMass in grams.

^bVolume in cm³.

^cDensity in grams/cm³.

FIGURE 13

FOAM DENSITY AS A FUNCTION OF TIME
OF PRODUCT A AT LOW TEMPERATURE (9°C)

Table 12. Linear Foam Shrinkage With Respect to Environmental Conditions

Environmental Conditions	Linear Shrinkage
High temperature, high relative humidity	2.7%
High temperature, low relative humidity	2.4%
Low temperature, high relative humidity	2.1%
Low temperature, low relative humidity	1.9%

FIGURE 14

EMISSION OF FORMALDEHYDE VERSUS TIME
FOR PRODUCT B AT HIGH TEMPERATURE (33°C)

FIGURE 15

EMISSION OF FORMALDEHYDE VERSUS TIME FOR PRODUCT B
AT LOW TEMPERATURE (7°C)

Figures 14 and 15 are summarized in Table 13.

Extractable Formaldehyde. The results of monitoring extractable formaldehyde for the high temperature condition over the period of observation are presented in Figures 16 and 17. As previously observed, the differences in extractable formaldehyde were primarily due to the difference in moisture content of the high and low humidity condition. This is reflected in the density differences of the two different humidity conditions (Table 14).

The low temperature condition results are presented in Figures 18 and 19. As can be seen, the attainment of a stable extractable formaldehyde level appears approximately the same for the humid and dry conditions. The levels, however, were found to be different when calculated on a mg/g basis.

Free Formaldehyde. Because of the poor results obtained with Product A, free formaldehyde was not determined on this series of samples.

Density. The mass, volume, and density of the foam samples under high and low relative humidity conditions at the two temperatures are presented in Table 14 and in Figures 20 and 21. At both temperatures the high humidity condition produced a foam of high density. This is attributed to the difference in water retention.

Product C

General. The foam blocks, along with the quality assurance panels, were foamed under conditions comparable to the other two products. This foam represents a "newer type" insulation product. The initial foam density was 0.045 g/cm^3 .

Formaldehyde Emission. Results of the formaldehyde emission study for Product B are presented in Figures 22 and 23. The formaldehyde emission profiles are similar to those of Products A and B. The same observations with respect to the temperature and humidity relationships can be made. Concentrations of formaldehyde varied the greatest with the high temperature, low humidity condition (1.8 to 1.7 ppm, ml/l) over the period of observation. Attainment of stable formaldehyde levels were more rapid for the high temperature conditions when compared to the low temperature observations.

The data for Figures 22 and 23 are presented in Table 15.

Table 13. Formaldehyde Emission from Product B

Age of Sample (days)	(HCHO) $\mu\text{g}/\text{m}^3$	(HCHO) $\mu\text{l}/\text{l}$, ppm
Low Temperature, High Humidity		
1.4	3.36×10^3	2.74
2.1	6.40×10^3	5.21
5.0	4.49×10^3	3.65
6.8	3.44×10^3	2.81
9.0	3.79×10^3	3.09
15.0	2.49×10^3	2.03
17.9	1.69×10^3	1.38
21.0	2.85×10^3	2.33
28.1	3.36×10^3	2.74
31.0	3.05×10^3	2.49
Low Temperature, Low Humidity		
1.4	6.01×10^3	4.90
2.1	9.29×10^3	7.57
5.0	6.39×10^3	5.21
6.8	5.17×10^3	4.21
9.0	4.19×10^3	3.41
15.0	4.25×10^3	3.47
17.9	1.69×10^3	1.38
21.0	3.66×10^3	2.98
28.1	1.68×10^3	1.37
31.0	2.45×10^3	1.83
High Temperature, High Humidity		
2.2	30.22×10^3	24.62
5.2	13.64×10^3	11.11
7.0	6.97×10^3	5.68
10.0	6.79×10^3	5.54
15.2	4.71×10^3	3.84
18.1	2.05×10^3	1.67
21.2	3.88×10^3	3.17
28.3	3.83×10^3	3.13
31.3	3.20×10^3	2.61

