# TOXIC GASES FROM PVC IN HOUSEHOLD FIRES

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THE smoke and toxic gases produced from combustible materials in a building on fire can reduce the chances of escape of the occupants and put their lives in jeopardy. Records show that roughly half the deaths in fires in the United Kingdom are attributable to smoke and gases. The principal toxic gas from burning traditional building materials, such as wood, is carbon monoxide, but newer combustible building materials, such as plastics, may evolve additional toxic gases.

The hazards due to cellulosic and other combustible building materials are being examined, with the aim of quantifying the toxic gas and smoke hazards. Some results obtained on the effect of the addition of PVC to cellulosic fire loads on the toxic gases produced in small scale laboratory fires are presented here.

## Tests and Results

The tests were made in a 0.9 m cubical compartment lined with asbestos, the front of which could be opened for loading the chamber with combustibles, and fitted at the top with a vent of the full width of the compartment and of adjustable depth. Fig. 1 shows the compartment with the front open containing the cellulosic fire (a crib of wood fibre insulating board) and wall linings of rigid PVC. The cellulosic crib was ignited electrically, and samples of gas were withdrawn from time to time during the test for analysis of permanent gases and hydrogen chloride. The temperature of the issuing combustion gases was measured during a test, their total rate of evolution was calculated using the flow equation of Kawagoe (the ventilating condition in these tests required the discharge coefficient to be altered to 0.9) and the rate of evolution of the toxic gases was then obtained from the composition of the combustion gas.(1) Tests were made with cellulosic fire loads of 6.4 and 12.8 kg in the crib and with vents of 5 cm (equivalent in an average room to an open fan-light) and 10 and 15 cm (equivalent in an average room to an open door).

In most tests the three fixed walls of the compartment were lined with 1.5, 3 or 6 mm thick sheets of rigid PVC. A few tests were made with a board consisting of 0.5 mm rigid PVC sheet laminated on to 4.5 mm hardboard. The effect of a different arrangement of the plastic in relation to the fire, as, for example, in furniture incorporating plastics was examined by further tests in which sticks of rigid PVC were incorporated in the cellulosic crib; the weights of plastic used were 2.8 and 5.6 kg, the latter being the weight of the 1.5 mm wall lining.

Temperature records were made for the gases emerging from the vent. In all tests burning started with the crib smouldering and producing dense white smoke for a few minutes, which was followed by a flash ignition of the smoke and a resulting sharp rise in temperature, up to about 700°C. In tests with the 5 cm vent, this was followed by smouldering combustion, the temperature of the emergent gases remaining at a steady low value of about 230°C. With the 10 cm vent, smouldering alternated with flash ignition in most tests, while at the largest vent size the flash ignition after initial smouldering was generally followed by continuous flaming combustion. Combustion usually proceeded to completion in tests at the two larger vent sizes, but in many tests at the smallest vent size the fire went out before combustion was complete.

The patterns of evolution of hydrogen chloride and carbon

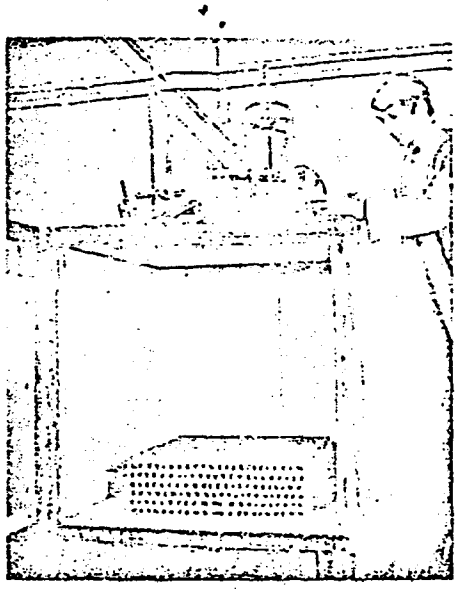

*Fig. 1. Model compartment showing wall linings and cellulosic crib*

evolved later than carbon monoxide, the delay increasing with decreasing vent size. In tests with the 5 cm vent, the delay was a minimum of 30 minutes, but usually much longer, for tests with the PVC present as wall linings. Shorter delays occurred when the PVC was incorporated in the crib, but the rates of evolution were lower than when the plastic was present as a wall lining. (Fig. 2).

In all tests carbon monoxide was evolved a few minutes after ignition. The rate of evolution was little affected by wall linings of PVC but was reduced in the test in which the larger weight of plastic was incorporated in the crib. (Fig. 3).

## Discussion

The results obtained in these tests may be used to assess the effect of PVC in burning compartments on the toxic gases escaping into the remainder of a building, for the worst condition in which no gases escape outside the building. The risk will then vary with the mode of burning and the time from ignition during which occupants are exposed to the gases. The growth of a flaming fire is rapid and escape or rescue must take place promptly to avoid exposure to excessive heat or toxic gases. However, gas evolution could occur more slowly, and without excessive heat production for longer times if the fire started by smouldering and continued with restricted ventilation before discovery; for this report exposure times of up to one hour before escape or rescue have been assumed.

The assessment of the effect of hydrogen chloride on escape is not straightforward. Atmospheres containing 100 parts per million or more of hydrogen chloride are intolerable to breathe,(2) while about 1,500 parts per million could prove lethal for exposures of half an hour.(3) The lower concentration could augment the effects of smoke and other gases in impeding escape, but on the other hand the irritancy of hydrogen chloride could give early warning to the occupants

## TOXIC GASES FROM PVC IN HOUSEHOLD FIRES

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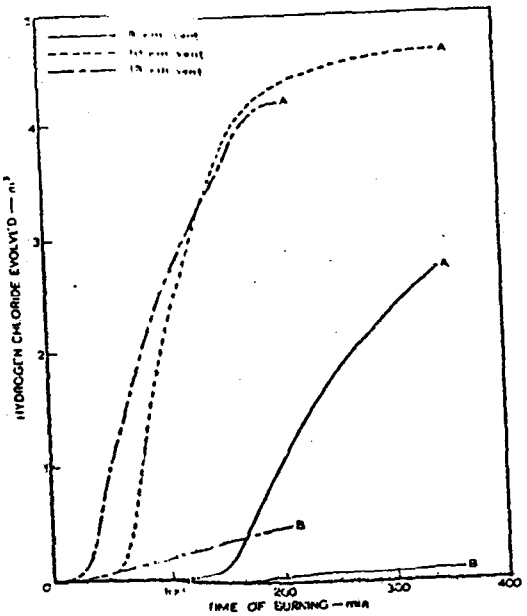


*Fig. 2. Evolution of hydrogen chloride. Fuel: Series A: 11 kg PVC wall lining, 12.8 kg wood fibre insulating board crib. Series B: 5.6 kg PVC incorporated in 12.8 kg wood fibre insulating board crib*

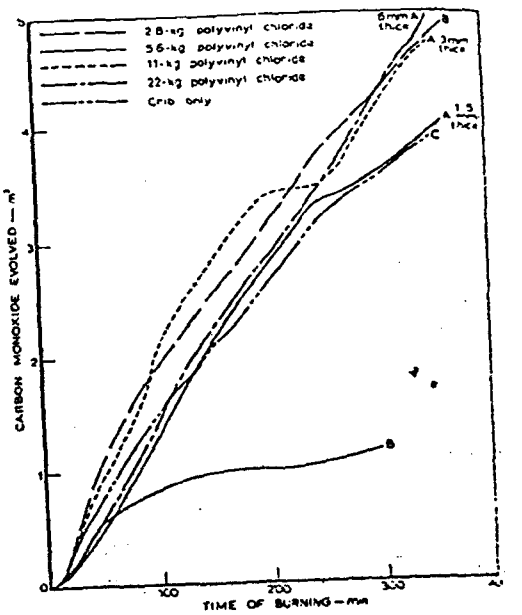


*Fig. 3. Evolution of carbon monoxide. Fuel: 12.8 kg wood fibre insulating board crib. Series A: PVC wall lining. Series B: PVC in wood fibre insulating board crib. Series C: wood fibre insulating board crib only*

remote from the compartment on fire. Thus the presence of hydrogen chloride could not be relied upon to ensure escape. The above values for hazardous levels of hydrogen chloride in air can be compared with the value of 3,000 parts per million of carbon monoxide which could prove lethal in half an hour; carbon monoxide is odourless and therefore may provide no warning of its presence.(3)

The results indicate that when the ventilation is small (5 cm deep vent, equivalent to an open fan-light) hydrogen chloride from PVC would make little or no contribution to the hazard already presented by carbon monoxide from traditional cellulosic combustibles. Assuming that the rate of burning is controlled solely by ventilation, it can be calculated from our results that about 30m³ of carbon monoxide would be generated in the first hour from a room 4 m x 4 m x 3 m high ventilated through an opening 1 m x 0.5 m at the top of the room. This quantity of carbon monoxide could contaminate 10,000 m³ to a level hazardous to life: as this volume is many times the volume of the average dwelling space, the hazard is a real one.

