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Frank H. Hengemihle, Norman Weberg and Chandru Shahani
Preservation Research and Testing Office

Preservation Directorate
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INTRODUCTION

Over the past several decades, ethylene oxide gained such wide acceptance in the library and archival preservation world, that in spite of the risks its usage presents, it has not been easy to replace with another fumigant. This biocide has an unparalleled track record of effectiveness against insects as well as microorganisms and also the absence of any significant ill effects on archival as well as museum collections themselves, although it is not entirely unblemished (Green, 1987).

A little over ten years ago, several public and private repositories routinely fumigated materials that were even remotely suspected of mold or insect infestation. For example, the U.S. National Archives subjected all incoming records to ethylene oxide fumigation as a precautionary measure for several decades. Now we know that ethylene oxide can be deadly not just for mold and insects, but also for us if it is not used within accepted limits (OSHA, 1982-5, Lewin, 1986). Chronic exposure to ethylene oxide can increase the risk of leukemia, brain tumors and other cancers; it can cause chromosome damage and may also affect the reproductive system.

It is now generally accepted that several natural, as well as synthetic polymeric materials tend to retain significant amounts of residual ethylene oxide subsequent to a fumigation treatment. The residual ethylene oxide is then gradually released into the environment over an extended period of time. Such offgassing phenomena are of particular concern since they extend the population that is routinely exposed beyond the limited numbers of workers who operate the sterilization/fumigation chambers, and who - one would expect - would be equipped to deal with the risk in an appropriate manner. In the case of fumigated library materials, this risk can be extended to unsuspecting and unprepared curators and other personnel who routinely service the fumigated materials. Researchers and readers exposed to such materials are also put at risk, although to an appreciably smaller extent since their exposure would be expected to be occasional, or short-term.

In 1984, the U.S. Occupational Safety and Health Agency (OSHA) specified a standard for occupational exposure to ethylene oxide, which among other provisions lowered the Permissible Exposure Level (PEL) from 50 ppm to 1 ppm (OSHA, 1984). In that document, OSHA reserved judgment on the need for and the appropriateness of a short-term exposure limit. Following scientific peer review and public comment on the issue of a short-term exposure limit, OSHA published its determination that the available evidence did not support the imposition of such a limit (OSHA, 1985).

The present work was undertaken to comprehend the capability of different library materials to offgas ethylene oxide. The objective was to obtain some understanding of the extent of aeration that different materials require after fumigation with ethylene oxide. Such knowledge would allow for better planning and control of the fumigation process and aid in the management of any risk that ethylene oxide offgassing may present to library personnel and users. It is not the intent of this work to suggest that such risk is unmanageable. Moreover, the rates of desorption of residual ethylene oxide observed in this work have no relevance on an absolute basis since desorption can be accelerated appreciably by raising the temperature and relative humidity levels of the air. The desorption rates observed here are useful only for the purpose of comparing these rates on a relative basis for different materials investigated in this work.

In 1982, OSHA issued an Advance Notice of Proposed Rule-making stating that the then-current occupational safety and health standard for ethylene oxide — 50 ppm measured as an 8-hour time-weighted average (TWA) — may be inadequate to protect exposed workers from significant risk (OSHA, 1982). At this point, it became clear to us that it was important to institute measurement of ethylene oxide concentration levels during the fumigation process. We began to monitor ethylene oxide by withdrawing gas samples from inside the fumigation chamber after successive air-changes before opening it up. The very first time that we started this practice, we were taken aback that after three evacuation-air change cycles, where we would have normally opened up the chamber, we still had an ethylene oxide concentration of several hundred parts per million within the chamber.

The materials being exposed at that time consisted mainly of wood, paper and interestingly enough — several bags of horse hair, which came not from the Library's collections but from the U.S. National Park Service. We had to exchange the air in the chamber as many as 28 times over several days before we could bring the ethylene oxide concentration to under 1 ppm. We speculated about the wood or horse hair being responsible for the strong retention of residual ethylene oxide. Clearly, we needed to know a lot more about the capability of different materials to retain residual ethylene oxide so as to exclude them or treat them separately. Hence the present series of experiments in which we simulated in the laboratory the operational conditions in our larger 500 cu. ft. fumigation chamber.

