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JOURNAL OF APPLIED POLYMER SCIENCE VOL. 13, PP. 377-391 (1969)

Analysis of the Volatile Combustion Products of Vinyl Plastics

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Synopsis

The extensive use of plastics for insulation and building materials has created interest in the possible toxicity of their combustion products. Three poly(vinyl chloride) homopolymers, a vinyl chloride-vinyl acetate copolymer, and formulations of two of the homopolymers and the copolymer have been examined to determine the composition and toxicity of their combustion products. Differential thermal analysis and thermal gravimetric analysis were used to study the breakdown process which occurred in several steps, the largest and first being the release of hydrogen chloride from the polymer at about 300°C. Approximately 50 products of combustion were then determined qualitatively by using either infrared spectroscopy or a combination of gas chromatography and mass spectroscopy. Quantitative analyses were carried out on 22 of the combustion products, and quantitative changes with varying air supply, temperature, and heating rate were determined. A comparison of the products of the polymers and their formulations is given.

INTRODUCTION

The use of plastics for wire insulation and other materials that may be intentionally or accidentally subjected to high temperatures has made it necessary for the environmental health scientist to know something about the nature and toxicity of their combustion products. The pyrolysis products of various polymers have been reported by others,¹⁻³ but much of this work has been carried out in inert atmospheres for the purpose of gaining information about polymer structure. Workers concerned with the combustion of vinyl chloride polymers examined these primarily to determine the amounts of HCl, CO₂, CO, and other gross products given off and the temperatures at which they were produced. Five such papers were published recently in German journals.⁴⁻⁸

In 1963, we began a program to determine the volatile combustion products of various plastics⁹ and to carry out animal exposure studies to determine the toxicity of these products. The combination of analytical data and acute toxicity studies is used to determine whether the compounds shown to be present can account for the overall toxicity of the decomposition products or whether synergistic effects may also be a factor to be taken into consideration. A prior knowledge of the physical nature and chemical

composition of these pyrolytic products provides a necessary guide animal exposures, both as to the extent of exposure and to the possible nature of the toxic effects.

This paper discusses the results of qualitative and quantitative analysis of the combustion products of poly(vinyl chloride) polymers and plastic. This particular group was selected, first, because of its wide application: electrical insulation and construction materials, second, because of the intensive work done in the pyrolysis of the basic polymers by others, third, because only limited knowledge is available on the quantities of compounds formed in combustion of plastic products of this type under various conditions.¹⁰ The portion of the study concerned with determining toxicity of the combustion products will be presented in another paper.¹¹

EXPERIMENTAL

The analytical portion of the study was carried out in three phases: (1) temperatures at which chemical and physical changes take place in a controlled air supply were determined; (2) compounds liberated at these temperatures were identified or characterized; (3) quantities of the products were determined either at the temperatures covering each decomposition step or for a sample collected over the entire combustion process.

The temperatures at which changes take place were determined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). In the second phase of the analysis, which involved identification of compounds liberated at the decomposition temperatures, two different approaches were taken. Gases collected from either the TGA apparatus combustion furnace were analyzed directly for major compounds by infrared absorption spectroscopy or mass spectroscopy. For positive identification of the minor constituents, it was necessary to collect the gases from a larger sample than the 200 mg that can be handled by the TGA apparatus. To do this, a combustion furnace with controlled temperature and air supply was used to carry out the combustion on a tenfold scale (2 g) but under same conditions as in the TGA apparatus. The furnace, controlled by a commercial programmer-controller, has a Vycor gas-tight core which supplied air from a tank of purified air. Products from the combustion furnace can be collected in several temperature or time fractions, depending on the collection method. The outlet of the core can be connected to a U-tube submerged in a cooling bath of Methyl cellosolve-Dry Ice followed by a plastic bag to collect the gaseous products in two phases (compounds boiling below -75°C and above -75°C), or it can be connected to a plastic bag and a single sample collected to be separated by gas chromatography. To establish that the products from the TGA apparatus combustion furnace were the same, a gas chromatogram of the furnace combustion products was compared with a chromatogram of the TGA combustion products over the same weight-loss range. Individual chromatographic peaks were collected by condensation at liquid air temperature and analyzed by mass spectroscopy.

The third phase, quantitative analysis of the identified products, was carried out by infrared spectroscopy for the principal constituents and by gas chromatography for the minor constituents.