The above assessments are made on the assumption that the size of the burning compartment has no effect on the rate of combustion of the plastic. Some large scale tests are in progress in a compartment, measuring 4 m x 8 m x 3 m high, using similar plastics materials to examine the effect of scale.

Conditions would, however, be different if the ventilation were substantially higher than that of an open fan-light. Provided enough PVC were present in a room on fire, the hydrogen chloride formed from its combustion would add to the risk presented by carbon monoxide from traditional cellulosic materials, which need not differ much from that given above.(4) If a flaming fire developed quickly a substantial part of the plastic would be burnt in the first hour. Therefore, since other workers have shown that for a wide range of conditions the chlorine content of burning PVC is released quantitatively as hydrogen chloride(5, 6) the maximum level of risk due to hydrogen chloride in this case can be calculated. It can thus be shown that the hydrogen chloride from a coating (usually less than 0.1 mm) of the plastic on wallpaper in a room does not add much to the risk presented by the normal content of cellulosic matter. For greater loads of PVC full account must be taken of the actual rate of evolution of hydrogen chloride, which has been shown to vary with time.

A fuller account of the programme of tests on the combustion of cellulose and PVC, including the series of full scale experiments will be published later.

### Acknowledgement

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## THE ECONOMICS AND PERFORMANCE OF LEAD STABILISERS

*(concluded from page 285)*

the volume reactivity of the PVC compound containing its stabiliser is extremely high.

In certain outlets such as the production of rigid pipe, profiles, sheet extrusion, and rigid injection mouldings, which have now become major growth areas in the consumption of PVC, tribasic lead sulphate is often used as the sole stabiliser because of the higher processing temperatures involved. Additional protection against ultra-violet light may be obtained by replacing part or all of this stabiliser by dibasic lead phosphite. The presence of this phosphite acting as an antioxidant in conjunction with the normal pigments used in rigid PVC can prolong the life of the fabricated article.

Summarising it can be said that the stabiliser should confer on the plastic the necessary properties for its end use. Where non-toxic properties and transparency are required the use of lead stabilisers should not be considered. However, if heat stability, resistance to degradation by ultra-violet light or good electrical properties are required lead stabilisers should be used as they confer these properties at the lowest cost to the compounder. This is particularly so when high temperature processing

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My Future with Plastics, Palmer House, Chicago, Ill., pg. 623, Soc. of Plastics Engrs., Chicago, Ill., May 15-18, 1972.

# GASES FROM BURNING PVC

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## INTRODUCTION

From the small beginnings about thirty five years ago -- and particularly since the end of World War II -- the plastics industry has become a major visible contributor to our life-style. This is quite evident in the improvement in quality and availability of those utilitarian and aesthetic things we consider necessary for living today.

Those of us who have played the part of contributor to this growing use of plastics in today's society are well acquainted with the excitement of these resin, processing and product developments. Our greatest goal has been, and is, to bring to the area of product development the best combination of those attributes that will serve the product's needs. These can be itemized in many ways but it will suffice to say that we seek to optimize desirable physical strength; chemical, flame and electrical resistance; total economics of materials and processing; as well as the aesthetic properties of color and transparency.

Safety for processors and consumers has been "part and parcel" of these product developments and the many acceptances in the market place are tribute to the success of these endeavors, particularly in the vinyl plastic industry. We see tough transparent containers that serve in an outstanding way the package requirements for content security and safety, that provide content visibility and that resist breakage which can result in injury and economic loss to the consumer. In like manner, we may also mention the flame resistance and toughness of such products as wire and cable insulation and sheathing, phonograph records, flooring, pipe and building products.

From this background on the detailed attention paid by you to plastic product development, it may seem strange that the whole industry, and vinyl plastics in particular, has been targeted, mostly in the lay press, as a serious threat to environmental quality. Please note Figure 1.

When you dig into the background of these expressed concerns you find that most of them have to do with the nature of gases evolved when Polyvinyl Chloride is forced to burn. This may be either the accidental burning of the PVC content of a building along with the more easily combustible other materials of construction or the burning of PVC along with other waste products in an incinerator. Some of the questions raised are shown in Figure 2.

It is our intent here to take a look at the results reported by scientists from different areas of the world so that we all may have a better understanding of just what does happen when PVC burns. That PVC is difficult to ignite is a well recognized fact and Hilado[1] reports the flash-ignition temperature of 391°C (735°F) and self-ignition temperature of 454°C (850°F).

We would consider the burning of PVC in line with the candle-type mechanism described by Fenimore[2,3,4] and others[5]. In this way we can model the burning by considering that exterior heat initiates thermal degradation or pyrolysis of the polymer in the condensed or solid phase to produce fuel for combustion in the gas phase. Pyrolysis of the material in the absence of oxygen, then, provides us with a means to determine the fuel components that would oxidize in the presence of oxygen.

## PYROLYSIS

The decomposition of PVC resin will produce a thermogravimetric plot such as that in Figure 3. This is a graphical picture of PVC weight loss when heated in an inert atmosphere. Here we can see that a large weight loss (approximately 58 per cent) occurs around 300°C (572°F) followed by a slower loss of volatiles (approximately 38 per cent) out to 600°C (1112°F) and leaving a small amount (approximately 4 per cent) of ash. We are, of course, curious about the chemical nature of these pyrolysis products.

Before we look into the reported analyses of pyrolysis and combustion products of PVC, I believe it is necessary that we look at these results with the knowledge that each investigator developed a method of thermal treatment and product analysis as dictated by his own approach and instrumentation available. I suppose I am really saying that each study is somewhat individual but that all represent the results of planned scientific experiments. Some of the major variables in these studies are the method and rate of application of the heat flux, static or dynamic gas flow, and the methods and techniques of the gas analyses. Since space does not allow the full incorporation of these analytical methods, the reader is directed to the full reports as indicated in the references.

In 1959, Stromberg[6] reported on thermal degradation of PVC in a vacuum by first stripping the resin of HCl at temperatures up to 350°C (662°F) for 30 minutes. The resulting residue was then heated in a furnace at 400°C (752°F) for 30 minutes and the volatile products from this second heating were identified by mass spectrometry. Stromberg identified approximately 25 hydrocarbon products with ethylene and benzene predominant. Earlier work by Bradt and Mohler[7] showed that HCl is the primary decomposition product from 127°C to 300°C (261°F to 572°F) along with some benzene; and, above 300°C (572°F), a great variety of hydrocarbons evolve. No chlorine nor chlorinated hydrocarbons were reported in the gases.

At a later time, Ohtami and Ishikawa[8] pyrolyzed PVC in a nitrogen atmosphere and analyzed the degradation products by infrared and ultraviolet spectroscopy. They found that: (1) the pyrolysis products, other than HCl, consisted of aromatic and aliphatic hydrocarbons, and (2) the types of pyrolysis products were influenced by the stereoregularity (tacticity) in the original polymer. Additional qualitative or quantitative measurements were not made.

Noffz and associates[9] used a high frequency pyrolyzer to degrade PVC as well as a number of other polymers. They separated the products from PVC by gas chromatography and reported that the hydrocarbon degradation products consisted only of aromatic compounds. Neither aliphatic hydrocarbon nor chlorine was identified in the volatiles.

In a more recent study O'Mara[10] degraded PVC and PVC plastisols with a radiant type furnace at 600°C (1112°F) in a helium gas stream and analyzed the products by a combination of gas chromatographic and mass spectrometric technique. 600°C was chosen to provide pyrolysis products in a manner similar to those existing under fire conditions. It is also noted that this temperature is above the self-ignition temperature (850°F) mentioned previously for PVC[1].

O'Mara reports no degradation products resulting from plasticizer interaction in the plastisols. He also reports that a stoichiometric amount of HCl is released (58.3 per cent) from PVC based on the chlorine in the polymer. The remaining products were hydrocarbons (~38 per cent) and a chlorine-free carbonaceous ash of 3 to 4 per cent of the original polymers.

