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THERMAL DEGRADATION OF POLYVINYLIDENE FLUORIDE AND POLYVINYL FLUORIDE BY OVEN PYROLYSIS

by
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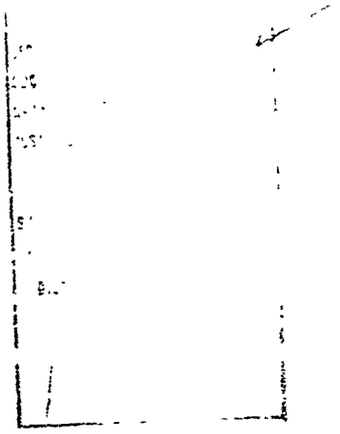
UNITED STATES ARMY
NATICK LABORATORIES
Natick, Massachusetts 01760

Clothing and Organic Materials Laboratory
C&OM-50



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FOREWORD

This report is based on a series of in-house studies made during the past four years on the thermal degradation of two fluoropolymers, polyvinylidene fluoride and polyvinyl fluoride. These studies were carried out as part of the research on Thermal Protection, Task 04, of Project 1T024401A329, Organic Materials Research for Army Materiel.

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ABSTRACT

The purpose of this study was to determine differences in the major thermal degradation products of polyvinylidene fluoride (PVF_2) and polyvinyl fluoride (PVF). Such differences might help explain the greater ability of PVF_2 to attenuate radiant energy from high-intensity thermal sources. Investigated were degradation of the polymers by oven pyrolysis, separation of the degradation products into major fractions, elemental analyses of the fractions, and identification of a number of the components of the volatile fractions.

During pyrolysis, both PVF_2 and PVF yielded hydrogen fluoride, complex mixtures of other volatile products, and residual char. The main differences were in the nature of the volatile products and the amounts of char formed. The volatile products from PVF_2 consisted largely of highly fluorinated nonflammable materials; those from PVF contained much less fluorine and were flammable. The amount of char formed from PVF_2 was approximately twice as great as that formed from PVF. Although the amounts of hydrogen fluoride yielded by each polymer were large, differences between them were small and not considered significant.

It is inferred that the greater ability of PVF_2 to attenuate energy from high-intensity thermal sources, as compared to that of PVF, may be attributed in part to its ability to produce nonflammable smoke. This would tend to scatter the radiant thermal energy and keep it from reaching the polymer surface, whereas the smoke from PVF would ignite and thus create an additional heat source. Another possible contributing factor to the greater energy-attenuating capability of PVF_2 is its ability to form much larger amounts of char than PVF.

Degradation mechanisms are postulated to explain the formation of several compounds which were identified in the volatile products from PVF_2.

THERMAL DEGRADATION OF POLYVINYLIDENE FLUORIDE AND POLYVINYL FLUORIDE BY OVEN PYROLYSIS

I. INTRODUCTION

The military has a definite and pressing need to develop materials to protect personnel and equipment against the thermal effects of a nuclear weapon detonation. The thermal behavior of polymers which appear to have capabilities for attenuating such energy is therefore of interest to the U. S. Army. If the overall processes or mechanisms by which such polymers degrade thermally could be established and related to the original chemical structure of the polymers, it might then be feasible to design other polymer structures that would have better energy-attenuating characteristics than presently available materials.

A previous study[1] of the thermal behavior of a series of fluoropolymers, made with the QM arc-image furnace used as a high-intensity thermal pulse generator, showed that polyvinylidene fluoride (PVF_2) had a greater energy-attenuating capability than polyvinyl fluoride (PVF). For example, when disks of the polymers (60 mils thick) were exposed in the arc-image furnace to a radiant flux of 23 cal cm^{-2} sec^{-1} for one second, PVF showed an average temperature rise (ΔT) on the back surface of the disk of 16.8°C, while PVF_2 showed an average temperature rise of only 10.8°C. Similar experiments with polymer disks ranging in thickness from 30 to 75 mils showed that invariably PVF_2 produced lower ΔT values than PVF under the same test conditions. The difference between the average ΔT values for PVF_2 and PVF tended to vary slightly with disk thickness, but those for PVF_2 were always significantly lower than those for PVF.

The gaseous degradation products of the polymers irradiated in the arc-image furnace were collected by a closed-cell technique and analyzed by gas chromatography. However, the quantities of the gaseous degradation materials obtained were so small that only a qualitative comparison could be made between the products from the two polymers. Therefore, satisfactory mechanisms or processes of degradation could not be postulated to explain the difference in their energy-attenuating characteristics until a more detailed study of their thermal degradation behavior was made.

The present report presents the results of a study made on the thermal degradation products obtained from the two fluoropolymers, PVF_2 and PVF, by oven pyrolysis. It describes the separation of the thermal degradation

products of the polymers into fractions, and reports the elemental analyses of these fractions, and the identification of as many constituents of these fractions as was feasible.

In planning this study it was realized that oven pyrolysis would not necessarily yield the same degradation products in the same amounts as would be formed by exposure of the polymers in the arc-image furnace. However, oven pyrolysis was chosen as the means for effecting the thermal degradation since relatively large amounts of polymer could be pyrolyzed and, accordingly, large amounts of degradation products would be obtained in each run. This would facilitate separation and identification of the degradation products, among which were fluorinated materials whose spectral characteristics were as yet unknown. Once identified and characterized, these materials could then be sought in the much smaller volumes of gaseous degradation products obtained from exposure in the carbon arc-image furnace using the closed-cell technique.

II. EXPERIMENTAL DETAILS

1. Materials

a. Polyvinylidene fluoride (PVF_2) - Commercial sample of "Kynar,"* vinylidene fluoride resin, Grade L109C05E, Lot 6404-1713, obtained from Plastics Department, Pennsalt Chemicals Corporation, Three Penn Center, Philadelphia, Pennsylvania.

b. Polyvinyl fluoride (PVF) - Laboratory sample No. 3670, obtained from Film Department, Yerkes Research Laboratory, E. I. duPont de Nemours and Co., Buffalo, New York.

Both polymers were in the form of powders, PVF_2 having a bulk density approximately twice that of PVF.

Elemental analyses were made on the original polymers, carbon and hydrogen being determined according to conventional methods, and fluorine calculated by difference. The results are given in Table I.

*Trade mark of Pennsalt Chemicals Corporation for polyvinylidene fluoride.

TABLE I

ELEMENTAL ANALYSIS OF ORIGINAL POLYMERS

	PVF_2 $\leftarrow CH_2\text{-}CF_2\rightarrow_n$		PVF $\leftarrow CH_2\text{-}CHF\rightarrow_n$	
	Calculated	Found	Calculated	Found
Carbon	37.51%	37.40%	52.17%	51.80%
Hydrogen	3.15	2.85	6.57	6.98
Fluorine	59.34	59.75	41.26	41.22

The results indicated that the polymers were reasonably pure and free from extraneous materials such as plasticizers or other additives.

Information from the manufacturers indicated that the molecular weight of the PVF_2 was at least 500,000 with considerable material of molecular weight up to several million; that of the PVF was approximately 375,000. Whether or not substantial amounts of lower molecular weight materials were present in either polymer was not known.

2. Procedures

a. Pyrolysis Conditions

All pyrolyses were run in an inert atmosphere by passing a stream of helium through the sample holder and trapping system. The helium flow was adjusted to 40 cc/min by a manually controlled micrometer valve between the helium tank and the sample holder; the flow was monitored by a rotameter at the exit of the trapping system.