Four polymers produced by two companies were analyzed, as were three formulations using three of these polymers. They are listed as follows with the approximate molecular weight (weight average) and approximate mesh size of each polymer sample: polymer A, a poly(vinyl chloride) homopolymer, MW 109000, mesh size 80; polymer B, similar to A but a later production, MW 111000, mesh size 80; polymer C, a poly(vinyl chloride) homopolymer produced by another company, MW 250000, mesh size 60; copolymer D, a 85:15 copolymer of vinyl chloride and vinyl acetate, MW 55000, mesh size 100; plastic E, a formulation commonly used for wire insulation, containing 57% polymer C; plastic F, a formulation used for floor tiles, containing 35% copolymer D; plastic G, a wire insulation formulation, containing 51% polymer B.

With one exception, polymers and formulations were standard commercial materials furnished by the polymer manufacturers. The last product, plastic G, was formulated for us in a development lab of one manufacturer, a "typical" wire insulation formula being used.

RESULTS AND DISCUSSION

Breakdown Process

Differential thermal analysis (DTA) was used to determine the temperatures at which chemical and physical changes take place. With this apparatus a record as shown in Figure 1 was obtained for polymer C when heated at 10°C/min in an excess of air. The polymer was mixed 1:1 with

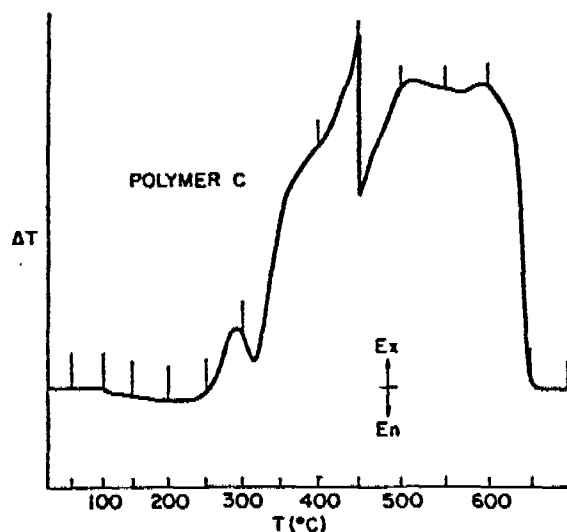


Fig. 1. Differential thermal analysis record of polymer C.

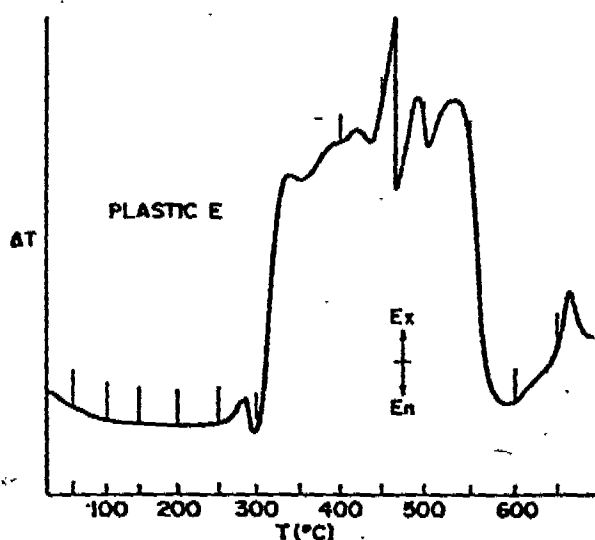


Fig. 2. Differential thermal analysis record of plastic E.

SiC and a 300 mg sample run, SiC being used as a reference. This record shows the heat absorbed (from an endothermic change) or liberated (from an exothermic change) as ΔT plotted against the temperature of the sample. Full-scale sensitivity, ΔT , is 1.82°C up to 450°C and 3.30°C from 450 to 600°C . Of significance is the endothermic peak with a maximum at about 300°C , which results from release of chlorine atoms in the polymer. Unfortunately it is here obscured by the start of the exothermic peaks which began at 300°C and continued to 600°C , at which temperature the sample is completely combusted. The dehydrochlorination peak varies in position