Table 13. Formaldehyde Emission from Product B continued

Age of Sample (days)	(HCHO) $\mu\text{g}/\text{m}^3$	(HCHO) $\mu\text{l}/\text{l}$, ppm
High Temperature, Low Humidity		
2.2	30.69×10^3	25.01
5.2	9.57×10^3	7.80
7.0	2.81×10^3	2.29
10.0	2.89×10^3	2.36
15.2	2.79×10^3	2.27
18.1	1.60×10^3	1.31
21.2	2.31×10^3	1.89
28.3	2.35×10^3	1.92
31.3	1.44×10^3	1.17

FIGURE 16

EXTRACTABLE FORMALDEHYDE OF PRODUCT B
AT HIGH TEMPERATURE (33°C)
mg/cm³

FIGURE 17

EXTRACTABLE FORMALDEHYDE OF PRODUCT B
AT HIGH TEMPERATURE (33°C)
mg/cm³

Table 14. Density Changes for Product B and a Function of Time

Time (days)	Dry Chamber			Humid Chamber		
	mass (g)	volume (cm ³)	density (g/cm ³)	mass (g)	volume (cm ³)	density (g/cm ³)
Temperature: 80°C Relative Humidity: "Dry" ~50% "Humid" ~90%						
0.4	132.31	4078	.0324	134.85	4002	.0337
1.0	129.71	4003	.0324	133.29	4002	.0333
2.2	125.87	4003	.0314	130.40	3935	.0331
4.0	121.89	3970	.0321	127.35	3970	.0321
7.0	115.27	3928	.0293	123.99	3914	.0317
9.0	109.11	3965	.0275	121.09	3900	.0310
13.2	95.83	3928	.0244	115.60	3900	.0296
15.2	89.40	3954	.0226	112.00	3887	.0288
17.2	85.60	3947	.0217	109.22	3900	.0280
21.3	74.13	3902	.0190	105.58	3889	.0271
24.2	66.28	3945	.0168	101.15	3846	.0263
28.4	52.80	3971	.0133	98.89	3839	.0258
31.0	51.61	3945	.0131	96.70	3839	.0252
Temperature: 33°C Relative Humidity: "Dry" <10% "Humid" ~80%						
0.4	133.76	3953	.0338	135.78	4074	.0333
1.0	110.18	3732	.0295	126.96	3871	.0328
2.2	85.50	3626	.0236	118.46	3786	.0313
4.0	50.77	3605	.0141	110.34	3754	.0294
7.0	47.88	3452	.0139	102.02	3749	.0272
9.0	47.71	3426	.0139	95.32	3671	.0260
13.2	47.35	3403	.0139	83.29	3665	.0227
15.2	47.36	3403	.0139	80.60	3654	.0221
17.2	47.23	3426	.0138	76.90	3646	.0211
21.3	47.04	3373	.0139	71.21	3613	.0197
24.2	47.01	3376	.0139	70.67	3606	.0196
28.4	46.92	3384	.0139	69.62	3606	.0193
31.0	47.08	3365	.0140	68.14	3606	.0189

FIGURE 13

EXTRACTABLE FORMALDEHYDE OF PRODUCT B
AT LOW TEMPERATURE (7°C)
mg/gm

FIGURE 19

EXTRACTABLE FORMALDEHYDE OF PRODUCT B
AT LOW TEMPERATURE (7°C)

FIGURE 20

FOAM DENSITY AS A FUNCTION OF TIME OF PRODUCT B
AT HIGH TEMPERATURE (33°C)

FIGURE 21

FOAM DENSITY AS A FUNCTION OF TIME OF PRODUCT B
AT LOW TEMPERATURE (7°C)

FIGURE 22

EMISSION OF FORMALDEHYDE VERSUS TIME FOR PRODUCT C
AT HIGH TEMPERATURE (33°C)

FIGURE 23

EMISSION OF FORMALDEHYDE VERSUS TIME FOR PRODUCT C
AT LOW TEMPERATURE (7°C)