The original purpose of the study was to obtain large amounts of gaseous degradation products of the polymers for separation into individual components by gas chromatography and identification of as many of these components as feasible by appropriate techniques. Therefore, relatively large samples (26g approximately) were pyrolyzed. The samples were placed in the large sample holder (see Appendix A, Note 1a) at room

temperature. The oven heaters were turned on fully, and the temperature allowed to rise to 455°C, where it was maintained for 30 minutes by a Thermac controller. The temperature of the pyrolysis sample was measured by a thermocouple. Since the oven and large sample holder together represented a considerable mass, there was an initial time lag in the heating-up period and the temperature rise was slow (approximately 6°C per minute).

The onset of pyrolysis caused a rapid evolution of gases that resulted in a marked increase in flow rate of the exiting helium. The temperature at which this occurred was recorded along with the elapsed time (approximately 30 minutes). After the onset of pyrolysis, the sample temperature was read at five minute intervals up to 455°C. The time required was close to 40 minutes. After reaching 455°C, the sample was held at this temperature for an additional 30 minutes. The overall time required for this type of pyrolysis run was approximately one hour and 40 minutes.

In later experiments to shorten the time of pyrolysis, smaller samples (2-3g approximately) were pyrolyzed in a small sample holder. This holder was similar to that previously described by Presser[2] et al, (see also Appendix A, Note 1a). The sample holder was brought to 455°C and the sample inserted. The sample temperature rose very rapidly and usually reached pyrolysis temperature within 2 to 4 minutes. Because of this rapid temperature rise, the temperature at which pyrolysis began could not be determined with any degree of accuracy. After the sample had reached 455°C, it was kept at that temperature for 30 minutes. The overall time for a run of this type was close to 34 minutes.

b. Fractions of Pyrolysis Products

The thermal degradation products of the fluoropolymers were separated into five fractions. These were designated by symbols adopted with some modifications from those used by Madorsky[3] as follows:

R - residue or char
V_{pyr} - materials that condense at room temperature
V_{hf} - hydrogen fluoride (HF)
V_{25} - materials that volatilize at 25°C and remain gaseous at higher temperature; however, they condense at -190°C
V_{-190} - materials that do not condense at -190°C

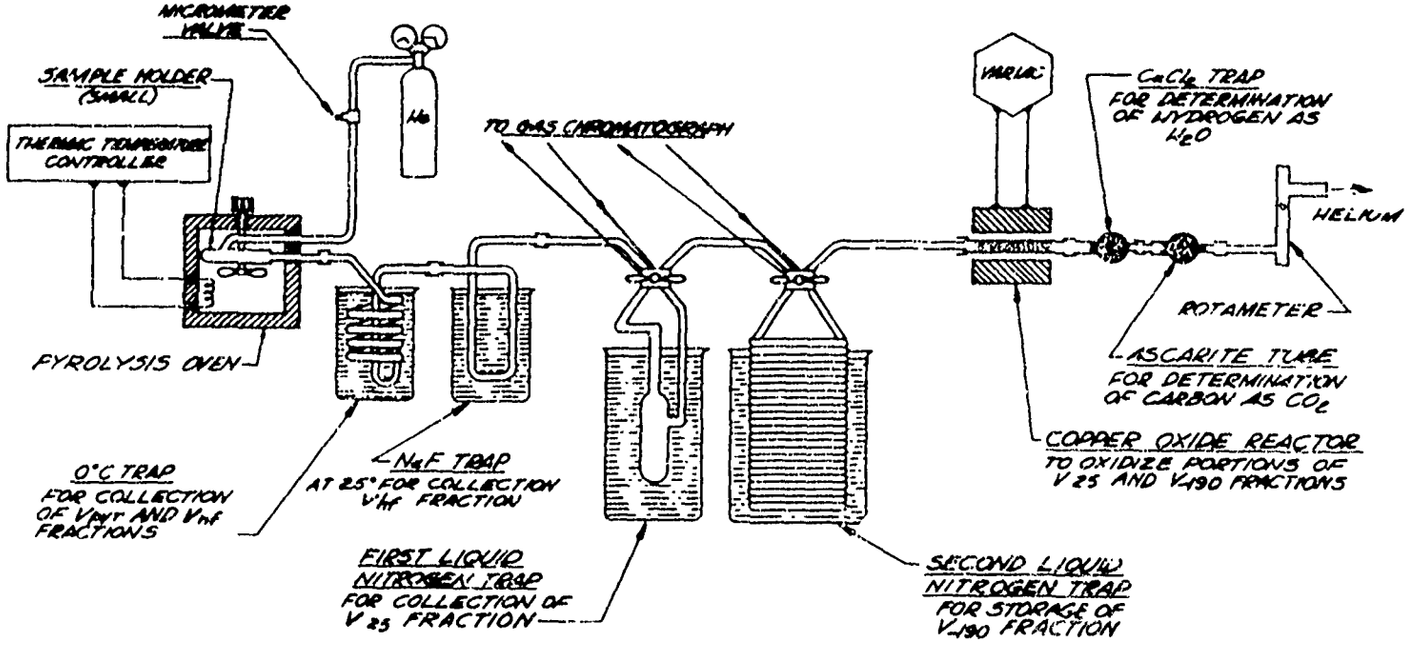


FIG. 1 SCHEMATIC DRAWING OF TRAPPING SYSTEM FOR FRACTIONATION OF PYROLYSIS PRODUCTS OF PVF_2 AND PVF

c. Separation of Fractions

During a pyrolysis, helium was passed through the sample holder at a predetermined rate, initially 40 cc/min (see Appendix A, Note 1(b)), sweeping the materials that were volatile at pyrolysis temperature into an elaborate trapping system (Figure 1) and leaving the char (R) in the oven. The volatile fractions were separated in the trapping system as described below.

(1) Residue Fraction

The weight of this fraction was determined by weighing the sample holder before and after a run. Samples of the R fractions from several representative runs of both types were taken for analysis. Hydrogen and carbon were determined by conventional methods. Fluorine was calculated by difference.

(2) V_{pyr} and V_{hf} Fractions

These two fractions condensed in the first trap which consisted of a polyethylene coil immersed in a bath kept at 0°C (see Appendix A, Note 2). The remaining fractions passed through.

When the pyrolysis run had been completed, the 0°C bath was removed and the trap allowed to warm slowly to room temperature (approximately 25°C), while the helium stream continued to flow through it. Fraction V_{pyr} remained in this trap, while the V_{hf} fraction was swept into the next trap. The trap containing the V_{pyr} fraction was then weighed and the weight of fraction V_{pyr} determined. The V_{pyr} fraction was removed from the trap by washing the trap with a suitable solvent, and aliquots were analyzed for carbon and hydrogen. Fluorine content of the fraction was calculated by difference.

The V_{hf} fraction was caught in a trap (see Appendix A, Note 3) packed with sodium fluoride (NaF) which reacted with the HF to form the complex, $NaHF_2$.

The weight of the V_{hf} fraction was determined by weighing the NaF trap before and after a run. Because of its toxicity, no effort was made to analyze for HF or determine its purity.

(3) V_{25} and V_{-190} Fractions

These fractions either did not condense at 0°C or else they volatilized when the trap was allowed to warm to 25°C. The materials

could be passed directly into the gas chromatograph for separation into components. Also, they could be separated, at least qualitatively, by means of two liquid nitrogen traps (Appendix A, Notes 4 and 5) into two fractions, one which condensed at -190°C (V_{25} fraction) and one which did not (V_{-190} fraction). The V_{25} fraction was caught in the first liquid nitrogen trap. The remaining material (V_{-190} fraction) was allowed to flow with the helium stream into the second liquid nitrogen trap for approximately 20 minutes after pyrolysis had begun. Then the trap was closed off and it acted essentially as a storage reservoir for any materials which had not been previously trapped. Portions of the V_{-190} fraction could be directed into the gas chromatograph, or back into the first liquid trap, or else passed into a copper oxide reactor.