Combining these background studies we can now put labels on the thermogravimetric plot we saw in Figure 3. Please note Figure 4.

Here we see that unburnable HCl is the primary product up to 300°C (572°F). Above 300°C we see the production of burnable volatile hydrocarbons and ash.

In the O'Mara[10] study the hydrocarbon fraction was further analyzed in a gas-chromatograph to provide a qualitative and quantitative analysis. In Table 1 we see the results of three runs that demonstrate the reproducibility of this technique.

Here we see that the pyrolysis of PVC at 600°C (1112°F) produces a series of aliphatic and aromatic hydrocarbons. The chromatograph areas shown closely reflect the mole per cent content. The amount of aromatic products is greater than that of aliphatics, and benzene is the major organic component of the more than 25 identified. Only one chlorinated product, chlorobenzene, was found in minor amounts. No chlorine was found.

In another recent study, O'Mara[11] described a highly reproducible method for HCl analysis from pyrolyzed PVC. He also showed that the outflow of HCl in the pyrolysis gas could be reduced by compounding with basic fillers such as calcium carbonate, potassium carbonate and magnesium oxide, among others. Under his conditions of short time flame exposure, the combustion of a number of pyrolysis residues in air revealed that the amount of HCl absorbed by the basic filler was retained in the non-carbonaceous ash.

COMBUSTION

Now that we have considered the nature of the gaseous products supplied by pyrolyzing PVC in the absence of oxygen, let's take a look at reports of scientific investigations of the, perhaps, more practical exposure, combustion.

Most of the combustion studies of PVC prior to 1959 analyzed the gases by colorimetric and gravimetric methods. An extensive review of these original scientific investigations was published in 1963 by Underwriters' Laboratories[12] and includes information on the combustion and pyrolysis of other polymers and natural building materials. It is consistently reported that combustion of PVC produces large amounts of hydrogen chloride, carbon dioxide and carbon monoxide and minor amounts of hydrocarbons. This was accompanied by severe oxygen depletion and, very occasionally, traces of phosgene and vinyl chloride.

Recent studies of the old colorimetric and gravimetric methods[13,14] have shown that the presence of large amounts of hydrogen chloride can interfere and cause erroneous reporting of the presence of phosgene.

In 1967, Tsuchiya and Sumi[15] decomposed PVC at 350, 600 and 800°C (662, 1112 and 1472°F) in a ceramic boat inserted in a furnace through which they passed helium gas for pyrolysis, or air in excess for complete combustion. When products of decomposition were analyzed, primarily by gas chromatography, they found that the main decomposition product in both cases was hydrogen chloride. The amount of hydrogen chloride produced in an inert atmosphere approached the theoretical value expected for PVC. Inasmuch as these investigators measured only gaseous hydrogen chloride, the amount determined in an oxidizing atmosphere was slightly lower because water vapor produced in an atmosphere of air absorbed some of the hydrogen chloride.

Under combustion conditions, the main change from pyrolysis gas effluent was the presence of large amounts of carbon dioxide and monoxide with a corresponding reduction in hydrocarbon content. Other oxidation products such as acid, aldehydes, alcohols and ketones were not found. Neither chlorine nor phosgene was detected though sensitive detection methods were used.

In a more recent report, Boettner and associates[16] reported combustion gas analyses on three PVC polymers, one copolymer with vinyl acetate and three related compounds. They analyzed the collected gases from combustion -- initially by infrared spectroscopy, and, in detail, by a combination of gas chromatography and a mass spectrometer. The combustion for quantitative gas analyses was done in a furnace by heating, after an initial heating at room temperature, from 200°C to 600°C (392 to 1112°F) at a rate of 3°C per minute. Air was supplied to the sample at a rate which, when integrated over the entire run, would result in about twice the amount of oxygen necessary to convert all carbon to carbon dioxide and at higher and lower levels as well. Under these conditions, the resin samples completely disappeared with no measurable residue and the compounds left a residue related to the presence of inorganic matter in the recipe.

Boettner reported that combustion gases from PVC resin contained approximately 50 different chemical compounds and quantitatively analyzed more than 20 of these. Although there are many analyses in this report -- including the effects of varying air supply and heating rate -- a typical analysis comparing a pure resin and a wire and cable compound (51 per cent PVC) is shown in Table 2.

Here we note the major constituents of the combustion gases to be carbon dioxide, hydrogen chloride and carbon monoxide. The other gaseous components are mainly hydrocarbons and the most abundant one is benzene. We note that the hydrocarbons produced from the compounds are much greater than that from PVC resin and this is attributed to the presence in the gases of breakdown materials from the phthalate plasticizer. These latter are a series of hydrocarbons similar to those produced by PVC. Hydrogen chloride in the gas reflects essentially complete conversion of the chlorine in the PVC. The only other chlorine compounds reported in the gas are vinyl chloride and methyl chloride in quantities less than 1 mg per gram of sample oxidized. Although detectors capable of measuring 0.1 ppm were used, no phosgene was found.

One of the more recent reports on PVC combustion studies was made by W. D. Woolley[17] in 1971. In this work gases from decomposition of PVC in air and nitrogen are analyzed by gas chromatography. PVC resin and unplasticized PVC sheet samples are compared and a special effort was made to detect phosgene and other oxygenated organic compounds. Decomposition of the 15 mg samples took place in a tube furnace at 300, 400, 450 and 500° (572, 752, 842 and 932°F) with a dry air or nitrogen flow of 100 ml per minute.

Woolley essentially verified the gas analyses of Boettner[16] in that the organic components consist mainly of aromatic and aliphatic hydrocarbons. He detected approximately seventy-five organic materials, about twenty-five more than Boettner. Although the products are modified by the presence of oxygen, no oxygenated species were detected. Phosgene was particularly looked for and was not detected.

The organic gaseous decomposition products from PVC polymer were found to be similar in identity -- but greater in quantity -- compared to those from the rigid PVC sheet. This could be reflecting the difference in the resin content of the samples: 100 per cent for the PVC polymer and approximately 90 per cent for the rigid PVC sheet.

In 1971 Kobayashi and associates[18] reported on analyses of combustion gases from PVC and PVC products in a comparative study with natural high polymer materials such as wood, paper, wool and silk. Their experiments were made by heating one gram samples in an electric furnace over a range of 300 to 700°C (572 to 1292°F) through which air flowed at a controlled rate (1.0-1.5 liters per minute) and at normal (21 per cent) and reduced (10.5 per cent) oxygen levels. The gases were analyzed by means of selected detector tubes.

Following is a quote from the report:

> "As for the gas composition generating from the PVC products at large, a major part consists of hydrogen chloride and carbon dioxide excepting hydrocarbons and water content, followed by carbon monoxide, but neither phosgene, chlorine, nitrogen dioxide, oxygen sulphide nor hydrogen sulfide were determined by the detector tubes."

Special effort was made to determine if phosgene were present in the combustion gases. The detection limit was determined to be 0.1 ppm. No phosgene was reported in any of the combustion gases.

Carbon monoxide and carbon dioxide from combustion of the natural polymers generally showed up in the gases at lower temperatures and at higher levels than with PVC. This was

related to the easier ignition of these products and the degree that hydrogen chloride does not evolve with these natural polymers in comparison with PVC.

In the comparison analysis with natural products, Kobayashi reported hydrogen cyanide in combustion gases from wool, and both hydrogen cyanide and ammonia in gases from burning silks. The maximum concentrations were reached at 400°C (752°F) and were as follows: wool -- hydrogen cyanide (1.2 per cent); silk -- hydrogen cyanide (0.36 per cent) and ammonia (0.5 per cent). For comparison the maximum concentration of hydrogen chloride in gases from burning PVC products was from 0.65 per cent at 500°C (932°F) for flexible auto cover leather to 12.0 per cent at 400°C (752°F) for PVC resin.

## TOXICITY

At the start we should recognize that the products of combustion of all organic products are toxic and this includes wood, paper, natural fibers, etc. This is, of course, because of two main occurrences in a fire: production of carbon monoxide and dioxide and reduction of the oxygen concentration. The latter is common to all organic combustion and this includes PVC.

Specific studies of the toxicity of gases from burning PVC have been conducted by various investigators over the years[12]. The most recent was reported by Cornish and Abar[19] of the University of Michigan. This investigation utilized the same samples of PVC as those described in the previously mentioned study of PVC combustion by Boettner[16]. All animals exposed to the combustion gases were male Sprague-Dawley rats. Autopsies were performed on all animals that died.

