Polyvinyl Chloride Film Thermal Decomposition Products as an Occupational Illness

I. Environmental Exposures and Toxicology

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Over the past several decades a variety of packaging materials and techniques have been utilized to wrap fresh meat. With the advent of refrigerated, self-service meat display cases came the popularity of clear plastic packaging films. Among film materials which have been widely used are cellophane, rubber hydrochloride, polyethylene, polystyrene, polyvinylidene chloride, and polyvinyl chloride.[1] Since its introduction in 1963-64, polyvinyl chloride (PVC) has grown to be the predominant fresh meat packaging material in use today. Usage estimates vary considerably, but approximately 80-90 million pounds of PVC film are used in the wrapping of meat each year. Another 30 to 35 million pounds are used to wrap produce and other products.[2]

Working Environment

Meat wrapping is usually performed in the meat departments of retail supermarkets. According to union and industry estimates, there are between 75,000 and 100,000 persons employed as meat wrappers in the United States.[2] The large majority of these meat wrappers work in the nation's 40,000 to 45,000 supermarkets, with the remainder employed by butchershops and packing houses.[3] Meat wrapping and labeling stations are typically located inside the mildly refrigerated meat departments. Minimal ventilation is supplied to these work areas to reduce refrigeration requirements and transportation of contaminants from other sections of the establishment into the meat cutting and wrapping area.

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Wrapping and Labeling Equipment/Hand Wrapping Procedure

A wide variety of hand operated, semi-automatic, and automatic meat wrapping and labeling equipment are in use. Semi-automatic and hand wrapping machines utilize hot or heated wire film cut-off. Price labels are printed, heated to activate the hot-melt adhesive, and then either manually or mechanically applied to the wrapped package of meat.

Although some of the newer wrapping equipment provides a means to control sealing temperature and cut-off wire temperature, most of the older equipment lacks one or both of these features. Hand wrapping equipment is durable, relatively uncomplicated, and can be expected to give several years of service. Consequently, many vintage machines are still in use today. A "typical" hand wrapping machine is shown in Figure 1.

The hand wrapping of meat involves: (1) pulling out a desired length of film; (2) wrapping the film around the tray or cut of meat; (3) severing the film from the supply roll using the hot-wire cut-off; (4) folding the film ends under the package; and (5) sealing the folded ends under the package by touching the package to the heated sealing pad. Most machines apply a mechanical tension to the film so that it retreats a few millimeters from the hot wire after cutting. This tension is intended to prevent the film from smoldering on the wire and causing it to become dirty and smoke. This tension also makes the film somewhat more difficult to pull from the supply roll and is often found to be improperly adjusted in the field. The sealing pad is maintained at a temperature sufficient to cause the film layers to adhere to one another after brief

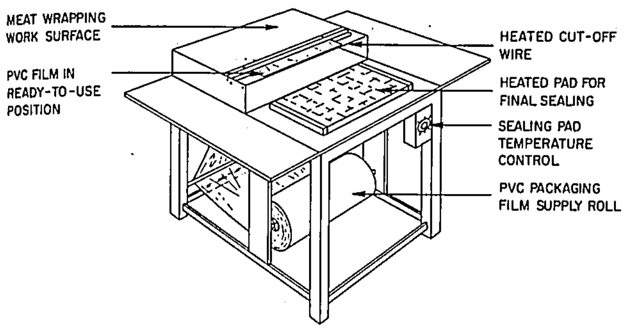

Fig 1. — Typical Hand-Wrapping Machine.

contact with the pad. Hand-held sealing irons are used very infrequently with PVC packaging films.

After wrapping, each package of meat is weighed and labeled. Printed labels are then heated to activate their adhesive coating and then applied to the package. The temperature of the label heating element can be regulated to suit the speed of the wrapping process and the surface temperature of the meat packages.

Manufacture of PVC Meat Packaging Film

PVC meat packaging film is made from PVC resin and selected additives. The additives serve to: (1) control deteriorative physiochemical reactions with the material during compounding, manufacture and film use; (2) impart desired properties (eg stretch, oxygen permeability, fog resistance, etc.), to the finished film product; and (3) control the migration of film constituents (eg monomer, plasticizer, etc.). Since the film does come into direct contact with meat, all film ingredients can potentially migrate into the meat and are therefore classified as "indirect" food additives. As such, film materials and ingredients are approved by the federal Food and Drug Administration.[4]

Commercially important PVC meat wrapping films have been found to have similar formulations (unpublished data). Plasticizers (di-2-ethylhexyl adipate, which is commonly referred to as dioctyl adipate, and epoxidized soybean oil) can comprise up to 30% of a film. Stabilizer (eg calcium-zinc stearate, epoxidized soybean oil), antifog agents (eg polyoxethylene derivatives of sorbitan monooleate, glycerol monooleate), lubricants (eg stearic acid) and colorants together make up 2 to 6% of a film. The above general formula information applies only to PVC films used to package fresh meat. PVC films used to wrap produce, cured meat, cooked meat, etc. may employ somewhat different additives.

