PVC only
K-25950-(100) FV

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K-25950-(100).

Thermal degradation products of polyvinyl chloride (PVC) food-wrap films were studied under simulated supermarket conditions using a commercial wrapping machine with either a hot wire or a cool rod cutting device. A sampling hood was constructed around the wire/rod to confine and allow collection of thermal degradation products produced. Compounds analyzed and normal concentration ranges found included hydrogen chloride (1-10 μg per cut), plasticizer (1-50 μg per cut), benzene and toluene (each <5-20 ng per cut), acrolein (25-150 ng per cut), and carbon monoxide (2-4 μg per cut) using the hot wire. Room air samples, collected during hot-wire cutting without the sampling hood, had <0.25 ppm hydrogen chloride. Using the cool-rod cutting device hydrogen chloride, benzene, and toluene were not detected. Plasticizer was detected (25-86 μg per cut) using the cool rod.

# Thermal degradation products from PVC film in food-wrapping operations*

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## introduction

Clear plasticized polyvinyl chloride (PVC) film is used extensively for packaging food products. The film is thermally cut for each package from a long roll using either a 0.508-mm (0.020-inch) diameter hot wire maintained at 200-350 °C or a 9.53-mm (0.375-inch) diameter cool rod maintained at 135 °C. The portion of the film in contact with the wire or rod during cutting may be subject to thermal degradation and/or volatilization of film components.

The thermal degradation products of unplasticized PVC have been thoroughly studied.[1] Between 240 and 310 °C, PVC undergoes nearly quantitative dehydrochlorination making hydrogen chloride (HCl) the major low-temperature thermal degradation product. Above 350 °C, oxidative reactions occur and carbon monoxide and carbon dioxide are the major products formed. Methane, benzene, and toluene are the major hydrocarbons produced, benzene in the same temperature range as HCl, and other hydrocarbons at somewhat higher temperatures.

PVC films contain 20-30% plasticizer, those most commonly used being di-(2-ethylhexyl) adipate (DOA), di-(2-ethylhexyl) phthalate (DOP), and acetal tributyl citrate (ATBC). These plasticizers generally have boiling points in excess of 300 °C, but they are liquids having small but significant vapor pressures at room temperature, and would be expected to volatilize to some extent at both the hot wire and cool rod temperatures.

Vandervort[2] studied the 200-230 °C thermal degradation products of PVC wrapping films using a micro furnace with ceramic sample boats and quartz combustion tubes. The major products were found to be benzene, toluene, chlorobutene, 1-chloro-2-ethyl hexane, 2-ethyl-1-hexanol, benzyl chloride, and hydrogen chloride. This experimental procedure discriminated in favor of benzyl chloride as it could decompose in the presence of hot metal, *e.g.* a hot cutting wire. In this same study the author found trace amounts of hydrogen chloride (well below the 5 ppm TLV[3]), but no detectable benzyl chloride, in field samples taken during the actual film cutting process.

In a study conducted at the Liberty Mutual Research Center[4] a hot wire film cutting device was operated in a sealed chamber while concentrations of hydrogen chloride, plasticizer, and total particulates were measured at different wire temperatures and at different heights above the wire. Hydrogen chloride again was found to be well below the TLV, and plasticizer concentrations did not seem sufficient to present a health hazard. A correlation existed between plasticizer and particulate concentrations produced.

A Borden study[5] of supermarket breathing-zone HCl levels using both hot wire and cool rod devices showed less than 1.5 ppm HCl using the hot wire and less than 0.1 ppm HCl using the cool rod. Substitution of the cool rod for the hot wire virtually eliminated smoke production during the cutting process. The present study was undertaken to further identify and quantitate major fume components produced by PVC films under simulated supermarket conditions using both the hot wire and the cool rod.

## description of samples

Five PVC film samples were provided by Borden Chemical and were plasticized as indicated in Table I. Three samples of RMF-61HY were used during the course of the study.

Solvent extracts of each film were prepared and analyzed by gas chromatography in order to detect the presence of major film additives. In addition to the plasticizers listed in Table I, films CW-65 and PC-63 produced an additional chromatographic peak which was identified by mass spectrometry as tributyl aconitate. Tributyl aconitate may be an impurity in commercial acetyl tributyl citrate.

*This research was supported by Borden Chemical.

**TABLE I**
**PVC Film Samples Analyzed**

| Designation | Use | Plasticizer 1 | Plasticizer 2 | Thickness mm (inches) |
|---|---|---|---|---|
| RMF-61HY (Batch 1959, Batch 1746A, Batch 1588) | Meat Wrap | DOA | – | 0.0165 (0.00065) |
| VF-71 (5630) | Produce Wrap | DOA | – | 0.0152 (0.00060) |
| VF-71 (64020) | Produce Wrap | DOP | – | 0.0152 (0.00060) |
| CW-65 | Carcass Wrap | DOA | ATBC | 0.0203 (0.00080) |
| PC-63 | Carcass Wrap | DOA | ATBC | 0.0173 (0.00068) |

DOA – Di-(2-ethylhexyl) adipate
DOP – Di-(2-ethylhexyl) phthalate
ATBC – Acetal tributyl citrate

## description of sampling hood

Several devices to allow sampling of fumes from the film cutter were considered, including a box-type enclosure of the whole apparatus. A two-part sampling hood surrounding the wire was decided upon for two reasons. First, it reduces surface adsorption problems; and second, it allows collection of all the fumes produced rather than the greatly diluted sample which would be obtained in a box, or in the actual meat-wrapping room environment. A sketch of this stainless steel hood is shown in Figure 1, and photographs are shown in Figures 2 and 3. The bottom portion of the hood is fixed beneath the wire and has five 6.3-mm (1/4-inch) diameter sampling holes along its length which are connected to a 6.3-mm (1/4-inch) diameter tubing manifold. The top portion of the sampling hood can be moved vertically on its support rods. During operation, the film is rolled from the top of the roll and stretched smoothly under the top part of the sampling hood, which is then quickly brought down to obtain a clean cut and held down for 30-90 seconds while the approximately 250 cc cylindrical volume, formed by the two parts of the hood, is swept with air and the gas collected in an impinger, charcoal tube, or other sampling device.