Cornish and Abar reported, "Without question, the major cause of death in this study of four polymers was the presence of relatively large amounts of carbon monoxide in the pyrolysis gas stream." They found relatively minor or no tissue damage in test animals exposed to hydrogen chloride from PVC decomposition.

## CONCLUSIONS

1. Phosgene and chlorine are not combustion products of PVC.
2. When PVC is forced to burn, the prime products are carbon monoxide, carbon dioxide, hydrogen chloride and water.
3. Minor gaseous products from burning PVC are aromatic and aliphatic hydrocarbons, predominantly benzene.
4. Carbon monoxide is the prime toxic component produced.
5. Hydrogen chloride from PVC pyrolysis or combustion is essentially stoichiometric.


## ACKNOWLEDGEMENT

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## FIGURE 1

NEW YORK TIMES, OCT. 22, 1969---
"NEW PLASTIC CAUSES AIR HAZARD"

CINCINNATI POST, OCT. 31, 1969---
"DISCARDED PLASTIC MATERIALS SUMMING UP INCINERATOR"

NBS NEWS RELEASE NOV. 1969---
"HAZARDOUS PRODUCT PRODUCED BY ELECTRICAL INSULATION"

INDUSTRIAL RESEARCH FEB. 1970---
"DECOMPOSITION OF PVC YIELDS HAZARDOUS GAS"

MODERN PACKAGING JAN. 1970---
"PVC AND THE CYCLAMATE SYNDROME"

DETROIT NEWS FEB. 24, 1970---
"NEW PLASTIC IS TOXIC WHEN BURNED"

NEW YORK DAILY NEWS JUL. 16, 1971--
"PLASTICS FIRMS SUE OVER TAX"

C & E NEWS NOV. 22, 1971---
"PLASTIC CONTAINER TAX RULED OUT IN NEW YORK"

## FIGURE 2

- HOW DOES PVC BURN?
- WHAT ARE THE MAJOR DECOMPOSITION PRODUCTS FROM PVC?
- WHAT ARE THE MAJOR COMBUSTION PRODUCTS FROM PVC?
- IS PHOSGENE A COMBUSTION PRODUCT?
- IS CHLORINE A COMBUSTION PRODUCT?
- ARE THE COMBUSTION PRODUCTS FROM PVC TOXIC?

FIGURE 3

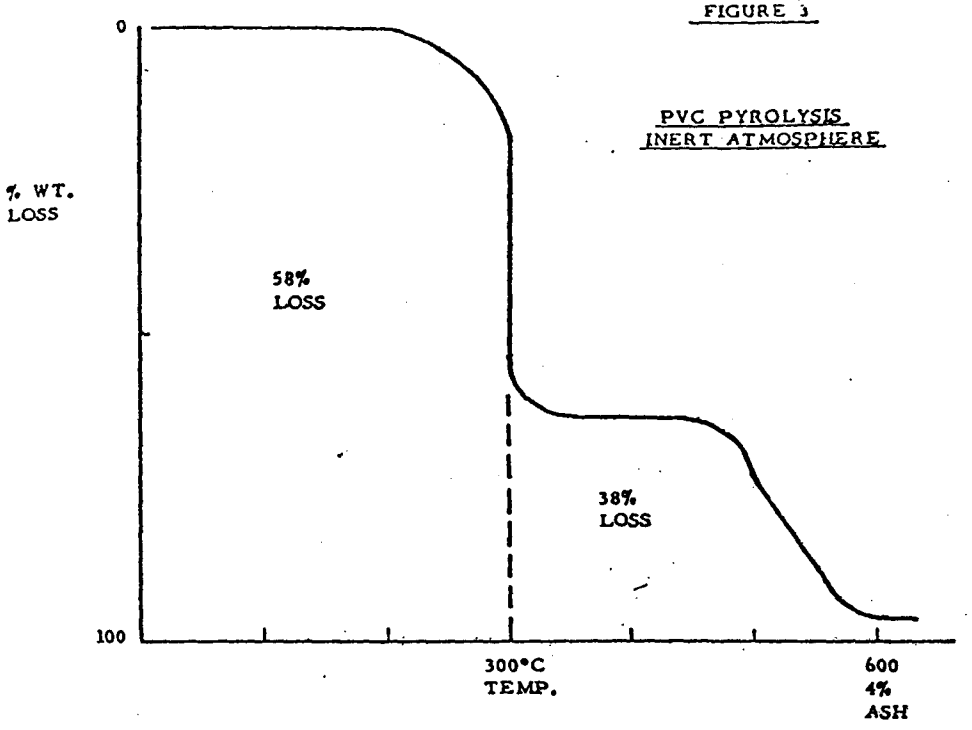


FIGURE 4

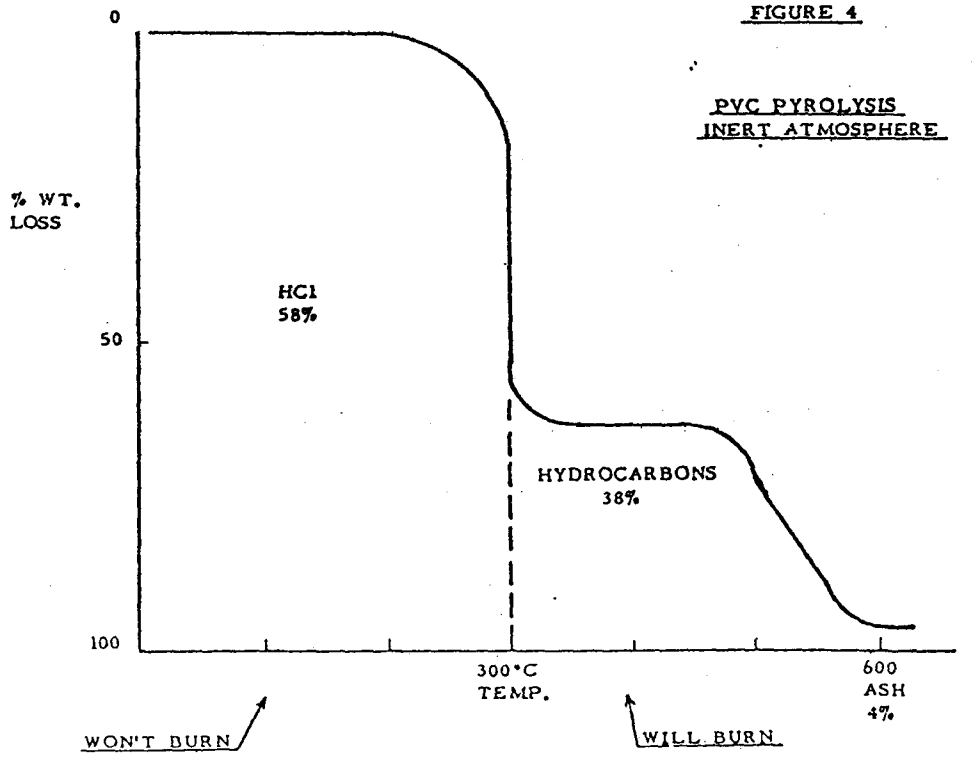


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FIGURE 5

## CONCLUSIONS

1. PHOSGENE AND CHLORINE ARE NOT COMBUSTION PRODUCTS OF PVC.
2. WHEN PVC IS FORCED TO BURN, THE PRIME PRODUCTS ARE CARBON MONOXIDE, CARBON DIOXIDE, HYDROGEN CHLORIDE AND WATER.
3. MINOR GASEOUS PRODUCTS FROM BURNING PVC ARE AROMATIC AND ALIPHATIC HYDROCARBONS, PREDOMINANTLY BENZENE.
4. CARBON MONOXIDE IS THE PRIME TOXIC COMPONENT PRODUCED.
5. HYDROGEN CHLORIDE FROM PVC PYROLYSIS OR COMBUSTION IS ESSENTIALLY STOICHIOMETRIC.

TABLE 1.