It is obvious from the foregoing that the separation and collection of the V_{-190} fraction could not be considered as quantitative by any means and the separation and collection of the V_{25} fraction as only semiquantitative at best.

The purpose of the copper oxide reactor train (Appendix A, Note 6) was to detect the presence in the V_{-190} fraction of any low molecular weight hydrocarbon materials which would pass through all the previous traps in the system. Such materials would be oxidized, at least partially, to water and carbon dioxide. The water would be caught in a calcium chloride trap, the carbon dioxide in an Ascarite trap.

d. Difficulties Encountered in Separation of Fractions

In the earlier studies in this series, the gaseous degradation products of the fluoropolymers were passed into a tube packed with glass wool, to trap out discrete particles or drops of liquid, and then directly into the gas chromatograph. It was found that the glass wool rapidly disintegrated and large peaks, apparently of SiF_4 and water, were obtained. These obviously resulted from the reaction of HF with the glass wool as follows:

$$4HF + SiO_2 \longrightarrow SiF_4 + 2H_2O$$

Material accounting for the suspected SiF_4 peak was trapped and identified by its IR and mass spectra.

Water did not give a sharp, discrete peak in the gas chromatograph and tended to smear other peaks and cause considerable "tailing." In consequence, the presence of water was deduced from its general behavior.

After a considerable period of trial and error, the present trapping system was evolved in which the HF was removed at an early stage in the fractionation process as described in Section 2c(2). When the HF was

removed by the NaF trap in front of the chromatograph, the SiF_4 peak disappeared completely and the difficulties of smearing and tailing of peaks were obviated.

Attention was then focussed on the mixture (as yet unseparated) that was composed of the V_{25} and V_{-190} fractions, with no attempt being made to study the R or V_{pyr} fractions. It became evident that the mixture was extremely complex with as many as 40 to 50 peaks appearing on the gas chromatographic record. Although some of the peaks could be identified by conventional means, many could not because of lack of information in the literature on their spectra. There was reasonable qualitative agreement in the chromatographic records from run to run, but quantitative agreement was poor. The second liquid nitrogen trap enabled some of the material representing major peaks to be concentrated and identified qualitatively by IR and mass spectrometry.

Efforts were made to determine what proportions of the original polymer were being accounted for by the various fractions. It was found that the R, V_{pyr} and V_{hf} fractions accounted for 80-90 percent of the total weight of the original polymer; thus the products that were volatile at 25°C and constituted the combined V_{25} and V_{-190} fractions on which the gas chromatographic runs were made represented only a relatively small proportion (20 percent or less) of the total weight of the thermal degradation products of PVF_2 and PVF. Since even the major peaks on the chromatographic charts represented only portions of the combined V_{25} and V_{-190} fractions, it became apparent that they accounted for only very small amounts (in some cases only trace amounts) of the original polymer weights. Thus, even if all the constituents in these two fractions were identified, it was highly unlikely that this knowledge would contribute materially to postulation of an overall process or mechanism to explain the differences in the energy-attenuating characteristics of PVF_2 and PVF. The complexity of the V_{25} and V_{-190} fractions, as indicated by the large number of chromatographic peaks, and the lack of IR, mass spectrometric and nuclear magnetic resonance data in the literature for many of the fluorinated compounds made the problem very difficult to solve within a reasonable time. Therefore, the direction of the investigation was changed. Emphasis was placed on acquiring at least semiquantitative information on the amounts of the fractions obtained: R, V_{pyr}, V_{hf}, V_{25} and V_{-190}, and as much qualitative information of their composition as could be derived from their elemental analyses.

e. Efforts to Determine Reproducibility of Separation of Fractions

After a large number of runs, made primarily to obtain V_{25} and V_{-190} fractions for gas chromatographic studies, a reasonably standardized

method of pyrolysis and separation of fractions was evolved Then as many replicate runs as time permitted were made. The four fractions, R, V_{pyr}, V_{hf} and V_{25}, were collected as quantatively as possible and their weights determined. Since the weights of the V-190 fractions could not be determined with any degree of accuracy, calculated values were used. This will be discussed in more detail later. From the weights of the first four fractions, calculations were made of their average weights, expressed in terms of percent of the original polymer weights.

Efforts were made to treat the data statistically, but it was found that they could not be treated rigorously enough to establish reasonable standard deviation values or confidence levels for the average fraction weights. The variations from run to run were attributed in part to the complexity of the pyrolysis oven/trapping system, and in part to the degradation processes themselves. As the research progressed, it became obvious from the nature of the degradation products that so many reactions were taking place, either simultaneously or in sequence, that it was practically impossible to sort them out. Although it was not possible to extract quantitative information from the data, nevertheless it was possible to establish definite qualitative differences between the thermal degradation processes of the two polymers.

III. RESULTS

1. Reproducibility of Separation of Fractions

Although not successful in establishing satisfactory statistical confidence levels for the average weights of the fractions, it was possible to make the following generalizations concerning the results:

a. The weights of the R fractions were more consistent than those of the others. This is understandable, since the R fraction weights could be determined more directly and more readily than those of the other fractions.

b. The weights of the fractions from PVF_2 were more reproducible than those from PVF.

c. The accuracy with which the weights of the V_{25} fractions could be determined was poor. This was due to the relatively low weight of the fraction (5g or less) in comparison to the weight of the liquid nitrogen trap (568g).

TABLE II

MATERIALS BALANCE FO' FRACTIONS OF PYROLYSIS* PRODUCTS
OF POLYVINYLIDENE FLUORIDE AND POLYVINYL FLUORIDE

(Weights of fractions expressed as percent
by weight of the original polymers.)

	Polyvinylidene Fluoride		Polyvinyl Fluoride	
Fraction	Run T53	Run T54	Run T58	Run T59
Residue	41.1	40.8	12.7	13.9
V_{pyr}	8.7	10.6	48.3	49.2
V_{hf}	20.7	28.6	29.2	27.5
V_{25}	19.5	19.3	8.1	9.0
Subtotal	99.0	99.3	98.3	99.6
V_{-190}	1.0**	0.7**	1.7**	0.4**
Total	100.0	100.0	100.0	100.0

*Total time required for each pyrolysis run was approximately one hour and 40 minutes

**The values for the V_{-190} fractions were calculated by subtracting the sum of the weight percent values of the other four fractions from 100 percent.

d. The V_{-190} fractions presented a similar, but greatly magnified, problem to that of the V_{25} fractions, because the second liquid nitrogen trap weighed 5,821g in comparison to the weight of the V_{-190} fraction (usually less than 1.5g). To obtain an estimate of the amount of material in the V_{-190} fractions, an indirect method was used to calculate possible weights of the V_{-190} fractions by subtracting the sum of the weight percentage values of the other four fractions from 100 percent. It is realized that this may create a fictitious appearance of accuracy in the results, so it should be emphasized that this method was used only to obtain an idea of the order of magnitude of the amounts of V_{-190} materials obtained.

2. Materials Balance for Fractions

a. Long Pyrolysis Time

To determine how much of original polymer was being accounted for, a material balance was determined using the first four fractions. The results for four representative runs (two for PVF_2 and two for PVF) carried out over a total time of approximately one hour and 40 minutes per run are shown in Table II.

The weights of the four fractions R, V_{pyr}, V_{hf} and V_{25}, accounted for more than 98 percent of the original polymer weights. This left less than 2 percent to be accounted for in the V_{-190} fraction of each polymer.

The amounts of the V_{hf} fractions were substantially the same for both the polymers, accounting for almost 30 percent of the original polymer weights.