Many volatile compounds are swept directly into the sampling device. However, compounds which are high boiling or tend to adsorb on surfaces condense in the system and the hood must be dismantled and washed with known volumes of solvent to obtain quantitative recovery.

During this study, an attempt was made to simulate the film cutting that occurs in a store using typical manual wrapping machines and experienced personnel. Accordingly, efforts were made to obtain cuts of the film which did not produce excessive smoke or char and to note when one or more excessively smoky cuts did occur in a series. The design of the sampling hood was such that the maintenance of some tension in the film while being cut

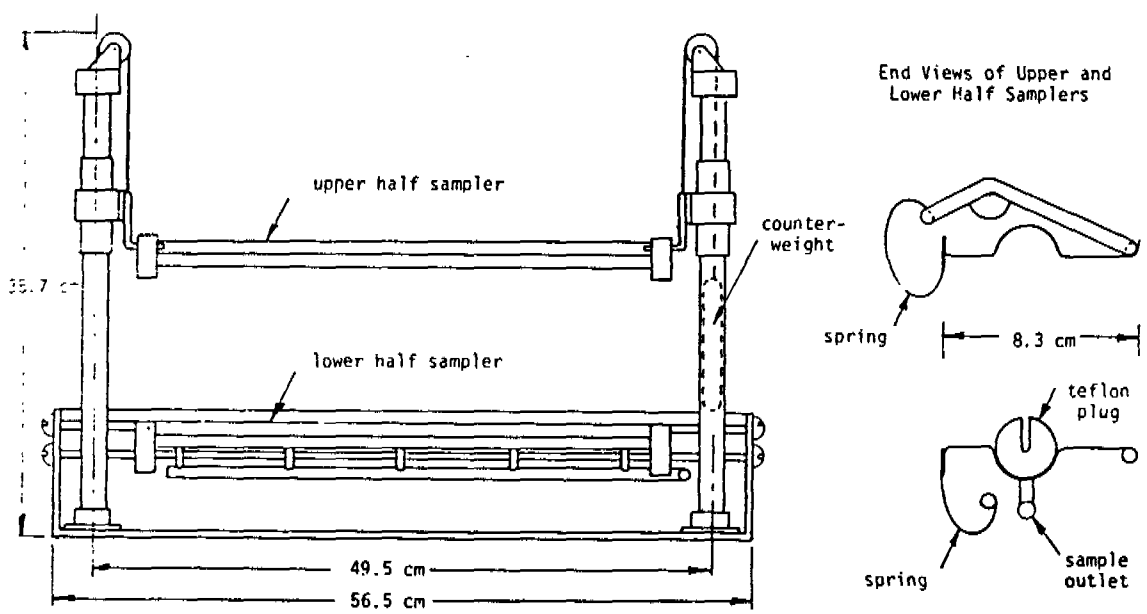


Figure 1 – Sketch of the sampling hood.

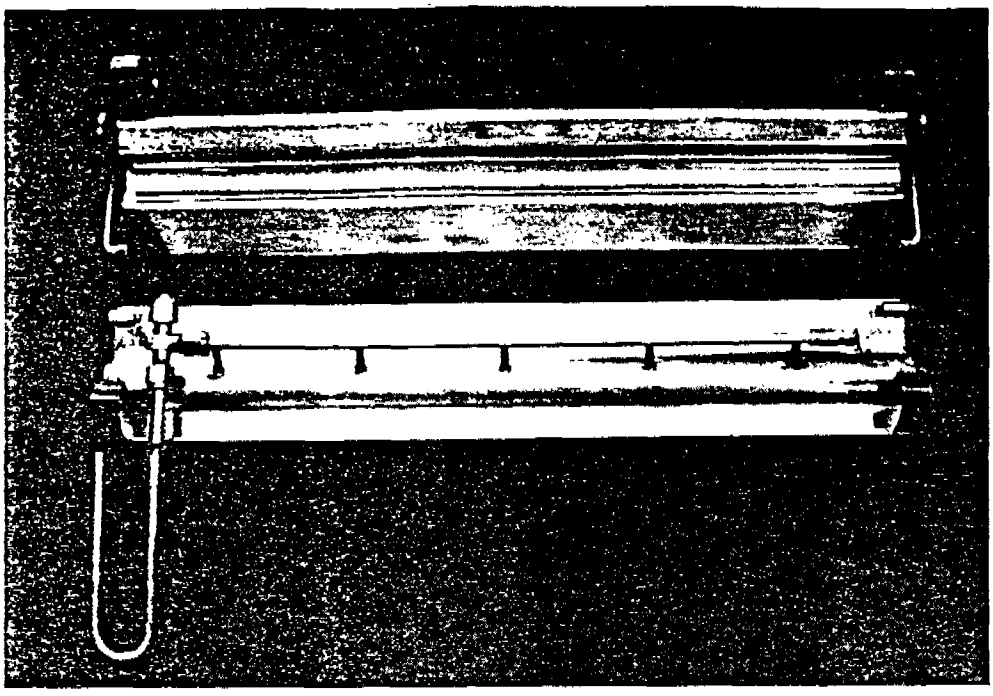

Figure 2 – Dismantled sampling hood, trap attached, showing sampling manifold.

