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1 2	61 62
	21
INDUSTRIAL HYGIENE EVALUATION OF TOXIC	22
DECOMPOSITION PRODUCT FROM PVC FILM IN MEAT-	23
WRAPPING OPERATIONS -- MEAT WRAPPERS ASTHMA,	24

PYROLYSIS.

Source (Journal, Vol., Number, Pages, Date)

1 2	61 62
AM IND HYG ASSOC J 41 510-517 1980	31
	32

Brief Summary

1 2 10	61 62
SUMMARY:	61
	62
	63
	64

An industrial hygiene evaluation is presented concerning experimental data included in the preceding paper on thermal degradation products from hot-wire and "cool"-rod cutting of PVC film but, in this paper, limited to film used in meat-wrapping operations. Room air concentrations of less than 0.2 ppm HCl and less than 0.05 ppm benzene can be maintained by a number of factors, including minimal dilution ventilation. Estimates of room air concentrations of degradation products are presented using average values of amounts produced per cut. The relation of these concentrations to TLV's is given, together with methods of suggesting TLV's for substances not listed by ACGIH or OSHA. Room air concentrations for the 12 degradation products for which TLV's are assigned, based on average values per cut, were no greater than 0.3% of accepted limits. Room air concentrations of DOA are not determinable from available data but present information does not indicate that exposure to DOA causes airway hyperreactivity. The cool rod, rather than the hot wire, is recommended as good industrial hygiene practice, producing no apparent PVC degradation products, even though similar amounts of DOA are volatilized.

Industrial hygiene evaluation of thermal degradation products from PVC film in meat-wrapping operations

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introduction

A number of studies have been made of potential hazards to employee health in meat wrapping departments of supermarkets. Most comprehensive are those conducted by the National Institute for Occupational Safety and Health (NIOSH) and its organizational predecessor, the Bureau of Occupational Safety and Health, U.S. Department of HEW, over the six years through 1977. An initial report[1] concluded that *"there appear to be no apparent health hazards presented by PVC film fumes generated in meat wrapping to normal healthy persons employed as meat wrappers."*

The NIOSH report[2] at the end of this period includes all known information on hot-wire cutting of PVC packaging film up to that time and a summary of NIOSH health hazard evaluation studies of meat wrappers and cutters. The conclusion after conducting these extensive studies was that *"it cannot be determined from these studies whether actual allergic sensitization and resultant bronchial asthma occurs from exposure to these contaminants."* It was noted that *"hot wire cutting of PVC meat wrapping films and thermal activation of price labels can release irritant substances into the meat wrapping work environment;"* but that *"breathing zone concentrations of the irritant substances emitted are low when compared to established occupational health exposure standards."*

Much of the information in the NIOSH report[2] has been published in two papers, one on environmental exposure and toxicology[3] and the companion paper on clinical studies.[4] In this latter, more recent paper, the conclusion quoted in the preceding paragraph was again stated.

A small number of degradation products on heating PVC film samples to the hot-wire temperature of 200-300 °C in a micro furnace were identified by NIOSH,[1] but in order to determine just what substances the meat wrapping operators were exposed to, there was a need for identification of all degradation products of significance from hot-wire film cutting and a determination of the amount of each substance produced.

This basic information has been provided through a research project that is the subject of a paper[5] in this issue of AIHAJ.

application of research data on thermal degradation products

An application of data developed in this research project[5] is the evaluation of exposures to these substances of persons engaged in PVC film meat wrapping operations. The research project included five types of films, only one of which, Type RMF-61HY, is used for meat-wrapping operations. This discussion is limited to industrial hygiene aspects of the experimental results utilizing Type RMF-61HY film, since the other four types included in the research project are used for such other purposes as produce wrapping and carcass wrapping, operations not under consideration here. Furthermore, data are included only on Batch No. 1588 of this type film, since only this batch of RMF-61HY film, as discussed in the research paper, was of sufficiently recent origin to be handled in a representative manner and consequently to produce representative results. The plasticizer used in this film is di-(2-ethylhexyl) adipate, commonly called dioctyladipate (DOA).

The experimental data in the following discussion are from the cited research project, except where specifically noted.

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breathing zone air samples

hydrogen chloride

Three air samples were collected during hot-wire cutting of PVC film RMF-61HY in a closed room 42.3 m^3 (1500 $ft.^3$) in volume with dimensions as given in the research paper that also notes the sampling point at the breathing zone of the operator. Even though an extremely sensitive analytical method was used, the amount of HCl in the air was not sufficient to permit a quantitative result. The largest sample collected, 75 liters, established that an average of less than 0.1 part per million (ppm) of HCl was present over the 75-minute sampling time. With 240 cuts of the PVC film being made during this period, the HCl concentration would have increased from zero at the start to something less than 0.2 ppm at the termination of the sampling period for the average to have been less than 0.1 ppm.