In contrast to the V_{hf} and V_{-190} fractions, the amounts of the other three fractions showed very large differences between the two polymers. The R fraction from PVF_2 was approximately three times as large as that from PVF. It was the largest fraction obtained from PVF_2, while it was a relatively small fraction from PVF. Similarly, the weight of the V_{25} fraction from PVF_2 was practically twice that of the V_{25} fraction from PVF. Conversely, the weight of the V_{pyr} fraction from PVF_2 was about only one-fifth that of the same fraction from PVF.

b. Short Pyrolysis Time

The results for four representative runs (two for PVF_2 and two for PVF) carried out over a total of approximately 34 minutes per run are shown in Table III.

TABLE III

MATERIALS BALANCE FOR FRACTIONS OF PYROLYSIS* PRODUCTS
OF POLYVINYLIDENE FLUORIDE AND POLYVINYL FLUORIDE

(Weight of fractions expressed as percent
by weight of the original polymers.)

	Polyvinylidene Fluoride		Polyvinyl Fluoride	
Fraction	Run T64	Run T66	Run T71	Run T72
Residue	45.9	46.2	22.9	25.0
V_{pyr}	7.1	5.3	29.0	27.3
V_{hf}	43.4	45.0	40.0	34.1
V_{25}	2.3	1.0	3.9	3.7
Subtotal	98.7	97.5	95.8	90.1
V_{-190}	1.3**	2.5**	4.2**	9.9**
Total	100.0	100.0	100.0	100.0

*Total time required for each pyrolysis run was approximately 34 minutes.

**The values for the V_{-190} fractions were calculated by subtracting the sum of the weight percent values of the other four fractions from 100 percent.

When compared with the R fractions from the long pyrolysis times, the R fractions from PVF_2 were found to have increased slightly (approximately 5 percent), while those from PVF practically doubled. However, those from PVF were still much less than those from PVF_2.

The V_{pyr} fractions from PVF_2 decreased slightly for the shorter pyrolysis time, while those from PVF decreased markedly. Nevertheless, the latter accounted for practically 30 percent of the original polymer weight and were four to five times as great as those from PVF_2.

The V_{hf} fractions increased markedly with the shorter pyrolysis times and those from PVF appeared to show more variation from run to run.

The V_{25} fractions decreased with shorter pyrolysis time, especially for PVF_2. The V_{-190} fractions from PVF_2 showed only minor differences between the long and short pyrolysis times. Those from PVF appeared to increase appreciably.

3. Comparison of Fractions and Their Elemental Analyses

a. Residue Fractions

The R fractions from both polymers were black, friable chars which did not differ appreciably in appearance. Their elemental analyses are given in Table IV. As might be expected, the major element in the R fractions was carbon, with fluorine next and hydrogen last. Less carbon was left in the R fractions of both polymers when the shorter pyrolysis time was used. The R fractions of PVF consistently contained about 5 percent more carbon than those from PVF_2, whereas with fluorine, the situation was reversed, the R fractions from PVF_2 contained 8 to 9 percent more fluorine than those from PVF.

The R fractions could not be further separated into sub-fractions or individual components because of their insolubility.

From the elemental analyses, possible carbon/hydrogen/fluorine ratios were calculated for comparison with the same ratios in the original polymers. To simplify interpretation of the ratios, they were calculated on the basis of the number of fluorine atoms being equal to one. The ratios are shown in Table VI, and their interpretations given in "Discussion of Results."

TABLE IV

ELEMENTAL ANALYSES OF ORIGINAL POLYMERS AND THEIR PYROLYSIS FRACTIONS

Average pyrolysis time - 100 minutes

	PVF_2			PVF		
	C	H	F*	C	H	F*
Original Polymer:	37.40	2.85	59.75	51.80	6.98	41.22
Pyrolysis Fractions						
Residue:	79.65	1.35	19.00	85.94	4.17	9.89
V_{pyr}:	41.33	3.04	55.63	82.28	7.99	9.73
V_{25} + V_{-190}: **	4.39	2.67	92.94	28.84	9.92	61.24

*Fluorine calculated by difference: 100%- (%C + %H)
**Calculated values for unseparated fractions; see text.

b. V_{pyr} Fractions

The V_{pyr} fractions differed considerably in appearance and physical characteristics; those from PVF_2 were black, viscous oil- or tar-like materials, while those from PVF consisted of a yellow, grease-like material sometimes mixed with a dark brown material having a waxy consistency.

The elemental analyses (Table V) showed that the V_{pyr} fractions from the tw polymers differed strikingly in chemical composition. The V_{pyr} fraction from PVF_2 contained approximately 55.6 percent fluorine (long pyrolysis time) and 50.9 percent fluorine (short pyrolysis time). Thus it appeared to consist of highly fluorinated materials. On the other hand, the V_{pyr} fraction from PVF contained relatively little fluorine (9 to 10 percent) but considerably larger amounts of carbon and hydrogen.

Tentative attempts were made to separate the V_{pyr} fractions into components by fractional distillation in vacuo and by extraction with various solvents. It became obvious such separation was not immediately feasible, so these attempts were abandoned.

Owing to the complexity of these mixtures, no efforts were made to determine molecular or average molecular weights. These mixtures had relatively low vapor pressures, since they did not distill readily even in vacuo. It was therefore assumed that their molecular weights were rather high.

From the elemental analyses, carbon/hydrogen/fluorine ratios were calculated as in the case of the R fractions (see Table VI and Discussion).

c. V_{hf} Fractions

As pointed out previously, the contents of the NaF trap were not analyzed for hydrogen and fluorine because of the toxicity of the materials in the trap. The total weight was determined by weighing the trap before and after a run, and the increase in weight was assumed to be due to HF. There is some risk in this assumption as it is possible that fluorinated materials, other than HF, might form complexes with the NaF. However, as far as it is known, no such materials have been reported in the literature.

When long pyrolysis times were used, the amounts of HF given off by the two polymers were of the same order of magnitude and amounted to

TABLE V

ELEMENTAL ANALYSES OF ORIGINAL POLYMERS AND THEIR PYROLYSIS FRACTIONS

Average pyrolysis time - 34 minutes

	PVF_2			PVF		
	C	H	F*	C	H	F*
Original Polymer:	37.40	2.85	59.75	51.80	6.98	41.22
Pyrolysis Fractions						
Residue:	75.53	1.78	22.69	80.75	5.09	14.16
V_{pyr}:	45.74	3.40	50.86	82.80	7.22	9.98
V_{25} + V_{-190}:	3.09	trace	96.91	79.27	13.47	7.26

*Fluorine calculated by difference: 100% -(%C + %H)
**Calculated values for unseparated fractions; see text.

approximately 30 percent of the original polymer weight. With the short pyrolysis times, considerably more HF was given off. For PVF_2 it amounted to 43-45 percent of the original polymer weight and for PVF, 34-40 percent.

d. Unseparated V_{25} and V_{-190} Fractions

As pointed out previously in Section 3(c), collection and separation of the V_{25} and V_{-190} fractions could be regarded at best as qualitative only. Nor was it feasible to take aliquots of these fractions for elemental analysis. Therefore, an indirect method was used for calculating possible elemental composition of the unseparated V_{25} and V_{-190} fractions.

For example, the carbon content was calculated in the following manner. The original polymer weight and the average weights of the R and V_{pyr} fractions were known with reasonable certainty. Therefore, by subtracting the weights of the R and V_{pyr} fractions from the original polymer weight, a calculated average weight was obtained for the unseparated V_{25} and V_{-190} fractions. This involved only one assumption, i.e., that no losses of these two fractions occurred by leakage. The elemental analyses gave the carbon contents of the R and V_{pyr} fractions. Subtracting these values from the values for carbon in the original polymer, values for the carbon contents of the unseparated V_{25} and V_{-190} fractions were obtained. From these values and the values for the weight of these fractions, the percentage of carbon in the unseparated fractions could then be calculated.