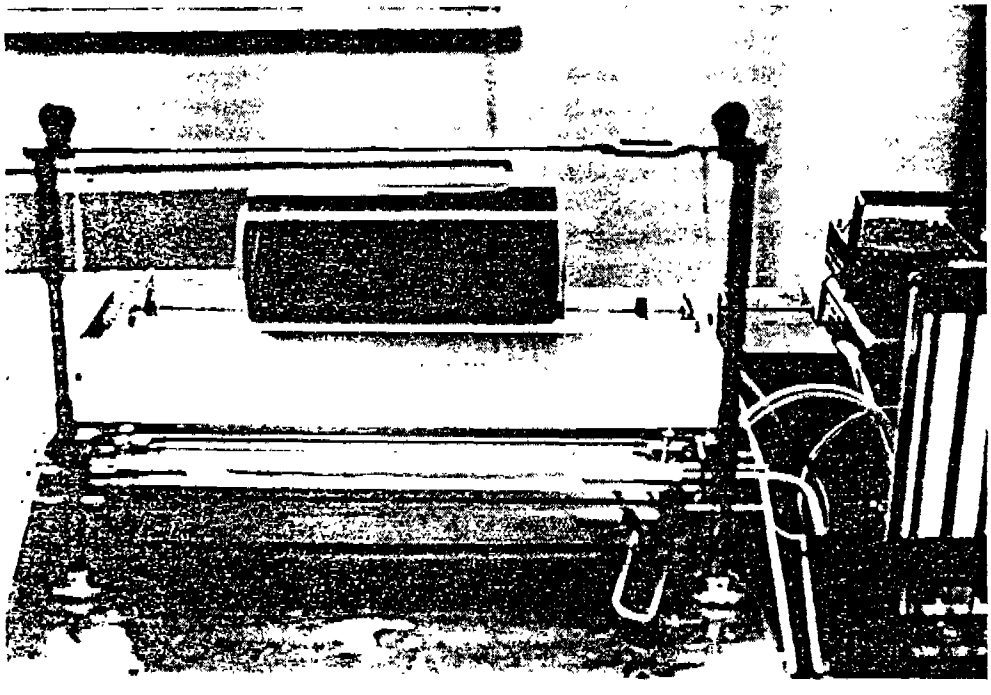

Figure 3 – Film cutting device with sampling hood (clamped in the closed position) and associated sampling equipment

depended on the film being sufficiently tacky. Two samples of film RMF-61HY, Batch Nos. 1959 and 1746A, had been stored in the laboratory for several years and had lost some of their ability to cling to the sampling hood surface. Thus the film would not retract from the hot wire following a cut resulting in abnormally smoky cuts and considerable char generation. Since our objective was to simulate actual supermarket film cutting conditions, a roll of RMF-61HY (Batch No. 1588) of more recent manufacture eventually was substituted. Even with this film, however, there were occasional smoky cuts. We are told that these excessively smoky cuts are not representative of the use of the film under ordinary conditions, but did not do a field study to verify this point.

The sampling hood described in the previous paragraphs was mounted directly on a Heat Sealing Equipment Manufacturing Company, Model No. 628, wrapping machine. The hot wire, which by necessity had become an integral part of the sampling hood, was wired directly to the wrapping machine with no change in the wiring circuits. The

hot-wire employed was the standard 0.508-mm (0.020-inch) diameter, 50.8-cm (20-inch) long unit supplied with the wrapping machine. The temperature of the hot wire was determined to be approximately 215 °C (420 °F). However, precise temperature control of this small-diameter wire is not achieved, and we are told there is a rather wide range of normal operating temperatures for the wire.[5] The cool rod employed was Model AT 1000 manufactured by Borden Chemical. This device is designed to operate at a temperature of 135 °C (275 °F). The temperature of the rod was determined to be within ± 10 °C (± 18 °F) of the stated temperature.

A Gast Manufacturing Corporation Model DOA-101 pump was used in all cases to draw air from the sampling hood through the sampling device. The sampling device was always attached directly to the hood's sampling manifold so that there was no possibility of sample loss or contamination in other units of the sampling train.

## methodology

### *hydrogen chloride*

An Orion model 94-17A chloride specific-ion electrode was used for HCl analysis. Samples were collected at 2 liters per minute in 15 mL collection reagent in single midget fritted bubblers. The collection reagent was 2M potassium nitrate and $3.13 \times 10^{-1}$ M lead nitrate which provided a solution of high ionic strength to overcome the ion activity dependence of the electrode and effectively removed any possible sulfide interference. The calibration curve is nonlinear at low concentrations making $\sim 1.75 \times 10^{-5}$ molar chloride ion the minimum level that can be quantitated with good precision.

Recovery of HCl gas from the sampling hood was established by comparing the response obtained when 0.5 mL of HCl gas was injected with a gas-tight syringe directly into absorbing reagent in a midget fritted bubbler, with the response obtained when 0.5 mL of HCl gas was injected into the closed sampling hood at the end opposite the sampling bubbler. The sampling hood was rinsed with a measured amount of surfactant-containing collection reagent which was analyzed separately in the recovery studies, but was combined with the bubbler solution for samples. In the first recovery test, 77% of the HCl was recovered. Of that 77%, 86% was on the sampling hood and 14% in the impinger. In the second test, the total recovery was 70.5%, with 74% and 26% on the sampling hood and in the impinger, respectively. The amount recovered on the sampling hood was somewhat dependent on the relative humidity at the time of analysis. A figure of 75% has been used for HCl results to correct for recovery efficiency.

