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B. F. Goodrich Chemical Company
A DIVISION OF THE B. F. GOODRICH COMPANY
DEVELOPMENT CENTER

Degradation and Combustion Products From Poly(vinyl chloride)

II - Description of Pyrolysis Unit and Initial Pyrolysis of PVC

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I - MAJOR OBJECTIVE:

The major objective in this work is the development of the necessary analytical tools for the rapid determination of the degradation and combustion products from PVC.

In addition to studies of PVC, the developed analytical-pyrolysis tool will be used in the following areas:

1. toxicity,
2. flammability,
3. polymer structure and stability,
4. efficiency of PVC stabilizers,
5. polymer identification (fingerprinting).

II - LIMITED OBJECTIVES

A pyrolysis unit that afforded the following capabilities was desired:

1. the temperature of pyrolysis accurately known,
2. wide range of pyrolysis temperatures possible,
3. all volatile pyrolysis products be admitted to the gas chromatograph for analysis,
4. capabilities for pyrolysis in an oxygen rich and oxygen poor atmosphere,
5. reproducibility.

III - SUMMARY OF CONCLUSIONS:

1. A radiant heat pyrolyzer having the necessary capabilities for degradation, toxicity, flammability and polymer characterization studies has been constructed.

2. Initial pyrolyses of PVC (Geon 103EP F-7) in both a nitrogen and helium atmosphere have been carried out. The result of these studies showed that at 600°C., PVC degrades to 21 major (identifiable) and 25 minor components.

3. The major degradation products have been identified by mass spectrometric techniques.

   These products are:

   1. HCl
   2. CO_2 (and N_2)
   3. ethane
   4. ethylene
   5. propane
   6. propylene
   7. butane
   8. butene
   9. butadiene
   10. diacetylene
   11. benzene

12. toluene
13. }
14. } 3 xylenes
15. }
16. chlorobenzene
17. ethyltoluene
18. indane
19. naphthalene
20. }
21. } 2 isomers of methylnaphthalene

4. A quantitative analysis encompassing volatiles and non-volatiles has been completed. The results of that determination are contained in the following table.

% Weight	Composition of Fraction
~58 (Theoretical)	HCl
~10	Carbonaceous Ash(non-volatile)
~32	Volatile Aliphatic and Aromatic Hydrocarbon Fraction

IV - FUTURE ACTION:

The next phase of this research problem is:

1. carry out the pyrolysis of PVC in varying levels of oxygen and compare and correlate the results with those pyrolysis results obtained under inert conditions.

2. pyrolyze copolymers of PVC and other polymers in order to obtain a catalog of reference pyrograms (polymer characterization)

3. a study of the flammability characteristics of PVC-Acrylate-PVDC-Phosphonate-Polymers has been initiated. (Preliminary results are very encouraging.)

4. initiate a program in the thermo-oxidative degradation of Hydrin 100 and 200. This work will be in support of current studies on the Hydrin process.

V - INTRODUCTION AND DISCUSSION

In a recent outline of objectives,[1] it was stated that a pyrolysis-gas chromatograph-mass spectrometer tandem system was being developed for purposes of carrying out polymer degradation studies. The gas chromatographic technology required for separating the typical degradation products from PVC has been developed and detailed in a status report.[2] The present paper deals with the pyrolysis apparatus that has been constructed for these studies, with initial pyrolysis of PVC and with the identification of the major pyrolysis products from PVC.

It was deemed necessary that the pyrolysis unit have a number of capabilities. These were:

