

# ES&T RESEARCH

## Removal of Aldehydes and Acidic Pollutants from Indoor Air

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■ Indoor pollutants such as formaldehyde or acidic gases such as SO<sub>2</sub>, NO<sub>2</sub>, and H<sub>2</sub>S can be removed from a house by a reactive method consisting of a coating on a furnace filter in a forced-air heating system. The coating is a polymeric substance with specific functional groups that react with the pollutant, which in the case of formaldehyde or other aldehydes, would be a polymeric amine such as polyethylenimine. The coating is plasticized with a low-volatility liquid such as glycerol in order to extend the useful life of the coating.

### Introduction

The extensive use of resin-bonded wood in construction and the continued expanding application of formaldehyde-based resins has resulted in formaldehyde becoming a major indoor contaminant (1). We have previously reported (2) on the use of polymeric amines and polyethylenediamine, which when sprayed onto fiberglass furnace filters could reduce the levels of formaldehyde from 0.16 to 0.01 ppm. However, the effectiveness of the filter was limited to ~2 weeks. We have now shown that by plasticizing the coating it has been possible to extend the usefulness of the coating to well over 1 month—the recommended life of a fiberglass furnace filter. Heavier coatings can be made to be effective for longer periods. We have also shown that the coatings can trap acidic gases such as SO<sub>2</sub>, NO<sub>2</sub>, and H<sub>2</sub>S.

### Experimental Section

**Reagents.** Polyethylenimine (PEI) was used as a 50% aqueous solution from Eastman and was shown by <sup>13</sup>C NMR (3) to consist of primary, secondary, and tertiary amine at 35%, 37%, and 28%, respectively. Glycerol was Fisher's USP grade. The gases H<sub>2</sub>S and SO<sub>2</sub> were obtained from lecture bottles of chemically pure grade from Matheson. The NO<sub>2</sub> was prepared by the action of HNO<sub>3</sub> on Cu and was stored in a plastic bag fitted with a septum. Formaldehyde gas was generated by flowing air over paraformaldehyde (Eastman) heated to 85 °C. The loss in weight of the paraformaldehyde was used to estimate the amount of formaldehyde generated.

**Measurement Methods.** **Method A.** Low concentrations of formaldehyde (0.3 ppm) were determined spectrophotometrically by the pararosaniline method at 570 nm in a 10-cm cell (2). Formaldehyde was collected for analysis by pulling air through a sintered glass bubbler, containing 25 mL of water, at a flow rate of 750 mL/min

for 20 min. A second bubbler in series showed no additional formaldehyde (2). Duplicated analysis showed ~5% precision.

Higher concentrations were measured by either a Miran IR analyzer, method B, or a CEA Model 555 air monitor, method C.

Analysis for H<sub>2</sub>S was made by passing the air through a sintered glass bubbler containing a known volume of a dilute solution of CuSO<sub>4</sub>.



The copper was determined (spectrophotometrically) with diethyldithiocarbamate (DDTC), and from the change in concentration, the amount of H<sub>2</sub>S that passed through the foam filter could be calculated.

For SO<sub>2</sub> the gas was absorbed in a dilute solution of KOH and the resulting solution was analyzed spectrophotometrically for SO<sub>3</sub><sup>2-</sup> either by Fuchsin or by K<sub>2</sub>HgCl<sub>4</sub>. It was found that O<sub>2</sub> in air tended to oxidize some of the SO<sub>2</sub> to SO<sub>3</sub> and this interfered with the analysis. Hence, N<sub>2</sub> was used instead of air as the carrier gas.

The determination of NO<sub>2</sub> was made by measuring the change in conductivity of distilled water in the absorber. A Radiometer CDM-2d conductivity meter was used for the measurements.

**Laboratory Evaluation.** Laboratory experiments on the trapping efficiency were done for formaldehyde and acidic gases.