EXPERIMENTAL

Materials

Carboxide™ gas, which is 10 percent ethylene oxide in carbon dioxide, was obtained from Linde Specialty Gases, a division of Union Carbide Company.

The fine wood pulp book paper used in this study is Springhill™ offset paper, which had been obtained one year prior to its use from the International Paper Company as a single roll from which 8 1/2"xll" sheets were cut for this experiment. This is an alum-rosin-sized paper with a pH value of 5.5 units. The newsprint paper was also obtained as

a single roll from the US Government Printing Office about 15 years prior to its use in this work. The newsprint paper has a pH value of 4.8, and was cut into 8"x10" sheets for this work. Leather scraps were an uncharacterized mix of several different kinds of leather from the Library's Book Conservation Section.

The vinyl audio records were typical 33 RPM long-play records from the Library's collection. They were fumigated without their covers.

Two different photographic films were used in these experiments. One was a 35 mm roll of black and white motion picture film on a cellulose acetate safety base, while the other was a 35 mm roll of color motion picture film on a polyester base.

For each of the materials selected for this study, exactly 1.4 Kg of the material was weighed out for treatment.

Experimental Setup

A 33-liter cylindrical, round-bottomed heavy-gauge glass chamber with an open top was used to contain the materials during exposure to Carboxide™ gas. This chamber was fitted with an air-tight half-inch thick Plexiglas™ (acrylic) cover with four openings. These openings were joined with air-tight fittings to (1) a Carboxide™ gas cylinder, (2) a Welch Duo-Seal Model 1400 vacuum pump through a trap and valve, (3) a Matheson pressure gauge through a valve, and (4) a flexible tubing that extended to the bottom of the chamber on one end and was equipped at the other end, outside the chamber with a needle valve.

This tubing at the fourth opening served as an inlet for air and also as an outlet for sampling and analysis of the air within the chamber. Air samples could also be withdrawn through a septum that covered an opening in the middle of the Plexiglas™ cover. A perforated stainless steel rack sitting about an inch above the bottom of the chamber supported the objects being fumigated. To the sides of the metal rack were attached an Airguide™ relative humidity gauge and
a Weston Model 4200 thermometer, both of which could be viewed plainly from outside the sealed chamber. This glass chamber was placed inside a fumehood, where all the work was carried out.

Fumigation Procedure

With the materials in place and the cover with all its fittings secured, the chamber was evacuated for 30 minutes. The pressure inside the chamber was well under 30 torr in the case of all the materials studied. The Carboxide™ gas was allowed into the chamber until the pressure was about 650 torr. The system was left undisturbed for 24 hours.

Two separate and independent procedures were followed to compare the relative affinity of library materials for ethylene oxide. In the first procedure, the air inside the chamber was changed several times, and the decreasing concentration of ethylene oxide was periodically monitored. At the end of the 24 hour fumigation period, and thereafter after every aeration step, the chamber was evacuated for 30 minutes and room air (40% RH) allowed to enter the chamber until a pressure of 650 torr was registered. The

ethylene oxide concentration inside the chamber was monitored constantly at regular intervals 20 to 40 minutes apart. The total contact time between the fumigated material and fresh air varied between 3 and 16 hours (longer times were for aerations that continued overnight).

In the second procedure, the evacuation of the chamber was initiated at the end of the 24-hour fumigation period, and continued for several hours while the ethylene oxide concentration at the vacuum pump exhaust was monitored at regular intervals. For experiments that could not be completed by the end of the workday, the system was sealed off overnight and the process continued the next morning.

No attempt was made in these experiments to introduce additional moisture other than that present in the room air and that given off by the materials themselves. The relative humidity varied from 25% RH under vacuum to 45% RH in the presence of air.

Ethylene Oxide Detection and Analysis

The work area and laboratory personnel were constantly monitored by EOTrak™ badges (Chemrox, Inc.) for ethylene oxide TWA exposure dose.