The amount of hydrogen chloride generated per cut is small, so that a number of cuts were required to obtain a measurable electrode response. In order to minimize the amount of hydrogen chloride lost by volatilization from the sampling hood while it was opened preparing for a subsequent cut in a series, the following protocol was adopted: The wire was turned on for a 30-second preheat, the cut was made, the wire was turned off 15 seconds after making the cut, and sampling was continued with the hood closed for one minute after turning the wire off. Heating of the metal sampling hood on which the hydrogen chloride deposited was thus reduced by turning off the wire for the bulk of the sampling period.

### *plasticizer*

Plasticizers were analyzed by gas chromatography, on a column of 1% SE-30 maintained at an isothermal temperature of 220 °C, using a flame ionization detector. Standards were prepared by direct injection of microliter quantities of plasticizer into known volumes of ethyl alcohol.

Two attempts to collect DOA in a midget fritted bubbler, direct collection and heating the hood after a number of cuts to force DOA into the bubbler, were unsuccessful. Due to its high boiling point, most of the DOA condensed on the surface of the sampling hood. Plasticizer could be recovered efficiently by rinsing the sampling hood with a measured amount of ethyl alcohol. Recoveries of each plasticizer by this method were determined by placing 1 $\mu$L quantities of plasticizer on the wire, closing the hood, turning the wire on for a few seconds to volatilize the plasticizer, and rinsing the volatilized plasticizer off the sampling hood with ethyl alcohol. Average recoveries of the three plasticizers were 80% for DOA, 77% for DOP, and 71% for ATBC. These averages have been used to correct plasticizer results for recovery efficiency. Plasticizer not recovered could have been lost in the washing process or thermally degraded on the wire.

The quantity of plasticizer produced by hot-wire cutting of each of the film samples was determined by making a series of five or ten cuts with an air flow of 200 cc per minute through the sampling hood and then washing the hood with a total of 25 milliliters of ethyl alcohol to recover the condensed plasticizer. Hood blanks, obtained by washing the hood with 25 milliliters of ethyl alcohol prior to making a series of cuts, were often taken to insure the absence of contamination or sample carry-over. The 25-milliliter samples were concentrated to 1.0 milliliter prior to analysis. Five microliter injections were made onto the chromatographic column.

### *benzene and toluene*

Benzene and toluene were collected from 2-5 cuts of film in 5-mm (0.20-inch) ID, 23-cm (9.1-inch) stainless steel U-shaped traps packed with 60-80 mesh Tenax GC® and connected to the sampling manifold of the hood. The flow rate was 600 cc per minute and the total sampling time was less than 9 minutes due to the ~5.5 L breakthrough volume of the trap. These traps were preconditioned 6-8 hours at 280 °C with a 50 mL/minute prepurified nitrogen flow, and were fitted with Swagelok® nuts and back ferrules with silicon O-rings for seals. The trap contents were introduced onto the gas chromatograph column (20% Carbowax 20M via a 4-port valve while the trap was heated. At the end of 4.0-minute heating period, the valve was positioned to tak the trap off-line and the column was heated to 75 °C in on minute and then programmed at 7.5 °/minute to 180 °C Detection limits were 15 nanograms of benzene and 2 nanograms of toluene.

TABLE II
Hydrogen Chloride Produced During Hot Wire Cutting of PVC Films

| Film | | µg/cut HCl Mean | S | Range |
|---|---|---|---|---|
| RMF-61HY (Batch 1959) | Total Runs (13) | 29 | 30 | 3-81 |
| | Smoky Runs (5) | 59 | 27 | 15-81 |
| | Clean Runs (8) | 10 | 9 | 3-31 |
| RMF-61HY (Batch 1588) | Total Runs (6) | 4 | 3 | 1-9 |
| VF-71 (5630), VF-71 (64020), CW-65, PC-63 | Total Runs (8) | 3 | 3 | 1-6 |

A gaseous benzene plus toluene standard was injected onto two traps linked in series to determine that trap breakthrough volumes were not exceeded. Traps which had contained sample or standard were stripped a second time to insure that trapped components had been quantitatively removed. No measurable amount of material was ever found on the second trap. Pure HCl gas was injected with a standard onto a trap to establish that no new peaks resulted from reaction between HCl and Tenax-GC, nor were the trapping characteristics of the material modified. The recoveries of benzene and toluene from the sampling hood were determined to average 95% and 83% respectively. To obtain the recovery data, the same volume of a particular standard was either injected directly onto the Tenax-GC trap, or injected into the closed, preheated sampling hood and collected at the opposite end of the hood, using the same collection conditions previously described.

*acrolein*

Acrolein was analyzed by the colorimetric method of Cohen and Altshuller.[6] The sample was collected in 15-20 milliliters of 4-hexyl-resorcinol absorbing reagent in a midget fritted bubbler attached to the sampling manifold. During analysis of the film samples, 30 cuts were made and the sampling hood was held together manually for 30 seconds between cuts with a 2 L/minute air flow through it. Total sampling time was approximately 25 minutes. The intensity of the color formed was read at 605 nanometers. The detection limit was 0.7 micrograms or approximately 25 ng/cut for a 30-cut sample. Calibration standards were prepared by injecting known amounts of a stock solution of acrolein in ethanol directly into the color-forming reagent. The only interferences reported are butadiene and pentadiene in large excess (1000×). It is unlikely that interfering quantities of these compounds would be formed from degradation of the plasticized PVC films, but the reported concentrations of acrolein may be regarded as "*less than or equal to*" values because the relative quantities of butadiene and pentadiene were not determined.

