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# Phosgene in the Thermal Decomposition Products of Poly(Vinyl Chloride): Generation, Detection and Measurement

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## Abstract

An analytical study was made to determine whether carbonyl chloride (phosgene) is formed during the thermal decomposition of poly(vinyl chloride), PVC. Four methods of decomposition were studied: (1) thermal degradation of PVC in a resistively heated furnace, (2) electrical overloading of a PVC clad wire, (3) electrical arcing between electrodes partially covered with PVC, and (4) electric arc initiated flaming combustion in a cup furnace. Results are reported which show that significant quantities of phosgene can be generated from PVC by the electric arc method. Lesser amounts were found in the other scenarios. The measurements, identification and quantification of phosgene in the decomposition product, were obtained through the use of gas chromatography, infrared spectroscopy and mass spectroscopy. While the study was not mechanistic in nature, phosgene is postulated to result from secondary reactions of the PVC products. Reaction mechanisms are suggested.

## Introduction

Vinyl chloride polymers are frequently used in many applications, perhaps the most familiar application is for electrical insulation. These polymers are also widely used in construction, in appliances, in furnishings and in transportation vehicles. Total production for 1978 is estimated to be 2.3 million metric tons (1). Buildings, including home furnishings and appliances, provide the major market for the production.

The role of poly(vinyl chloride), PVC, in leading to human fire fatalities has been the subject of a number of investigations (2,3,4). In addition, the thermal degradation of PVC has been studied extensively from an analytical point of view (5,6) and various reviews of such studies have been prepared (7,8,9). Toxicological studies involving the exposure of animals to the thermal degradation products of PVC have also been reported (2,3).

Unanswered by these various studies is whether or not carbonyl chloride\* is a product of thermal degradation of PVC. A toxicological study by Barrow et al (2) suggests that the toxicity of PVC decomposition products is due principally to HCl, with little contribution from other components. The

work reported by Woolley (6) and Tsuchiya et al (5) seems to lend support to Barrow's conclusion. However, Woolley's negative results regarding phosgene are limited by an instrumental detectability of 50 ppm, a level that would be quite significant toxicologically (10).

On the other hand, Baltatis et al (11) reported the presence of phosgene in the combustion products of two PVC composite materials which were burned in a closed container. These workers reported that burning 0.5 g of PVC from conveyor belts and cables gave respectively 0.0019 and 0.0135 per cent of  $\text{COCl}_2$  in a 5 liter chamber. Earlier Coleman and Thomas (12) reported  $\text{COCl}_2$  concentrations up to 3 ppm and to 1 ppm respectively for unstabilized PVC and stabilized PVC composites burned at 900°C in a closed environment.

In fatal fires involving PVC, various claims have been made which attribute at least part of the toxicological hazard to phosgene (13,14). The bases for the claims, however, are not well documented in those reports. Nevertheless, the reports do raise a fundamental question that the analytical measurements referred to above do not clearly resolve, either as a consequence of instrumental limitation or the limitation imposed by the type of decomposition scenario chosen.

Based on these uncertainties and the toxicological significance of phosgene, a study was carried out in which analyses for  $\text{COCl}_2$  were performed on decomposition products obtained by four methods, each of which represents a potential real situation.

The four methods are: (1) direct thermal degradation of PVC in a resistive furnace; (2) electrical overload of a copper wire wrapped with PVC insulation; (3) an electrical discharge between wires covered by PVC insulation; and (4) electric arc initiated flaming combustion in a cup furnace.

The first method is equivalent to the analytical type of studies already referenced in the literature. The most significant difference between this study and other work is that more sensitive analytical techniques were used in this study. More importantly, the second and third methods were not previously represented and were chosen based on expected modes of degradation involving electrical overload and arcing conditions (e.g. reference (7)).

\* Carbonyl chloride whose formula is  $\text{COCl}_2$  has three well known synonyms: phosgene, chloroformyl chloride, and carbonic acid dichloride. In the following text the synonym phosgene and the formula are used interchangeably to denote this compound.

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

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

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### introduction

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

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

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

Vandervort<sup>(2)</sup> studied the 200-230 °C thermal degradation products of PVC wrapping films using a micro furnace with ceramic sample boats and quartz combustion tubes. The major products were found to be benzene, toluene, chlorobutene, 1-chloro-2-ethyl hexane, 2-ethyl-1-hexanol, benzyl chloride, and hydrogen chloride. This experimental procedure discriminated in favor of benzyl chloride as it

could decompose in the presence of hot metal, e.g. a hot cutting wire. In this same study the author found trace amounts of hydrogen chloride (well below the 5 ppm TLV<sup>(3)</sup>), but no detectable benzyl chloride, in field samples taken during the actual film cutting process.

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

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

### description of samples

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

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

\*This research was supported by Borden Chemical.

# Polyvinyl Chloride Film Thermal Decomposition Products as an Occupational Illness

## I. Environmental Exposures and Toxicology

Robert Vandervort and Stuart M. Brooks, M.D.

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.<sup>1</sup> 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.<sup>2</sup>

### 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.<sup>3</sup> 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.<sup>3</sup> 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.