PVC PYROLYSIS PRODUCTS

OVERALL DEGRADATION PROFILE

| | %, Wt. |
|---|---|
| HCl | 58.3 |
| Hydrocarbons | 37.0 |
| Carbon Char | 4.7 |

HYDROCARBONS PROFILE
(Gas Chromatographic Area)

| | Area, % | | |
|---|---|---|---|
| | Run 1 | Run 2 | Run 3 |
| CO | 0.6 | 2.2 | 0.8 |
| Methane | 8.8 | 7.8 | 9.3 |
| $CO_2$ | 0.4 | 0.3 | 0.2 |
| Ethylene | 3.5 | 3.5 | 3.8 |
| Ethane | 4.8 | 5.1 | 5.5 |
| Propylene | 2.9 | 2.6 | 3.0 |
| Propane | 3.0 | 1.9 | 2.3 |
| Butane, butene<br>Butadiene, diacetylene | 2.5 | 2.1 | 2.1 |
| $C_5$ and $C_6$ hydrocarbons | 1.9 | 1.8 | 1.3 |
| Benzene | 51.2 | 50.8 | 50.1 |
| Toluene | 5.3 | 5.9 | 5.8 |
| Chlorobenzene | 1.1 | 1.1 | 1.3 |
| Xylene | 1.9 | 2.1 | 2.3 |
| Allylbenzene | 1.3 | 1.4 | 1.6 |
| $C_9H_{12}$ | 0.4 | 0.5 | 0.5 |
| $C_9H_{12}$ | 0.2 | 0.2 | 0.3 |
| Indane | 0.2 | 0.3 | 0.3 |
| Indene<br>Ethyltoluene | 0.9 | 1.4 | 0.9 |
| Methylindane | 0.5 | 0.5 | 0.5 |
| Methylindenes | 1.1 | 1.3 | 1.0 |
| Napthalene | 4.8 | 4.6 | 4.5 |
| Dimethylindane | 0.7 | 0.8 | 0.8 |
| Methylnaphthalene | 0.8 | 0.7 | 0.7 |
| Methylnaphthalene<br>Acenaphthalene | 1.2 | 1.0 | 1.1 |

RE: O'Mara, M.M., J. Polym. Sci. A-1, 8, 1970, p. 1893

TABLE 2.

COMPARISON OF COMBUSTION PRODUCTS
PVC RESIN VS. WIRE & CABLE COMPOUND
(POLYMER B* VS. PLASTIC G*)

COMBUSTION PRODUCTS, mg/g

| Material | PVC Resin | Wire & Cable Compound (51% PVC) |
|---|---|---|
| HCl | 583 | 273 |
| $CO_2$ | 729 | 616 |
| CO | 442 | 67 |
| Methane | 4.6 | 6.6 |
| Ethylene | 0.58 | 2.3 |
| Ethane | 2.2 | 3.0 |
| Propylene | 0.47 | 2.0 |
| Propane | 0.84 | 1.7 |
| Vinyl Chloride | 0.60 | 3.3 |
| 1-Butene | 0.18 | 1.1 |
| Butane | 0.28 | 1.1 |
| Isopentane | 0.02 | 0.15 |
| 1-Pentene | 0.06 | 0.35 |
| Pentane | 0.16 | 0.58 |
| Cyclopentene | 0.05 | 0.14 |
| Cyclopentane | 0.05 | 0.16 |
| 1-Hexene | 0.05 | 0.24 |
| Hexane | 0.12 | 0.49 |
| Methylcyclopentane | 0.14 | 0.14 |
| Benzene | 36.0 | 10.0 |
| Toluene | 1.3 | 0.94 |
| Residue** | ------ | 159 |

* RE: Boettner et al, J. Appl. Sci., 13, February 1969, p. 390

** Residue is what remained in combustion boat.

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# Toxicity of Pyrolysis Products of Vinyl Plastics

*Herbert H. Cornish, PhD, and Ellen L. Abar, MA, Ann Arbor, Mich*

Polyvinyl chloride polymers and formulations were pyrolyzed in a stream of air by gradually raising the temperature from ambient to approximately 600 C. The pyrolysis air stream was diluted with twice its volume of room air, and rats were exposed to it. Exposure to an air stream containing the pyrolyzed products of 1 to 2 gm of polyvinyl chloride polymer resulted in the death of 50% of the animals. Most deaths were due to carbon monoxide (CO), and carboxyhemoglobin (COHb) levels correlated well with the amount of plastic pyrolyzed. Little histological evidence of lung damage was evident. When oxygen ($O_2$) was added to the air stream to prevent deaths from CO, pulmonary edema and interstitial hemorrhage developed. The lungs of some animals exposed to high levels of pyrolysis products of vinyl chloride-vinyl acetate copolymer also showed focal edema and intra-alveolar hemorrhage. Polyvinyl chloride formulations, containing additives and inert materials, were in general less toxic per gram of sample pyrolyzed.

THE WIDESPREAD use of plastics in the manufacture of commercial and household products raises the question of potential hazards associated with burning these materials. This is not a new problem; it was investigated by Berger et al[1] in a study of thermosetting plastic materials used for insulating electrical conduits. They determined some products produced during pyrolysis of phenolic and melamine plastics—carbon monoxide (CO), cyanides, and ammonia. Watson et al[2] reported the chemical identification of pyrolysis products of foamed polyvinyl chloride. Zapp's[3] investigations revealed pulmonary congestion and edema in rats exposed to the pyrolysis products of polyurethane foam. The quantity and nature of pyrolysis products of Teflon depends on degradation temperature. Waritz and Kwon[4] reported no adverse effects in rats exposed to products of Teflon heated to 400 C, while pyrolysis at 450 C produced acute pulmonary hemorrhage and edema. Coleman et al[5] suggest that at 550 to 700 C, carbonyl fluoride may be a major toxic product of Teflon degradation.

MacFarland and Leong[6] studied the toxicity of pyrolysis products of polyurethane and polyurethane-coated nylon. Acute asphyxia from occlusion of the upper respiratory tract was apparently the mechanism of death of animals exposed to pyrolysis products of polyurethane, whereas with nylon products, death occurred from slowly developing pulmonary edema. Thrune[7] reported the chemical analysis of products of combustion of halogen containing epoxy resins, while Leong and MacFarland[8] reported on the hazards from thermodecomposition of epoxy resins. On the basis of animal studies they suggest that pyrolysis products of epoxy resins may constitute a hazard under circumstances realizable in practice.

Boettner and Weiss[9] described an analytical system for identifying the volatile pyrolysis products of a virgin homopolymer polyvinyl chloride (PVC) resin. In another study, Boettner et al[10] noted that three distinct breakdown temperature ranges occurred as temperature was increased. The pyrolysis products released during these three weight loss periods differed markedly. The present study is an extension of their work to include toxicological investigations of the pyrolysis products of polyvinyl chloride plastics. The samples and sample designations are those of Boettner et al.[10]

## Materials and Methods

Materials.—The materials consist of four polymers produced by two companies and three formulations which utilize three of the polymers. The materials were classified as follows.

Sample A. A polyvinyl chloride homopolymer in which approximately 20% of the particles fall within the range of 100μ to 250μ, with most of the remainder falling below 100μ in size.

Sample B. Similar to A but of somewhat

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smaller particle size, with 85% of the particles within the 75μ to 200μ range, and the remainder below 75μ.

Sample C. A polyvinyl chloride homopolymer (powder) produced by a different company.

Sample D. A copolymer of vinyl chloride and vinyl acetate (powder) in the approximate ratio of 85:15.

Sample E. A formulation commonly used in electrical wire insulation utilizing polymer C (small cubes, approximately 5 mm).

Sample F. A formulation commonly used for floor tile utilizing copolymer D (fluffy powder containing asbestos).

Sample G. A formulation commonly used in wire insulation utilizing polymer B (sheets cut into approximately 5-mm cubes).

Animals.—All animals included in the present study were male Sprague-Dawley rats. The animals ranged in weight from 200 to 300 gm and were maintained on an ad libitum diet of commercial rat chow and water except during the exposure periods. At autopsy, animals were anesthetized with ether, and blood was removed by heart puncture for the determination of carboxyhemoglobin (COHb) and other blood studies. In most cases, blood was also obtained for COHb measurement in animals dying during the exposure periods. In some cases, blood for COHb determinations was obtained from the tail vein. Tissues were promptly removed and small sections fixed in 4% formaldehyde and stained with hematoxylin and eosin. Animals surviving the exposures and not killed were maintained for a minimum of two weeks and observed for latent effects.