The recovery of acrolein from the sampling hood was approximately 94%, the value used in correcting acrolein concentrations. During some recovery experiments, the hood was coated with a few microliters of DOA to insure that plasticizer did not cause acrolein to be lost by deposition on the hood surface.

*carbon monoxide*

Available analytical methods did not have the sensitivity necessary to analyze carbon monoxide (CO) directly. Several gas chromatographic columns will separate CO from air, but the only available chromatographic detector was of the thermal conductivity type, which has a detection limit of approximately 200 parts per million. Because of this problem, a semi-quantitative method involving use of either MSA no. 91229 or Dräger 10/b detector tubes was employed. By attaching the tube to the sampling hood and continuously drawing air at 400 cc per minute from the hood through the tube, the response produced during hot-wire cutting can be compared with the response produced by injecting standards of CO into the sampling hood.

The CO detector tubes can be used in either direction, so a measured amount of standard can be injected into the sampling hood and collected on the opposite end of the tube from the sample. In this way, each tube can be calibrated, an important feature since the tubes are being used in a manner for which they were not intended. All results reported have been calculated using standards injected onto the detector tube through the sampling hood.

*other hydrocarbons*

Other compounds were collected on Tenax-GC or Porapak® P traps as described for benzene and toluene. Since these compounds were generally present in lesser quantities, 15 cuts of film were sampled onto the trap at 1 liter per minute with a 1 minute per cut sampling time. Porapak P retains low-boiling compounds more efficiently than Tenax-GC, and was used where the breakthrough volume might have been exceeded on Tenax-GC during the approximately 20 minutes it took to sample 15 cuts.

TABLE III
Plasticizer Produced During Hot Wire Cutting of PVC Films

| Film | | µg/cut Plasticizer Mean | S | Range |
|---|---|---|---|---|
| RMF-61HY (Batch 1959) | Total Runs (3) | 225 | 111 | 100-313 |
| RMF-61HY (Batch 1746A) | Total Runs (4) | 137 | 75 | 45-200 |
| RMF-61HY (Batch 1588) | Total Runs (9) | 36 | 44 | 3-118 |
| VF-71 (5630) | Total Runs (9) | 100 | 94 | 4-295 |
| | Smoky Runs (4) | 180 | 81 | 110-295 |
| | Clean Runs (5) | 37 | 37 | 4-95 |
| VF-71 (64020) | Total Runs (6) | 29 | 24 | 1-68 |
| CW-65 DOA | Total Runs (7) | 17 | 26 | 1-75 |
| CW-65 ATBC | Total Runs (7) | 13 | 22 | 1-62 |
| PC-63 DOA | Total Runs (6) | 27 | 52 | 1-[illegible] |
| PC-63 DOA | Clean Runs (5) | 6 | 7 | 1-[illegible] |
| PC-63 ATBC | Total Runs (6) | 20 | 39 | 1-[illegible] |
| PC-63 ATBC | Clean Runs (5) | 4 | 4 | 1-9 |

**TABLE IV**
**Benzene and Toluene Produced During Hot Wire Cutting of PVC Films**

| Film | | ng/cut Benzene Mean* | S* | Range | ng/cut Toluene Mean* | S* | Range |
|---|---|---|---|---|---|---|---|
| RMF-61HY (Batch 1746A) | Total Runs (5) | 1030 | 650 | 190-1660 | 240 | 175 | 42-470 |
| RMF-61HY (Batch 1588) | Total Runs (12) | >90 | 170 | 6->450 | <53 | 111 | <7-392 |
| | Clean Runs (10) | 19 | 20 | 6- 64 | <14 | 20 | <7- 68 |
| VF-71 (5630) | Total runs (5) | 18 | 18 | 9- 50 | < 7 | 3 | <7- 7 |
| VF-71 (64020) | Total Runs (6) | 45 | 39 | 17- 120 | <17 | 8 | <7- 24 |
| | Clean Runs (5) | 30 | 15 | 17- 50 | <15 | 8 | <7- 20 |
| CW-65 | Total Runs (8) | 37 | 49 | 7- 155 | < 9 | 4 | <7- 16 |
| | Clean Runs (7) | 20 | 12 | 17- 38 | < 8 | 3 | <7- 10 |
| PC-63 | Total Runs (3) | 1150 | 1990 | 3-3450 | <91 | 146 | <7-260 |
| | Clean Runs (2) | 7 | 5 | 3- 10 | < 7 | 1.5 | <7- 8 |

*Where > or < values are reported, means and standard deviations have been calculated using the figure given in the Range column.

Porapak P is less thermally stable than Tenax-GC, however, and was stripped at 200 °C.

Compounds collected from the film cutter could be stripped from a trap directly onto a Pye series 104 gas chromatograph interfaced using a membrane separator to an AEI MS30 mass spectrometer for identification. A smoky cut or a longer series of cuts was required to see compounds occurring at <50 ng per cut by mass spectrometry.