### 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

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# Polyvinyl Chloride Film Thermal Decomposition Products as an Occupational Illness

## 2. Clinical Studies

Stuart M. Brooks, M.D. and Robert Vandervort

In 1973, Sokol et al reported three cases of workers employed as meat wrappers who developed respiratory symptoms when exposed to fumes of polyvinyl chloride (PVC) film cut with a hot wire.<sup>1</sup> The patients were middle-aged women who smoked cigarettes and demonstrated reversible airway obstruction on pulmonary function testing. The patients were not studied at work, but reported to a hospital where examinations and laboratory studies were performed. In an epidemiologic study conducted in 152 supermarkets in Houston, Tex., approximately 10% of the meat wrappers studied reported multiple respiratory symptoms at work which included wheezing, shortness of breath, and chest pain or tightness.<sup>2</sup> A significantly greater prevalence of symptoms suggesting eye, nose and throat irritation was also found. Andrasch et al conducted a questionnaire survey of 165 meat wrappers in the Portland, Ore. metropolitan area.<sup>3</sup> Fifty-seven percent of the symptomatic workers reported respiratory symptoms and 30% reported symptoms suggestive of nose and throat irritation. Several workers reported the occurrence of acute asthmatic attacks while at work. Bronchial inhalation provocation studies with emissions from hot-wire cutting of PVC films conducted on 11 selected meat wrappers demonstrated rhinorrhea in seven wrappers, cough, tightness of the chest, and sore throat in five, dyspnea, exhaustion and wheezing in four, and throat soreness in two subjects. These studies were conducted in a laboratory away from work. Nine of 13 patients who were then challenged with emissions from heating price label material developed immediate acute asthmatic reactions. Four of these subjects also experienced a delayed asthmatic reaction which occurred six to eight hours after exposure. The authors concluded that the emissions from thermally activating price labels were the principal cause of "meat wrappers asthma," but that the entire spectrum of this disease had to be interpreted as a complex

response from exposure to both emissions from hot-wire cutting of PVC film and from thermal activation of price labels. Other investigations of respiratory illness in meat wrappers have also been reported.<sup>1-6</sup>

The Bureau of Occupational Safety & Health received complaints associated with exposure to air contaminants generated by the hot wire cutting of PVC meat packaging film as early as the summer of 1969. Beginning in 1972, The National Institute for Occupational Safety & Health conducted clinical studies of meat wrappers in response to requests for Health Hazard Evaluations in supermarket meat departments. The present report contains the results of these clinical studies. Investigation of many of these cases was in collaboration with the Department of Environmental Health, University of Cincinnati College of Medicine.

### Materials and Method

Twenty-four meat wrappers, eight meat cutters and 20 control subjects (office personnel and store clerks) make up the population studied. Data concerning age, sex and smoking history of the subjects are shown in Table 1. While meat wrappers were commonly women, meat cutters were usually men. The three groups were of similar age, but there was a greater number of meat wrappers who were cigarette smokers. The mean duration of wrapping in the meat wrappers was 12.5 years (range 1 to 26 years).

Investigations were performed at or near the workplace in each case. The meat cutters worked in the same general area as the meat wrappers. Each subject was administered a modified respiratory questionnaire which included questions on past medical history, cigarette smoking, previous occupational exposures, current respiratory status and adverse effects allegedly arising from work.

Pulmonary function testing was performed on each of the 53 workers at the beginning and end of the work shift. Thirty-seven subjects were tested using a waterless, high fidelity, precalibrated spirometer equipped with an air temperature probe (Ohio Medical

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## Vinyl Chloride Formation from the Thermal Degradation of Poly(Vinyl Chloride)

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The volatile products from the thermal degradation of poly(vinyl chloride) (PVC) resins and compounds are shown to contain trace amounts of vinyl chloride. Data presented show the effect of temperature and resin type on the amount of vinyl chloride formed. At the maximum temperatures involved in PVC processing which may reach 210°C, vinyl chloride monomer (VCM) evolution amounts to less than 1 ppm (resin basis). A technique employing a thermogravimetric balance and charcoal adsorption of volatiles is described for studying thermal degradation of PVC. The volatiles are analyzed for vinyl chloride by gas chromatography. Peak identity was confirmed by mass spectrometry.

### INTRODUCTION

Numerous studies and surveys have been published describing the thermal degradation and pyrolysis products of poly(vinyl chloride) (PVC). These studies have shown that at elevated temperatures essentially quantitative dehydrochlorination of PVC occurs, resulting in the formation of a complex mixture of aromatic and aliphatic hydrocarbons with benzene being the largest single component (1-8). Stromberg, *et al.* (1) studied the decomposition of PVC under vacuum at temperatures up to 400°C and measured the variations in the decomposition products as a function of temperature. They did not indicate the formation of any vinyl chloride monomer (VCM) under these conditions. Boettner, *et al.* (2) investigated the thermal degradation of PVC in air up to 600°C. Using infrared spectroscopy and gas chromatography-mass spectroscopy, they identified approximately 50 volatile degradation products and measured the rate of formation of the major products as a function of temperature. Their data indicate that up to 600 ppm of VCM is formed from PVC homopolymer and up to 3000 ppm from PVC compounds. Although no mention is made of residual VCM in the polymer, the bulk of the VCM was detected in the 280-430°C range and it is inferred that VCM is produced during the thermal decomposition. Woolley (3) reported low levels of VCM in PVC pyrolysis products but did not measure residual VCM, and it is not clear whether any VCM was actually formed during the decomposition. Lewis (4) has recently reported degradation studies of a homopolymer having a residual VCM content of < 0.5 ppm and found a maximum VCM formation of 35 ppm at 350°C.

