Bull. Environm. Contam. Toxicol. 20, 418-422 (1978)

A Water-extractable Toxic Compound In Vinyl Upholstery Fabric

V. D. Ahrens[1], J. D. Henion[2], G. A. Maylin[2], L. Leibovitz[3], L. E. St. John, Jr.[4], and D. J. Lisk[4]

[1]College of Home Economics, University of Delaware, Newark, Del. 19711,
[2]Veterinary Diagnostic Laboratory, [3]Department of Avian and Aquatic Animal Medicine,
[4]Pesticide Residue Laboratory, Department of Food Science,
Cornell University, Ithaca, N.Y. 14853

INTRODUCTION

Commercial plastics typically contain many additives which impart specific properties to the finished material. These may include plasticizers, stabilizing agents, fillers, colorants, antistatic agents, flame retardants and many others. A number of studies have been conducted showing the release of plasticizers and other additives from plastics into contacting biological solutions and food products and such studies have been reviewed (AUTIAN, 1975). Recently studies have shown the release of the flame retardant, tris (2,3-dibromopropyl) phosphate from polyester sleepwear into water and its high toxicity to goldfish (GUTENMANN and LISK, 1975; MAYLIN et al., 1977). In the work reported, release of a compound from vinyl (polyvinyl chloride) automotive upholstery fabric highly toxic to goldfish has been found and identified.

EXPERIMENTAL

Eleven vinyl and several other viscose or nylon automotive upholstery fabrics were obtained locally. All of the vinyl materials had a calendered finish and a backing material consisting of cotton or cotton/polyester bonded to the vinyl without adhesives (PENN, 1971). The viscose and nylon fabrics had no backing material. Each material was cut into pieces 9 x 15 inches in size. A 7 x 15 inch area of these pieces was immersed in 20 liters of well water (electrical conductivity, 290 micromhos/cm, temperature 20° C) contained in a glass fish tank. Six goldfish (Carassius auratus), about 3 inches long, were placed in the tank and their activity and behavior were observed during 24 hours of exposure. Analysis of water extracts of the fabrics for possible released additives was conducted using gas chromatography with a flame ionization and a flame photometric detector in the specific phosphorus mode. Pieces of the fabrics 4 x 9 inches in size were each shaken with 500 ml of the well water for 24 hours. Fifty ml of the water was shaken with 10 ml of benzene. The benzene was concentrated to 0.1 ml and analyzed. The gas chromatograph was a Tracor Model MT 220. The column was glass, 3 feet long and containing 5% FFAP on 80 to 100 mesh Gas Chrom Q. Column Temperatures of 205 and 230° C were employed.

0007-4861/78/0020-0418 $01.00

Electron impact (EI) mass spectra were obtained using a Model 1015 Finnigan quadrapole mass spectrometer operating at an ionizing energy of 70 eV and an emission current of 100 microamperes. This instrument was interfaced to a Systems Industries Model 150 data system which controlled the mass spectrometer in the full scan mode. The above benzene equilibrates of the water extracts of the materials were evaporated to dryness. The residue was then dissolved in 0.1 ml of ethyl acetate and 1 microliter of the solution was injected into a gas chromatographic column prior to mass spectrometric analysis. The column was glass, 3 feet long and contained 3% OV-101 on 80 to 100 mesh Gas Chrom Q. The temperature of the column and injector were, respectively, 210 and 280° C.

RESULTS AND DISCUSSION

Only an expanded vinyl with a cotton polyester backing used as Ford car seat cover upholstery fabric resulted in the death of fish, all succumbing within 24 hours. Death was preceded in turn, by hyperactivity, disoriented swimming, sluggishness, aimless drifting and often a peculiar desire of the fish to maintain a vertical position in the water with head down and tail up. This Ford fabric was removed from the fish tank, rinsed and placed in a second tank containing fresh water and fish and left 24 hours. At the end of this period the fish were still alive but showed the above described toxic symptoms. They were then removed and examined histopathologically.