## results of hot wire cutting

All results reported from hot wire cutting have been corrected to 100% recovery of the compound from the sampling hood. Results have also been normalized to a film thickness of 0.0165 mm (0.00065 inch) and a film width of 33 cm (13 inches). In some cases a distinction has been made between smoky runs when char on the wire or other evidence of incomplete combustion was observed in one or more cuts in a series, and runs having only the clean cuts normally obtained.

### *hydrogen chloride*

HCl results are reported in Table II. Results on film RMF-61HY (Batch 1959) include trials with both excessively smoky and clean cuts as these were obtained with the several-year-old material and prior to development of some consistency of the cutting technique using the sampling hood. Remaining results represent normal cuts and yield hydrogen chloride values that generally fall into the range of 1-10 micrograms per cut.

### *plasticizer*

Plasticizer results are shown in Table III. Plasticizer values fall within a rather wide range of 1-100 micrograms per cut, with excursions up to 300 micrograms per cut when there were smoky cuts in the series.

### *benzene and toluene*

Benzene and toluene results are shown in Table IV. All results have been background corrected for the small amount of benzene or toluene occasionally found in the laboratory air, using a blank taken prior to each sample. Results for film RMF-61HY (Batch 1746A) are considerably higher than results for other films, as it was difficult to obtain clean cuts with this film. Runs where benzene exceeded 100 nanograms per cut included at least

**TABLE V**
**Acrolein Produced During Hot-Wire Cutting of PVC Films**

| Film | ng/cut Acrolein |
|---|---|
| RMF-61HY (Batch 1959) | 120 |
| VF-71 (5630) | 151 |
| VF-71 (64020) | 80 |
| CW-65 | 27 |
| PC-63 | 57 |

**TABLE VI**
**Carbon Monoxide Produced During Hot-Wire Cutting of PVC Films**

| Film | Run Number | µg/cut CO |
|---|---|---|
| RMF-61HY (Batch 1588) | 1* | 2 |
| | 2 | 1.5 |
| VF-71 (5630) | 1 | 2 |
| | 2 | 3 |
| VF-71 (64020) | 1 | 4 |
| | 2 | 1.5 |
| CW-65 | 1 | 2 |
| | 2 | 1.5 |
| PC-63 | 1 | 2 |
| | 2 | 3 |

*In each case, CO Run no. 1 was performed using the MSA tube, and CO Run no. 2 was done using the Dräger tube.

**TABLE VII**
**Identified V latiles Collected on Porapak P Traps and Stripped onto a 3% OV-17 Column**

| Compound | RMF-61HY (Batch 1588) | | VF-71 (5630) | | VF-71 (64020) | |
|---|---|---|---|---|---|---|
| | Quality* (as Proportion of Benzene) | Concentration Range* ng/cut Clean Cuts - Smoky Cuts | Quality (as Proportion of Benzene) | Concentration Range ng/cut Clean Cuts - Smoky Cuts | Quantity (as Proportion of Benzene) | Concentration Range ng/cut Clean Cuts - Smoky Cuts |
| enzene | | 5 - 1000 | | 5 - 1000 | | 5 - 1000 |
| -Ethyl-1-hexene | ~2× Benzene | 10 - 2000 | ~2× Benzene | 10 - 2000 | ~2× Benzene | 10 - 2000 |
| oluene | ~2/3× Benzene | 3 - 700 | ~1/2× Benzene | 2 - 500 | Trace | |
| thylbenzene | ~1/5× Benzene | 1 - 200 | ~1/10× Benzene | <1 - 100 | ~1/5× Benzene | 1 - 200 |
| Styrene | ~1/3× Benzene | 2 - 350 | ~1/5× Benzene | 1 - 200 | ~1/5× Benzene | 1 - 200 |
| Propylbenzene | ~1/3× Benzene | 2 - 350 | ~1/5× Benzene | 1 - 200 | | |
| 2-Ethylhexanal** | | | ~2/5× Benzene | 2 - 400 | ~1/5× Benzene | 1 - 200 |
| Propenylbenzene** | ~1/8× Benzene | <1 - 125 | | | | |
| Indene** | ~1/8× Benzene | <1 - 125 | | | | |
| Naphthalene** | ~1/20× Benzene | ≪1 - 50 | ~1/20× Benzene | ≪1 - 50 | | |

*See text

**Unconfirmed identifications.

one excessively smoky cut. For a series of clean cuts, benzene falls in the range of 5-20 nanograms per cut and toluene in the range of >7-20 nanograms per cut. In one run a high benzene value was not accurately measured, and in several runs toluene was below the 7 ng/cut detection limit of the analytical method, leading to some greater- or less-than values in Table IV with consequent uncertainties in the means and standard deviations. When plasticizer, benzene, and toluene were measured on the same run, high benzene and toluene values were generally associated with high plasticizer values. However, occasionally plasticizer values were high when benzene and toluene values were low. This may be due to volatilization of plasticizer from the film during cutting, without degradation of the PVC.

***acrolein***

Acrolein results are reported in Table V. Acrolein concentrations are a factor of 10-100 less than HCl or plasticizer concentrations, and of the same order of magnitude as benzene concentrations.

***carbon monoxide***

Carbon monoxide results, as determined by the semi-quantitative detector tube method, are shown in Table VI. Room air blanks did not produce any CO detector tube response, while the response increased progressively during hot-wire cutting. The amount of CO produced falls within the range of 1-5 micrograms per cut for each of the films tested.

***other compounds***

Methyl palmitate and methyl stearate were detected after derivitization with boron trifluoride/methanol of a concentrated ether rinse of the sampling hood made after 30 cuts of film RMF-61HY. Calcium and magnesium were also detected in this sample by emission spectroscopy, indicating that calcium and/or magnesium palmitate and stearate may have been added to the film during processing. These compounds were not quantitated.