Table 15. Emission of Formaldehyde Over Time for Product C

Age of Sample (days)	(HCHO) $\mu\text{g}/\text{m}^3$	(HCHO) $\mu\text{l}/\text{l}$, ppm
Low Temperature (8°C), High Humidity (90% R.H.)		
1.0	4.23×10^3	3.45
3.3	3.86×10^3	3.14
8.8	5.33×10^3	4.34
10.9	3.74×10^3	3.05
12.9	2.79×10^3	2.27
14.9	3.61×10^3	2.94
20.1	2.19×10^3	1.78
22.0	2.07×10^3	1.68
26.1	2.73×10^3	2.23
28.8	2.01×10^3	1.65
Low Temperature (8°C), Low Humidity (70% R.H.)		
1.0	5.81×10^3	4.73
3.3	6.59×10^3	5.37
8.8	5.01×10^3	4.07
10.9	3.81×10^3	3.11
12.9	3.03×10^3	2.47
14.9	4.91×10^3	4.01
20.1	2.54×10^3	2.07
22.0	2.13×10^3	1.73
26.1	3.51×10^3	2.86
28.8	1.75×10^3	1.43
High Temperature (33°C), High Humidity (85% R.H.)		
1.9	15.20×10^3	12.39
3.3	5.19×10^3	4.23
8.9	4.49×10^3	3.67
10.9	2.52×10^3	2.05
13.0	2.15×10^3	1.75
16.0	2.08×10^3	1.69
20.2	1.55×10^3	1.27
22.2	1.63×10^3	1.33
26.2	1.97×10^3	1.61
28.9	1.15×10^3	0.94

Table 15. Emission of Formaldehyde Over Time for Product C,
continued

Age of Sample (days)	(HCHO) $\mu\text{g}/\text{m}^3$	(HCHO) $\mu\text{l}/\text{l}$, ppm
High Temperature (33°C), Low Humidity (10% R.H.)		
1.0	21.45×10^3	17.48
3.3	5.79×10^3	4.72
8.9	3.23×10^3	2.63
10.9	2.69×10^3	2.19
13.0	2.61×10^3	2.12
16.0	3.32×10^3	2.71
20.2	2.05×10^3	1.67
22.1	2.39×10^3	1.95
26.2	1.64×10^3	1.33
28.9	2.05×10^3	1.67

Extractable Formaldehyde. The results of monitoring extractable formaldehyde for the high temperature conditions is presented in Figures 24 and 25. As can be seen the data indicates that there is little difference between the humid and dry exposure samples with respect to extractable formaldehyde. In addition, the levels of extractable formaldehyde are significantly lower than for the other two products. This indicates that the long term hydrolysis of the material may be decreased to a significant degree.

The results of the low temperature exposure are similar to those of the other products tested. However, the levels of extractable formaldehyde in this product are lower when compared to the previous two materials (Figures 26, 27).

Free Formaldehyde. Because of the poor results obtained with Product A, free formaldehyde was not determined on this series of samples.

Density. The mass, volume and density of the samples under high and low relative humidity conditions at the two temperatures is presented in Table 16 and Figures 28 and 29. At the high temperature condition the densities of the high and low humidity samples were essentially the same. The volume and mass of the sample exposed to humid conditions were slight higher than the dry condition indicating a low level retention of water.

The low temperature observations indicate that the dry condition density stabilized to the density of the high temperature conditions. The volume and mass, however, in the low temperature condition were higher for the reduced temperature. The sample exposed to humid conditions did not attain density equilibrium.