A similar scheme was followed for hydrogen except that the hydrogen content of the V_{hf} fraction was calculated. This involved the assumption that the V_{hf} trap caught only HF and did not catch any other highly fluorinated materials. Thus, values for hydrogen contents of the R, V_{hf} and V_{pyr} fractions were subtracted from the value for the hydrogen content of the original polymer to give a value for the hydrogen content of the unseparated V_{25} and V_{-190} fractions.

Values for fluorine were calculated throughout by difference, i.e., 100% -(%C + %H). Thus any errors in the fraction weights or analyses would be cumulative and the values for fluorine are probably the most uncertain.

The values calculated for the elemental composition of the unseparated V_{25} and V_{-190} fractions of PVF_2 indicated that these materials are highly fluorinated for both long and short pyrolysis times, the pyrolysis time having only a small effect on the composition of the fractions (see Tables IV and V). In the comparable fractions from PVF, the materials appeared to be much less highly fluorinated, especially in the fractions obtained with short pyrolysis times.

The experiments with the CuO reactor were highly qualitative. Only small amounts of H_2O and CO_2 were caught in the $CaCl_2$ and Ascarite traps. These amounts were of the order of magnitude of centigrams. Because of considerable scatter in the results, no definite conclusions could be drawn as to differences between the products from PVF_2 and PVF or differences between the long and short pyrolysis times. The results, however, did show definitely that there were very small amounts of hydrocarbon-like materials which could not be condensed into the liquid nitrogen traps at -190°C. No conclusions could be drawn as to their degree of saturation or of fluorination.

IV. DISCUSSION OF RESULTS

1. Qualitative Chemical Composition of the Fractions: Carbon/Hydrogen/Fluorine Ratios

The R fractions, as pointed out previously, were not separable into components for further identification because of their insolubility, nor were the V_{pyr} fractions separable into components either by fractional distillation or by extraction with solvents.

The details of the attempts made with gas chromatography to separate the large number of components of the V_{25} and V_{-190} fractions are being presented in a separate report(4). Therefore, no effort is made to discuss them here.

To obtain a qualitative view of the chemical nature of the components of the fractions, calculations were made from their elemental analyses (Tables IV and V) of possible carbon/hydrogen/fluorine (C/H/F) atomic ratios for the fractions. To simplify comparison of the ratios, they were calculated on the basis of one fluorine atom. These ratios are shown in Table VI.

a. R Fractions

The C/H/F ratios for the R fractions from PVF_2 are consistent with the process of elimination of HF from the polymer to leave mainly C atoms in the residue. The ratio of H/F in the R fractions is about 1.4/1 compared with 1/1 in the polymer. This might indicate that relatively more F than H had been eliminated. This would occur if highly fluorinated compounds were formed. The C atoms left in the R fractions are probably arranged in long chains corresponding to the

TABLE VI

C/H/F ATOMIC RATIOS IN ORIGINAL POLYMERS
AND OVEN PYROLYSIS FRACTIONS

	PVF_2 C / H / F	PVF C / H / F
Original Polymer:	1 /1 / 1	2 /3 / 1
Residue:		
Long Pyrolysis Time	6.6/1.3/ 1	13.7/8 / 1
Short Pyrolysis Time	5.3/1.5/ 1	9 /6.8/ 1
V_{pyr}		
Long Pyrolysis Time	1.1/1.0/ 1	13.7/16.4/1
Short Pyrolysis Time	1.4/1.3/ 1	13.1/13.6/1
$V_{25} + V_{-190}$		
Long Pyrolysis Time	0.1/0.5/ 1	0.8/ 3.0/1
Short Pyrolysis Time	0.1/tr*/ 1	17.3/35.0/1

*tr≈ trace amount

original carbon skeleton of the polymer, with one H and one F attached randomly to approximately every fifth or sixth C atom. Differences between the two pyrolysis times produced practically no change in the chemical composition of the R fractions.

For PVF with long pyrolysis times, the atomic ratios of the R fractions show that relatively little fluorine is left in these fractions in comparison with H and C. The residue is, of course, mainly carbon with one H per two C atoms and one F per 14 C atoms. For shorter pyrolysis times, relatively more F and H appeared to be left in the R fractions, one F per 9 C atoms and practically one H per C atom.

b. V_{pyr} Fractions

The C/H/F ratio for the V_{pyr} fraction from PVF_2 with long pyrolysis time is very interesting in that it is practically identical to that for the original polymer. This could result from scission of the PVF_2 polymer chain into rather large fragments with little loss of HF, i.e., a partial "unzipping" of the polymer. These fragments might be expected to have a range of molecular weights such that they would not readily distill even in vacuo. Like the original polymer they are saturated and highly fluorinated compounds. A decrease in pyrolysis time had only a small effect namely, to increase the ratios of C and H to F very slightly.

The C/H/F atomic ratio for the V_{pyr} fractions of PVF shows that the relative amounts of C/H are practically 1/1 and that these are approximately 13-16 times the amount of F. Therefore, these materials are mainly unsaturated hydrocarbons containing relatively small amounts of F. The C/H/F ratio for the V_{pyr} fraction differs very much from that of the original PVF, so that evidently the PVF has not "unzipped" like the PVF_2 but has undergone a more random degradation. A decrease in pyrolysis time had practically no effect on the C/H/F ratio for these fractions.

c. Unseparated V_{25} and V_{-190} Fractions

Owing to the method by which the C/H/F ratios for these fractions were calculated, these values can be considered as offering only a very general indication of the chemical nature of these materials. The fractions from PVF_2 are apparently saturated hydrocarbons having a high degree of fluorination.

If the unzipping process, mentioned above, proceeded far enough, one would expect the monomer ($CH_2=CF_2$) to be formed. Since this monomer

has a low boiling point (-51°C), it would therefore be expected to appear in the unseparated V_{25} and V_{-190} fractions.

The C/H/F ratios for the V_{25} and V_{-190} from PVF suggest that they contain materials which are mainly saturated hydrocarbons containing little fluorine.

2. Comparison with Results Reported in the Literature

The thermal degradation of organic polymers has been studied in detail by many investigators. The literature on the subject is so voluminous that no attempt is made in this report to review it in detail. Perhaps the most succinct and recent treatment of the thermal degradation of fluoropolymers is that of Madorsky[5]. The following summary compares Madorsky's method of attack on the problem with the one used in this study and points out similarities and/or differences in the results.

Madorsky's oven pyrolyses were carried out in pyrex/quartz systems using very small weights of polymer (20-50 mg) at very low pressures (down to 10^{-5} torrs*). PVF_2 was pyrolyzed for 30 minutes at temperatures ranging from 372°C to 480°C. For each polymer the rate of volatilization was measured as a function of time. The growth rates of two fractions, V_{pyr} and V_{25} (HF), were also calculated as functions of pyrolysis time. The HF was not determined directly, since it reacted with the glass of the equipment to give SiF_4 and H_2O, as noted previously in Section 2d of Procedures. The V_{25} fraction obtained by Madorsky was, therefore, found to consist of SiF_4 and H_2O. The values were calculated back to HF.

In the study conducted at the U. S. Army Natick Laboratories, oven pyrolyses were carried out in stainless steel/copper equipment with polyethylene traps and connectors in the separation train. Large amounts of polymers (up to 25g) were pyrolyzed at a single temperature range (455°C) for 30 minutes. As noted previously, both short and long pyrolysis times were used. HF was removed from the system by reaction with NaF; as a result this acid could be determined directly. Furthermore, SiF_4 and H_2O were prevented from forming and the difficulties caused by these two compounds in the gas chromatograph were thus eliminated. The fraction weights were determined experimentally or by calculation after a pyrolysis, with no attempt being made to determine pyrolysis rates. Elemental analyses for C and H were made on the three fractions: residue, V_{pyr} and V_{25}; F content of these was calculated by difference.