Two gas chromatographs were employed at different points in this study. One of these was an HNU Systems Model 301 gas chromatograph equipped with a HayeSep D 80/100 stainless steel column (4'xl/8"), and a photoionization detector (PID) was used to measure ethylene oxide concentration inside the chamber. This gas chromatograph was equipped with a microprocessor programmed to measure the ethylene oxide concentration repeatedly over pre-determined intervals by monitoring the response of the detector at 10.565 eV, the ionization potential for ethylene oxide. This instrument was also used periodically to monitor ethylene oxide concentration in the work area. The other gas chromatograph used was a Varian Model 3700 which was equipped with an HNU Systems Model 52 PID detector. A Porapak Q column was used at 135˚C. The gas chromatographs were calibrated with two standard mixtures of ethylene oxide in air (5.4 ppm and 19.1 ppm) obtained from MG industries.

Results and Discussion

Two parallel studies were completed to compare the relative capacity of selected library materials for offgassing of ethylene oxide. One of them monitored the progressive increase in ethylene oxide concentration within a contained environment after successive infusions of fresh air. In the other study, a constant vacuum was applied after the fumigation step, and the ethylene oxide concentration monitored at the vacuum pump exhaust.

Figure 1 presents the data collected by monitoring the progressive accumulation of ethylene oxide above fumigated vinyl audio records in successive changes of air. Only a few selected air changes are shown here as an illustration of the pattern that was generally observed after each change of air with the vinyl platters, as well as with other materials. As each fresh volume of air begins to interact with the fumigated material, the concentration of ethylene oxide in the air continues to increase towards an equilibrium

value where it ultimately levels off. In about two hours after a fresh volume of air is introduced, the ethylene oxide concentration approaches to within 10 percent of the equilibrium value. In the interest of efficiency, it was decided to plot the data for all air changes with different materials in the manner illustrated by the data in Figure 1 and read off the near-equilibrium concentration at 2.0 hours.

Table I presents these experimental data for all of the materials studied here with the single exception of the data for the second motion picture film. The two sets of data obtained with the black and white film on a cellulose acetate base and the color film on a polyester base were almost identical. Therefore, the second data set has been excluded. The single data set presented here represents both the color film on a polyester base and the black and white film on acetate base. The only material that the two films had in common was the emulsion layer. The high and almost identical affinity that both the films exhibit for residual ethylene oxide suggests that it is mainly the gelatinous emulsion layer that interacts with ethylene oxide.

Besides the different materials, Table I also presents data for desorption of the fumigant from the empty chamber. Considering the size of the chamber and its large surface area, it would not be unexpected to find a small, but measurable concentration of ethylene oxide in the first few changes of air. However, it is surprising to note that the amount of ethylene oxide dislodged in the presence of 1.4 Kg of leather is even less than that observed for the empty chamber. When the data for each air-change for individual materials is corrected for the ethylene oxide given off by the empty chamber, the leather would appear to have actually absorbed some ethylene oxide. This fact suggests that leather probably interacts chemically with ethylene oxide. This comment is not expressed without reservation since we have not observed any direct and convincing proof for this deduction, which, however, does appear logical. These data suggest the need for further work to clarify this issue. However, such work was beyond the scope our immediate objective.

The data from Table I were corrected for the ethylene oxide given off by the empty chamber. The corrected data are presented in Figure 2. The book paper studied here is a commercial acidic alum-rosin-sized chemical wood pulp paper that we considered to be representative of today's acid-sized fine paper. Evidently, it does retain residual ethylene oxide to a relatively high enough extent to suggest the use of caution and adequate aeration if such paper is fumigated with ethylene oxide. Newsprint shows an even higher retention, which is exceeded by wood, probably because of its smaller porosity. The vinyl records, with an appreciably smaller surface area exposed to the fumigant, show a much smaller retention than the fine book paper. However, they need just as many air-changes to reduce the level of the ethylene oxide concentration to an acceptable level.