FIGURE 24

EXTRACTABLE FORMALDEHYDE OF PRODUCT C
AT HIGH TEMPERATURE (33°C)
mg/gm

FIGURE 25

EXTRACTABLE FORMALDEHYDE OF PRODUCT C
AT HIGH TEMPERATURE (33°C)
mg/cm³

FIGURE 26

EXTRACTABLE FORMALDEHYDE OF PRODUCT C
AT LOW TEMPERATURE (7°C)
mg/cm³

FIGURE 27

EXTRACTABLE FORMALDEHYDE OF PRODUCT C
AT LOW TEMPERATURE (7°C)

Table 16. Mass, Volume, Density Relationship of Product C

Time (days)	Dry Chamber			Humid Chamber		
	mass (g)	volume (cm ³)	density (g/cm ³)	mass (g)	volume (cm ³)	density (g/cm ³)
Temperature: 33°C Relative Humidity: "Dry" <10% "Humid" ~85%						
.25	197.71	5095	.0388	189.03	5061	.0373
1.0	144.79	5015	.0289	167.32	5061	.0330
3.9	59.43	4794	.0124	134.68	5496	.0245
7.8	56.19	4489	.0125	54.60	4565	.0120
9.8	55.81	4463	.0125	58.79	4816	.0122
13.7	55.69	4430	.0126	58.42	4773	.0122
16.0	55.98	4482	.0125	57.55	4738	.0121
18.2	55.74	4462	.0125	58.00	4746	.0122
20.9	55.89	4397	.0127	59.43	4761	.0125
22.9	55.64	4410	.0126	57.87	4746	.0122
24.9	55.84	4410	.0127	57.61	4723	.0122
27.8	55.69	4371	.0127	57.66	4731	.0122
30.0	55.60	4346	.0128	57.24	4642	.0123
Temperature: 8°C Relative Humidity: "Dry" ~70% "Humid" ~90%						
.25	189.38	5073	.0373	195.71	5113	.0383
1.0	175.98	5040	.0349	186.84	5154	.0362
3.9	161.51	4984	.0324	179.12	5095	.0352
7.8	140.93	4905	.0287	164.05	4952	.0331
9.8	130.00	4848	.0268	159.29	4874	.0327
13.7	111.40	4861	.0227	148.78	4839	.0307
16.0	103.68	4848	.0214	143.40	4867	.0295
18.2	93.36	4853	.0192	138.38	4845	.0286
20.9	83.63	4883	.0171	131.50	4817	.0273
22.9	74.43	4883	.0152	127.55	4817	.0265
24.9	67.89	4883	.0139	124.11	4768	.0260
27.8	62.56	4897	.0128	118.74	4816	.0247
30.0	61.47	4872	.0126	114.66	4761	.0241

FIGURE 28

FOAM DENSITY AS A FUNCTION OF TIME OF PRODUCT C
AT HIGH TEMPERATURE (33°C)

FIGURE 29

FOAM DENSITY AS A FUNCTION OF TIME OF PRODUCT C
AT LOW TEMPERATURE (7°C)

SUMMARY

Emission of formaldehyde from the foamed polymer produced from urea-formaldehyde resin and the surfactant-catalyst mixture has been reported (28). However, the duration and concentration levels of emission were not determined. The data shown in the previous section indicates that the emission of formaldehyde can occur at appreciable levels and for long periods of time.

In general, the maximum concentration values measured for the high temperature exposure resulted in a large difference between the high and low humidity conditions. The humidity for both chambers was initially high due to the amount of water present in the foam samples. However, the relative humidity decreased to low levels rapidly under the high temperature condition. The humidity differences at the initial measurement is assumed to be large enough to account for the difference in concentrations of the two chambers.

All urea-formaldehyde resin mixtures used in the production of the foams contained a certain amount of unreacted formaldehyde. Some of the free formaldehyde reacts when mixed with the foaming agent/catalyst mixture; however, much of it is uncombined and is incorporated into the foam. Measurement of free formaldehyde in resin and in the foam resulted in values for Product A of 0.8% and 0.5%, respectively. These values are reported as free aldehydes. Free formaldehyde in the foam samples is shown to be present at an appreciable level.

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 ($-\text{CH}_2\text{OH}$) 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 A 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.

An exponential fit of the data was suggested from the emission versus time curves. Since two sources of formaldehyde are suspect, independent rates for the sources may be possible. Both processes, emission from free and hydrolyzed formaldehyde, would occur simultaneously. The rate of emission from free formaldehyde would prevail initially with hydrolysis being manifested when the amount of free formaldehyde has been reduced.