*torr = 1mm Hg

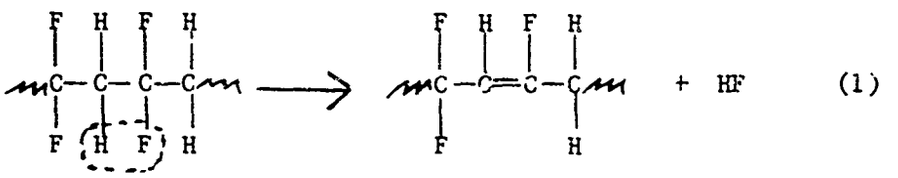
It would appear that our V_{hf} fraction corresponds to Madorsky's V_{25} (HF) and our combined V_{25} and V_{-190} fractions to his V_{pyr} fraction. Apparently Madorsky did not isolate a fraction or investigate materials which would correspond to our V_{pyr} fraction.

Madorsky states that PVF_2 yields, on pyrolysis, larger amounts of HF than does PVF. The results obtained in this study with short pyrolysis times (Table III) agree well with Madorsky's on the HF yields. However, when long pyrolysis times were used, the yields of HF were practically the same from each polymer (Table II).

Madorsky also states that "loss of HF (from PVF_2) results in the formation of double bonds in the chain so that it becomes thermally more stable. This in turn results in carbonization of the residue, more so in the case of PVF_2 than of the other two hydrofluoropolymers (PVF and polytrifluoroethylene)." Here again the results obtained in this study are in agreement with his, since the amounts of residual char obtained from PVF_2 were two to three times those obtained from PVF, depending on the pyrolysis time.

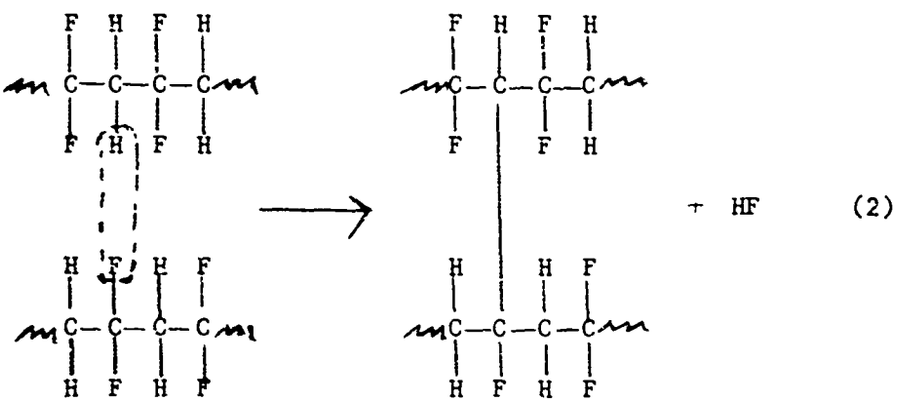
3. Possible Mechanisms for Thermal Degradation of PVF_2

Madorsky postulates two possible mechanisms for loss of HF from PVF_2:



(1)

or

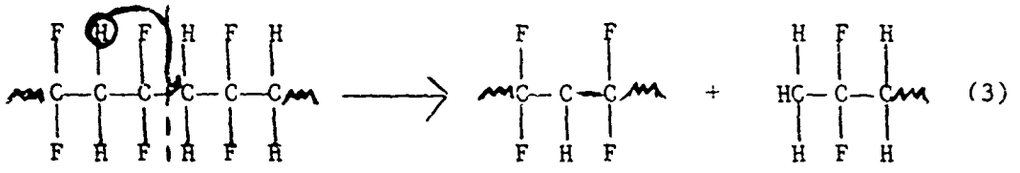


(2)

Mechanism (1) would be expected to lead to highly fluorinated compounds in the volatile fractions. This is consistent with the results obtained in this study for the C/H/F ratios for our V_{pyr} and combined V_{25} and V_{-190} fractions which indicated a high ratio of F to C and H, especially in the V_{25} and V_{-190} fractions. Further confirmation is the fact that the components of the V_{25} and V_{-190} fractions that could be identified in the NLABS study were highly fluorinated (Table VII).

Mechanism (2) could yield residues with C/H/F ratios close to 1.1/1/1. Since we find ratios having much higher C to H and F (Table VI), considerably more HF must be split out than indicated by this mechanism, and the residue would be largely carbon containing little H and F.

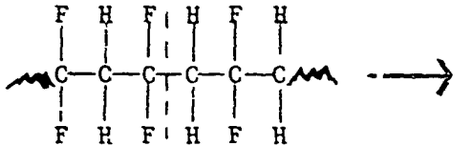
A third mechanism postulated by Madorsky is:



(3)

This, like (1), would lead to highly fluorinated volatile materials and is consistent with the results obtained in this study.

Madorsky also postulates the formation of free radicals:

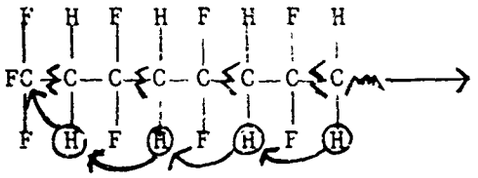


2 free radicals (4)

which would then unzip into the monomer. Because of difficulties caused by the reaction of HF with the pyrex/quartz pyrolysis systems which he used, Madorsky was unable to confirm this. However, in this study, these difficulties were obviated and appreciable amounts of monomer, $CH_2=CF_2$, were found in the volatile products formed both in pyrolysis in the arc-image furnace and in oven pyrolysis (Table VII). Thus, Madorsky's free radical postulation appears to be supported.

In the pyrolysis products, a small amount of CHF_3 was identified in this study. However, since the amount of CHF_3 was small, this could

indicate the probability of another process involving the terminal carbon atom and an unzipping mechanism alternate to that of (4) above. If the terminal carbon is stabilized as $-CF_3$, a simple mechanism can be formulated which would result in continuous production of monomer:



$$\longrightarrow \quad CF_3H + n(CH_2{=}CF_2) \qquad (5)$$

However, since the total monomer produced was small, it is unlikely that this mechanism, although possible, is the primary mode of thermal degradation of the PVF_2.

4. Comparison of Results of Arc-Image Furnace Pyrolysis with Those of Oven Pyrolysis

In the previous study[1] made with fluoropolymers in the carbon arc-image furnace it was possible to collect (by means of a closed-cell technique) volatile degradation products which were analogous to the unseparated V_{25} and V_{-190} fractions obtained by oven pyrolysis. The R fraction remained on the exposed surface of the test disk and the fraction corresponding to the V_{pyr} fraction condensed on the walls of the closed cell. The R and V_{pyr} fractions were not investigated in this earlier study. However, the volatile degradation materials were analyzed by gas chromatography and two peaks were identified for PVF_2 and five peaks for PVF. These are shown in Table VII for comparison with the components identified in the combined V_{25} and V_{-190} fractions. It is realized that this comparison is limited, since not all of the components of the volatile fractions have been identified. However, even this limited comparison yielded interesting information. In spite of the fact that the method of pyrolysis in the arc-image furnace was drastically different from oven pyrolysis, there were striking similarities between the results.

By either method, PVF yielded a larger number of degradation products than PVF_2. In consequence, the volatile fractions from PVF were much more complicated than those from PVF_2. This would indicate that PVF may undergo a more random process of degradation than PVF_2.