Figures 3 and 4 show the data obtained from the second set of experiments in which the fumigated materials were subjected to a constant vacuum and the ethylene oxide concentration measured at vacuum exhaust. In these experiments too, the data for the two photographic films overlapped so closely that one set of data is presented to represent the two films. The same order for increasing affinity for residual ethylene oxide is displayed here as observed in the experimental approach in which the near-equilibrium concentration in successive air-changes was measured, namely, leather < vinyl records ≈ book paper < newsprint < wood < photographic film. In general, paper does not pose much of a problem.

Some library books studied as a part of this work, but not reported here, lost the residual gas even more easily than the Springhill offset paper, for which the ethylene oxide concentration dropped under 1 ppm after 5 air-changes. On the other hand, the ethylene oxide concentration over pine scraps was still over 1 ppm after 23 air changes, and it was 38 ppm over photographic film after 25 air-changes (Table I).

This work demonstrates that offgassing of ethylene oxide by library materials is a reality. Vigilance needs to be exercised by confining fumigated materials to a restricted, but well-ventilated area where the ethylene oxide concentration can be monitored. The fumigated materials should be added to the collections only after the ethylene oxide concentration is decisively under 1 ppm. The data presented here offer a comparison of the relative capacity of different library materials to offgas residual ethylene oxide. However, it needs to be noted that no attempt was made here to facilitate the desorption of ethylene oxide. The introduction of moisture into the chamber or raising the temperature of the air would have accelerated the rate of desorption of ethylene oxide. The optimization of this process was beyond the scope of this study.

Acknowledgment

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Table 1.
Effect of Successive Air changes on Residual Ethylene Oxide Concentration (ppm) over Fumigated Materials

. Fumigation mixture: Carboxide (10% ethylene oxide in carbon dioxide)
. Volume of chamber: 33 Liters
. Mass of material: 1.4 Kg
. Carboxide pressure: 650 Torr
. Fumigation period: 24 Hours
. Evacuation conditions: 30 Minutes at 5 Torr
. Aeration conditions: 20 Hours at 650 Torr

Air Changes	Control: empty chamber	Leather scraps	Wood pulp	Newsprint Paper	Pine Wood	Motion picture film	Vinyl audio records
1	21.0	13.0	1000	980	920	1000	180
2	8.5	.60	255	370	415	1000	35
3	0.44	---	105	180	280	780	---
4	---	---	17.3	110	210	570	---
5	---	---	8.7	56	113	380	---
6	---	---	6.1	26	65	---	7.5
7	---	---	4.9	17.7	---	---	---
8	---	---	1.9	10.2	43	---	---
9	---	---	---	7.3	41	245	2.8
10	---	---	---	6.0	37	---	---
11	---	---	---	5.1	---	---	---
12	---	---	---	2.9	31	---	---
13	---	---	---	2.0	16	87	---
15	---	---	---	---	---	66	---
18	---	---	---	---	---	57	---
25	---	---	---	---	---	38	---