The recent findings (9) of carcinogenicity on prolonged exposure of test animals to elevated concen-

trations of vinyl chloride in the air and of cases of angiosarcoma in vinyl chloride workers have caused serious concern about the effects on workers involved in all phases of PVC manufacture and fabrication. Although present day manufacturing processes have reduced the residual VCM content of PVC resins and compounds to very low levels (10), the possibility of forming VCM by degradation of the polymer during calendaring, extrusion, and thermoforming operations is still a cause of concern.

There is very little likelihood of VCM formation during thermoforming of PVC for food packaging application since this operation is carried out under mild conditions (90-120°C for a few seconds). It has been demonstrated previously that no detectable VCM is formed in up to 1 h exposure at 130°C, using an analytical method capable of detecting 1 part per billion of VCM (10).

During calendaring and extrusion operations, however, temperatures may reach the 175-210°C range for brief time periods. We know of no published information involving VCM formation under these conditions. Our present work involved the investigation of the thermal degradation of PVC over the 130-500°C temperature range with special emphasis on VCM formation at 210°C, the upper limit used in PVC fabrication.

### EXPERIMENTAL

Thermal degradation studies were carried out using a duPont Model 950 thermal balance which provided a convenient method for accurately controlling the temperature and heating rates. Samples of 80-100 mg were placed in a platinum foil boat suspended on the thermal balance sample holder. The furnace tube surrounding

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# THERMAL DECOMPOSITION PRODUCTS OF POLYVINYL CHLORIDE

By YOSHIO TSUCHIYA and KIKUO SUMI

When plastics are involved in a fire they may yield toxic decomposition products. Some quantitative data on the decomposition products of plastics are available in the literature, but it is difficult to assess the danger from the different amounts of various products because of the absence of a suitable method of evaluation. The authors have proposed a method of evaluation based on pyrolysis followed by gas chromatographic analysis and have used it to assess toxicity from various thermal decomposition products of polyvinyl chloride. Hydrogen chloride was found to be the main toxic decomposition product.

## Introduction

The increasing use of plastics and other organic polymers raises the possibility that when involved in a fire they may yield toxic decomposition products in quantities sufficient to produce a dangerous atmosphere. Some quantitative results on the decomposition products of plastics are available in the literature, but it is difficult to compare data because of differences in experimental methods and differences in presentation of experimental data.

It is also difficult to assess the danger from the different amounts of various decomposition products because of the absence of a suitable method of evaluation. In view of the above factors, the authors believe that a need exists for a systematic study to provide quantitative results on the volatile decomposition products of a wide variety of plastics in both inert and oxidising atmospheres. A need also exists for a method of assessing danger from the different quantities of decomposition products. This investigation was carried out to meet these needs.

Polyvinyl chloride (PVC) is the plastics material that has probably received the most attention from fire authorities because of its relatively wide use and the possibility of its thermal decomposition leading to the formation of toxic gaseous products. This polymer was, therefore, selected for the present study.

Coleman & Thomas<sup>1</sup> determined the combustion products of PVC and other chlorinated plastics using a static system. The specimens were decomposed in a flask over a temperature range of 300 to 1000°. The ratio of plastics to air was varied by using different weights of sample, and the combustion products were analysed by conventional methods. Schriesheim<sup>2</sup> employed a similar method over a temperature range of 250 to 550° and analysed the products of combustion by a mass spectrometer and chemical methods. Stromberg *et al.*<sup>3</sup> studied the mechanism of thermal decomposition of PVC in vacuum. The volatile products were analysed by mass spectrometry and found to consist almost entirely of hydrogen chloride and small proportions of benzene, toluene and other hydrocarbons. Gilbert & Kipling<sup>4</sup> investigated the carbonisation of PVC and other vinyl polymers by decomposing the specimens, under vacuum, in an inert atmosphere and in air. After removal of hydrogen chloride the residue was decomposed and the products were analysed by gas chromatography.

In the present investigation the thermal decomposition products of PVC were determined, firstly, in an inert atmosphere and, secondly, in air. A flow system was adopted

instead of the static system used by other investigators,<sup>1-3</sup> because the decomposition conditions during an experiment can be more closely defined in a flow system than in a static system.

## Experimental

### Material

The PVC used in this study was a commercially available, general purpose resin in powder form. It did not contain any plasticiser.

### Thermal decomposition

PVC was decomposed in a furnace through which inert gas or air was passed and the gaseous products were collected in a flask. The sample was weighed in a ceramic boat, to which a stainless steel wire and a piece of iron were attached, so that it could be moved inside a 19-mm diameter tube to the hot zone of the furnace by means of an external magnet. The furnace temperature was maintained at isothermal values of 350, 600 or 850°. Helium was used to provide an inert atmosphere in one series of experiments and air was used to provide an oxidising atmosphere in the other series. After some preliminary studies a gas flow rate of 450 cm<sup>3</sup> per min was adopted. This corresponded to a mean linear velocity of about 160 cm per min. The sample weights selected for this study were 0.5 g in helium atmosphere and 0.5 and 0.25 g in air. The amount of air used during each experiment was slightly in excess of that required for complete combustion of 0.5 g of PVC to carbon dioxide, water and hydrogen chloride. The smaller weight of 0.25g was also used in an effort to examine the influence of effectively increasing air supply on the formation of decomposition products.

The higher boiling components of the decomposition products were collected in a U-tube filled with glass beads and maintained at 0°. The unreacted gas and the remainder of the volatile decomposition products were collected in a 3-litre flask that had been evacuated prior to the experiment. The sample was kept in the furnace until the gases filled the flask. Each experiment lasted about 8 min.