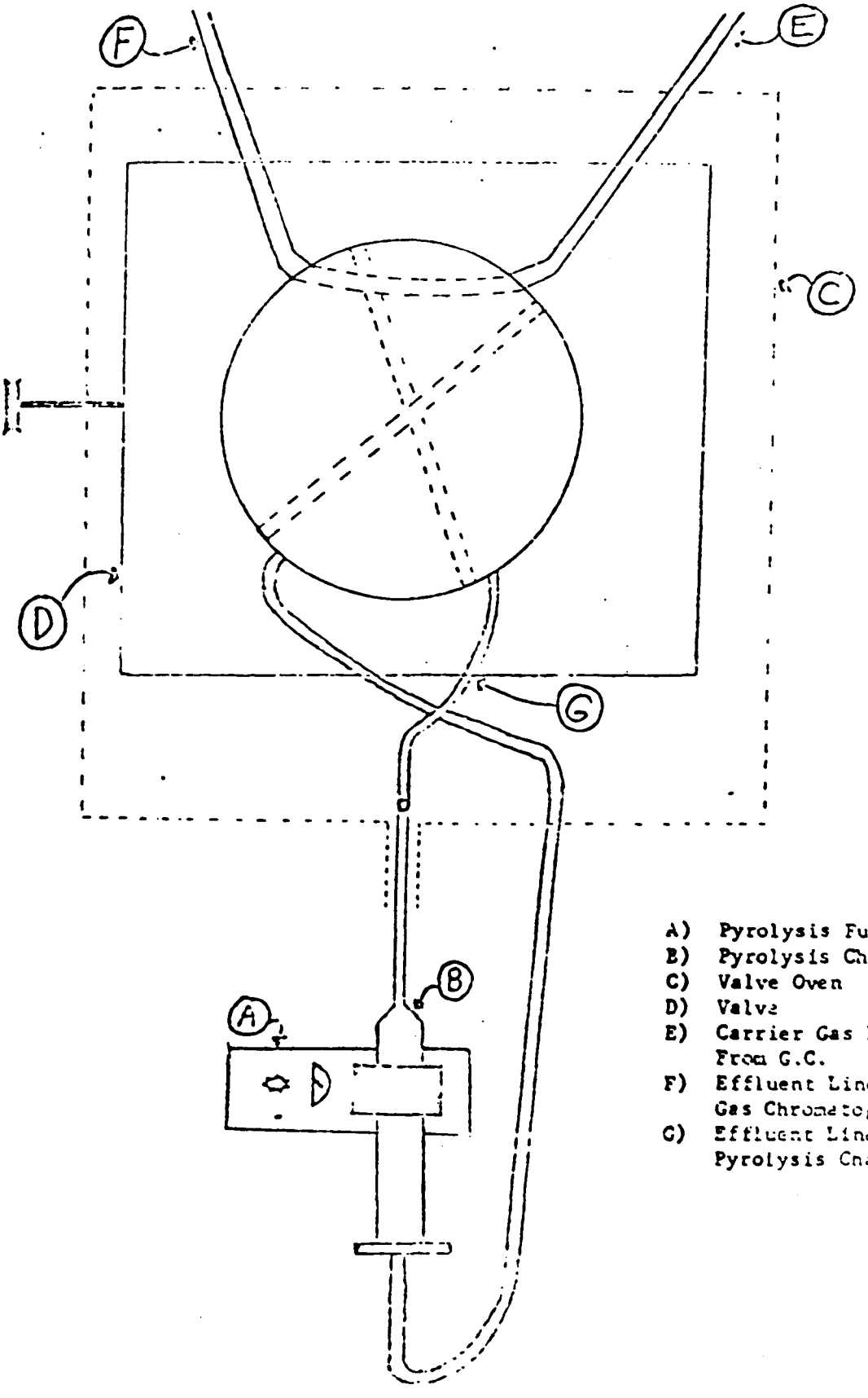
1. that the temperature of pyrolysis be accurately known,
2. that a wide range of pyrolysis temperatures be possible,
3. that all pyrolysis products be admitted to the gas chromatograph for analysis,
4. that pyrolysis could be carried out under an oxygen rich and oxygen poor atmosphere, and
5. that some degree of reproducibility exist.

In all of the areas in which this pyrolysis-gas chromatographic-mass spectrometric tool will be used (See I, Major Objectives), it will be important that all volatile degradation products be analyzed. For studies in which polymer structure is to be correlated with degradation products, the temperature of pyrolysis must both be accurately controlled and known. Similarly, the capability of a wide range of pyrolysis temperatures is important. The need for being able to control pyrolysis atmosphere is important with respect to simulating usual combustion conditions. Finally without some degree of reproducibility, correlations of degradation products and toxicity, or flammability, for example, would be impossible.

