

Pyrolytic Evaporation of a Plasticizer from Polyvinyl Chloride Meat Wrapping Film

by

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Recent interest in the environmental and health effects of plasticizers from polyvinyl chloride (PVC) formulations has centered around the reports of STALLING *et al* (1973) and JAEGER *et al* (1973, 1972). In these reports, tissues from fish and humans have been found to contain the plasticizer, di-2-ethylhexyl phthalate (DEHP¹). In the case of human tissue, the contamination presumably resulted from the administration of blood which was stored in PVC plastic. In another report (JAEGER, 1971), another plasticizer, di-2-ethylhexyl adipate (DEHA¹) was found to be extracted by human blood from PVC tubing. In still other reports in the popular press, plasticizers from PVC have been implicated in the "new car smell". However, with the exception of unpublished work currently in progress, little information is available to demonstrate the safety or hazard of PVC plasticizers which may contaminate the internal or external environment.

An unpublished report (VANDERVORT, 1971) from the Bureau of Occupational Safety and Health (NIOSH-USPHS) has concerned itself with the PVC film used to wrap meat. This work which is ongoing was begun as a result of workers' complaints of lung, throat and eye irritation during the heat cutting and sealing processes used to wrap meat. In the preliminary communication cited above, it was stated that chlorobutane, benzene, toluene, 1-chloro-2-ethyl hexane, 2-ethyl-1-hexanol, benzyl chloride and hydrogen chloride were released from the PVC film when it was heated to 200° C (app. 400° F).

The present report was conducted as a result of litigation involving a manufacturer of PVC plastic food wrap. In this case the worker's complaints were similar to those cited above. Additionally, the worker noted an oily material in the vicinity of the meat wrapping machinery. An investigation was begun to determine if the plasticizer in the PVC wrap was DEHA, and to determine if this material would evaporate from the film when it was heated.

¹ DEHP and DEHA are frequently and erroneously referred to as DOP and DOA.

MATERIALS AND METHODS

A sample of PVC food wrap was obtained from the Boston office of the manufacturer. A 10 g sample was inserted into a one inch glass tube of sufficient length to act as an air condenser. The glass tube had previously been cleaned with dichromate solution and rinsed with reagent grade acetone. Plugs of acetone-washed glass wool were tamped on either side of the PVC sample, and the entire assembly was placed in a tube furnace that had previously been heated to 400° F. Air from a compressed air tank was passed down the tube, and allowed to escape on the other side of the furnace. The material was heated for 1.5 hr. at 275-350° F. During this time, a brown oily liquid was observed to collect in the condenser. At the same time, an acrid gas was released (presumed to be HCl).

The oily liquid was collected in acetone by careful washing of the distal end of the glass tube-air condenser. No attempt was made to quantify the volume released from the 10 g sample of PVC film nor were attempts made to recover more volatile materials such as reported by VANDERVORT (1971).

The recovered acetone soluble material was analyzed in a Varian 1700 gas chromatograph (GC) equipped with a flame ionization detector. A 5 ft. column (stainless steel, 1/8 inch) packed with 5% SE-30 on Gas Chrom Q (80-100 mesh) was employed. Nitrogen was the carrier gas and the oven temperature was 250° C.

An acetone extract of the PVC film was made. The manufacturer confirmed the plasticizer to be DEHA. Samples of the acetone extract of the film and the pyrolytically evaporated material were submitted for computerized, combined gas chromatography, mass spectrometry (GC-MS).