TABLE VII

COMPARISON OF COMPONENTS IDENTIFIED IN THE UNSEPARATED V_{25} AND V_{-190} FRACTIONS PRODUCED BY ARC-IMAGE FURNACE PYROLYSIS AND BY OVEN PYROLYSIS

Pyrolysis in Arc-Image Furnace[1]	Oven Pyrolysis[3]
Polyvinylidene Fluoride PVF_2	
CF_4	---
---	CHF_3
---	$CH_2{=}CHF$
$CH_2{=}CF_2$	$CH_2{=}CF_2$
---	symmetrical trifluoro benzene
two unidentified components	---
---	CO_2*
Polyvinyl Fluoride PVF	
CH_4	CH_4
$CH_2{=}CH_2$	$CH_2{=}CH_2$
$CH_3\text{-}CH_3$	$CH_3\text{-}CH_3$
$CH_2{=}CHF$	---
$CH_2{=}CF_2$	---
---	$CH_3\text{-}CH_2\text{-}CH_3$
---	$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_3$
---	C_6H_6 (benzene)

*See text

The only materials which were identified in the volatile fractions obtained from PVF_2 by either method of pyrolysis were fluorinated hydrocarbons. This is consistent with the high ratio of F to C and H indicated above by the atomic ratios. Carbon arc-image furnace pyrolysis yielded the monomer ($CH_2=CF_2$) along with carbon tetrafluoride (CF_4) and two components which were not identified. Oven pyrolysis also yielded the monomer and, in addition, three other fluorinated compounds identified as CHF_3, $CH_2=CHF$ and symmetrical trifluoro benzene. Also among the products formed during oven pyrolysis in a pyrex sample holder was a small amount of CO_2. This will be discussed later.

The monomer is undoubtedly formed by the "unzipping" process discussed previously. It is interesting to note that this takes place under the two very different conditions of pyrolysis.

More degradation products were identified in the volatile fractions from PVF and from PVF_2. From PVF these were preponderantly unfluorinated saturated hydrocarbons. This is consistent with the C/H/F ratios calculated for the unseparated V_{25} and V_{-190} fractions noted previously. The same three hydrocarbons, methane (CH_4), ethylene ($CH_2=CH_2$), and ethane (CH_3-CH_3), were identified in the products formed by either carbon arc-image furnace pyrolysis or oven pyrolysis. Only two fluorinated compounds, the monomer, $CH_2=CHF$, and $CH_2=CF_2$, were identified, and these were found only in the degradation products obtained by the carbon arc-image pyrolysis. Three additional saturated hydrocarbons, propane ($CH_3-CH_2-CH_3$), butane ($CH_3-CH_2-CH_2-CH_3$), and benzene (C_6H_6) were found in the products of oven pyrolysis.

Considering the two very different methods of pyrolysis, and changes in the gas chromatographic procedures (e.g., some operators using an early model of the chromatograph and other operators using a highly modified and sophisticated version of the chromatograph), it is felt that the overall consistency of the results is good.

The finding of CO_2 in the volatile degradation products of oven pyrolysis of PVF_2 was not too surprising. In 1947, White and Rice reported[6] that a fluorine-containing compound reacted with a glass container to produce CO_2. They suggested that the reaction might proceed as follows:

$$2C_2F_6 + 3SiO_2 \longrightarrow 2CO + 2CO_2 + 3SiF_4$$

In 1953, Madorsky et al. established[7] the presence of small amounts of CO_2 and CO in the thermal degradation products of Teflon $(C_2F_4)_n$ and polytrifluoroethylene $(CHF\text{-}CF_2)_n$ when these polymers were pyrolyzed in vacuo. They attributed the finding of CO_2 in the volatile pyrolysis products to either:

(1) the presence of oxygen in the fluoropolymers as part of their structure; and/or

(2) the reaction of fluorocarbons with glass as suggested by White and Rice[6].

In 1965, Barnes and Yelland[1] found CO_2 in the volatile thermal degradation products of polytrifluoroethylene $\leftarrow CHF\text{-}CF_2 \rightarrow_n$ when pyrolyzed in a helium atmosphere in a glass cell in the carbon arc-image furnace.

In the present work small amounts of CO_2 were found only in the earlier experiments in which PVF_2 was pyrolyzed in a helium stream with a Pyrex sample holder in the oven. When the Pyrex holder was replaced by a stainless steel/copper holder, CO_2 could no longer be found in the volatile thermal degradation products. This would appear to confirm the postulation of White and Rice that CO_2 is produced by the reaction of fluorocarbon materials with the Pyrex.

V. SUMMARY OF THERMAL DEGRADATION PROCESSES OF PVF_2 AND PVF DURING OVEN PYROLYSIS

During oven-pyrolysis of PVF_2, the predominant reaction appears to be the elimination of HF, either by stripping it off the main polymer chain or by removal of H from one chain and F from the chain next to it. In either case there is formed a large amount (40 percent b.w. of the original polymer) of a highly carbonaceous char containing small amounts of hydrogen and fluorine. Simultaneously, a very complicated mixture of highly fluorinated compounds is produced, including some of the original monomer. Some of these (amounting to 7 percent or less of the original polymer) condense at room temperature; others (less than 3 percent of the original polymer) condense at -190°C, while a few (again less than 3 percent of the original polymer weight) do not condense even at -190°C. Since the fluorine content of the volatile products is high, these products would be expected to be nonflammable.

Mechanisms have been postulated, by Madorsky and by the authors, to account satisfactorily for the few compounds which were identified in the fractions which are volatile at 25°C and below. However, from the amounts of these compounds found in these fractions, it is obvious that these mechanisms are of very minor importance compared to that which causes elimination of HF and formation of char.

Under the same conditions of oven pyrolysis as those used for PVF_2, PVF behaves very differently. Although elimination of HF from PVF is a major degradation process, it is evidently not as predominant as with PVF_2 and the subsequent results are not the same. Much less residue (approximately one half as much as from PVF_2) is produced and considerably larger amounts of volatile products are formed. These are even more complex mixtures than the analogous products from PVF_2 and they appear to be largely hydrocarbons containing relatively little fluorine. Because of this, these materials would be expected to be highly flammable.

Undoubtedly, mechanisms could be postulated that would satisfactorily explain the production of each compound. However, it was felt that the amount of effort involved would not be justified by the results, since most of the products were found only in small (sometimes trace) amounts and were very likely of minor importance in the overall degradation process.

VI. POSSIBLE EXPLANATIONS FOR THE DIFFERENCE IN ENERGY-ATTENUATING CAPABILITIES OF PVF_2 AND PVF

Attenuation of high-intensity thermal pulses by organic polymers may be accomplished by one or more of the following:

(1) Smoke, generated at a very early stage in the polymer degradation, that prevents much of the energy from impinging on the polymer by scattering the energy;

(2) Endothermic degradation reactions that cause the polymer to act as a chemical heat sink;

(3) Formation on the exposed surface of the polymer of a char that is a poor heat conductor and therefore can be considered as acting as a physical heat sink or thermal barrier.

It is realized that the conditions (time, temperature and rate of energy input) under which oven pyrolysis takes place differ drastically from those of pyrolysis in the arc-image furnace. However, because of the overall consistency of the results on the volatile products obtained by both methods of pyrolysis, it is felt that possible explanations of the difference in the energy-attenuating capabilities of the two polymers in the carbon arc-image furnace can be inferred from the oven-pyrolysis results.