### Analysis

Gas chromatography was the main method used in the analysis of decomposition products. As these were composed of widely differing materials, three chromatographic conditions had to be employed (two with a thermistor-type thermal conductivity cell detector, with different columns).

First a molecular sieve 5A (60- to 80-mesh) column of length 2 m and diameter 1/8 in. (0.6 cm) was used with the

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January 1974

# Smoke and toxic gases from burning plastics

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# MEASUREMENT OF HYDROCHLORIC ACID EMISSION FROM BURNING PVC COMPOUNDS

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## ABSTRACT

The development of a novel Micro/TG method for measuring HCl emission from PVC compounds and optimization of operation conditions are described. The main problem with conventional large scale methods is the loss of HCl due to leaks and condensation in the system leading to erroneous results. The Micro/TG method overcomes many of the problems inherent in the large scale method. Comparison with results obtained by the large scale method showed that the total balance of chlorine content determined by the Micro/TG method is closer to the theoretical in all of the formulations tested. Any chlorine in the form of organic-chloride (RCl) will not be detected by the Micro/TG method, a limitation shared by the large scale method. The Micro/TG method offers other advantages such as automation, short experimental time and direct measurement of chloride ion concentration by ion selective electrode.

## INTRODUCTION

PLASTICISED PVC IS WIDELY USED FOR THE INSULATION AND sheathing of cables because of its low flammability (when used with flame retardant plasticisers), satisfactory electrical properties and low cost [1,2]. The emission of large quantities of hydrochloric acid (HCl) when it burns, however, is an unacceptable disadvantage for some applications. Even if the PVC compound does not actually ignite in a fire, it may still be heated sufficiently to evolve HCl. Quite small amounts of

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## Hydrochloric A

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## Current Metho

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1. Loss of volat
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## EXPERIMENTA

### Materials Used

Breon S125/14  
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# Combustion Gases Generating from Polyvinyl Chloride and Its Products

## —Model Experiment in Case of Fire—

By Yoshitaka Kobayashi<sup>\*)</sup>, Masahiro Hori<sup>\*)</sup> and Hisako Murata<sup>\*)</sup>

### 1. Introduction

IN building fires, death has been caused in many cases recently by generating gases rather than by the fire itself. The increase of disasters resulting from such generating gases depends to some extent on building construction but to a greater extent on the change of composition of generating gases.

The change of gas composition has been brought about by the fact that building materials have been changing from natural materials such as wood, etc. to synthetic high polymer materials.

With the development of high polymer materials in recent days, a variety of plastics or synthetic fibers has been utilized for interior materials or furniture, with many of these materials having thermal decomposing properties or burning properties differing from those of natural high polymers<sup>1)</sup>.

It is considered from the difference of the gas composition, therefore, that many problems are involved in application in consideration of fire prevention or escape.

Among synthetic high polymer materials, polyvinyl chloride (PVC) is one of those which are most commonly utilized. Building materials made chiefly of the resin are floor tiles, roofing, walling, gutters, various piping, partitions, accordion curtains, chair upholstery, etc., and more recently, PVC is used for a

diversified range of application including large building exteriors and interiors as well as for wooden houses by laminating onto metal, wooden and other plastics bases.

Some studies were conducted on the thermal decomposition of PVC in vacuum and air at an elevated temperature<sup>2-4)</sup>, but in this experiment, investigation was especially made on various processed PVC products recently marketed in Japan.

The method of elevating temperature was adopted according to the fire resistance test (JIS 1304) for building construction elements, and combustion gases generating at each temperature level were determined. Comparative study was also made for natural high polymer materials such as wood, paper, etc., and PVC products. Besides, stress was especially placed on generation of minute toxic gases when burning conditions such as air supply, etc. were changed.

### 2. Method of Experiment

#### 2-1. Materials Tested and Device

Materials tested were PVC raw material and 8 kinds of PVC products presented in Table 1. Among PVC building materials are included flexible and rigid products in plate or film form, and the materials tested can be classified into 4 according to the quantity of stabilizer added.

In addition, natural high polymer materials such as wood, etc. and other plastics materials such as melamine resin, etc. were selected

and a comparison carried out.

The equipment shown in Fig. 1 was used as a combustion gas generating device. Heating is provided by use of an electric furnace, and the method of elevating temperature was adopted according to the fire resistance test for building construction parts (JIS 1304) (ca. 100°C/min.).

Readers are recommended to refer to Fig. 2.

Specimens were heated in a magnetic boat placed in a quartz tube having a diameter of 2.5 cm and a length of 30 cm in the electric furnace. Supplying air at a constant flow speed by means of a compressor and nitrogen bombe, the specimens were burned and generating gases gathered.

The electric furnace is preheated, then 1 gram of specimen is fed into the burning tube, and the air supply quantity is adjusted to a constant flow speed. Heating is immediately conducted, and part of the exhausted gases including excess air and generating combustion gases is gathered in a glass cylinder at 300, 400, 500, 600 and 700°C for rapid analysis.

The temperature inside the furnace is determined by a thermocouple attached to the magnetic boat.

As for PVC raw material, changing the air flow speed from 1 l/min. to 1.5 l/min., and also changing the oxygen ratio in air supplied from 21 to 10.5 per cent, the influence on the generated gas composition was studied. Experiments were re-

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by so doing, it having been shown that the mechanism, and a great deal of this can be made in the design specification and the chances of successful performance can be improved.