Actually, the increase in the concentration time would not be a straight line but would be a hyperbolic curve asymptotic to a maximum at equilibrium between introduction of HCl into the air and the several factors causing its removal from the air. These factors include solubility of the HCl in moisture (a greater factor in meat-wrapping rooms than in the test room), adsorption on and reaction with the surfaces contacted, and a small but definite amount of dilution from convection currents through loosely fitting doors and intermittent opening of doors.

The investigators note that the value of less than 0.1 ppm is less than 1/50 of the threshold limit value (TLV) for HCl; but conservatively, recognizing a build-up with passage of time, suggest that the continuing exposure might be on the order of less than 1/10 of the TLV.

A series of laboratory tests conducted by other investigators[6] using artificially severe operating conditions causing excessively smoky cuts gave results of 1.9 ppm HCl at a sampling location 7 in. above the hot wire and 0.2 ppm HCl at breathing level 17-18 in. above the sealing pad.

A calculation is of interest of the amount of diluting air that would be required to keep the concentration of HCl below 1/10 of its TLV using the formula in the Industrial Ventilation Manual of the American Conference of Governmental Industrial Hygienists (ACGIH).[7] The amount of HCl released into the air per minute was calculated from the amount per cut (4 micrograms – the average of six cuts with Batch 1588 of film RMF-61HY) times the operating rate of 192 cuts per hour (240 actual cuts over a 75-minute period). A K value is incorporated in the formula to serve as a multi-purpose safety factor to maintain air concentrations well below the TLV. The K value may vary from 3 to 10 with the latter resulting in the highest amount of dilution air required. Using this maximum K value of 10, the amount of dilution air required for each hot-wire cutting unit would be only 0.17 m^3 (6 $ft.^3$) per hour. More than this amount of air change occurs normally even without benefit of mechanical ventilation.

For comparisons of the findings under these test conditions with results of air analyses taken at the breathing zone of the operator during hot-wire cutting of PVC film in four different stores under normal operating conditions, James[8] reports that the average of eight determinations was 0.57 ppm HCl, close to 1/10 of the TLV, with a maximum of 1.49 ppm HCl.

benzene

Following the 240 hot-wire cuts in the test room prior to ventilating the room, an air sample was collected for 20 minutes for determination of low-boiling hydrocarbons such as benzene and 2-ethyl-1-hexene. No low-boiling hydrocarbons were found, using the GC/MS unit capable of detecting benzene in the order of 3 micrograms. With the 20-liter air sample, as little as 0.05 ppm would have been detected. Accordingly, the accumulated concentration of benzene produced was necessarily less than 1/20 of the proposed OSHA TLV limit of 1 ppm and less than 1/200 of the existing OSHA TLV of 10 ppm.

estimates of room-air concentrations of degradation products from PVC film type RMF-61-HY (batch 1588)

data used in estimates

In calculating the estimates of room-air concentrations of degradation products, the average amount from 250 cuts, essentially the same as the maximum number of cuts used in the breathing zone samples, was related to a room of 42.3 m^3 (1500 $ft.^3$), the volume of the test room. With this number of cuts, it was considered that equilibrium conditions would be reached.

For the degradation products, HCl, plasticizer (DOA), benzene, toluene, carbon monoxide, the average of all test runs on Batch 1588 as reported in the research paper[5] are used in the calculations. Since only Batch 1959 was used for the acrolein tests, these results were used. For benzyl chloride, negative results from 15 cuts indicated less than 1 μg, the mass spectrometer detection limit. For the remainder of the degradation products as listed in Table I, determinations were conducted by gas chromatograph/mass spectrometer. As discussed in the research paper,[5] smoky cuts were required to produce enough degradation product for quantitative results with this latter group of degradation products. As benzene amounts could be determined from normal cuts as well as from smoky cuts, the ratio of these values for benzene was applied to the smoky cut results of these other products to obtain a value for normal cuts. The average values for these additional degradation products have been taken as 9/10 of those listed from Batch 1588 in Table VII of the research paper[5] for clean cuts and 1/10 of those listed for smoky cuts since, according to the investigators, approximately one of ten cuts tended to be smoky.

threshold limit values

Threshold limit values are listed in Table I for each of the substances for which these have been established by ACGIH or OSHA except that for benzene for which the value currently proposed by OSHA is listed.