Exposure Techniques.—The exposure chamber utilized in early studies was a 7-liter desiccator with the animals maintained on a grid 4 to 5 cm above the bottom. Four rats were normally exposed at one time. The weighed plastic was decomposed in a ceramic boat placed in a combustion furnace programmed for increasing temperature (three degrees per minute). This programming technique was recently described by Boettner and Weiss.[9] Temperature was measured in the combustion boat by a thermocouple and reached a maximum of 550 C after 115 to 140 minutes at which time pyrolysis was essentially complete. Animals were removed at or near the end of this time period unless death occurred earlier. During pyrolysis, 2 cu ft of air per hour passed over the plastic. The pyrolysis stream was cooled and diluted by the addition of 4 cu ft of air per hour prior to entry into the animal chamber. Temperature in the animal exposure chamber did not rise above 29 C, with an average of 27 C. The ash remaining in the ceramic boat or in the boat and combustion tube was weighed at the end of the exposure to determine the extent of pyrolysis. Periodic measurements of hydrochloric acid (HCl) and CO were made both in the entrance and exit air streams of the exposure chamber, utilizing a gas sampling pump and detector tubes. Unfortunately, HCl detector tubes did not go above 500 ppm. Previous studies by Boettner et al.[10] however, show that HCl is released over a relatively short time during pyrolysis. Thus, maximum concentrations can be estimated with a fair degree of accuracy.

In early studies the level of HCl in the air leaving the exposure chamber (desiccator) was markedly lower than that entering the chamber. Thus, in subsequent studies, exposure chambers in which only the animal's nose protruded into the pyrolysis airstream were utilized. Plastic baby bottles, attached to small nose funnels, opened into a large vinyl tubing through which the airstream was passed. This type of exposure eliminated the absorption of HCl, and possibly other vapors in the urine which accumulated in the bottom of the small chamber. It also prevented animal crowding and the adsorption of pyrolysis products on animal fur. Hydrochloric acid and CO concentrations were measured in samples taken from the moving air stream.

Blood Analysis.—Blood carboxyhemoglobin was determined by the micro-method of Scholander and Roughton[11] and was always done in duplicate or triplicate. Serum glutamic oxaloacetic transaminase (SGOT) was determined by the method described by Steinberg et al.[12] Hemoglobin levels were measured spectrophotometrically in dilute ammonia.

## Results

The results of the first study utilizing varying amounts of PVC homopolymer (sample A) are shown in Table 1. The animals were exposed in a 7-liter dessicator. Note that pyrolysis was essentially complete, and that quantities of ash remaining in the ceramic boat were negligible. Although the level of CO in the air was greater than 3,000 ppm for some time during each of the exposures, the COHb levels varied greatly among the different groups. However, the COHb levels correlate well with the amount of plastic pyrolyzed. Exposures to increasing amounts of sample A demonstrate this correlation. The quantity of pyrolyzed plastic which killed 50% of the

Table 1.—Effect o

| Quantity Pyrolyzed (gm) | Weight of Residue (gm) | Exp T (n |
|---|---|---|
| 0.8 | <0.01 | 1 |
| 1.0 | <0.01 | 1 |
| 1.2 | | |
| 1.4 | <0.01 | |
| 1.5 | 0.03 | |

*Animal deaths.
†Numerator, deaths; den

animals under these
($LC_{50}$) was approxim
In all exposures, anim
of nasal and eye irri
charge, salivation, an
Convulsions were a
the animals with high

Since the work of
had indicated that H
PVC at relatively l
mals were exposed i
early pyrolysis produ
ple A, and remove
affected by large qu
were killed 24 hou
exposed animals su
loss during the exp
not completely rest
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were not significantl
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tered, or were SG
utilized as a mea
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er, kidney, and spl
between exposed an

In the subsequ
were exposed by
nose into the pyr
scribed in the meth

Table 1.—*Effect of Pyrolysis Products of Polyvinyl Chloride Homopolymer (Sample A)*

| Quantity Pyrolyzed (gm) | Weight of Residue (gm) | Exposure Time (min) | CO Max Conc (ppm) | Rat No. | Blood Hb (gm/100 cc) | Blood COHb (vol %) | Mortality† |
|---|---|---|---|---|---|---|---|
| 0.8 | <0.01 | 130 | >3,000 10-15 min | 1 | 16.2 | 14 | 0/4 |
| | | | | 2 | 15.3 | 14 | |
| | | | | 3 | 16.2 | 5 | |
| | | | | 4 | 17.1 | 8 | |
| 1.0 | <0.01 | 135 | >3,000 10-15 min | 1 | 15.3 | 15 | 1/4 |
| | | | | 2 | 15.7 | 7 | |
| | | | | 3 | 18.1 | 38* | |
| | | | | 4 | 16.2 | 8 | |
| 1.2 | | 135 | >3,000 15-20 min | 1 | 15.3 | 65* | 2/4 |
| | | | | 2 | 16.2 | 78* | |
| | | | | 3 | 15.0 | 11 | |
| | | | | 4 | 15.7 | 65 | |
| 1.4 | <0.01 | 125 | >3,000 15-20 min | 1 | 17.6 | 65* | 3/4 |
| | | | | 2 | 16.6 | 19 | |
| | | | | 3 | 16.6 | 55* | |
| | | | | 4 | 15.7 | 68* | |
| 1.5 | 0.03 | 120 | >3,000 15-20 min | 1 | | 42* | 4/4 |
| | | | | 2 | | 55* | |
| | | | | 3 | | 40* | |
| | | | | 4 | | 45* | |

*Animal deaths.
†Numerator, deaths; denominator, total.

animals under these exposure conditions ($LC_{50}$) was approximately 1.2 gm of PVC. In all exposures, animals showed symptoms of nasal and eye irritation with nasal discharge, salivation, and chromodacryorrhea. Convulsions were a common occurrence in the animals with high COHb levels.

Since the work of Boettner and Weiss had indicated that HCl was released from PVC at relatively low temperatures, animals were exposed in the desiccator to the early pyrolysis products of 2.0 gm of sample A, and removed before they became affected by large quantities of CO. Animals were killed 24 hours after exposure. The exposed animals suffered a slight weight loss during the exposure period which was not completely restored by the following day. Liver and kidney body weight ratios were not significantly different from control animals. Hematocrit values were not altered, nor were SGOT levels which were utilized as a measure of tissue damage. Histopathological examination of lung, liver, kidney, and spleen showed no differences between exposed and nonexposed rats.

In all subsequent studies, the animals were exposed by the insertion of only the nose into the pyrolysis air stream as described in the methods.

The results of exposure of animals to PVC homopolymer B is shown in Table 2. All animals exposed to 0.8 gm of pyrolyzed plastic survived. Maximum COHb levels were 17 and 21 vol% in two of four rats. At 1.2 gm of plastic, one animal with 66 vol% COHb died. The surviving animals had considerably lower COHb levels. At 1.4 gm, three of four animals did not survive the exposure. The single surviving animal again had a relatively low COHb level of 13 vol%, as compared with 65 to 75 vol% in the other three animals.

An attempt was made to overcome the acutely toxic effects of CO and possibly allow other aspects of toxicity to become evident. Animals were exposed to PVC pyrolysis products as previously described with air passing over the sample at 2 cu ft/hr, but with replacement of the air dilution stream by oxygen (4 cu ft/hr). In separate studies, 3.5 gm of samples A and B were pyrolyzed and animals exposed to the pyrolyzed air streams. All animals survived these exposures which, without oxygen ($O_2$) would have been lethal. Calculations of HCl release would predict levels above 6,000 ppm for 15 to 30 minutes during this exposure. Animals were killed 24 hours after exposure and lung tissue taken for histopatho-

Table 2.—*Effect of Pyrolysis Products of Polyvinyl Chloride Homopolymer (Sample B) and Formulation (Sample G)*

| Quantity Pyrolyzed (gm) | Weight of Residue (gm) | Exposure Time (min) | CO Max Conc (ppm) | Rat No. | Blood Hb (gm/100 cc) | Blood COHb (vol %) | Mortality |
|---|---|---|---|---|---|---|---|
| Sample B | | | | 1 | 17.1 | 17 | |
| 0.8 | <0.01 | 130 | >3,000 | 2 | 16.2 | 21 | 0/4 |
| | | | | 3 | 15.7 | 7 | |
| | | | | 4 | 13.7 | 5 | |
| | | | | 1 | 17.1 | 66* | |
| 1.2 | <0.01 | 130 | >3,000 5-10 min | 2 | 16.6 | 19 | 1/4 |
| | | | | 3 | 15.3 | 9 | |
| | | | | 4 | 17.1 | 11 | |
| | | | | 1 | 16.6 | 74* | |
| 1.4 | <0.01 | 130 | >3,000 10-20 min | 2 | 14.5 | 68* | 3/4 |
| | | | | 3 | 15.3 | 13 | |
| | | | | 4 | 17.1 | 69* | |
| Sample G | | | | 1 | 13.0 | 7 | |
| 6.0 | 0.93 | 105 | 800 | 2 | 15.3 | 7 | 0/4 |
| | | | | 3 | 12.0 | 9 | |
| | | | | 4 | 12.7 | 3 | |

*Animal deaths.
†Numerator, deaths; denominator, total.

logical examination. Of the animals exposed to sample A, all showed evidence of pulmonary edema and intra-alveolar and interstitial hemorrhage. Several of the hemorrhages were associated with angular fibers and sheets of foreign material within the alveoli. Examination of the lungs of animals exposed to sample B revealed pulmonary edema and interstitial hemorrhage, but no traces of foreign material.