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Attachment VIII

## Toxic products from plastics materials in fires

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**Abstract:** Over one-half of the fatalities in fires are caused by smoke and toxic gases. Work is in progress at the Fire Research Station to study the production of toxic gases when plastics materials are decomposed under controlled laboratory conditions involving pyrolysis at temperatures up to 1000°C and in full-scale fires using a special compartment with a variable ventilation slit (door) leading to a corridor. When heated above about 150°C, PVC releases the toxic gas hydrogen chloride. At 300°C this dehydrochlorination is rapid and quantitative. In fires involving wood and PVC fuels the main toxic products are carbon monoxide and hydrogen chloride and the contribution of hydrogen chloride to the over-all toxicity depends upon the fuel loadings and ventilation. Pyrolysis of flexible polyurethane foam at about 300°C releases a polymeric 'yellow smoke' which decomposes at temperatures above 600°C in nitrogen (500°C in air) to give a range of nitrogen-containing compounds, particularly hydrogen cyanide. Fires involving industrial loads of foam show that temperatures in excess of 1000°C (sufficiently high to decompose the yellow smoke) are attained within a few minutes. During the early stages of the fire the toxic hazard from hydrogen cyanide can approach the same order of magnitude as that from the carbon monoxide.

### 1 Introduction

Last year in the United Kingdom approximately 1000 persons died as a direct result of fire. Evidence indicates that over one-half of the fatalities were caused by the combined effects of smoke and toxic gases and that the remainder were due to burns and other injuries. In addition, many thousands of persons were involved in potentially hazardous fire situations.

The effects of smoke and toxic gases can be considered separately. The main effect of smoke is that it reduces visibility and hence hinders escape, whereas the effect of toxic gases, coupled with oxygen depletion of the atmosphere and heat exposure, is to kill. Certain toxic gases at sub-lethal levels can directly hinder escape by producing

severe eye and inhalation irritation. Other toxic gases that are odourless kill rapidly without warning.

This paper will outline the current work being carried out at the Fire Research Station to study the release of toxic products when building and furnishing materials are involved in fires. As examples the paper will report the results of two well known and topical materials, namely polyvinyl chloride (PVC) and polyurethane foam.

Essentially, the research is divided into two main areas involving, first, small-scale laboratory decomposition experiments under simulated fire conditions, and, secondly, full-scale fire tests. It is relevant in this report to discuss the experimental facilities and procedures and then give a broad survey of the results.

### 2 Experimental procedures

#### 2.1 Laboratory experiments

In the laboratory studies, small samples of material are decomposed in a furnace system under the conditions likely to be encountered in fires, i.e. temperature up to and in excess of 1000°C in environments ranging from air to a serious deficiency of oxygen. This is in fact a study of the

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**FLAME RESISTANCE** of compositions of neoprene and Hypalon via the Oxygen Index Method indicate that both polymers have a high degree of flame resistance. Pyrolysis and combustion tests show that hydrogen chloride evolution from these materials can be minimized by compounding.

BY CHARLES E. McCORMACK

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Public concern regarding atmospheric pollution and governmental regulations aimed at consumer protection have caused the spotlight to be focused on what happens to materials when they are exposed to conditions of pyrolysis and combustion. There is evidence that industry is aware of the challenges and is in the process of dealing with them.

In considering matters such as pyrolysis, combustion and flame resistance, neoprene, the first general-purpose synthetic elastomer commercially introduced in 1932, merits special attention. Right from the start, it was recognized as flame-resistant. Of course, if it had only flame resistance to recommend it, it would not have attained the hundreds of millions of lbs/yr. status it enjoys today. It is noteworthy, though, that flame resistance is the key property in many applications such as wire and cable (mining cable, telephone drop wire, appliance cord), conveyor belting and flame-resistant latex foam. In each of these applications, other properties such as physical strength, oil and ozone resistance, have played strong supporting roles.

The results of some recent studies on the flame resistance of compositions of neoprene and Hypalon judged by the Oxygen Index Method, and on the

products of their pyrolysis and combustion with particular emphasis on the control of hydrogen chloride evolution are covered in this paper.

#### Oxygen Index Flammability Ratings

The higher the oxygen concentration required to support the combustion of a material, the better its flame resistance. This is the basis for oxygen index flammability ratings, which are numerically equal to the minimum volume percentage of oxygen in a slowly rising mixture of oxygen and nitrogen which will support candle-like burning. The test method, as described in ASTM Method D-2863, fills a long felt need for a relatively simple, reproducible test for the characterization of materials. Of particular appeal are its applicability to all types of polymeric materials, regardless of whether or not they normally support combustion in air, and its simple numerical index which permits a ready comparison of materials.

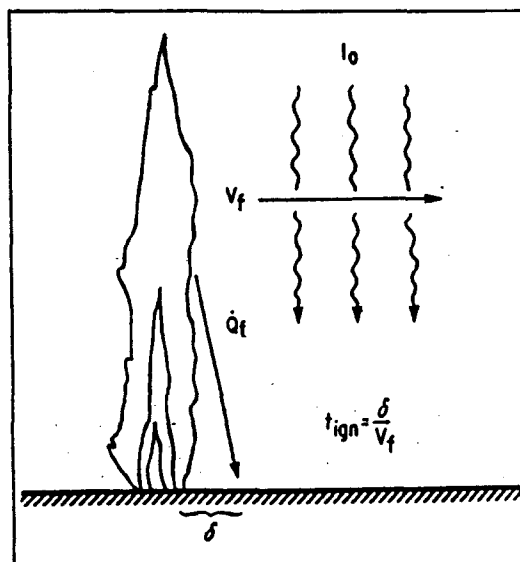
Oxygen index levels easily attainable with neoprene are shown in Table I. All of the values are well above the index level of 27 considered to indicate self-extinguishing characteristics. No attempt is made here to isolate the effect of various compounding ingredients on oxygen index. It is evident, however, that com-

This report provides a framework for understanding the principles that are important in correlating small- and large-scale fires by describing a selected series of small-scale tests in terms of such fire concepts as ignition, propagation, heat release, and smoke generation. All of the methods have limitations and cannot completely evaluate fire performance, but they offer a baseline for continued development of tests to provide better correlations with real-fire performance.