RESULTS AND DISCUSSION

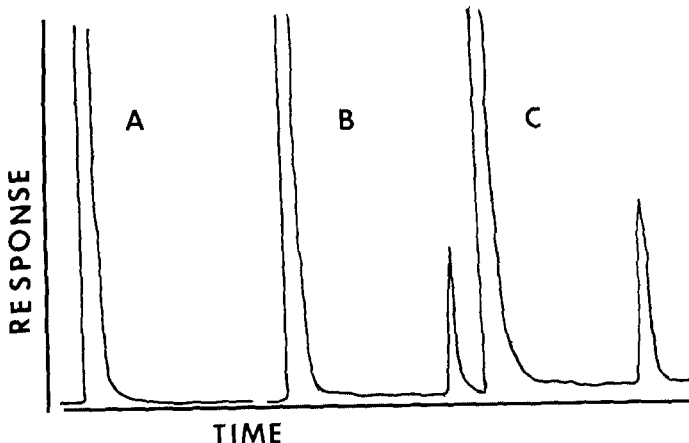


FIGURE ONE

In figure one above, the results of the 3 GC determinations are shown: A represents acetone alone; B represents the acetone extract of the PVC film; C represents the GC pattern of the material recovered from the pyrolytic distillation of the PVC film. Since the manufacturer stated that the plasticizer shown by B is DEHA, and the retention time of B and C are similar, the data suggests that DEHA does, in fact, pyrolytically evaporate from PVC food wrap.

To confirm the supposition of identity, the material from C was analyzed by GC-MS. The data is shown in table one. The information is derived from computer analysis of the MS output.

The spectrum of relative intensity for each m/e value can be read as follows; m/e is represented by the arithmetic sum of the value given at the top of the column plus the value shown at the left of the row. The intensity corresponds to the value shown at the intersection of the row and column for each m/e value. The spectrum shown below is consistent with the published spectra of DEHA. The GC retention time was also consistent. The characteristic masses are m/e of 129 (intensity=99), 147 (17), and 112 (24). The species at m/e 129 is the protonated anhydride of adipic acid.

TABLE ONE
Mass Spectrum

| | 20 | 34 | 48 | 62 | 76 | 90 | 104 | 118 | 132 | 146 | 160 | 174 | 188 | 202 |
|----|----|----|----|----|----|----|-----------|-----------|-----|-----------|-----|-----|-----|-----|
| 0 | | 0 | 0 | 0 | 0 | | 0 | 0 | 0 | 2 | 1 | | 0 | |
| 1 | | 0 | 0 | 1 | 3 | 2 | 1 | 1 | 2 | <u>17</u> | 0 | 0 | 0 | 0 |
| 2 | | 1 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 2 | | 0 | | 0 |
| 3 | | | 1 | 1 | 1 | 1 | 0 | 1 | 4 | 2 | 0 | 1 | 1 | 1 |
| 4 | | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 1 | 1 | | 0 | 0 | 0 |
| 5 | | 4 | 1 | 3 | 2 | 1 | 1 | 0 | 1 | 0 | 1 | 1 | 1 | 8 |
| 6 | | | 2 | 2 | 4 | 2 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 2 |
| 7 | | 16 | 26 | 9 | 21 | 2 | 21 | 0 | 0 | 0 | 0 | 0 | 1 | 2 |
| 8 | | 5 | 13 | 33 | 11 | 1 | <u>24</u> | 0 | 0 | 0 | 1 | | 0 | 0 |
| 9 | | 20 | 44 | 37 | 3 | 1 | <u>14</u> | 1 | 1 | 0 | 0 | 0 | 3 | 1 |
| 10 | 1 | 7 | 2 | 2 | 1 | 6 | 1 | 4 | 3 | 0 | 0 | 0 | 0 | 1 |
| 11 | 1 | 1 | 3 | 13 | 6 | 8 | 1 | <u>99</u> | 1 | 1 | | 0 | 1 | 0 |
| 12 | | | 1 | 1 | 0 | 3 | 0 | 9 | 0 | 1 | 0 | 0 | 0 | 0 |
| 13 | | 0 | 1 | 1 | 0 | 1 | 1 | 2 | 0 | 0 | | 0 | 0 | |

This demonstration of DEHA release from PVC film under conditions which approximate use should be carefully considered. The previous report by VANDERVORT (1971) in conjunction with the observations reported above suggest that additional investigations should be undertaken². There exists a possibility for

²Dr. Vandervort, in a personal communication, has confirmed the presence of DEHA as a pyrolysis product from PVC film. A more complete report including a safety evaluation of the material is currently being prepared by NIOSH.

interaction between the plasticizer and other decomposition products. Such a possibility may compound the slight hazard associated with the irritation observed by workers who must use the material. Certainly long term investigations under conditions of use are indicated. A complete evaluation of pulmonary function in workers with a predisposition to respiratory complications would be a minimum prerequisite.

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