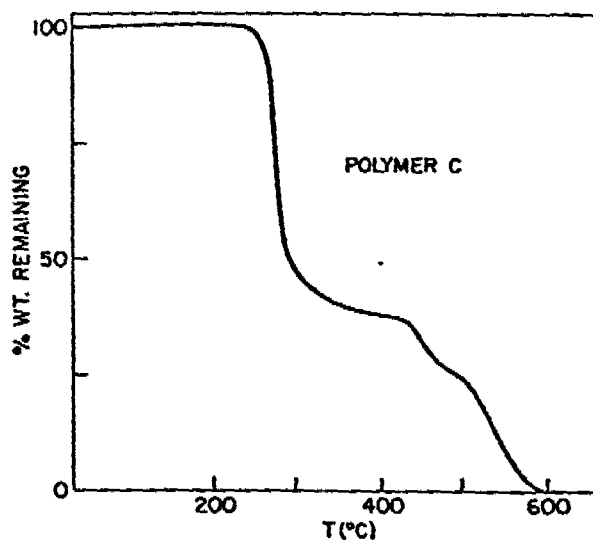


Fig. 3. Thermogravimetric analysis record of polymer C heated at $3^{\circ}\text{C}/\text{min}$ in

by $\pm 20^\circ\text{C}$ and, as this variation seems to be erratic and independent of the sample, it is assumed that it is associated with some experimental parameter such as rate of sample melting, etc. Figure 2 shows a DTA record of plastic E which was formulated from polymer C. The only gross difference is a steeper slope in the exothermic peak at 325°C .

Because of the limited amount of interpretation that could be extracted from these curves, information derived from the DTA technique did not prove as helpful to our study as did thermogravimetric analysis, where a recording of weight change with increasing temperature is obtained. Figure 3 shows a TGA record for polymer C heated at $3^\circ\text{C}/\text{min}$ in air. Here a rapid weight loss at 300°C is observed, corresponding to the endothermic peak in the DTA record. On collecting the combustion gases up to 300°C and analyzing them by infrared absorption, it was found that the 60% weight loss was almost entirely due to removal of chlorine in the form of hydrogen chloride gas and, by calculation, it appeared that the amount corresponded to almost all the chlorine atoms in the polymer. Above 300°C , the TGA record shows a slower but gradually increasing rate of weight loss up to 600°C , corresponding to the exothermic peaks in the DTA record. This weight loss appears to take place in five stages. First is the rapid loss up to 280°C ; second, a decreasing rate of loss up to 350°C ; third, a slow constant rate of loss to 430°C ; fourth, a more rapid rate of loss to 510°C ; and finally, a faster rate of loss for the remainder of the sample. These particular temperature ranges are used later (Table IV) in describing the change in composition of combustion products with temperature. Figure 4 shows a similar record for plastic E, which contains polymer C. The height of the 300°C step, attributed in Figure 2 to removal of chlorine, is as high here, although this plastic contains only 57% of the polymer. The remainder of the weight loss is due to boiling-off of the plasticizer, a phthalate which has a boiling point of about 280°C .

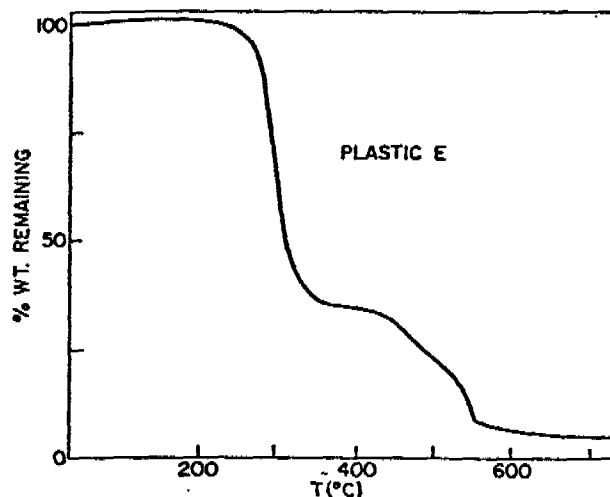


Fig. 4. Thermogravimetric analysis record of plastic E heated at $3^\circ\text{C}/\text{min}$ in air.