Film ingredients are melted or dissolved, mixed, blown-bubble extruded or solvent cast, and the finished film is wound on rolls and cut to size for sale. Although these film making processes are widely applied in industry, the operating parameters, techniques and accessory equipment are basically developed by each manufacturer and are considered proprietary. The finished film has a thickness of several ten-thousandths of an inch (typically 0.00075 inches).

Thermally Activated Price Labels-Adhesive Composition and Label Manufacture

Adhesives used in price labeling must securely affix the labels to meat packages so that they cannot be easily removed by shoppers, and the label must stay in place even at low temperatures. To achieve these adhesive performance characteristics, label manfacturers are currently using a hot-melt or thermally activated adhesive containing a solid plasticizer. On heating, the plasticizer softens and application to a package of meat wrapped in PVC film forms a film-label bond which can be as strong or stronger than the film. To some degree the adhesive becomes part of the film.

Since the early 1960's label adhesives have contained dicyclohexyl phthalate (a solid plasticizer) as a major constituent (more than 60% by weight) and small amounts of a variety of polymers and elastomers which do not contain halogens and are not epoxy or urethane compounds.[2] Prior to the use of dicyclohexyl phthalate, diphenyl phthalate was utilized in label adhesives.

Adhesive ingredients are combined in a water emulsion/dispersion and applied to the paper stock by a knife coating process. Coated label stock is dried and wound into rolls. Later the label stock is printed with the design/advertising requested by the customer. Label stock can be stored for long periods (years) provided that the material is kept cool and dry. Some of the adhesive ingredients do tend to sublime, however.

Emissions from Hot-Wire Cutting of PVC Packaging Film

The thermal degradation of PVC alone (not the film) has been studied extensively.[5-9] The Bureau of Occupational Health has studied the thermal decomposition products of PVC meat wrapping film. In a study directed toward identifying the "volatile" irritant/toxic decomposition products, samples of film from several manufacturers were heated for one hour at temperatures ranging 200-230 C. The decomposition products were separated by gas chromatography and the most prominent substances were found to be emitted by all film samples: hydrogen chloride, chlorobutane, benzene, toluene, 1-chloro-2-ethyl hexane and 2-ethyl-1-hexanol. The latter two substances were assumed to be plasticizer breakdown products. Benzyl chloride was randomly found as a decomposition product from a few film samples. An oily substance, presumed to be the film plasticizer, was observed to condense in the analytical apparatus but was not positively identified. Subsequent environmental measurements made in supermarket meat departments under working conditions detected only trace concentrations (less than 1 ppm) of hydrogen chloride.

Bovee et al examined the thermal decomposition of meat packaging films from six manufacturers.[10] This study found the chromatograms of the different films to be similar at a decomposition temperature of 180 C with one film showing two unique additives displaying adipate-like mass spectra. The primary decomposition product of the various films was found to be a plasticizer identified as diisooctyl adipate (di-2-ethylhexyl adipate). Isooctanol (2-ethyl-1-hexanol), a plasticizer breakdown product, was emitted from all film samples and varying amounts of Ionol (butylated hydroxy toluene) was emitted by several of the films. A number of substances were observed to be present in very small quantities and were not identified. The hot wire was observed to sluggishly melt through films at 150 C; smoke was observed above 175 C; and hydrogen chloride was detected above 230 C. Analysis of the smoke from the hot wire showed it to be 99% diisooctyl adipate (di-2-ethylhexyl adipate).

In a study undertaken to learn more about air contamination generated by the actual wrapping process, Van Houten et al installed a film cutting and sealing machine in a sealed laboratory chamber.[11] Wrapping conditions were varied from normal to artificially severe. Air contaminants were collected at a point directly over the cut-off wire and in the meat wrapper's breathing zone. Under the most severe test conditions, (ie operating the machine at a "greatly exaggerated production rate" and allowing the film to decompose and smolder on the cut-off wire maintained at 183 C) a breathing zone hydrogen chloride concentration of 0.3 mg/M³ (0.2 ppm) and a total particulate concentration (directly over the wire) of 19 mg/M³ were measured. Subsequent analysis of total particulate samples by extraction and gas chromotography showed them to contain approximately 75 to 80% dioctyl adipate (di-2-ethylhexyl adipate). Under normal operating conditions concentrations of total particulate and dioctyl adipate measured directly over the wire were 0.7 and 0.25 mg/M³ respectively at a cut-off wire temperature of 183 C. Operating normally at a wire temperature of 105 C, 0.35 mg/M³ of total particulate and 0.14 mg/M³ of dioctyl adipate were found directly above the wire. Although breathing zone hydrogen chloride concentrations were not measured under normal operating conditions, they can be safely assumed to have been much below the 0.3 mg/M³ (found directly over the wire) and less than 0.1 mg/M³ (found in the breathing zone) at wire temperature of 183 C and 105 C respectively. It was determined that a cut-off wire temperature of 102 to 110 C was satisfactory for the film used in this study. Reducing the cut-off wire temperature from 183 C to 105 C afforded a near 50% reduction in emission of total particulate and dioctyl adipate under normal operating conditions.