**Gordon M. Kline, technical editor**

Many small-scale tests are in use. In the past, results were often described by such terms as "flame spread" or "flammability index." The ability to predict actual fire performance was sometimes implied. Experience has shown that this approach generally is not valid. For example, ASTM D-1692, a standard test method for rate of burning or extent of burning of cellular plastics, specifies a horizontal sample orientation producing results vastly different from those obtained using a vertical orientation with

In defining chemical factors affecting polymer fire performance, heat of combustion offers a reasonable starting point. Heat of combustion is related to bond strengths, and can be determined by oxygen bomb calorimetry. In this context, it is the total heat energy released when a material is ignited and burned in a pure oxygen atmosphere. An examination of heat-of-combustion data, however, indicates that heat of combustion is not sufficient to rank materials in terms of potential fire performance. Based on heat-of-combustion data (Table I), and assuming equivalent burn-



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## Toxic Gases from Fires

James B. Terrill, Ruth R. Montgomery, Charles F. Reinhardt

According to ancient Greek mythology, Prometheus suffered extreme torture for giving men heavenly fire. However, without fire it is difficult to envision how humans could have advanced beyond the caves. As people crowded together in cities, the occasional, unwanted fire problem escalated drastically. Some dramatic examples include the Great Fire of London in 1666, the Chicago Fire in 1871, and the destructions of Tokyo, Dresden, and Hamburg during World War II.

Frequent fires in American cities

certed efforts of materials suppliers, fire-fighting officials, fire code groups, and the insurance industry.

In the United States today, fire exacts an annual toll of some 8000 to 9000 deaths and property losses amounting to some \$3 billion to \$4 billion (2). The survivors may also experience severe anguish. Approximately 70 percent of the 1976 fire deaths occurred in residential fires. To reduce this fire fatality rate, it will be necessary to assess the potential life hazard from dwelling fires or fires in general. The factors leading to fire tox-

**Summary.** The major lethal factors in uncontrolled fires are toxic gases, heat, and oxygen deficiency. The predominant toxic gas is carbon monoxide, which is readily generated from the combustion of wood and other cellulosic materials. Increasing use of a variety of synthetic polymers has stimulated interest in screening tests to evaluate the toxicity of polymeric materials when thermally decomposed. As yet, this country lacks a standardized fire toxicity test protocol.

stimulated efforts to test the fire performance of materials to minimize potential fire damage. The American Society for Testing and Materials (ASTM) accordingly devised the first scaled test procedures: door fire resistance [ASTM E-152 (1940)] and wall fire resistance [ASTM E-119 (1917)], ignition resistance [ASTM D-1692 (1959)], and flame spread [ASTM E-84 (1950); E-162 (1960)] (1). These procedures were devised through the con-

icity must be examined. This knowledge must then be applied toward developing reliable test procedures that will make it possible to evaluate the potential of a combustible material to create an extraordinary toxic gas hazard in a fire.

The total life hazard in fires results from a composite of at least four interlocking and variable sets of conditions, as shown in Fig. 1 (3). A few decades ago, the main lethal factors were frequently identified as burns, hot gases, and smoke poisoning. Disastrous fires such as the Cleveland Clinic fire in 1929 (4), the Coconut Grove fire in 1942 (5), the Hartford Circus fire in 1944 (6), and the S.S. *Noronic* fire in 1949 (7) raised serious questions about how people die

in fires. These and other fires resulted in more detailed fire investigations that, together with laboratory experiments with animals, made it possible to begin to identify the lethal factors in fires.

### Epidemiologic Study

The first major epidemiologic study was retrospective. The Columbia Presbyterian Hospital team led by Zikria (8) conducted an extensive analysis of autopsy records of New York City fire victims during 1966 and 1967. Carbon monoxide (CO) poisoning was noted in 70 percent of all victims with a primary diagnosis of smoke poisoning or asphyxia. Among victims who died in less than 12 hours, 59 percent of the 70 percent who were tested had lethal or significant exposure to CO as determined by the blood carboxyhemoglobin (COHb) concentration (COHb is stable in postmortem tissue); CO poisoning was found almost equally in the presence or absence of surface burns (in 50 percent of the victims with burns and 39 percent of the victims without burns).

An ongoing epidemiologic study was started in September 1971 under the joint auspices of the Johns Hopkins University Applied Physics Laboratory and the Maryland State Medical Examiner's Office (9, 10). This study was limited to autopsied victims who died within 6 hours after a particular fire. Data obtained from more than 200 victims through the end of 1974 (9) indicate that 50 percent died from CO poisoning (COHb > 50 percent); 30 percent died from CO poisoning plus contributory factors such as heart disease, alcohol, or burns; 10 percent died from causes other than CO poisoning (probable laryngeal spasm, burns, or heart failure); and 10 percent died from undefined causes.