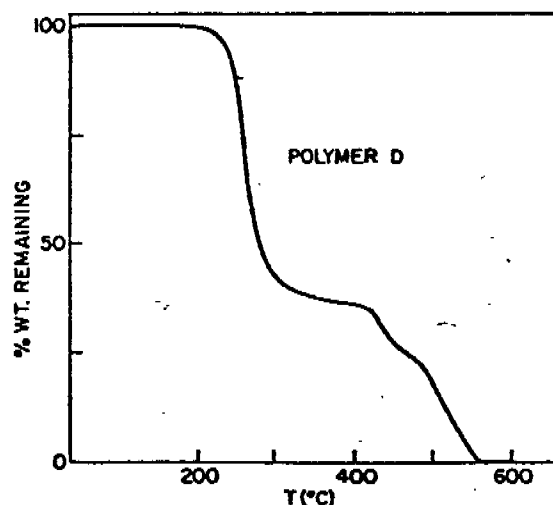


Fig. 5. Thermogravimetric analysis record of copolymer D heated at 3°C/min in air.

Figure 5 is the TGA record of copolymer D, and it can be seen that the weight loss proceeds in the same manner as the previous polymer, except that here the initial weight loss is due to the removal of both chlorine atoms and acetate groups. Figure 6 is of plastic F, the floor tile formulation that contains about 35% of polymer D. This formulation contains a considerable amount of inorganic minerals, such as asbestos, which is the reason for the limited amount of weight loss up to 600°C.

Qualitative Analysis

This study was primarily concerned with the "volatile products" of combustion, those compounds boiling up to about 150°C being defined as

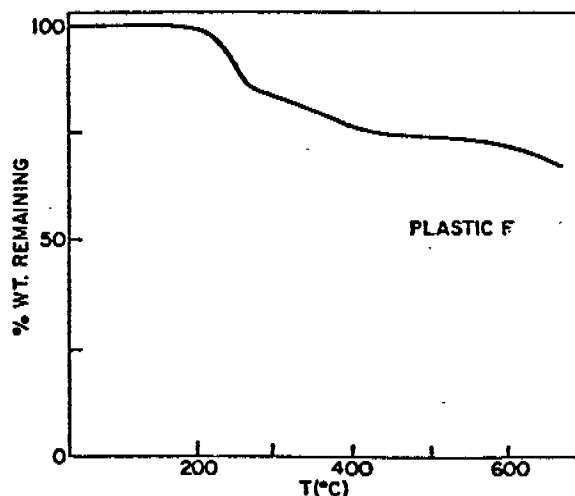


Fig. 6. Thermogravimetric analysis record of plastic F heated at 3°C/min in air.

volatile. As a result, although the TGA record of plastic E (Fig. 4) shows a weight loss due to boiling off of the phthalate plasticizer, this compound is not listed in our results. Compounds that remained in the combustion boat or condensed in the sample bag or at the exit end of the combustion tube were not analyzed, although an attempt was made to determine the weight of this remainder to assure that the volatile fraction was all accounted for.

When the products of combustion were analyzed by infrared spectroscopy, collecting the total products in gas form and introducing them into long-path gas cells, absorption bands of HCl, CO₂, CO, and benzene were found, along with other bands in the 3000 cm⁻¹ region indicating the presence of compounds containing C—H groups. It was evident that identification of other compounds should be carried out by separating them from the mixture and collecting them in individual quantities that would permit identification by infrared or mass spectroscopy. For this gas chromatography was employed, using sufficiently large columns to permit the introduction of up to 30 ml of sample. To separate the low-boiling compounds, i.e., those boiling at temperatures less than 0°C, a Porapak Q column was used; to separate higher-boiling compounds a column of 5% squalane on Chromosorb P was used. Columns were temperature programmed at 10°C/min to 110°C after an initial period of 5–15 minutes at 25°C. A stream splitter on the column outlet of the chromatograph passed one hundredth of the gas through a hydrogen flame detector. The remaining 99 parts emerged from the column through a two-way valve and were diverted into a U-tube when a particular compound was eluted. The U-tube, filled with glass beads, was cooled with liquid air to condense out everything except the helium carrier gas. The U-tube and its cooling flask were then transferred to the inlet system of the mass spectrometer.