***gas chromatograph/mass spectrometer (GC/MS) results***

GC/MS results are reported qualitatively and semiquantitatively in Tables VII and VIII. The 0.1-microgram detection-limit range of the mass spectrometer required some cuts in a series of 15-30 that produced significant smoke, so that these results may not simulate actual supermarket conditions, where minimal smoke should be produced. The assumption has been made that compounds formed during these moderately smoky cuts were formed in the same ratios as during clean cuts, only in higher quantities since more material is being volatilized at the same wire temperature. Results are related to benzene production so that they may be scaled up or down to semiquantitatively determine the range of concentrations of each compound that would be produced by clean through excessively smoky cuts. Relationships were established on the basis of total ion current chromatogram peak areas.

Benzyl chloride was not detected by GC/MS in a 15-cut sample of film RMF-61HY (Batch 1588). The detection limit of the mass spectrometer for this compound is about one microgram. However, using gaseous and liquid benzyl chloride standards and the hot-wire cutting device, it was found that benzyl chloride could not be recovered either in a the gas phase or in a concentrated hood wash. The decomposition of this compound in the presence of hot iron may account for its absence.

Several identifications in Table VII were not confirmed due to the low quantity of the compound produced, the existence of many isomers of the same molecular weight, or the absence of molecular ions by electron impact mass spectrometry. RMF-61HY produced two unidentified

**TABLE VIII**
**Identified Volatiles Collected on Porapak P (CW-65) or Tenax-GC (PC-63) Traps and Stripped onto a Porapak P Column**

| Compound | CW-65 | | | PC-63 | | |
|---|---|---|---|---|---|---|
| | Quantity* (as Proportion of Benzene) | Concentration Range* ng/cut Clean Cuts | Smoky Cuts | Quantity (as Proportion of Benzene)* | Concentration Range ng/cut Clean Cuts | Smoky Cuts |
| Acetic Acid | | | | ~1/2× Benzene | 2 - | 500 |
| Butyraldehyde | ~1× Benzene | 5 - | 1000 | | | |
| 1-Butanol | ~10× Benzene | 50 - | 10 000 | ~1/4× Benzene | 1 - | 250 |
| Benzene | | 5 - | 1000 | | 5 - | 1000 |
| 2-Ethyl-1-hexene | ~5× Benzene | 25 - | 5000 | ~1/4× Benzene | 1 - | 250 |
| Toluene | ~2× Benzene | 10 - | 2000 | ~1/10× Benzene | <1 - | 100 |
| Styrene | | | | ~1/20× Benzene | ≪1 - | 50 |

*See text

peaks which are not included in Table VII, at the ~1/2× and ~1/20× benzene level. VF-71 (5630) and VF-71 (64020) each produced one unidentified peak at the ~1/8× benzene level. The ATBC plasticizer in CW-65 and PC-63 contributes some compounds which are not seen with the DOA- or DOP-plasticized films, as shown in Table VIII. CW-65 results in Table VIII probably represent a run having several very smoky cuts in the series, as this film and PC-63 often produced lower quantities of volatiles than the other films. There are at least four unidentified volatiles produced by hot wire cutting of CW-65 and PC-63.

### breathing-zone hydrogen chloride concentrations produced by film RMF-61HY

The experimental work to this point involved use of the sampling hood to facilitate the collection of evolved gases. To assist in relating data generated in this manner to the actual wrapping environment, a series of measurements were made simulating the use of the film cutter in such a workroom.

The hood was removed from the hot wire cutter and the device was placed in a room 5.07 m (16.63 ft) long × 2.78 m (9.12 ft) wide × 3 m (9.84 ft) high for this series of tests. The volume of the room was 42.3 $m^3$ (1492 $ft^3$). During each test the doors and window of the room were closed and the blower for the heating/air conditioning unit was turned off in order to provide minimum ventilation. A midget fritted bubbler containing 15 milliliters of chloride-absorbing reagent was placed with its intake approximately 17 inches above the film-cutting device in the breathing zone of the operator. During each test room air was drawn through the bubbler at the rate of 800-1000 cc/minute, and a cut of film RMF-61HY (Batch 1588) was made every 15 seconds. An attempt was made to produce normal cuts. However, smoke was readily visible in about 10% of the cuts. Test no. 1 was carried out for 30 minutes making 120 cuts. Following this test, which was done in the morning, the doors and window to the room were opened for three hours to provide maximum ventilation. Test no. 2 was then carried out for 60 minutes with 240 cuts after the room had again been closed off and the temperature allowed to equilibrate. Test no. 3 was also carried out for 240 cuts, but on a different day, and sampling was continued for 15 minutes following cutting.

Each of the three samples had less chloride ion than the lowest standard used, which was 0.625 mg/L or $1.75 \times 10^{-5}$ M. This corresponds to room air concentrations <0.25, <0.13, and <0.1 ppm HCl for the 30, 60, and 75 minute tests, respectively, since the detection limit varies with the volume of air sampled. A room air blank taken prior to sampling produced a chloride level slightly below that found in Tests no. 1 and no. 2, and slightly above that found in Test no. 3. From 45-70 minutes into Test no. 3 several MSA no. 91636 and Dräger 1/a detector tube samples were taken for HCl. The Dräger tube should be sensitive to <1 ppm and the MSA tube to <2 ppm HCl. Not a trace of color change was observed with either brand of tube.