Hydrogen cyanide (HCN), hydrogen chloride (HCl), and other gases associated with the thermal decomposition of synthetic materials did not appear significant in the deaths of the Maryland fire victims. Synthetic materials likely to produce such gases were "the primary articles burning in only 5% of the fires reported" (9).

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## MECHANISM OF THE THERMAL DEGRADATION OF POLY(VINYL CHLORIDE)

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### SYNOPSIS

The kinetics for dehydrochlorination and benzene formation has been studied during the degradation of two samples of poly(vinyl chloride) (PVC) at 180–200°C under vacuum with and without the removal of hydrogen chloride. The effects of various additives, such as organic phosphites, mercury, silver, gold, and glass upon the thermal degradation of PVC were investigated. Mercury, silver, and glass decrease the rate of autocatalytic dehydrochlorination of the polymer in the presence of hydrogen chloride but silver and glass do not affect PVC degradation rate in the absence of HCl. PVC thermal decomposition under vacuum with removal of HCl mostly proceeds by a molecular mechanism. At the same time, radical reactions take place. But there are some very endothermic stages of chain propagation, this is why in this case, the radical mechanism of PVC dehydrochlorination does not compete with the molecular one. In the presence of HCl, the rate of radical reactions increases and predominates over rate of molecular reactions.

### INTRODUCTION

The thermal degradation of poly(vinyl chloride) (PVC) is accompanied by a dehydrochlorination reaction, color change, and crosslinking of macromolecules. Some theories explaining these processes have been offered.<sup>1</sup> Braun<sup>2</sup> has discussed in detail the molecular-ionic mechanism for the thermal degradation of PVC.

One of the most important questions of PVC decomposition is the elucidation of the nature of the weak structures in macromolecules from which the polymer degradation begins. On the basis of investigation of the thermal decomposition of model compounds and detailed study of various structures of PVC, it has been proved<sup>2</sup> that the chloroallylic groups, distributed at random over the polymer chain, are the most unstable structures. In PVC macromolecules the amount of double bonds is about 1.6 per 1000 monomer units.<sup>3</sup>

Geddes<sup>4</sup> found the average length of polyenes in degraded PVC to be 10–15 by comparing the quantity of evolved HCl with the number of formed polyenes which was determined by ozonolysis. On the basis of electron

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# Toxic Gas and Smoke Assessment Studies on Vinyl Floor Coverings with the Fire Propagation Test

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The Fire Propagation Test (BS 476 Part 6) has been used with the discharge of combustion products into a small test room, to provide a fire hazard assessment of some polyvinylchloride floor covering systems, and includes measurements of fire propagation, smoke, CO and HCl production. Particular attention has been given to the change in the HCl concentration of the room atmosphere during the test and the influence of relative humidity and the nature of the surface linings of the room. The results have been discussed as a contribution to the understanding of the role of HCl in toxicity of fire atmospheres. Some approaches for improving further the reproducibility of the test method are indicated and support is given to the Japanese proposal that such a test be standardized to enable comparison of fire hazard potential of lining systems used in buildings.

## INTRODUCTION

The Fire Propagation Test (British Standards Institution BS 476 Part 6) was previously studied<sup>1</sup> as a method for assessing both the fire spread and smoke production potential of modern interior lining materials. It was shown that both parameters could be measured simultaneously in the one test and it was argued that such a procedure was necessary for valid consideration of fire hazard potential because smoke production is a by-product of fire and dependent upon the nature and extent of fire propagation. Both parameters were so much higher under flaming conditions that only this condition and not pyrolysis (non-flaming) was assessed. Assessment of smoke was done in an unstirred room for which condition correlation of fire propagation with simulation room and corridor fires had been established.<sup>2</sup> It should be noted that the correlation relates to the spread of a developed fire from the room down the corridor after flash-over and that the position of the lining, whether floor or wall covering, is irrelevant, the test method relating to both.

A recent review<sup>3</sup> indicates extensive research and International Standards activity on toxicity of combustion products, but little attention to the mode of combustion degradation. Since the main problem of gaseous combustion products is the hazard to people, and hazard assessment by definition should relate to a fire scenario, it follows that the combustion degradation methods associated with toxic gas studies should also relate to fire scenarios. The Fire Propagation Test is one of the simpler methods that conforms to this requirement. As indicated previously,<sup>1</sup> the major concern is the hazard to people in dwelling fires and the role of smoke and combustion products in retarding egress. There is evidence<sup>4</sup> to suggest that the floor is the element most frequently damaged in building fires. Since it is also known<sup>5</sup> that products made of polyvinylchloride (PVC) may emit copious smoke and hydrogen chloride

(HCl), which is highly lachrymatory, as well as carbon monoxide (CO), which is the major established cause of non-burn fire fatalities, it was decided to assess the fire hazard of PVC floor coverings with the Fire Propagation Test, including combustion propagation, smoke obscuration and principal toxic gas production (HCl and CO).

## PVC COMBUSTION PRODUCTS

It is known that PVC will evolve HCl at relatively low temperatures. Small losses of HCl are believed to be responsible for discoloration of *unstabilized* PVC when heated at 76 °C for several weeks in relation to weathering studies<sup>6</sup> and of stabilized PVC at 180 °C for several hours in relation to processing studies.<sup>7</sup> At about 300 °C the loss of HCl is stoichiometric (58.6%), and weight loss at this temperature may be used to determine PVC resin content in vinyl floor coverings.<sup>8</sup> The rate of loss of HCl has been determined by Woolley<sup>9</sup> at 200 and 300 °C, which are considered important temperatures for surfaces exposed to early development of fire in a room. At 200 °C, 50% of theoretical dehydrochlorination occurs in 882 min in nitrogen and 403 min in air, while at 300 °C these times reduce to 0.38 and 0.51 min respectively. While the rate of HCl emission is influenced by oxygen concentration, dehydrochlorination will occur without the presence of air or flame.