Figure 7 shows the separation of the first eight compounds. These are primarily paraffins and olefins through butane, and are identified in Table I according to peak number. These peaks were identified by using the

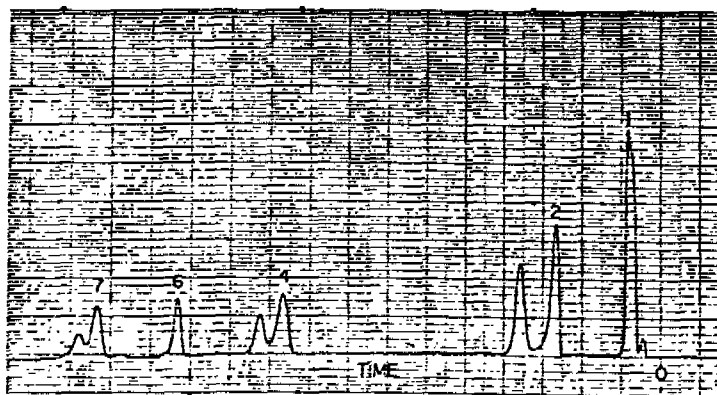


Fig. 7. Chromatogram of low-boiling combustion products of polymer A on a Porapak Q column.

TABLE I. Identification of Chromatogram Peaks

Peak no.	Identification
Air	
1	Methane
2	Ethylene
3	Ethane
4	Propylene
5	Propane (methyl chloride)
6	Vinyl chloride
7	1-Butene (isobutane-butadiene)
8	Butane
9	<i>trans</i> -2-Butene
10	<i>cis</i> -2-Butene
11	3-Methyl-1-butene
12	Isopentane (1,4-pentadiene)
13	1-Pentene
14	Pentane
15	<i>trans</i> -2-Pentene
16	<i>cis</i> -2-Pentene
17	2-Methyl-2-butene
18	<i>cis</i> or <i>trans</i> -1,3-Pentadiene
19	<i>cis</i> or <i>trans</i> -2-Penten-4-yne
20	Cyclopentene
21	Cyclopentane
22	2-Methylpentane
23	1-Hexene (3-methylpentane)
24	Hexane
25	2-Hexene
26	Methylcyclopentane
27	1-Methylcyclopentene
28	Benzene
29	Cyclohexane
30	1-Heptene
31	1,4-Dimethylcyclopentene*
32	Heptane
33	
34	3-Ethylcyclopentene
35	Methylcyclohexane
36	Ethylcyclopentane
37	1,2-Dimethylcyclopentene*
38	1- or 4-Ethylcyclopentene
39	1-Methylcyclohexene
40	Toluene
41	
42	
43	Octane
44	
45	
46	
47	
48	Ethylbenzene
49	<i>p</i> -Xylene
50	<i>m</i> -Xylene
51	<i>o</i> -Xylene

* Tentative.

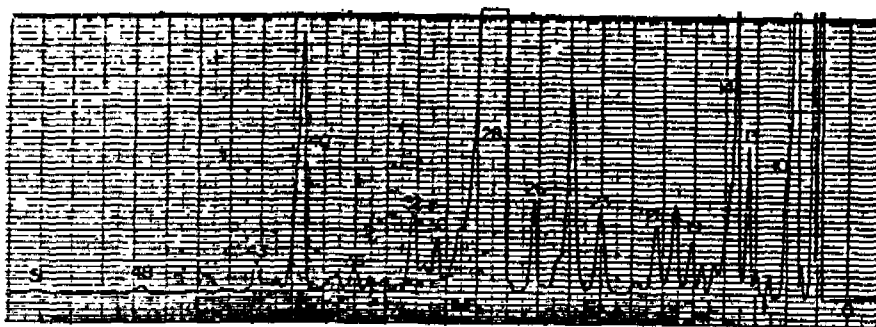


Fig. 8. Chromatogram of the combustion products of polymer A on a column of 5% squalane on Chromosorb P.

collection technique described to transfer the compound to the mass spectrograph. Mass spectrographic identification was then cross-checked by injecting the pure compound on the chromatograph to establish that its elution time was the same as the collected peak.

A chromatogram on the squalane column is shown in Figure 8. Here, in addition to straight-chain paraffins and olefins, both branched and cyclic compounds are found. These are again identified in Table I.

There are minimally 59 volatile products of combustion, totaling the three compounds identified by direct infrared analysis and 51 chromatographic peaks, at least four of which represent more than one compound. Of this minimum figure of 59, we have identified 52 compounds. Because of the similarity in molecular weights and limited mass spectral reference data, positive identification of the remaining peaks has been difficult. These are higher-boiling compounds and are present in very small quantities, i.e., less than 30 $\mu\text{g/g}$, and therefore are of limited interest from the standpoint of toxicity. The qualitative picture was similar for all PVC polymers tested, with only a few differences found in the higher-boiling products and the formulations.