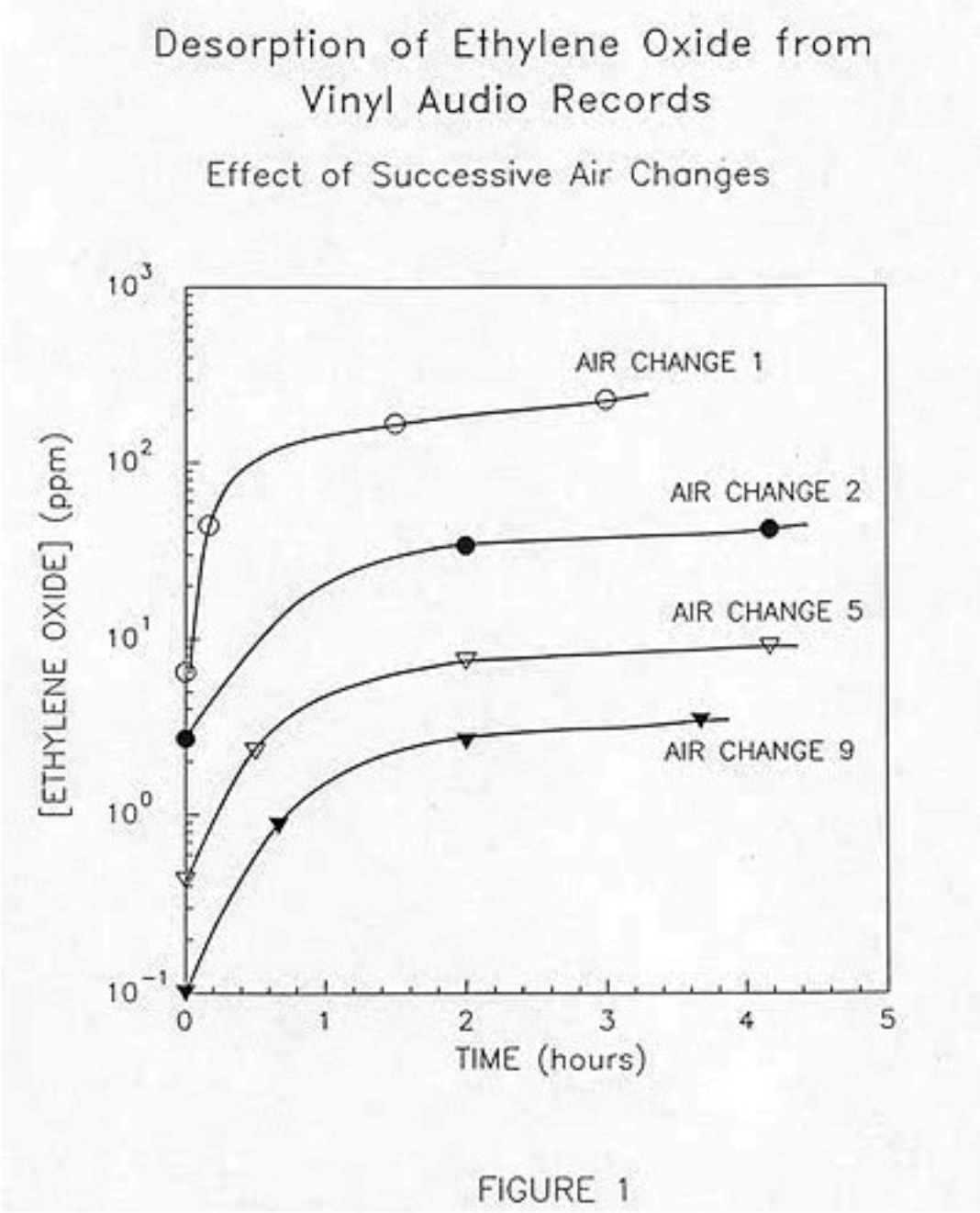
Desorption of Ethylene Oxide from
Vinyl Audio Records
Effect of Successive Air Changes
[ETHYLENE OXIDE] (ppm)
10^3
10^2
10^1
10^0
10^{-1}
AIR CHANGE 1
AIR CHANGE 2
AIR CHANGE 5
AIR CHANGE 9
0
1
2
3
4
5
TIME (hours)