Sampling at the 5 ppm TLV level of HCl at one liter per minute for 15-75 minutes should produce chloride ion concentrations in the range of $2.0 \times 10^{-4}$ to $1.0 \times 10^{-3}$ M. The chloride concentrations found in the three tests, $<1.75 \times 10^{-5}$ M, correspond to room air concentrations well below the TLV: *i.e.* <1/50th of the TLV for the average room air concentration, and <1/10th of the TLV assuming all the exposure to HCl occurred during the last 15 minutes of the test. This assumption was made because it takes the HCl concentration some time to build up as cuts are made, so that the maximum concentration should occur toward the end of the test. This assumption, however, is complicated by the fact that an equilibrium is established between buildup of HCl in the room and deposition of HCl on various room and furnishing surfaces. This equilibrium was not studied and will differ for each room, depending on surface area, materials in the room, temperature, humidity, and other factors.

A Porapak P trap sample was collected at one liter per minute for 20 minutes following Test no. 3, and was run by gas chromatography/mass spectrometry. No low-boiling hydrocarbons such as benzene or 2-ethyl-1-hexene were

detected in this test. Sampling benzene onto a trap at its 1 ppm TLV level at one liter per minute for 15-75 minutes should result in collection of 50-240 micrograms of benzene. This amount is at least twenty times greater than the detection limit of the mass spectrometer. Thus, benzene was not detected at levels less than one twentieth of its TLV. Plasticizer was not measured during this test.

## cool rod analyses

A Borden Model AT100 cool rod film cutting device was installed and used with the previously described sampling hood without modification, except to widen the U-shaped slots in the Teflon ® sealing plugs at each end of the hood in order to accommodate the rod. This device has been reported to reduce volatile products during cutting.[5] Initial observations indicated this to be the case, as even leaving a film draped over the rod produced some odor of plasticizer but no visible smoke. Cool rod analyses for hydrogen chloride, plasticizer, and volatile hydrocarbons were made on film RMF-61HY (Batch 1588). Analyses were performed in the same manner as for products from the hot wire, except that the rod was not turned off during sampling for HCl and plasticizer because it required longer than the 1.5 minutes between cuts to cool appreciably.

### *hydrogen chloride*

One sample of film RMF-61HY (Batch 1588) was analyzed for chloride ion, but the sample did not differ from the blank analysis. To determine whether or not it was possible for the PVC to break down and form HCl at the temperature of the rod, an experiment was set up whereby a large amount of film could be heated. A stoppered 250-mL round-bottom flask was enclosed in a heating mantle. The temperature of the heating mantle, measured by a thermocouple embedded in it, was adjusted so that when equilibrium was reached the resulting air temperature inside the flask was 135 ± 1 °C (275 ± 2 °F), as measured by a thermometer. The flask was also connected via a glass bridge to a midget fritted bubbler and a small amount of room air (4 cc/min) was used to flush air from the flask through the bubbler. Neither a blank nor a sample of 6.1 grams of film heated for two hours produced any detectable chloride ion, even though the film discolored during the long heating period. Since HCl condenses readily on surfaces, the flask, the glass transfer bridge, and the plastic were separately rinsed with 10-20 mL of chloride absorbing reagent and found to contain 3, 0.8, and 2.5 micrograms of HCl per gram of plastic respectively. Hot wire cutting of this same film resulted in 1-7 micrograms of HCl per cut and since a cut represents less than a milligram of plastic, the amount of HCl produced at the cool rod temperature is at least a factor of 1000 less than the amount produced by hot-wire cutting.

### *plasticizer*

Plasticizer was analyzed as reported previously except that, since the rod was not turned off during sampling, more plasticizer remained volatile and a 7.6 cm × 4 mm (3 inch × 0.16 inch) glass wool trap was attached to the sampling manifold to condense and collect it. The air flow through the sampling hood was approximately 500 cc per minute and the hood was kept closed for 1.5 minutes following a cut. Two recovery studies were done, placing 2 microliters of DOA on the rod, closing the sampling hood and turning on the rod. Recoveries were 109% and 116%, indicating approximat[illegible] quantitative recovery, most of the inaccuracy being due the fact that it is difficult to measure the viscous DOA using a microliter syringe. The sampling hood, the rod, and the trap were each washed with known volumes of ethyl alcohol and measured separately. Most of the plasticizer was recovered in the glass wool trap sample, indicating that the DOA can be volatilized at the temperature of the cool rod.

Three 10-cut samples of film RMF-61HY (Batch 1588) were analyzed for DOA and produced 86, 70, and 25 micrograms DOA per cut. These values are within the range of values produced by hot wire cutting of the same film.

### *hydrocarbons*

Volatile products from a 15-cut sample of film RMF-61HY (Batch 1588) were collected on a Porapak P trap using a 1 liter per minute air flow and 1 minute per cut sampling time, and analyzed on a Porapak P column. Benzene and toluene were not detected above the blank level, providing another indication that the PVC does not thermally degrade at the cool rod temperature.

## conclusions

On the basis of the above tests and measurements, the following conclusions can be made:

1. The cutting process is such that using the hot wire, and less so the cool rod, the amount of plastic melted and/or combusted will vary considerably (up to two orders of magnitude) from cut to cut. Operator experience plays a major role in this process. However, even in the case of cuts resulting in the largest amounts of combustion products, the quantities are such that the operator is exposed to levels of identified products considerably below their threshold limit values.
2. Quantities of combustion products resulting from the use of the cool rod are considerably lower (and in most cases nondetectable), than those resulting from use of the hot wire.

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