Quantitative Analysis

All the quantitative work was done on the 22 compounds present in the greatest quantities. As a uniform condition for intercomparing the polymers and formulations of the polymers, the following combustion conditions were adopted:

The rate of air supply was 60 cc/min which, when integrated over the entire run, would result in about twice the amount of oxygen necessary to convert all of the carbon to carbon dioxide. However, this was not true for any particular time in the combustion process, in that first, the carbon was not available to form carbon dioxide until higher temperatures were reached and second, the air flow pattern was such that all of the oxygen was not in the immediate vicinity of the sample. The plastics were heated, (after an initial heating from room temperature) from 200°C to 600°C at a rate of 3°C/min.

During the study several parameters were examined that could affect the quantities of the various compounds of combustion, and these are reported as follows:

(1) the variation in quantity within a class of compounds and between classes of compounds for the polymers; (2) changes with varying air supply; (3) changes with temperature; (4) changes with varying heating rates; (5) changes between the plastics and their polymers.

Variation in Quantity within a Class of Compounds and between Classes of Compounds for the Polymers

Table II shows the volatile products of combustion of polymer B. Quantities of these products are representative of the other two homopolymers. Also in this table are the same products from copolymer D. All quantities given are in mg of compound per gram of polymer. In polymer B, chlorine is almost completely accounted for in the form of HCl gas (583 mg found, 584 mg possible). The only other chlorine compounds found, methyl chloride and vinyl chloride, are present in quantities of less than 1 mg. Some investigators have reported finding phosgene intermittently in very small quantities (0.1 ppm) but, using detector tubes of this sensitivity, we could not detect this compound. Carbon dioxide and carbon monoxide, which are formed at higher combustion temperatures, are present in quite large

TABLE II
Volatile Combustion Products of Polymer B and Copolymer D

Compound	Combustion products, mg/g	
	Polymer B	Copolymer D
HCl	583.	500.
Acetic acid	—	96.
CO ₂	729. = 735	923.
CO	442. = 440	292.
Methane	4.6	4.4
Ethylene	0.58	0.60
Ethane	2.2	2.3
Propylene	0.47	0.56
Propane	0.84	0.88
Vinyl chloride	0.60 = 0.0006	0.72
1-Butene	0.18 = 1.00	0.22
Butane	0.28	0.29
Isopentane	0.02 = 0.0002	0.02
1-Pentene	0.06	0.09
Pentane	0.16	0.21
Cyclopentene	0.05	0.05
Cyclopentane	0.05	0.06
1-Hexene	0.05	0.08
Hexane	0.12	0.17
Methylcyclopentane	0.04	0.05
Benzene	36.	28.
Toluene	1.3	0.96

amounts. The most abundant hydrocarbon is benzene (35 mg/g). Decreasing in quantity with increasing molecular weight are the straight chain aliphatics, starting with methane. Olefins and side-branched aliphatics are generally present in lesser quantities than the corresponding aliphatics. Note that quantities of these compounds for the polymer and copolymer are very similar, except that some of the HCl is replaced by acetic acid. In these samples, volatile combustion products account for approximately 100% of the original polymers, and no residue remained in the combustion boats.

Changes with Varying Air Supply

One sample (polymer A) was combusted by use of three different conditions of air supply. The first provided the minimum amount of oxygen for complete combustion of all carbon to CO_2 (30 cc air/min). The second was about twice this amount (60 cc/min), and the third was with a large excess of oxygen.