Sample C is a PVC homopolymer produced by another company. The results of exposure to the pyrolysis products of this material are shown in Table 3. Exposure ranged from 1.2 gm where all animals survived, to 2.3 gm where all animals died. In general, COHb levels correlate well with the degree of exposure and the mortality data. The acute $LC_{50}$ under these conditions is approximately 2.0 gm of pyrolyzed plastic. Surviving animals were killed 24 hours after exposure. Tissues of exposed animals were comparable to control animals. Serum SGOT levels, however, showed some elevations suggestive of tissue damage.

The results of the exposure of animals to the pyrolysis products of the vinyl chloride-vinyl acetate copolymer (sample D) are shown in Table 4. The pyrolysis of quantities greater than 2.0 gm resulted in deaths of animals even though they had relatively low COHb levels. Rats died after exposures to pyrolysis products of 2.5 and 2.8 gm of sample D with COHb levels of 12.3 to 14.5 vol%. These COHb levels do not appear to b high enough to be responsible for the death which occurred during and shortly afte exposure. SGOT levels of all rats exposed 2.0 gm were slightly elevated, suggestive d tissue damage.

Histological sections of lung, liver, ar kidney of all animals exposed to 2.0 gm d product were not different from those control animals. The lungs of some but n all animals exposed to 2.5 to 2.8 gm d pyrolysis product showed focal edema wi areas of acute suppuration and occassiona intra-alveolar hemorrhage.

Sample E is a formulation of polymer C commonly used in wire insulation applic tions. The results of this study are shown i Table 5. Even at levels as high as 3.0 gm c formulation, CO levels did not reach 1,00 ppm in the air stream, compared with va ues as high as 3,000 ppm with 1.2 gm c homopolymer. Hydrochloric acid levels i the 4.0-gm sample air stream were in exces of 500 ppm. All animals survived exposure ranging from 3.0 to 4.0 gm of pyrolyzed material. Carboxyhemoglobin levels did no rise above 23 vol% in any of the exposed animals, and no animals died during th exposure period. Animals not killed fo COHb levels were maintained for 24 hours then killed and examined for histological evidence of lung damage. In all cases, th

Table 3.-

| Quantity Pyrolyzed (gm) | Weight Resid (gm) |
|---|---|
| 1.2 | <0.0 |
| 1.5 | 0.0 |
| 1.8 | ... |
| 2.1 | <0.( |
| 2.3 | 0.( |

Controls

*Animal deaths.
†Numerator, de

lungs of expo to controls.

Three of fo the pyrolysis formulation. ( and two oth hours. Carbo high as 30 rats exposed gm of PVC fo ately after ex for histopat was no evid exposed grou

Sample F. tion of samp of inert mat 6.0 gm of total residue of the origi 1.4 gm of posed. All vol%. The after expos lungs and S controls.

The pyrol (wire formu the 16 rats cal evidenc

Table 3.—*Effect of Pyrolysis Products of Polyvinyl Chloride Homopolymer (Sample C)*

| Quantity Pyrolyzed (gm) | Weight of Residue (gm) | Exposure Time (min) | CO Max Conc (ppm) | Rat No. | Blood Hb (gm/100 cc) | Blood COHb (vol %) | Lung (%) (Body Weight) | SGOT (units) | Mortality† |
|---|---|---|---|---|---|---|---|---|---|
| 1.2 | <0.01 | 130 | >3,000 | 1 | 15.0 | 7 | ... | ... | 0/4 |
| | | | | 2 | 15.0 | 0 | ... | ... | |
| | | | | 3 | 16.2 | 0 | ... | ... | |
| | | | | 4 | 14.1 | 0 | ... | ... | |
| 1.5 | 0.02 | 135 | >3,000 | 1 | 20.4 | 30 | 0.38 | 69 | 1/4 |
| | | | | 2 | 12.3 | 64* | 0.38 | ... | |
| | | | | 3 | 13.7 | 42 | 0.47 | 127 | |
| | | | | 4 | 14.5 | 24 | 0.46 | 124 | |
| 1.8 | ... | 135 | >3,000 | 1 | 15.3 | 42 | 0.50 | 99 | 0/4 |
| | | | | 2 | 15.7 | 28 | 0.51 | 132 | |
| | | | | 3 | 14.5 | 38 | 0.58 | 123 | |
| | | | | 4 | 15.0 | 15 | 0.47 | 109 | |
| 2.1 | <0.01 | 130 | >3,000 | 1 | 13.7 | 46* | 0.41 | ... | 2/3 |
| | | | | 2 | 17.6 | 21 | 0.47 | ... | |
| | | | | 3 | 17.5 | 44* | 0.50 | ... | |
| 2.3 | 0.02 | 135 | >3,000 | 1 | 16.2 | 41* | 0.50 | 134 | 4/4 |
| | | | | 2 | 15.3 | 30* | 0.50 | 103 | |
| | | | | 3 | 15.3 | 39* | 0.56 | ... | |
| | | | | 4 | 15.7 | 61* | 0.52 | 164 | |
| Controls | | | | 6 rats | | | 0.53 | 67 | |

*Animal deaths.
†Numerator, deaths; denominator, total.

lungs of exposed animals were comparable to controls.

Three of four rats died when exposed to the pyrolysis products of 6.0 gm of this formulation. One died during the exposure and two others died within the next 16 hours. Carboxyhemoglobin levels ranged as high as 30 vol%. An additional group of rats exposed to the pyrolysis products of 6.0 gm of PVC formulation were killed immediately after exposure and lung sections taken for histopathological study. Again, there was no evidence of lung pathology in the exposed group of animals.

Sample F, which is a floor tile formulation of sample D, contained large amounts of inert material. Pyrolysis (up to 550 C) of 6.0 gm of this material (Table 4), left a total residue in the boats of 4.6 gm of 76% of the original material. Thus, only about 1.4 gm of material was actually decomposed. All COHb levels were below 5.0 vol%. The animals were killed 24 hours after exposure. Histological sections of lungs and SGOT levels were comparable to controls.

The pyrolysis of 1.2 to 2.5 gm of sample G (wire formulation) produced no deaths among the 16 rats used in these studies. No histological evidence of lung damage occurred in these animals. The results of the exposure to pyrolysis products of 6.0 gm of sample G are included in Table 2 since this is a formulation of sample B. Even at this high level of exposure, no animals died and all COHb levels were below 10 vol%.

## Comment

The toxicological findings in pyrolysis studies will depend, to a large extent, on methodology. This includes such factors as presence or absence of oxygen during combustion, air flow rates, dilution of pyrolysis stream, presence of particulates, and type of exposure chamber utilized. In spite of the variables involved, certain valid comparisons can be made utilizing standardized conditions of pyrolysis and exposures.