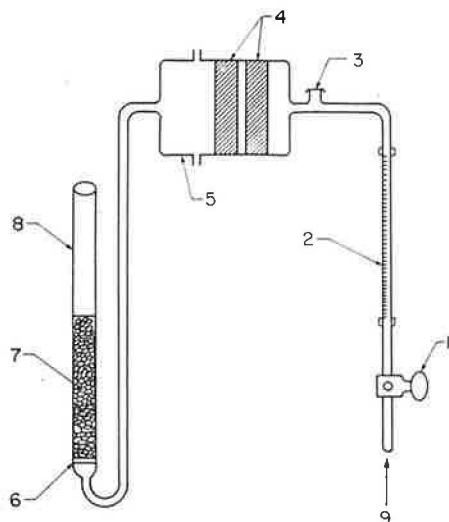
**Formaldehyde.** (a) A short column (1/2 in. i.d. × 1 in. long) of 7–10 mesh alumina beads coated with PEI/glycerol was evaluated for the trapping of formaldehyde in a single pass. Analysis was performed by method C.

(b) A test chamber was constructed from part of a small laboratory, which was partitioned off with polyethylene (10 mil) but not thoroughly sealed. The dimensions of the test chamber was approximately 5 ft × 6 ft × 10 ft high. A small fan operating continuously at a constant rate thoroughly mixed the air in the chamber while formaldehyde was introduced into the chamber.

A filter was fitted to a box fan (20 in. × 20 in.) that was placed in the chamber. The fan could be turned on or off from outside the chamber. Analysis was performed by method A.

**Acidic Gases.** To test the coatings for their effectiveness in removing acidic gases from air two open cell reticulated (45 pores per inch) polyurethane foam sponges (each 7 cm diameter, 2.3 cm thick) were coated with polyethylenimine/glycerol (two parts of 50% PEI to one part of glycerol by volume) and fitted into a glass cylinder through which the gases could be passed.

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**Figure 1.** Apparatus used to test the removal of acidic gases from a flowing air stream. (1) Flow rate controller, (2) flow meter, (3) septum, (4) coated foam filters, (5) glass filter holder, (6) fritted disk, (7) absorbing solution, (8) glass absorber, (9) gas input.

A diagram of the apparatus is shown in Figure 1. The coated, air-dried filters (4) were placed in the glass cylindrical filter holder (5), which was connected to a calibrated flow meter (2) and air supply (9). The rate of flow of gas was controlled by the valve (1). A septum (3) between the flow meter (2) and the filter (4) allowed for the injection of small amounts of gases to be tested. These gases were carried through the filter by the air flow (9) and were absorbed by a reactive solution (7), which was placed in the absorber (8) and which was fitted with a fritted disk (6) to disperse the gas into fine bubbles to ensure dissolution or reaction of the gas with the solution. By analysis of the solution it was possible to determine the effectiveness of the polymeric amine in removing the acidic gases injected into the gas stream. Blank tests without the coating were used for comparison.

**Field Evaluation.** Field evaluation of the coatings were limited to formaldehyde. One home, which had urea formaldehyde foam insulation, (formaldehyde analyzed by method A) and a new mobile home constructed with particle board and plywood was tested for formaldehyde by method B.

## Results and Discussion

**Laboratory Evaluation. Formaldehyde.** (a) When formaldehyde at 2, 5, and 10 ppm was passed through the PEI/glycerol-coated alumina column at a flow rate of 500 mL/min (contact time 0.4 s), approximately 96% of the formaldehyde was trapped. (We are grateful to Teledyne Water Pik of Fort Collins, CO, for conducting this test.)

(b) The results for tests in the chamber are shown in Table I and indicate that the coating was effective in lowering the concentration of formaldehyde.