The evolution of HCl in actual fires is known to have caused corrosion of building materials<sup>10</sup> and to be implicated in injury (including one fatality) to firemen,<sup>11</sup> although studies on civilian fire victims<sup>12</sup> have only confirmed carbon monoxide as the toxic gas primarily responsible for death. It is well known that a wide range of organic compounds is present in the gaseous products from PVC pyrolysis; however, concentrations of these are low and, compared to HCl and CO, con-

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## COMBUSTION OF PVC

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Abstract - thermal decomposition and combustion mechanisms of PVC are examined.

With respect to thermal decomposition, the results of a deuterium labeling (d-PVC) study indicate that the mechanism of benzene formation involves an intramolecular cyclization step rather than an intermolecular Diels-Alder condensation step.

With respect to combustion, the evolution and ultimate fate of hydrogen chloride and other combustion gases generated under NBS Smoke Density Chamber conditions is described. The combustion of rigid PVC, flexible PVC and rigid PVC-wood mixtures has been carried out. It was observed that under smoldering conditions, rigid PVC evolves combustion gases in a sequence that agrees with the current mechanism of decomposition. It was discovered that under flaming conditions, the concentration of hydrogen chloride in the NBS Smoke Density Chamber rapidly decreases and that the decay follows first order kinetics. Analytical data is presented which shows that this decay is due to HCl condensation on the chamber walls and is not an experimental artifact. The data from these experiments indicate that water generated during combustion plays a key role in this condensation.

Recent data published on the exposure of test animals to the combustion gases from PVC are reviewed in light of the above findings.

## INTRODUCTION

The combustion of polyvinyl chloride (PVC) has been the subject of considerable research over the past 20 to 30 years. The excellent ignition-resistant properties of rigid PVC and modified flexible PVC were responsible for many of its initial uses and for its continuing growth rate since the late 1930's to become the second most widely used plastic material in today's world market. The wide use and acceptance of PVC in applications demanding improved fire performance is well documented (1). More recently however, combustion research relating to PVC as well as other construction materials has been directed toward the by-products of combustion: heat, gases, aerosols, particulates and the effects of those by-products on biological systems. Indeed, one of the purposes of the present symposium is to delve into the complexity of just this issue, to determine what is known and what is not known and, hopefully, to outline what remains to be done. In this spirit then, this paper on the combustion of PVC will prove into the thermal decomposition of PVC (mechanisms), the combustion products from PVC, methods of altering the combustion profile of PVC and finally into the question of exposing test animals to the combustion products from PVC. Since the thrust of this paper will be directed toward the analytical chemistry of PVC combustion, it is relevant to ask what is the relationship between combustion toxicology or biological response and analytical chemistry. While some have suggested that the latter can predict the former (2, 3), recent published work on urethane foams, which produced a highly toxic bicyclic phosphate ester during combustion, completely invalidates this approach when it is applied to broad classes of materials. In other words, a knowledge of the combustion gases released from a material does not allow one to predict, a priori, a biological response (4). However as was shown in this same report, ultimately it was analytical chemistry (specifically, phosphorous -31 nuclear magnetic resonance spectroscopy and chemical ionization mass spectrometry) that unraveled the cause and effect observed in the biological testing. In essence, both disciplines are necessary and complement each other in providing an improved understanding of combustion toxicology.

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## Investigations of the Thermal Decomposition of Polyvinyl Chloride by Means of Gas Chromatography

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### INTRODUCTION

The course of thermal decomposition of polyvinyl chloride has already been widely investigated. The patterns of decomposition products are fairly differentiated and depend on both the reaction conditions and on the nature of accompanying substances (1-3, 6, 7, 9-13). The obtained reaction products, hydrochloride being the main one, strongly influence the kinetics and mechanism of the discussed process (3-5, 8, 10). These facts explain the necessity of further investigations aiming at a better understanding of the decomposition process of polyvinyl chloride.

This paper discusses thermal decomposition of polyvinyl chloride with particular attention on chromatographic identification of the obtained reaction products and the role of oxygen in the process.

### EXPERIMENTAL

#### *Characteristics of the Applied Polyvinyl Chloride (PVC)*

Polymeric, emulsive PVC (in form of a powder): E 68 (in the range of the K number from 68 to 72); flow weight, 0.56 g/cm<sup>3</sup>; volatile part, 0.3% (mainly moisture); thermal stability at 180°C, 32 min; PVC stabilized with the 0.3% addition of Na<sub>2</sub>CO<sub>3</sub>.

#### *Conditions of Thermoxidative Separation and of GC Analysis*

Thermal decomposition of the polymeric PVC E 68 was performed inside the silite oven in a stream of air, its flow rate 1 cm sec<sup>-1</sup>, the reaction time 15 min, at 300, 400, 500, and 600°C.

The sample of 1000 ± 5 mg in a quartz vessel was introduced into a quartz pipe placed in an oven at a demanded temperature. The temperature regulation of the oven allowed a measurement correctness in the

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Report of Investigations 8235

# Coal Mine Combustion Products: Ingredients of Conveyor Belts

By Theodore Christos, David R. Forshey, and Arthur M. Hartstein



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