It is felt that the pyrolysis unit constructed and described in detail below meets the above requirements.

A. Description of the Pyrolysis Unit

The unit basically consists of a quartz chamber which is heated by an external furnace. The furnace is that which is provided with the P and E commercial unit and temperatures of up to 1000°C. are possible. The quartz chamber contains an inlet line through which carrier gas (He) can be admitted to the pyrolysis chamber and an effluent (exit) line through which the degradation products (and carrier gas) are carried. These two lines have been connected to an F and M Gas Sampling Valve in such a way so as to replace the normal "sampling loop". A carrier gas line from the chromatograph leading to the valve and an effluent line leading from the valve to the injection port of the chromatograph have also been constructed.



A) Pyrolysis Furnace
B) Pyrolysis Chamber
C) Valve Oven
D) Valve
E) Carrier Gas Line From G.C.
F) Effluent Line to Gas Chromatograph
G) Effluent Line From Pyrolysis Chamber (B).

With the valve in the "in" position, carrier gas by-passes the pyrolysis chamber (i.e., the "sample loop") through the valve and travels directly to the injection port of the gas chromatograph. With the valve in this position, the pyrolysis unit is then loaded with a porcelin boat containing sample, the hot zone of the chamber is brought to temperature and the entire unit is purged with N_2 or N_2/O_2. The boat is then moved into the hot zone where degradation is carried out. Once the degradation period has been completed, the gas sampling valve is switched to the "out" position. Carrier gas is then admitted to the pyrolysis unit and the degradation products are carried from the unit, through the heated sampling valve to the injection port of the chromatograph. (See accompanying block diagram).

All effluent lines through which the pyrolysis products pass, as well as the gas sampling valve itself, are heated. Provisions were made during the construction of the effluent line to the injection port of the chromatograph for "on-column" injection.

A calibration was made between the temperature read-out on the pyrolysis unit and the actual temperature inside the hot zone of the pyrolysis chamber so that the true temperature of pyrolysis could be known.

B. Volatilization of an Analytical Sample in the Pyrolysis Chamber.

An analytical sample of benzene, toluene and naphthalene was prepared and analyzed on the gas chromatograph by two methods. The first was the usual direct injection procedure (Method A) while the second involved placing the mixture in a sample boat, volatilizing the sample in the hot zone of the pyrolyzer and sweeping the vapor from the pyrolyzer to the chromatograph (Method B) for analysis. The results of these two runs are contained in Table I.

It is believed that the 3% difference in analysis is a result of the differences in the two methods and not due to a "selective extraction" of one of the products while in transit from the pyrolysis chamber to the gas chromatograph. If this were happening, one would expect the naphthalene content to be low in the analysis obtained by Method B. However, the opposite of this results: Naphthalene is 3% higher when the analysis is carried out by Method B.

TABLE I - G.C. Analysis of Analytical Mixture. Method A: Direct Injection; Method B: Sample Volatilized in Pyrolysis Chamber.

	Method A	Method B
	%	%
Benzene	41	38
Toluene	48	48
Naphthalene	11	14

It should be noted that while in Method A the chromatographic peak due to benzene is sharp with no tailing, the same peak by Method B is broad and tails considerably. This factor is the most probable source of error in this analytical determination.

C. Initial Pyrolysis of PVC. Identification of Major Degradation Products

Preliminary degradations of PVC were carried out at 600°C. for 5 minutes in an inert atmosphere (N_2 or H_e). Initially, sample sizes in the 5 to 10 mg. range were used but due to the preponderence of products (other than HCl), amounts in the 20-30 mg. range were necessary. Since HCl has an adverse effect on the chromatographic column used for separating the degradation products (SE52 on ABS), it was removed through reaction with copper powder.

In a typical pyrolysis run, a 25 mg sample of PVC (Geon 103EP F-7) produced, upon thermal decomposition, 21 major and 25 minor products. The identification of the major products has been completed and the results of these identifications are contained in Table II.