FIGURE 1

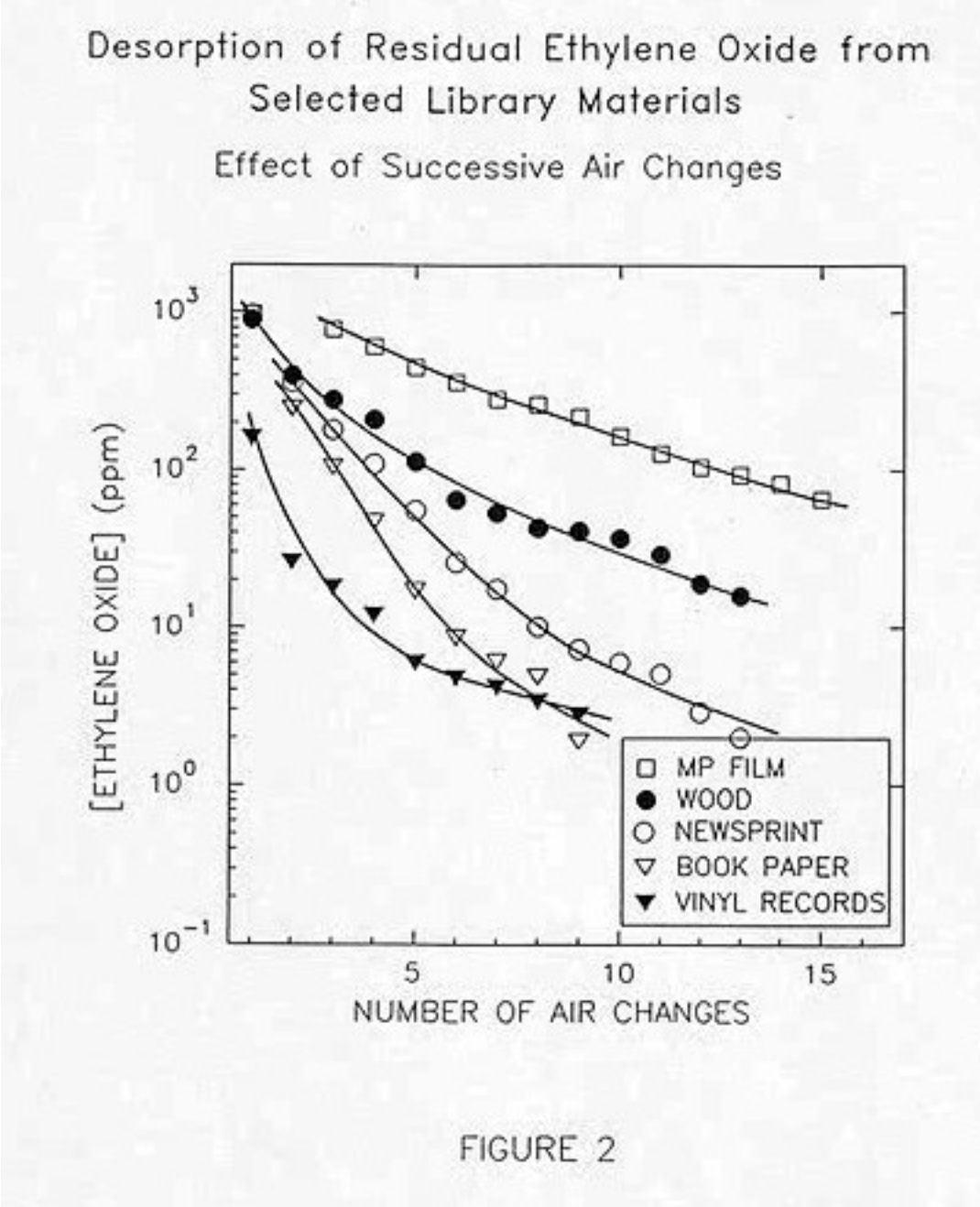
Desorption of Residual Ethylene Oxide from Selected Library Materials
Effect of Successive Air Changes
[ETHYLENE OXIDE] (ppm)
10^3
10^2
10^1
10^0
10^{-1}
5
10
15
NUMBER OF AIR CHANGES
MP FILM
WOOD
NEWSPRINT
BOOK PAPER
VINYL RECORDS