Figures 30, 31, 32, 33, 34, and 35 present plots of the logarithm of the formaldehyde concentration versus time for the three products described previously. For the high and low temperature observations for these products it is possible to identify qualitatively two slopes. This is presumed to be associated with two different mechanisms of formaldehyde emission, a short term (possibly free formaldehyde) and a longer term (possibly hydrolysis) process.

FIGURE 30
 LOGARITHM OF THE CONCENTRATION OF FORMALDEHYDE
 VERSUS TIME FOR PRODUCT A
 High Temperature (33°C)

FIGURE 31
LOGARITHM OF THE CONCENTRATION OF FORMALDEHYDE
VERSUS TIME FOR PRODUCT A
Low Temperature (7°C)

FIGURE 33

FIGURE 34

FIGURE 35

CONCLUSIONS

Urea-formaldehyde foam polymers used in the insulation of buildings have a number of undefined properties. The emission of formaldehyde during the curing process and after curing has been observed: the temperature and humidity dependence of the emission also has been shown. Emission of formaldehyde can result from three sources: free, and hydrolyzed formaldehyde and paraformaldehyde. Two of these, free and hydrolyzed (or paraformaldehyde) are indicated. Emission of formaldehyde is dependent upon temperature and humidity. In addition, temperature and humidity affect the physical structure of the foam. Increased humidity and temperature increases the rate of hydrolysis which ultimately will cause deterioration of the polymer structure. This was evident upon examination of the foam samples after being exposed to high humidity and high temperature. The foam lost its rigidity and crumbled when handled. In general, the presence of both high humidity and high temperature accelerated the property changes of the foams. Examination of the samples from the low temperature, high humidity chamber, presented some disintegration but not to the extent of that found in the high temperature, high humidity sample.

Extractable formaldehyde was used as a measure of weakly bound and free formaldehyde in the foam products. The majority of the bound formaldehyde determined was believed to be a result of the hydrolysis of methylol end groups. This being the case, decreases in extractable formaldehyde levels should be an indication of formaldehyde losses as free and hydrolyzable formaldehyde. Hydrolysis of urea-formaldehyde foam should be a function of relative humidity and temperature. Experimental results support the hydrolysis hypothesis where the greatest decreases occurred in extractable formaldehyde at high temperature and relative humidity. The greatest shrinkage was also observed for the foam at high temperature and high relative humidity indicating a general degradation of the foam under those environmental conditions.

In summary, this indicates the following:

1. Temperature affects the levels of formaldehyde emission from urea-formaldehyde foam products. An increase in temperature results in an increase in formaldehyde vapor levels.

2. Humidity affects the levels of formaldehyde emission from urea-formaldehyde foam products. An increase in humidity results in an increase in formaldehyde vapor levels.
3. Two emission processes are indicated. A short term process attributed to the release of free formaldehyde and a longer term emission which is believed to be associated with hydrolysis of the polymer.
4. Recent advances in urea-formaldehyde foam chemistry exhibited by product C indicate that formaldehyde emissions can be controlled. Such advances in technology coupled with a reasonable government regulatory program may make it possible for our society to continue to use urea-formaldehyde foam insulation in efforts to conserve energy in buildings.

The results of these series of studies are with respect to the three insulation products tested and are not necessarily indicative of the characteristics of the myriad of urea-formaldehyde products available.

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APPENDIX I

Graphs were plotted by computer which fit the data to a least squares exponential equation. The weighted variance is an indication of how well the resulting line fit the data:

$$\text{Variance} = \frac{\sum (y_i^{\text{obs}} - y_i^{\text{calc}})^2}{N - p}$$

where: y_i^{obs} = observed value

y_i^{calc} = calculated value

N = number of data points

p = number of parameters

Data was fit to the exponential function:

$$Y = Ae^{-\alpha X} + C$$

Y = concentration

x = time

Parameters A , α , and C were optimized.

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