The amount of formaldehyde in the air of the chamber is of the order of 1–3 mg. The theoretical amount of formaldehyde that the PEI can react with is determined by the number of amine groups available. This is (6.2 g divided by 43 g/mol) = 0.14 mol or 0.14 mol × 30 g/mol or approximately 4.2 g of formaldehyde. However, formaldehyde only reacts with primary and secondary amines, but PEI also contains some tertiary amines (28%), which are ineffective. Hence, the capacity is  $0.72 \times 4.2$  or 3.0 g. Thus, an attempt was made to determine the capacity of the filter to absorb formaldehyde in terms of the functional amine groups available. The results are presented in Table

**Table I. Formaldehyde Removal by PEI/Glycerol-Coated Filter Formaldehyde Introduced into Test Chamber at a Constant Rate**

Feb date	conditions	[H <sub>2</sub> CO], ppm
11 (a.m.)	no coating on filter	0.102
12 (a.m.)		0.391
12 (p.m.)	coated filter installed (fan on)	0.242
13 (a.m.)		0.116
13 (p.m.)		0.078
14 (a.m.)		0.045
15 (a.m.)		0.031
16 (a.m.)	fan turned off	0.021
17 (a.m.)		0.051
18 (a.m.)		0.081
18 (p.m.)		0.215
19 (a.m.)		0.370
19 (p.m.)	fan turned on	0.364
20 (a.m.)		0.328
20 (p.m.)		0.195
21 (p.m.)		0.123
22 (p.m.)		0.106
23 (a.m.)	fan turned off filter still in chamber	0.046
24 (a.m.)		0.034
24 (p.m.)		0.024
25 (a.m.)		0.373
25 (p.m.)		0.368

**Table II. Test Chamber Results for Capacity of PEI/Glycerol Filter<sup>a</sup>**

time, h	rate of wt loss (CH <sub>2</sub> O) <sub>n</sub> <sup>b</sup> mg/h	[HCHO], ppm	time, h	rate of wt loss (CH <sub>2</sub> O) <sub>n</sub> <sup>b</sup> mg/h	[HCHO], ppm
-10	10	0.250	122	13	0.044
0 <sup>c</sup>	10	0.250	144	15	0.057
8	13	0.160	170	18	0.088
26	11	0.054	191	20	0.126
47	17	0.060	218	18	0.173
74	11	0.041	239	16	0.266
95	21	0.065			

<sup>a</sup>Theoretical capacity, 3.0 g of HCHO. <sup>b</sup>(CH<sub>2</sub>O)<sub>n</sub>, paraformaldehyde. <sup>c</sup>Fan on filter turned on and left on.

II. It is assumed that when the concentration of formaldehyde in the chamber is constant then the rate at which formaldehyde is introduced into the chamber ( $R_i$ ) is equal to the rate at which the formaldehyde leaks from the chamber ( $R_l$ ) plus the rate at which the formaldehyde is absorbed by the filter ( $R_f$ ). If it is assumed that  $R_l$  is proportional to the concentration of formaldehyde in the chamber, then it is possible to estimate the value of  $R_f$ . Before the box fan is turned on  $R_i = R_l = 10$  mg/h and [H<sub>2</sub>CO] = 250 ppb. When the fan is on,  $R_i = 16$  mg/h (average value) and since [H<sub>2</sub>CO] ~ 50 ppb,  $R_l \sim 2$  mg/h.

Therefore,  $R_f = 14$  mg/h. The total formaldehyde absorbed by the filter is 14 mg/h × 180 h or approximately 2.5 g. This value is consistent with the estimated capacity of formaldehyde (3.0 g) based on the amount of PEI present on the filter.

The results thus show that almost all of the available polymeric amine is used to react with the formaldehyde. When the glycerol was not present in the filter coating only a small fraction of the amine was utilized because of the lack of diffusion in the film coatings. It is possible to use other polymeric primary amines such as polyvinylamine or polyallylamine, and under such conditions (with glycerol), a higher efficiency with formaldehyde would be expected because of the absence of tertiary amines.

The data in Table II also clearly show that eventually the PEI in the filter is consumed and the level of form-



aldehyde in the chamber then rises.