Reduction of emissions from thermal cutting of PVC film by lowering cutting element temperature has also been recently reported by James.[12] It was demonstrated that emissions of hydrogen chloride were significantly less from a "cool rod" cutter (approximately 135 C) than from the uncontrolled hot-wire cutters. Average hydrogen chloride concentrations measured in the breathing zones of meat wrappers performing normal wrapping procedures were found to be 0.57 ppm using the hot-wire cutting elements and 0.03 ppm using the "cool rod" cutting element.

In a recent study a sample of film known to contain di-2-ethylhexyl adipate was pyrolyzed at 135 to 177 C for 1.5 hours.[13] Gas chromatographic and mass spectrophotometric analyses of the acetone soluble decomposition products contained di-2-ethylhexyl adipate which confirmed the pyrolytic evaporation of the intact plasticizer.

NIOSH has conducted a limited amount of field environmental sampling and evaluation work.[2] With the cooperation of a grocery chain a series of experiments was performed using three commercially available PVC packaging films and several film cutting/wrapping machines. The film cutting/wrapping machines utilized were modified so that the cutting element temperature could be varied over a wide range. Even under the most severe operating conditions (ie, piling large amounts of film on the cutting element) no vinyl chloride monomer was detected over the entire range of operating temperatures. Under the operating conditions, the lower limit of detection for the instrument used (Wilks Miran Infrared Gas Analyzer) was approximately 1 to 2 ppm of vinyl chloride monomer. Measurements for vinyl chloride monomer were also made at supermarkets involved in NIOSH health hazard evaluations. Operating conditions were varied over a wide range and again, no vinyl chloride monomer was detected in the plume of emissions for the cutting elements. The lower limit of detection ,for the charcoal tube collection and gas chromatograph analysis method utilized was approximately 0.2 ppm of vinyl chloride monomer.

In these same NIOSH hazard evaluations, measurements for hydrogen chloride revealed concentrations of 1 ppm in the meat wrappers' breathing zones. Under very severe conditions, a few parts per million (less than 5 ppm) of hydrogen chloride were found in the plume of emissions an inch or so from the cutting element. Gas detector tubes were utilized to make these field determinations.

Table 1. — Thermal Decomposition Products of Dicyclohexyl Phthalate (Sample Heated at 200 to 210 C for 30 & 60 Sec.)

	30 Sec.	60 Sec.
Cyclohexanol	90 ppm	130 ppm
Cyclohexyl Ether (Dicyclohexyl Ether)	43 ppm	92 ppm
Phthalic Anhydride	10 ppm	113 ppm
Cyclohexyl Benzoate (Cyclohexyl Ester of Benzoic Acid)	5 ppm	38 ppm

Emissions from Thermal Activation of Price Label Hot-Melt Adhesive

Thermal activation of adhesive coated price labels is performed by heating the label from the printed side. The activation temperature achieved by this process is a function of the heating element temperature, the thickness of the label paper, and the duration of label contact with the heating element. With contact times of less than a second, a heating element temperature of 149 to 205 C is commonly required to provide adequate activation. Whenever the contact time at a particular heating element temperature exceeds the time necessary for adequate activation, the potential exists for excess emissions from the activation process. A jam in the flow of packages can result in prolonged contact of the labeling material with the heating element.

By examining the formulation of price labeled adhesive it was determined that either the major ingredient, dicyclohexyl phthalate, or its breakdown products, or both, comprise an important portion of the emissions from the adhesives during activation. Other proprietary adhesive ingredients (ie thermoplastic polymers and elastomeric polymers not containing halogens) individually present in small quantities, are recognized to have known breakdown products comprised basically of hydrocarbons and small amounts of aldehydes, alcohols, carboxylic acids etc.

Information is available on the thermal decomposition products of dicyclohexyl phthalate.[2] A ten milligram sample of dicyclohexyl phthalate was placed in a boat contained in a heated tube and heated for 30 and 60 seconds at 200-210 C. The emissions from the sample were directly analyzed by gas chromatography and mass spectrometry. The materials emitted, expressed in terms of parts per million based on sample weight, are shown in Table 1. Under these experimental conditions the plasticizer itself did not volatilize appreciably.