No threshold limit value has been suggested by these

TABLE I

Estimation of Average Room-Air Concentrations of Degradation Products Resulting from Hot-Wire Cutting of PVC Film Type RMF-61HY (Batch 1588)

Degradation Product	TLV (ppm)	Average Amount Produced per Cut	Average Concentration in 1500 ft.³ Room from 250 Cuts	Percent of TLV
Hydrogen chloride	5	4 μg	0.016 ppm	0.3
Plasticizer (DOA)	[A]	36 μg	0.014 ppm	[A]
Benzene	1[B]	92 ng	0.0002 ppm	0.02
Toluene	100	53 ng	0.00008 ppm	0.00008
Acrolein	0.1	120 ng	0.0003 ppm	0.3
Carbon monoxide	50	1.75 μg	0.01 ppm	0.02
Benzyl chloride	1	0.07 μg	0.0002 ppm	0.02
2-Ethyl-1-hexene	[A]	210 ng	0.0003 ppm	[A]
Ethyl benzene	100	21 ng	0.00003 ppm	0.00003
Styrene	100	37 ng	0.00005 ppm	0.00005
n-Propylbenzene	100[A]	37 ng	0.00005 ppm	0.00005
Propenylbenzene[C]	100[A]	13 ng	0.00002 ppm	0.00002
Indene[C]	10	13 ng	0.00002 ppm	0.0002
Naphthalene[C]	10	6 ng	0.00001 ppm	0.0001
Unidentified	[A]	52 ng	0.0003 m/m³	[A]
Unidentified	[A]	6 ng	0.00004 m/m³	[A]

[A]Refer to text

[B]Proposed OSHA value

[C]Unconfirmed identification

agencies for DOA. An experiment of an 8-hour exposure of rats to saturated vapor resulted in no deaths.[9] NIOSH[2] cites a Monsanto Company report that *"10 rats were exposed for 4 hours to 900 mg/m³ (59 ppm) generated at 89 °C and observed for 14 days. None of the rats died and no untoward behavioral reactions were observed."* Later experiments[10] with 6-hour exposure to 200 mg/m³ gave similar results. Slight irritation occurred from 24-hour contact of rabbit skin (1.9/8.0) and from liquid DOA in the eye (1.4/110.0) with normal appearance 48 hours later. The LD_{50} on intravenous injection of the rat has been reported[11] as 900 mg/kg and of the rabbit as 540 mg/kg, indicating DOA as *"slightly toxic."*[12,13] These inhalation studies included only survival or death on acute exposure and observation over 14 days. Toxicological data on substances of similar constitution are sometimes helpful in suggesting a probable TLV but we know of no substances similar to DOA with such information.

Although neither ACGIH nor OSHA have TLV's for n-propylbenzene or propenylbenzene, the close structural analogy of the former substance with ethylbenzene and of the latter substance with styrene indicates a TLV of 100 ppm as applicable to each of these substances.

No TLV has been published for 2-ethyl-1-hexene; but from analogy with similar unsaturated hydrocarbons,[14] its principal action may be expected to be asphyxiant and anesthetic.

Suggestions for threshold limit values for the substances that caused film RMF-61HY to produce the two unidentified peaks noted in the research paper and included in Table I present a problem. An approach to whether there is a reasonable probability that concentrations f these unidentified substances as low as 0.0003 mg/m³ r 0.00004 mg/m³ could cause a physiological effect such as airway hyperreactivity may best be through a comparison with concentrations of known sensitizers at their threshold limit values. Of nearly 600 chemical substances for which TLV's have been published by ACGIH,[15] the substances that must be kept at the lowest concentrations to avoid causation of airway hyperreactivity are the isocyanates, of which toluene diisocyanate (TDI) has been most extensively studied. A recent criteria document published by the National Institute for Occupational Safety and Health[16] stipulates a limiting concentration of 0.005 ppm for diisocyanates. F r TDI, this value is equivalent to 0.035 mg/m³. This standard is *"designed to protect the health and provide for the safety of employees for up to a 10-hour workshift, 40-hour workweek, over a working lifetime."* The concentrati ns of 0.0003 mg/m³ and 0.00004 mg/m³ are thus 0.9% and 0.11%, respectively, of what is considered an acceptable concentration for the most severe sensitizer on which quantitative exposure/response data are available. Comparison values for these unidentified substances must be in terms of milligrams per cubic meter as lack of knowledge of their molecular weights prevents calculation of the corresponding parts per million values.