**Acidic Gases.  $H_2S$ .** Air was allowed to pass through the apparatus (shown in Figure 1) at a flow rate of 400 mL/min. The foam filters were coated and air-dried before being tested. When the filters were absent the amount of  $CuS$  precipitated was of the order of 70–100% of the expected value when 0.3 mL of  $H_2S$  at NTP was injected into the air stream over a 10-min period. This corresponds to a peak concentration in the air stream of  $0.3/(400 \times 10) = 75$  ppm. When the filter was coated with glycerol and water, the amount of this  $H_2S$  that passed through the system was closer to 50%. However, when the filter was treated with PEI in glycerol and water, the amount of  $H_2S$  that passed through the filter was less than 2% when as much as 8 mL of  $H_2S$  was injected. This did not change even after 25 mL of  $H_2S$  was injected. Hence, the capacity of the coated foam to trap  $H_2S$  is not trivial.

**$SO_2$ .** When 0.5 mL of  $SO_2$  was injected during a 10-min interval before a PEI/glycerol-coated filter with  $N_2$  flowing at 400 mL/min, no  $SO_2$  was detected in the absorber. This corresponds to a peak concentration of  $\sim 125$  ppm of  $SO_2$ .

Similar results were obtained after 1, 5, and 10 mL of  $SO_2$  were introduced into the gas stream. When the PEI was absent in the coating,  $\sim 60\%$  of the  $SO_2$  passed through the filter. This is similar to results obtained with  $H_2S$  and means that the glycerol dissolves some gas.

**$NO_2$ .** When 1 mL of  $NO_2$  at NTP was injected into the air stream (flow rate 400 mL/min, 250 ppm  $NO_2$ ) before the filter coated with PEI/glycerol, the conductivity of the distilled water did not change from  $2.5 \mu\text{ohm}^{-1}$ . When 5 mL of  $NO_2$  was injected the conductivity rose to  $4 \mu\text{ohm}^{-1}$  or to  $\sim 10\%$  of the value attained in the absence of the filter, thus indicating that PEI is effective in reducing the concentration of  $NO_2$  in air.

Tertiary amines are stronger bases than secondary or primary amines and therefore bind weak acids more strongly. Thus, the use of commercial polyethylenimine is a versatile coating for the absorption of aldehydes as well as acidic gases. This is due to the fact that commercial PEI contains all three types of amines.

**Field Evaluation. Formaldehyde.** The effect of the glycerol on the duration of the usefulness of the polyethylenimine coating was evaluated. A one-story bungalow (with basement), which had urea formaldehyde foam insulation, had levels of formaldehyde that were from 0.085 to 0.120 ppm. When a fiberglass furnace filter (16 in.  $\times$

20 in.  $\times$  1 in.) was treated by spraying with polyethylenimine, 150 mL of 5% PEI in water, 6.2 g of PEI on filter, the level of formaldehyde dropped to 0.015 ppm within 1 week but after an additional 10 days rose to 0.095 ppm. When a similar filter was treated with 150 mL of a 5% polyethylenimine solution of glycerol/water, 30/70 by volume, the level of formaldehyde remained below 0.040 ppm for 1 month after which testing stopped. Testing for longer periods is planned.

A new mobile home was tested for formaldehyde and an initial concentration of 0.46 ppm was determined. When a coated filter and fan was installed, the concentration of formaldehyde dropped to 0.29 ppm in 3 h. After 1.5 h of discontinued use the formaldehyde concentration rose to 0.40 ppm. (We are grateful to Trion Inc. of Sanford, NC, for conducting this test.)

### Conclusion

We have shown that plasticized polyethylenimine is an effective trap for formaldehyde as well as acidic gases such as  $H_2S$ ,  $SO_2$  and  $NO_2$  and that the reaction can be considered quantitative. The trapping efficiency is high even for high concentrations of the gases in air. Single-pass experiments do not show complete removal of the pollutant because of insufficient contact time. This is readily improved upon in recirculating systems (4).

It remains to test the trapping efficiency of the coating for longer periods of time and at very low level commonly found in indoor air.

**Registry No.** PEI, 9002-98-6;  $H_2S$ , 7783-06-4;  $SO_2$ , 7446-09-5;  $NO_2$ , 10102-44-0; formaldehyde, 50-00-0; glycerol, 56-81-5.

### Literature Cited

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