The results are shown in Table III. The data show that all of the hydrocarbons except benzene decrease in quantity with increasing air. Although a change in the amount of air affects the quantity of hydrocarbons generated, surprisingly it has little effect on the quantity of CO and CO_2 generated, which showed no trends using these air flows. However, it should be noted that the quantities of CO_2 varied erratically in most of our combus-

TABLE III
Variation of the Combustion Products of Polymer A with Oxygen

Compound	Combustion products, mg/g		
	Air, 30 cc/min	Air, 60 cc/min	Air, 25 cc/min + oxygen, 21 cc/min
CO_2	861.	619.	814.
CO	357.	429.	401.
Methane	6.7	4.7	3.8
Ethylene	0.76	0.53	0.28
Ethane	2.6	2.1	1.7
Propylene	0.80	0.53	0.28
Propane	1.3	1.0	0.66
Vinyl chloride	0.51	0.59	0.66
1-Butene	0.25	0.18	0.06
Butane	0.53	0.31	0.15
Isopentane	0.02	0.02	0.01
1-Pentene	0.10	0.08	0.04
Pentane	0.26	0.20	0.11
Cyclopentene	0.07	0.05	0.03
Cyclopentane	0.08	0.07	0.03
1-Hexene	0.07	0.06	0.03
Hexane	0.16	0.14	0.09
Methylcyclopentane	0.06	0.05	0.03
Benzene	35.	31.	32.
Toluene	1.5	1.1	0.68

tion runs, possibly because of sample ignition at higher temperatures. The amount of benzene seems to be independent of air conditions. The amount of HCl, 580 ± 5 mg/g (not listed in the table), is also independent of air conditions and accounts for nearly all the chlorine atoms of the polymer. Vinyl chloride increases consistently with increasing air supply, but this increase is not enough to affect the HCl concentration significantly.

Changes with Temperature

Table IV shows the variation in quantities of products of combustion as a function of temperature. The products were collected in five fractions during a single heating run. Fractions were selected on the basis of inflections on the TGA curve shown in Figure 3. During the first temperature fraction almost 80% of the benzene is formed along with a small amount of toluene and some unsaturated hydrocarbons. Production of HCl (not listed) roughly parallels that of benzene.

TABLE IV
Variation of Combustion Products of Polymer A with Temperature

Compound	Combustion products, mg/g				
	25- 280°C	280- 350°C	350- 430°C	430- 510°C	510- 580°C
CO ₂	—	9.7	181.	244.	237.
CO	—	20.	46.	151.	181.
Methane	—	0.20	1.3	1.8	0.31
Ethylene	0.04	0.33	0.39	—	—
Ethane	—	0.12	0.94	0.41	—
Propylene	0.06	0.11	0.31	—	—
Propane	—	0.08	0.44	0.11	—
Vinyl chloride	0.04	0.25	0.17	0.02	—
1-Butene	0.02	0.04	0.08	—	—
Butane	—	0.03	0.20	0.02	—
Isopentane	—	—	0.005	0.001	—
1-Pentene	—	0.01	0.03	—	—
Pentane	—	0.01	0.08	0.01	—
Cyclopentene	—	0.02	0.01	—	—
Cyclopentane	—	0.01	0.02	—	—
1-Hexene	—	0.01	0.02	—	—
Hexane	—	0.01	0.05	0.01	—
Methylcyclopentane	—	—	0.02	—	—
Benzene	24.	6.6	0.35	0.16	—
Toluene	0.12	0.18	0.55	0.03	0.01

In the second fraction (280–350°C), CO₂ and CO appear, toluene continues to increase, but HCl and benzene are already decreasing and continue to decrease through the higher ranges. HCl is present only in trace amounts after 300°C. Additionally, in the second fraction the maximum amount of vinyl chloride is formed. As expected, CO₂ and CO reached their maxima at higher temperatures.

Methane reached its maximum in the fourth step, but was still generated at higher temperatures. The other straight-chain aliphatics reached their maxima in the third step and were present in the last step in very small quantities. Olefins began to form in the first step, reached their maxima in the third, and did not appear in the last two fractions.

Changes with Varying Heating Rates

The data on Table V represent what happens when the heating rate is increased considerably. An increase in the heating rate results in increased hydrocarbon production, and of note is that unsaturated compounds increase by a greater amount than the saturates. As a result, with an exceptionally fast heating rate, olefins will be present in greater quantities than aliphatics. This is illustrated in the chromatogram shown in Figure 7, where the products were collected from a run in which the controlling thermocouple burned out, with the result that a heating rate greater than 80°C/min was attained. Also to be noted is that at higher heating rates production of CO₂ and CO decreases. The heating rate has no significant effect on the amount of HCl produced.