Samples of the Ford fabric were equilibrated with the well water for 24 hours and the water was extracted with benzene and analyzed using gas chromatography employing both flame ionization and the specific phosphorus (flame photometric) detectors as described (see Experimental Section). The gas chromatogram showed one major peak by either detection mode which eluted symmetrically with retention times of 32.4 and 12.4 minutes at column temperatures of 205 and 230° C. Peak response by equivalent sample injections was much greater using the flame photometric as compared to the flame ionization detector thereby indicating that the compound may have contained phosphorus.

The above benzene extract representing the Ford vinyl fabric was evaporated, the residue dissolved in ethyl acetate and this solution analyzed using the gas chromatograph-mass spectrometer with the operating parameters described earlier. The gas chromatogram showed a single major peak eluting at 8.5 minutes. The EI mass spectrum of it (see Figure 1) as obtained was subjected to the probability based matching library search (PESYNA et al., 1976) via direct computer access to an IBM 370-168 computer. The best matching spectrum reported was that of triphenyl phosphate. A reference spectrum of this material (STENHAGEN et al., 1974) verified this assignment and a mass spectrum of authentic triphenyl phosphate (also having a retention time, 8.5 min) obtained under identical instrumental conditions confirmed the major component of the aqueous extract of the Ford fabric as triphenyl phosphate.

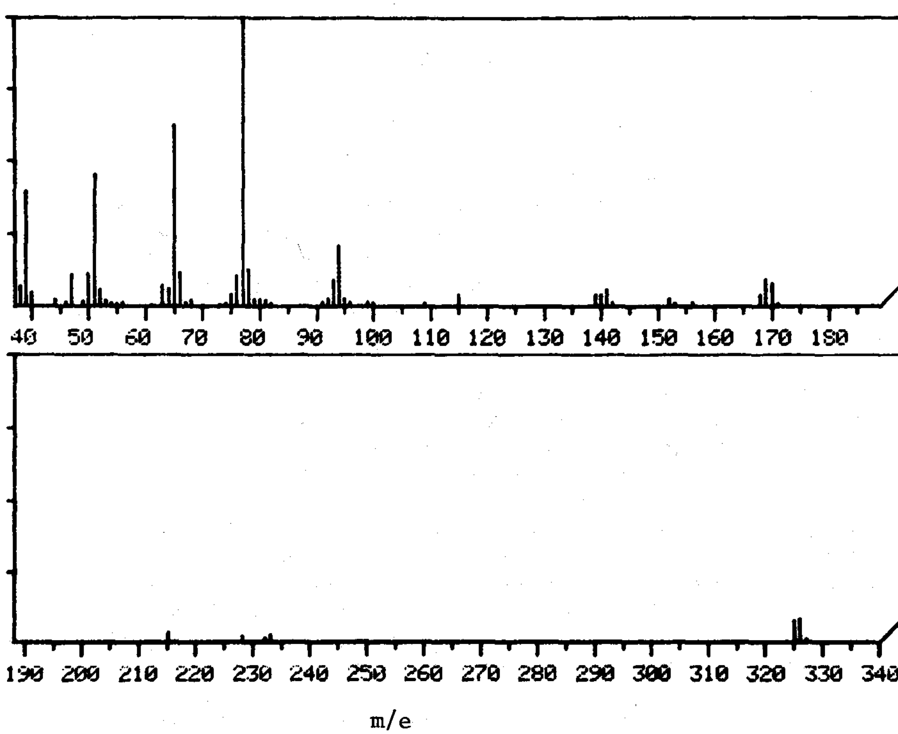

Figure 1. Mass spectrum of aqueous extract of vinyl upholstering fabric (Code No. 1).