TABLE II - Products From the Thermal Degradation of PVC at 600°C.

HCl
CO_2
Ethane
Ethylene
Propane
Propylene
Butane
Butene
Butadiene
Diacetylene
Benzene
Toluene
Xylene (3 isomers)
Chlorobenzene
Ethyl toluene
Indane
Naphthalene-
β-Methylnaphthalene
α-Methylnaphthalene

A typical pyrogram of PVC can be divided into three regions: volatile gases (CO_2 C_2H_4, C_2H_6, etc.), low boiling saturated and unsaturated hydrocarbons (C_4-C_6) and high boiling aromatics (benzene, toluene, naphthalene). In order to more fully investigate the volatile gas products (the low end of the pyrogram), gas chromatographic separation of these particular pyrolysis products on a Porapak QS column was necessary. Thus, in order to identify all degradation products, analysis on a Porapak and on an SE-52 column had to be carried out.

The minor degradation products from PVC could not be identified due to sensitivity limitations in the mass spectrometer. However, the majority (18 of 25) of these minor products appear in the "aromatic region" of the PVC pyrogram while the remaining minors (7) are in the light hydrocarbon region.

Boettner and Weiss[3] have reported that both aliphatic and aromatic products are evolved when PVC is degraded in the presence of air (TABLE III). A more recent report[4] by Noffz indicates that the only degradation products from PVC (aside from HCl) are aromatic type compounds (TABLE IV).

TABLE III - Weight Loss vs. Degradation Products from PVC in Air.[3]

HCl (97%), Benzene (3%)	Aromatic (40%) Aliphatic (30%) CO and CO_2 (30%)	CO CO_2
100%	40%	20% 0%

weight loss

TABLE IV - Degradation Products From PVC[4]

1. Benzene
2. Toluene
3. Ethylbenzene
4. Xylene
5. Chlorobenzene
6. Xylene
7. Styrene
8. n-Propylbenzene
9. Allylbenzene
10. α-Methyl styrene
11. Azulene
12. Indane
13. Methylindane
14. Indene
15. Tetralin
16. Methylindane
17. Naphthalene
18. Methylnaphthalene
19. α-Methylnaphthalene
20. Diphenylmethane
21. $C_{12}H_{12}$

The results from the work described in the present paper correspond fairly closely to the findings of Boettner and Weiss. Although Noffz has reported that the only products arising from the thermal degradation of PVC are various aromatics, the actual state of affairs appears to be that both aliphatic, olefinic hydrocarbons and aromatics are formed.

One of the more interesting aspects of the degradation products coming from PVC is the large amount of CO_2. Direct probe experiments involving the degradation of PVC in the heated inlet system of the mass spectrometer have verified that a large amount of CO_2 is released during degradation in vacuum. This result reflects one of two situations: a considerable amount of absorbed oxygen on the PVC resin or oxygen chemically bonded to the backbone of the polymer. In order to further investigate this, a sample of the resin was placed in the cold zone of the mass spectrometer inlet system and evacuated overnight (10^{-6} mm Hg). The sample was then moved to the hot zone of the inlet system where degradation proceeded. The amount of CO_2 released from the degassed sample of PVC was identical to that released from a sample that had not undergone overnight degassing. The results, however, cannot be construed as evidence for oxygen bonded into the PVC polymer. It may well be that the released CO_2 results from absorbed gen that is not effectively removed during the vacuum treatment. .s phenomenon of CO_2 generation during the pyrolysis of PVC in an inert atmosphere is being further investigated.

Another factor that requires limited investigation is the effect of secondary reactions on the types of degradation products. Since the pyrolysis products from PVC reside in the hot zone of the pyrolyzer for relatively long periods (5 minutes) of time, secondary degradations of primary products are quite possible. This important factor will be further investigated by varying the temperature and time of degradation.

D. Quantitative Analysis

Summary:

A quantitative analysis of the degradation products from PVC at 600°C. reveals that approximately 58% (by weight) of the polymer is converted to HCl, 32% to aliphatic and aromatic hydrocarbons and 10% remaining as a carbonaceous ash.