FIGURE 2

Desorption of Ethylene Oxide under Vacuum

Paper, Wood and Leather

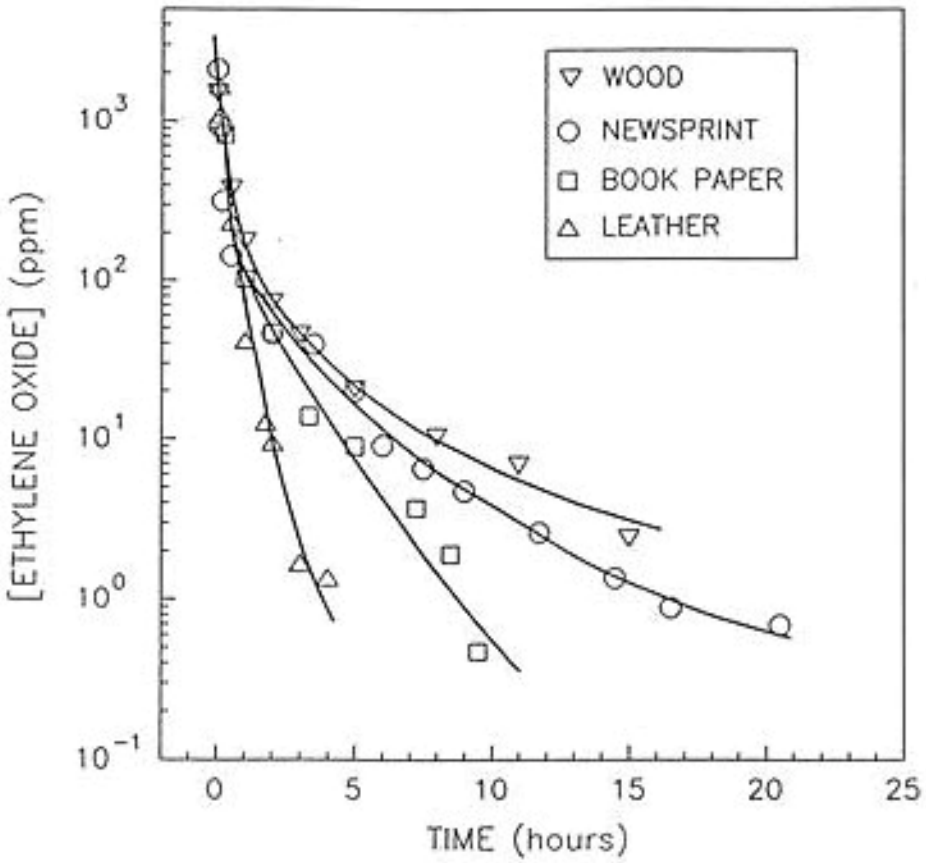

FIGURE 3

Desorption of Ethylene Oxide under Vacuum

Photographic Film and Vinyl Audio Records

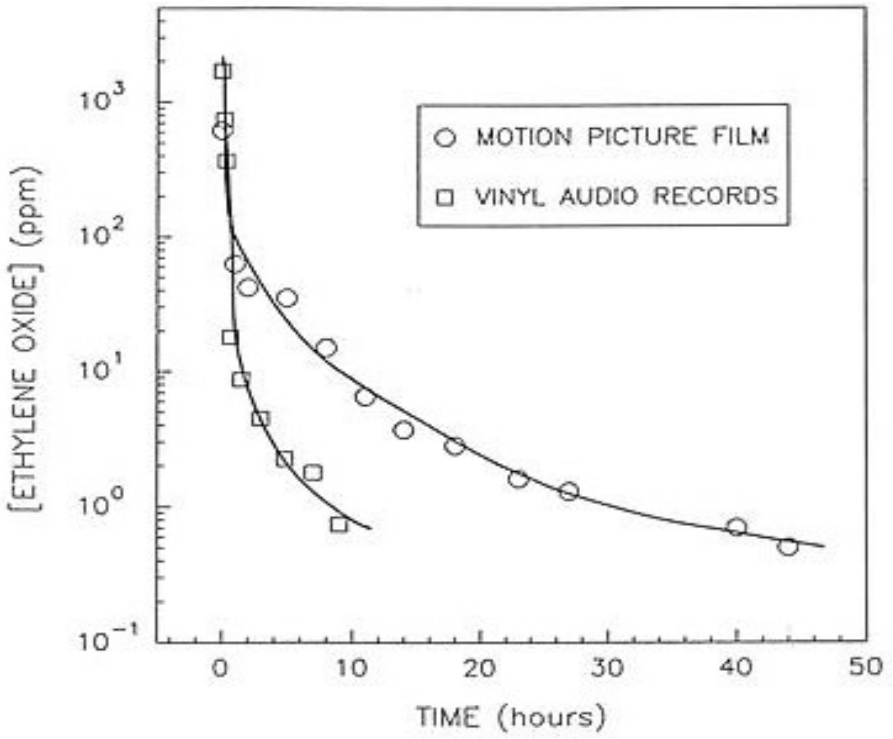

FIGURE 4