Triphenyl phosphate is listed as a flame retardant plasticizer used in vinyl products (ANONYMOUS, 1974; 1975-1976). The toxicity of pure triphenyl phosphate to goldfish was observed. Four ml of acetone containing 20 mg of the compound was dissolved in 20 liters of well water (1 ppm) in a tank containing 6 goldfish. The fish showed the same sequence of toxic symptoms (including the vertical positioning) as when the Ford fabric was immersed in their water. All fish were dead within 8 hours. At concentrations of 3 and 5 ppm of the compound all fish died within five hours and 1 hour, respectively. Fish held as controls in 20 liters of water containing 4 ml of acetone for 96 hours showed no toxic symptoms.

Gold fish that were exposed to either the Ford vinyl fabric or triphenylphosphate, showed histopathologic lesions. Unexposed goldfish maintained as experimental controls were free of neurologic signs and lesions. Histopathologic changes in affected fish were characterized by congestion, degeneration and hemorrhage from the smaller blood vessels, principally venules and capillaries. Such vascular pathology was most pronounced in the gills, where the capillaries of the gill lamellae were dilated and frequently ruptured. Free blood escaped from the ruptured lamellar capillaries, through the broken epithelial covering, into the peribranchial spaces. Swollen edematous lamellae and globate-clavate dilations of the lamellae were also present. The lumina of the venules of the gill filaments and arches were frequently dilated and congested with blood elements and free hemoglobin (intravascular hemolysis). Similar but less pronounced congestion of the smaller blood vessels were noted in the brain, spinal cord, pseudobranchs and kidneys.

The fish showed some sluggishness within 2 hours after either of two other expanded vinyl fabrics (labelled Naugahyde") were immersed in their water but the fish did not die or show other toxic symptoms during 24 hours of exposure. Gas chromatographic analysis of the water equilibrated with these latter two fabrics revealed no evidence of phosphorus-containing compounds. No toxic symptoms were observed in fish exposed to any of the other fabrics.

Triphenyl phosphate is incorporated in many other plastic products including photographic film, phonograph records, vacuum cleaner parts, housings for clocks and applicances, parts for Christmas tree lighting sets, cellulosic coatings, coatings for flash bulbs and sometimes as a component of shellac. Whether applications of triphenyl phosphate to such products, especially those which are heated (lights, flash bulbs, vinyl upholstery fabric in vehicles in hot weather) and from which the compound may vaporize, would constitute a hazard to users requires further investigation.

SUMMARY

A compound, highly toxic to goldfish, was found to be released from a vinyl (polyvinyl chloride) automotive upholstery fabric when the material was immersed in their water. The compound, a flame retardant used in such material, was identified by specific detector gas chromatography and mass spectrometry as triphenyl phosphate. Fish exposed to the immersed fabric or pure triphenyl phosphate showed neurologic intoxication and extensive histopathologic lesions.

REFERENCES

ANONYMOUS: J. Amer. Assoc. Textile Chemists and Colorists 6, 401 (1974).

ANONYMOUS: Modern Plastics Encyclopedia 1975-1976. Vol. 52. McGraw-Hill Inc. New York, New York. page 665.

AUTIAN, J.: "Toxicology of Plastics", Chapter 24, pages 604-626 in Toxicology - The Basic Science Of Poisons. Eds., Louis J. Casarett and John Doull. Macmillan Publishing Co., Inc., New York, 1975.

GUTENMANN, W. H. and D. J. LISK: Bull. Environ. Contam. and Tox. 14, 61 (1975).

MAYLIN, G. A., J. D. HENION, L. HICKS, L. LEIBOVITZ, V. D. AHRENS, M. GILBERT and D. J. LISK: Bull. Environ. Contam. and Tox. 17, 499 (1977).

PENN, W. S.: PVC Technology. 3rd. ed. Wiley Interscience, London pp. 431-432 (1971).

PESYNA, A. G. M., R. VENKATARAGHAVEN, H. E. DAYRINGER and F. W. MCLAFFERTY: Anal. Chem. 48, 1362 (1976).

STENHAGEN, E., S. ABRAHAMSSON and F. W. MCLAFFERTY (Editors): Registry Of Mass Spectral Data 3 (1974). John Wiley & Sons, New York. Spectrum No. 2035-4.