In several of the early studies described here, animals were exposed in a small desiccator in which urine and feces accumulated during the exposure period of one to three hours, and vapor collected on the chamber walls. Measurement of HCl gas at the inlet and outlet of this chamber indicated a considerable loss of HCl as the air stream passed through the chamber. Although most of this loss may have been due to solution in liquid, some may also have deposited on the animal's fur. Subsequent studies utiliz-

Table 4.—*Effect of Pyrolysis Products of a Vinyl Chloride-Vinyl Acetate Copolymer (Sample D) and Formulation (Sample F)*

| Quantity Pyrolyzed (gm) | Weight of Residue (gm)* | Exposure Time (min) | CO Max Conc (ppm) | Rat No. | Blood Hb (gm/100 cc) | Blood COHb (vol %) | Lung (%) (Body Weight) | SGOT (units) | Mortality‡ |
|---|---|---|---|---|---|---|---|---|---|
| Sample D | | | | 1 | 12.0 | 12 | 0.57 | 100.5 | |
| 2.0 | 0 | 112 | 8,000 >3,000 5 min | 2 | 13.7 | 18 | 0.58 | 84.0 | 0/4 |
| | | | | 3 | 15.3 | 12 | 0.56 | 143.5 | |
| | | | | 4 | 14.3 | 8 | 0.52 | 135.5 | |
| | | | | 1 | 13.3 | 56† | 0.60 | ... | |
| 2.5 | 0.16 | 103 | >3,000 5 min | 2 | ... | 13† | 1.38 cyst | ... | 4/4 |
| | | | | 3 | ... | 21† | 0.53 | ... | |
| | | | | 4 | 14.5 | 54† | 0.48 | ... | |
| | | | | 1 | 14.1 | 32 | 0.53 | ... | |
| 2.8 | 0.10 | 105 | 7,000 >3,000 5 min | 2 | 13.0 | 50† | 0.60 | ... | 3/4 |
| | | | | 3 | ... | ...† | 0.58 | ... | |
| | | | | 4 | 12.3 | 61† | 0.99 | ... | |
| Sample F | | | | 1 | 14.5 | 5 | 0.48 | 80 | |
| 6.0 | 4.6 | 130 | >3,000 5 min | 2 | 14.1 | 5 | 0.55 | 55 | 0/4 |
| | | | | 3 | 15.3 | 5 | 0.50 | 72 | |
| | | | | 4 | 15.0 | 5 | 0.52 | 56 | |
| Controls | | | | 12 rats | | | 0.60 | 67 | |

*Residue in boat plus residue in combustion tube.
†Animal deaths.
‡Numerator, deaths; denominator, total.

ing an air stream into which only the animal's nose protruded overcame these difficulties.

Without question, the major cause of death in this study of four polymers was the presence of relatively large amounts of carbon monoxide in the pyrolysis air stream. The blood carboxyhemoglobin levels, in general, correlated well with the amount of pyrolyzed PVC. However, rather marked exceptions occurred within groups. For example, in three of four rats exposed to 1.2 gm of polymer A, COHb levels were above 65 vol%. In the fourth rat, the blood COHb level was only 11.4 vol%. Other similar irregularities can be noted throughout the study. When animals were exposed in a desiccator chamber, it was felt that animal crowding might have played a role in these inconsistent findings. However, similar findings will be noted in the subsequent studies when only the animal's nose was exposed to the air stream. Perhaps a partial explanation may relate to the animal's respiratory rate at the time of high CO levels in the air stream. This period of high CO levels was relatively short compared to the total exposure time, CO levels being greater than 3,000 ppm for less than 20 minutes during most exposures, and in some cases such levels may have been reached for only a few minutes. With exposure to relatively large amounts of pyrolysis products, the animals died quickly due to carbon monoxide poisoning, thus the effects of HCl could not be demonstrated. However, when animals did survive exposure to lesser amounts of pyrolysis products, the histopathological findings in the lung were not remarkable. In the two studies where sufficient $O_2$ was added to the airstream so that animals did not succumb to CO effects, pulmonary edema and interstitial hemorrhage were noted in all animals. In one instance, this was associated with the presence of angular fibers and sheets of foreign material within the lung. No attempt was made to remove particulate matter from the air stream. Perhaps in this one instance, a sudden eruption of material from the pyrolysis boat could account for the findings of particulate matter in the lung.

The lungs of some animals exposed to 2.5 to 2.8 gm of pyrolysis product of copolymer D showed focal edema with several areas of acute suppuration and occasional intra-alveolar hemorrhage. It is interesting to note that the analytical data of Boettner et al[9] indicate that this pyrolyzed sample (D) has HCl concentrations quite comparable to samples A, B, and C, but CO production is approximately one half that of the previous samples. Thus in this instance the irritant effects of HCl becomes more pronounced in

olymer (Sample D) and

| | SGOT (units) | Mortality‡ |
|---|---|---|
| 57 | 100.5 | |
| 58 | 84.0 | 0/4 |
| 56 | 143.5 | |
| 52 | 135.5 | |
| 60 | ... | |
| cyst | ... | 4/4 |
| 53 | ... | |
| 48 | ... | |
| 53 | ... | |
| 60 | ... | 3/4 |
| 58 | ... | |
| 99 | ... | |
| 48 | 80 | |
| 55 | 55 | 0/4 |
| 50* | 72 | |
| 52 | 56 | |
| 60 | 67 | |

yrolysis products, the due to carbon monox- ne effects of HCl coulc i. However, when ani- osure to lesser amount s, the histopathological were not remarkable. In ere sufficient $O_2$ wa it that animals di effects, pulmonary ede hemorrhage were note one instance, this wa presence of angula foreign material withi it was made to remov om the air stream. Per tance, a sudden erup m the pyrolysis boa findings of particulat

animals exposed to 2 s product of copolyme na with several areas c nd occasional intra-a It is interesting to not lata of Boettner et al rolyzed sample (D) ha quite comparable t , but CO production i alf that of the previou is instance the irritan nes more pronounced i

Table 5.—*Effect of Pyrolysis Products of Sample E (Formulation of Sample C)*

| Quantity Pyrolyzed (gm) | Weight of Residue (gm)* | Exposure Time (min) | CO Max Conc (ppm) | Rat No. | Blood Hb (gm/100 cc) | Blood COHb (vol %) | Lung (%) (Body Weight) | SGOT (units) | Mortality‡ |
|---|---|---|---|---|---|---|---|---|---|
| 3.0 | 0.70 | 135 | 850 10-15 min | 1 | 13.3 | 17 | 0.57 | 83 | |
| | | | | 2 | 12.3 | 11 | 0.57 | 74 | 0/4 |
| | | | | 3 | 13.3 | 18 | 0.55 | 100 | |
| | | | | 4 | 14.1 | 12 | 0.54 | 101 | |
| 3.6 | 0.98 | 135 | 850 10-20 min | 1 | 13.3 | 6 | 0.49 | ... | |
| | | | | 2 | 13.6 | 7 | 0.50 | 81 | 0 |
| | | | | 3 | 13.3 | 7 | 0.52 | 86 | 4 |
| | | | | 4 | 12.7 | 9 | 0.54 | 85 | |
| 4.0 | 0.96 | 135 | 2,000 3-5 min | 1 | 15.3 | 23 | 0.50 | 87 | |
| | | | | 2 | 14.1 | 7 | 0.54 | 67 | 0/4 |
| | | | | 3 | 14.5 | 2 | 0.53 | 88 | |
| | | | | 4 | 11.7 | 4 | 0.55 | 98 | |
| 6.0 | 1.20 | 140 | 2,000 5-10 min | 1 | 16.6 | 20 | 0.75 | 98 | 4 |
| | | | | 2 | 14.5 | 30† | ... | ... | 3/4 |
| | | | | 3 | 18.1 | 7† | ... | ... | |
| | | | | 4 | 18.1 | 24† | 0.43 | ... | |
| 6.0 | 1.19 | 137 | 3,000 few min | 1 | 17.1 | 15 | 0.51 | 81 | |
| | | | | 2 | 14.1 | 11 | ... | 95 | Killed |
| | | | | 3 | 13.7 | 20 | 0.51 | 72 | |
| | | | | 4 | 13.7 | 10 | 0.57 | 151 | |
| Control | | | 8 rats | | | | 0.54 | 59 | |

*Residue in boat plus residue in combustion tube.
†Animal deaths.
‡Numerator, deaths; denominator, total.

exposed animals since larger quantities can be pyrolyzed without producing lethal COHb levels.

Three PVC formulations were also studied. The analytical data[9] indicated that sample E contained approximately 50% as much chlorine per gram as do the PVC homopolymers, indicating the presence of about 50% of materials other than PVC. The analytical data also indicated 30% as much CO was produced from this sample. In the present studies, doubling the usual amount of material to be pyrolyzed did not produce unusually high COHb levels in the exposed animals. In fact, the pyrolysis of 6.0 gm of PVC formulation resulted in maximum COHb levels of 30 vol% in the exposed animals, compared with COHb levels of 24 to 64 vol% after pyrolysis of only 1.5 gm of the homopolymer. However, three of four animals in this group died. Histopathological studies showed that the lungs of the exposed group were not different from controls, thus the cause of death is not apparent. Anoxia, resulting from irritant laryngospasm, could be a factor in these mortalities.

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