TABLE V
Variation of Combustion Products of Polymer A with Heating Rate

Compound	Combustion products, mg/g	
	3°C/min	50°C/min
CO ₂	619.	397.
CO	429.	269.
Methane	4.7	8.7
Ethylene	0.53	2.3
Ethane	2.1	3.5
Propylene	0.53	1.5
Propane	1.0	1.3
Vinyl chloride	0.59	0.64
1-Butene	0.18	0.67
Butane	0.31	0.69
Isopentane	0.02	0.02
1-Pentene	0.08	0.18
Pentane	0.20	0.29
Cyclopentene	0.05	0.19
Cyclopentane	0.07	0.11
1-Hexene	0.06	0.13
Hexane	0.14	0.20
Methylcyclopentane	0.05	0.08
Benzene	31.	43.
Toluene	1.1	3.5

Variations between Plastics and their Polymers

A comparison of the combustion products of the three plastics with the combustion products of their polymers is given in Table VI. Except for

the aromatic compounds, the hydrocarbons in plastics E and G have all increased in quantity by factors ranging from 1.3 up to 8 times, the average being about 4 times. Likewise, the amount of vinyl chloride appears to be about 5 times as great in these samples. Most of the increases are attributable to the breakdown of the phthalate plasticizer, which forms a series of hydrocarbons similar to those produced by PVC. The plasticizer, either dioctyl phthalate or diisodecyl phthalate, cannot be directly responsible for the increase in vinyl chloride. It is presently not clear if this increase is real or if there has been some chromatographic interference with an unidentified compound being eluted at the same time as vinyl chloride. The plasticizers do form several oxygenated compounds such as ethylene oxide, acetone, and at least one alcohol which have not been fully investigated.

TABLE VI
Comparison of Combustion Products of the Plastics with the Combustion
Products of their Polymers

Compound	Combustion products, mg/g					
	Polymer B	Plastic G	Polymer C	Plastic E	Co- polymer D	Plastic F
HCl	583.	273.	584.	333.	500.	73.
Acetic acid	—	—	—	—	96.	20.
CO ₂	729.	616.	730.	1182.	923.	456.
CO	442.	67.	403.	90.	292.	31.
Methane	4.6	6.6	5.8	6.8	4.4	0.30
Ethylene	0.58	2.3	0.33	2.0	0.60	0.13
Ethane	2.2	3.0	2.5	2.9	2.3	0.13
Propylene	0.47	2.0	0.56	1.4	0.56	0.11
Propane	0.84	1.7	1.1	1.4	0.88	0.10
Vinyl chloride	0.60	3.3	0.52	2.6	0.72	0.30
1-Butene	0.18	1.1	0.28	0.58	0.22	0.06
Butane	0.28	1.1	0.39	0.74	0.29	0.05
Isopentane	0.02	0.15	0.02	0.04	0.02	0.01
1-Pentene	0.06	0.35	0.11	0.15	0.09	0.01
Pentane	0.16	0.58	0.27	0.38	0.21	0.02
Cyclopentene	0.05	0.14	0.58	0.07	0.05	0.004
Cyclopentane	0.05	0.16	0.07	0.09	0.06	0.003
1-Hexene	0.05	0.24	0.09	0.18	0.08	0.01
Hexane	0.12	0.49	0.25	0.35	0.17	0.01
Methylcyclopentane	0.14	0.14	0.07	0.09	0.05	—
Benzene	36.	10.	29.	11.	28.	0.86
Toluene	1.3	0.94	1.1	1.0	0.96	0.04
Residue*	—	159.	—	61.	—	709.

* Residue is what remained in combustion boat. It does not include products which condensed at the end of the combustion tube.

Different results are noted for plastic F, the floor tile formulation made from copolymer D. This product contains about $\frac{1}{4}$ copolymer D, but the hydrocarbon products generated, especially saturated aliphatics and ben-

zene, are considerably less than $\frac{1}{2}$ the amount generated in copolymer D. Likewise, the amount of HCl to CH_3COOH is only 20%, rather than the 33% expected. This product contains about 70% inert material, such as asbestos and calcium carbonate, which may play a part in inhibiting breakdown of the polymer and production of hydrocarbons. It should be stated that plastic F has three compounds with boiling points in the vicinity of 120°C that have not been identified, which are present in quantities of 1-5 mg/g and probably arise from combustion of the plasticizer.

This investigation was supported in part by Public Health Service Research Grant No. UI-00485 from the National Center for Urban and Industrial Health.

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Received October 7, 1967