Discussion

From the data available, it appears that the major emissions from the hot-wire cutting of PVC meat wrapping film are di-2-ethylhexyl adipate and hydrogen chloride. Di-2-ethylhexyl adipate is not a significant irritant to the skin or eye.[14] Little information is available regarding inhalation toxicity of this compound. In a report of an unpublished study, ten rats were exposed for four hours to 900 mg/M³ (59 ppm) of di-2-ethylhexyl adipate at 89 C and observed for 14 days.[2] None of the rats died and no untoward behavioral reactions were observed.

Hydrogen chloride can be detected by most persons at concentrations of 1 to 5 ppm. At slightly higher concentrations (5 to 10 ppm), it is immediately irritating and disagreeable.[15, 16] The current health standard for occupational exposure to hydrogen

Table 2. — Occupational Health Exposure Standards/ACGIH TLV's.

Substance	Permissible Exposure
Hydrogen Chloride*	5 ppm (7 mg/M³)
Cyclohexanol†	50 ppm (200 mg/M³)
Phthalic Anhydride†	2 ppm (12 mg/M³)

ppm = parts of vapor or gas per million parts of contaminated air.
mg/M³ = approximate milligrams of substances per cubic meter of air.

*Ceiling value: Employee exposure should never exceed permissible exposure.
†Time-weighted-average standard: Employee exposure averaged over 8 hours should not exceed permissible exposure.

chloride (see Table 2) of 5 ppm (7 mg/M^3) is based on data which were interpreted as indicating that a ceiling exposure level of 5 ppm would be " . . . sufficiently low to prevent toxic injury, but on the border of severe irritation".[17]

In the process of cutting PVC film with a hot-wire, an aerosol of di-2-ethylhexyl adipate is formed. It is possible that some of the hydrogen chloride emitted absorbs to aerosol particles of di-2-ethylhexyl adipate. This type of gas/particle interaction has been observed in other situations (eg sulfur dioxide and soot particles), in particular, with hydrogen chloride and soot/water particles associated with fires involving chlorinated polymeric materials.[18, 19] Hydrogen chloride deposited on aerosol particles, less than 5 micrometers in diameter, could get past the defenses of the upper respiratory tract and deposit in the small bronchioles and alveoli resulting in lung irritation or injury.

Complete information regarding the total spectrum of emissions from the thermal activation of price labels is not available. Some information is available on the thermal decomposition products of dicyclohexyl phthalate, the major ingredient of price label adhesives. Pertinent toxicologic information dealing with cyclohexyl ether (dicyclohexyl ether) and with cyclohexyl benzoate (cyclohexyl ester of benzoic acid) could not be found in the literature. The effects of cyclohexanol at moderate and low exposure levels are basically irritative in nature. After three to five minutes of exposure to 100 ppm of cyclohexanol, human subjects found the effects of the vapors on the eyes, nose and throat to be objectionable. The current health standard for eight-hour time-weighted-average occupational exposure to cyclohexanol of 50 ppm (200 mg/M^3) (see Table 2) is based on this information and the absence of strong evidence suggesting more serious systemic toxicity.[17]

Phthalic anhydride is known to be a potent skin, eye and upper respiratory irritant.[20] Pulmonary sensitization to phthalic anhydride can cause bronchial asthma and may be associated with specific IgE antibody against phthalic anhydride when measured by the radioallergosorbent test (RAST).[21] The current health standard for eight-hour time-weighted-average occupational exposure to phthalic anhydride of 2 ppm (12 mg/M^3) (see Table 2) is derived from information regarding the toxicity of this compound as well as other strong irritants (ie sulfuric and nitric acids).[17, 20]

Only limited data concerning the toxic effects of the combined thermal degradation emissions from dicyclohexyl phthalate are available. One of six rats died within 24 hours following a 6 hour exposure to a vapor concentration of 9,000 mg/M^3 generated by heating dicyclohexyl phthalate to 205 C.[2] No gross pathologic changes were observed in the surviving rats which were observed for 14 days and sacrificed. During exposure, the animals were noted to have ocular discharge and labored breathing.

The standard sources of criteria used to assess workroom concentrations of air contaminants are: (1) recommended threshold limit values (TLV's) and their supporting documentation as set forth by the American Conference of Governmental Industrial Hygienists, ACGIH (1974); and (2) occupational health standards as promulgated by the U.S. Department of Labor (Federal Register, June 27, 1974, Title 29, Chapter 17, Subpart G, Table G-1). Recommended TLV's and Federal Standards are the same for the irritant materials listed in Table 2. TLV's and federal standards have not been established for the plasticizers (di-2-ethylhexyl adipate and dicyclohexyl phthalate) and for cyclohexyl ether and cyclohexyl benzoate. Furthermore, in general, information on inhalation toxicology of plasticizers and their thermal degradation products is limited.

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