The TLV of HCl is well established at 5 ppm, but e particulate DOA is present as an aerosol on which some of the HCl may become attached, the questi n arises as to

whether concentrations of somewhat less than 5 ppm may, through this mechanism, reach the lower respiratory areas and cause irritation in these areas. Such gas/particle interaction has been discussed in relation to fire situations,[17,18] but in the experiment with HCl/soot aerosol reactions,[17] the concentrations of HCl were over 100 ppm, and in that with HCl/water aerosol reactions,[18] concentrations of 60, 600, and 6000 ppm gas-phase HCl were used. All of these concentrations are far beyond the range of HCl produced in hot-wire cutting of PVC film and so not applicable to the operations under consideration.

The most extensive researches on potentiation of the effect of an irritating gas by aerosols are those conducted over more than a decade by an investigator using sulfur dioxid as the irritating gas. In one of these research projects where the irritant gas was inhaled with each of a variety of aerosols,[19] it is stated that *"It is plain from the data presented in this paper that all aerosols do not potentiate the response to sulfur dioxide,"* and in a subsequent paper,[20] that *"neither iron oxide nor open hearth furnace dust affect the response to sulfur dioxide."* On the basis of these results, it cannot be assumed that any given aerosol will potentiate the action of an irritant gas without demonstration through specific research. Such research has not been conducted c ncerning the potentiation of sub-TLV levels of HCl by DOA aerosol.

All of the substances listed in Table I are readily volatile liquids or gases with the exception of DOA and naphthalene. It was found by the research investigators that most of the DOA volatilized by the hot wire condensed on the surrounding hood surfaces, the portion remaining as a vap r to be collected by an impinger being too small for quantitative measurement in an initial experiment. It is believed that, in use of hot-wire film cutters in meat-wrapping operations, a portion of the DOA will condense onto adjoining surfaces but that some portion of the amount volatilized will reach the breathing zone of the operator. As no publications of results of air analyses for DOA at the operator's breathing zone under normal operating conditions are available, just what this portion or the total am unt volatilized will be remains conjectural. From the calculation of the average amount recovered from washings of the hood surfaces on making cuts of film Batch 1588, this concentration would be some value less than 0.014 ppm.

As listed in the final column of Table I, the concentrations of the degradation products for which TLV values are assigned on hot-wire cutting of RMF-61HY film, Batch 1588, on 250 cuts in a 1500 cubic foot room are no greater than 0.3% of their respective TLV's.

cool rod PVC film cutting

On finding no HCl evolved when the so-called cool rod cutting device was used or in the air flushed from the top of a flask in which a sample of film Batch 1588 was maintained at the cool rod temperature of 135 °C (275 °F), it appears probable that PVC does not degrade at the cool rod temperature. The finding of a total of 6.3 micrograms of HCl in rinses of surfaces of the flask and tubing leading to the sampling bubbler indicates either that the amount f HCl that may have been produced by degradation was a thousandth r less of that produced by hot-wire cutting or that this minute amount may represent contamination.

Negative results for benzene and toluene also indicated that PVC does not thermally degrade at the cool rod temperature.

The amount of DOA volatilized by the cool rod device within the hood was in the same range as when using the hot wire, this result being ascribed to the fact that the rod was not being turned off during sampling. Keeping the cool rod turned on during sampling would increase the temperature within the hood, thus causing more of the plasticizer to remain volatile.

conclusion

An analysis of the results of the research[5] on thermal degradation products of PVC film using the hot-wire cutting device in meat-wrapping operations showed that the average concentration of hydrogen chloride as produced in a closed room by hot-wire film cutting was less than 2 percent of the OSHA TLV and that of benzene less than 5 percent of the proposed OSHA TLV and less than 0.5 percent of the current OSHA TLV. Just how much less these values actually were is indicated by the results of the experimental gas chromatograph/mass spectr graph results as presented in Table I.

These GC/MS results indicated that the concentrati n of degradation products for which TLV's are assigned would be no greater than 0.3% of acceptable limits and in most instances much lower. Thus it would appear that any workroom exposures to such products w uld be insignificant from an industrial hygiene standp int. F r the DOA, the concentration is less than 0.014 ppm; how much less is not determinable due to the presence of the close surrounding hood structure under experimental conditions, a factor that is not existent under actual operating conditions. Information presently available does not indicate that exposure to DOA causes airway hyperreactivity.

Investigation of the cool rod PVC film cutting devic indicated that PVC does not degrade at the temperature o the cool rod but that the amount of DOA volatilized withi the hood was comparable to that using the hot-wire device The continued elevated temperature within the closed hoo would not be a factor in the actual meat-wrapping peratio and lesser volatilization of the DOA would accordingly b expected even though in meat wrapping the cool rod is kep on.

In accordance with the industrial hygiene viewp int tha all exposures should be kept as low as is practicably feasibl the cool rod device is to be recommended.

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