It has previously been stated that the large amount of CO_2 generated during the pyrolysis of PVC cannot be explained in the absence of further data.

The amount of CO_2 generated during a typical pyrolysis accounts for over half of the volatile fraction of the degradation products. In view of this discrepancy, a precise quantitative analysis is not possible at this time. However, a fairly good approximation of the quantity of volatile products in relation to the quantity of starting polymer can be made. Since only 30% of the polymer is coverted into a hydrocarbon and CO_2(?) fraction, uncertainty in the origin of the CO_2 does not result in too large of an error.

In order to determine the amount of residue that results from the 600°C. degradation of PVC in an inert atmosphere, a 21.7 mg. sample of the polymer was pyrolyzed at 600°C. for 5 minutes in the absence of copper powder. The residue (2.10 mg) thus accounts for approximately 10% of the sample, by weight. Since 58% by weight of the polymer is HCl, this leaves approximately 32% of the original polymer that is converted into the hydrocarbon and CO_2 (?) fraction. [Boettner and Weiss have reported that 16% (TABLE III) of PVC is converted into aromatic and aliphatic hydrocarbons]

The following analysis (TABLE V) is of this 32% volatile fraction that is produced during the pyrolysis of PVC at 600°C.

In each of the two quantitative analyses that were carried out, two exact weight samples of PVC were degraded (for each analysis) under the same conditions. The products from one of the degradations were analyzed on the Porapak QS column while the products from the second degradation were analyzed on the SE52 column. In this way, both the volatile gases and the higher molecular weight aromatics could be precisely analyzed. This dual degradation-analysis procedure was carried out twice and the results of these two analyses are presented in Table V.

The results demonstrate the excellent reproducibility that is obtained in these pyrolysis experiments. For example, in only one instance do the two analyses differ by more than 2% absolute. In that case (butane, butadiene, butene, diacetylene), the calculation of the gas chromatographic peak area was difficult due to the dissymmetry of the peak (See Appendix).

Approximately half of the volatile fraction consists of saturated and unsaturated hydrocarbons while the remaining products are the aromatics. Of these, 68% is benzene.

It should be noted that the CO_2 content that results in each analysis is not included in the calculations. Thus, the quantitative analysis involves only the hydrocarbon fraction. This analysis can be adjusted if it is found that the large amount of CO_2 does indeed result from the degradation of PVC.

TABLE V - Quantitative Analysis of the Volatile Fraction (32% by weight) from PVC.*

Component	Analysis I G.C. Peak Area	%	Analysis II G.C.P.A.	%
N_2	127.1	-	31.2	-
CH_4	58.2	18	38.2	20
CO_2	367.4	-	232.0	-
C_2H_4	21.7	7	12.6	7
C_2H_6	30.2	9	17.2	9
C_3H_6	25.7	8	11.4	6
C_3H_8	9.5	3	3.6	2
Butane Butadiene Butene Diacetylene(?)	23.2	7	8.0	4
Benzene	109.4	34	67.2	35
Toluene	14.8	5	9.5	5
Xylenes (3 isomers)	7.7	2	4.7	2
Chlorobenzene	7.4	2	5.3	3
Indane	1.3	~1	1.5	~1
Ethyltoluene	1.7	~1	1.4	~1
Napththalene	7.7	2	5.6	3
Methylnaphthalene (α-?) Methylnaphthalene (β-?)	3.2	1	3.1	2
Σ	321.7	100	189.3	100

1. L.B. Crider, M.M. O'Mara - "A Study of the Degradation and Combustion Products from Polymers. Objectives and Problem Description" Inter-Organization Correspondence. B.F.G. Chemical Company, August 2, 1968.

2. M.M. O'Mara, "Degradation and Combustion Products From Poly(vinyl chloride) : Part I, September, 1968.

3. Boettner and Weiss, American Industrial Hygiene Assoc. Journal 28, November-December, 1967.

4. Noffz, Benz, Pfag, Z. Anal. Chem. 235 #1 p. 121-37 (1968).

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