1. Smoke Formation

Observations made on the behavior of disks of PVF_2 and PVF, during exposure to high-intensity thermal energy in the carbon arc-image furnace, have shown that both polymers produced copious amounts of smoke. Because of a lack of equipment, it was not possible to determine whether there were differences in the amounts of smoke produced by the two polymers. The losses in weight of the polymer disks during exposure in the carbon arc-image furnace were of the same order of magnitude. This implies, but does not prove, that the amounts of smoke produced were approximately the same. Nor was it possible to measure possible differences in the size of the particles in the smokes. Particle size has a marked effect on light energy scattering as has been shown by Butler and Erbaugh who reported[8] that optimum diameter for light energy scattering is in the range of 0.1 to 1.0 microns. So no inferences can be drawn from the amounts of the smokes produced or their particle size.

However, there was a great difference in flammability between the smokes from the two polymers. It was noted that the smoke from PVF_2 rarely ignited, while that from PVF always ignited. This is consistent with the observation that the volatile materials obtained from PVF_2 by oven pyrolysis were highly fluorinated, while those from PVF were not. Ignition, or flaming, would act as an additional heat source. So this may explain, at least in part, the poorer energy-attenuating capabilities of PVF in comparison to PVF_2.

2. Possible Endothermic Processes

According to Pauling,[9] the elimination of HF from compounds is endothermic. However, the amount of energy absorbed is not large, 69.9 Kcal/mole of HF (see Appendix B for calculations). Also, differences between the amounts of HF evolved from PVF_2 and PVF are relatively small. Furthermore, Butler and Erbaugh[8] have shown in

DTA-TGA studies that the overall thermal degradation processes for PVF_2 and PVF are exothermic. Therefore, it is believed that the energy-attenuating capabilities of PVF_2 and PVF cannot be attributed to endothermic reactions producing a chemical heat sink.

3. Char Formation

The role of char formation in attenuating thermal energy has been demonstrated by G. T. Holmes, who reported[10] that, when a 3-layered fabric system, consisting of wool/rayon fabric, a nylon fabric and a cotton fabric, was exposed to high-intensity thermal radiation with the wool/rayon fabric facing the oncoming radiation, considerable char was formed by the wool/rayon and was held in place by the nylon. This completely protected the cotton fabric up to an irradiation level of 16 cal cm^{-2} sec^{-1}. In a similar system, wool/rayon:cotton:nylon, exposed with the wool/rayon fabric again facing the radiation, the char from the wool/rayon fabric was retained on the surface of the cotton and afforded partial protection of the nylon up to 30 cal cm^{-2} sec^{-1}. Other permutations of this layering system, in which a char was either not formed or else not held in place, offered very little protection to the third or inner layer.

In the early work,[1] the possible importance of the role of char formation as a means of attenuating thermal energy was not suspected. Therefore, measurements were not made on the relative amounts and thicknesses of the char layers produced. Visual observation of the polymer disks, after exposure in the arc-image furnace, indicated that both polymers produced considerable char. The char from PVF appeared to be more vitreous than that from PVF_2, while the latter appeared to be more porous. Unfortunately, time limitations precluded repetition of the previous work so that quantitative measurements could be made on the char layers. Therefore, it cannot be stated conclusively that differences in the char layer formation on the exposed surfaces of the polymer disks were responsible for the differences in their energy-attenuating capabilities. However, if the char formation results of oven pyrolysis and arc-image furnace pyrolysis are as consistent as the results on the volatile products, it could be inferred that char formation is a highly plausible factor contributing to the difference in energy-attenuating capabilities of the two polymers.

VII. FUTURE WORK

No further investigation of fluoropolymers of the aliphatic PVF_2-PVF type is planned for two reasons: (1) Since this type of polymer gives off large amounts of HF during thermal degradation, an additional hazard to personnel would be created because of the extremely corrosive action of HF on the skin and eyes; and (2) in the concomitant studies on screening polymers in the carbon arc-image furnace, several polymers (e.g., nitroso rubber, polytrifluorostyrene and zein) have been found that are measurably better energy attenuators than PVF_2 and PVF. Therefore, it is felt that expenditure of further time and effort on these fluoropolymer studies is not warranted.

The thermal program is being broadened to include studies of the thermal-physical properties of polymers, e.g., specific heats of nylon, cotton and nylon/cotton (Nyco) blends; also enthalpy changes in these polymers up to and including the point of decomposition. In these studies data will be obtained by means of a Differential Scanning Calorimeter and a Cahn Electrobalance with auxiliary gas chromatographic equipment. Temperature gradients and profiles will be determined on polymer systems (in fabric or film form) during exposure to thermal radiation by means of a Mach-Zehnder interferometer. The parameters determined in these studies will be used eventually in heat-flow and heat-transfer equations previously developed as mathematical models to predict the behavior of polymeric materials under thermal stress.

VIII. ACKNOWLEDGMENTS

For the extensive technical assistance received in this investigation, the authors wish to express their appreciation to a number of colleagues as follows:

In the Clothing and Organic Materials Laboratory: Dr. R. A. Prosser, for his ingenuity and untiring efforts in modification of the gas chromatograph and in designing and setting up the pyrolysis ovens and the trapping system to separate the volatile fractions of the pyrolysis products; and Mr. Robert Sacher for assistance in making infrared spectroscopic measurements.

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mass spectroscopy measurements; Dr. Julius Weinstein and Dr. Aaron L. Bluhm for infrared spectroscopic measurements; and Mr. Frank H. Bissett for nuclear magnetic measurements.

The authors also wish to express their thanks to Mr. David Feldman, Clothing and Organic Materials Laboratory, for his suggestions in interpreting the data and for his constructive criticisms throughout the research and preparation of the report.

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APPENDIX A

NOTE 1(a). Pyrolysis Oven and Sample Holders

The pyrolysis oven was a box constructed of 3/4-inch thick plywood. Its external dimensions were 13 1/4-inch x 13 1/4-inch x 14 1/2-inch. This was lined with Fiberglas* batts approximately 1 inch thick, held in position by stainless steel plates. Inside these were Transite* plates, 1/2-inch thick, to whose inner surfaces were attached aluminum sheets to provide heat reflection. Internal dimensions of the oven were 10 inches x 10 inches x 10 inches.

A fan motor was mounted on top of the removable oven cover, the shaft and blade extending into the cavity. A 1-inch diameter hole in one side of the oven provided a path for gas exit tubing and thermocouple wire. Heat was supplied by four 350 watt, 57.7 volt chromel wire heaters which were mounted one in each corner of the cavity. Temperature was controlled by a Thermac, Model SPY 5212 (Research, Inc., Minneapolis, Minnesota). Four thermocouples were positioned inside the oven cavity to check the temperature uniformity.

The large sample holder was a 1-liter stainless steel beaker equipped with copper gasket and tight-fitting steel cover plate. A brass ring was fitted below the lip of the beaker and held in place by a lower plate which was bolted to the cover plate. A leak-proof seal was assured when each heat-treated bolt was adjusted to 15-18 pounds pressure per square inch. The cover plate was further fitted with: (a) a helium inlet stainless steel tubing (1/4 inch OD x 7/32 inch ID); (b) chromel-alumel thermocouple sheathed in 1/4 inch OD tubing for monitoring internal oven temperature changes; and (c) an exit tube (1/2-inch OD x 7/16-inch ID) for pyrolyzates.

The small sample holder described[2] previously uses a preheated helium stream in addition to external heaters to heat the polymer undergoing pyrolysis and to sweep the volatile pyrolyzates out of the oven.

*Registered trade marks

NOTE 1(b). Helium Flow Rate

The flow rate of the carrier gas, helium, must be controlled carefully during the pyrolysis. If it is too rapid, portions of the V_{pyr} fractions may be swept into the NaF trap, designed to catch only HF, and give anomalous results. Also, the V_{25} and V_{-190} fractions may not be caught in the appropriate liquid nitrogen traps and thus be lost. The helium flow rate is manually controlled by a micrometer valve between the helium tank and the inlet tube. It is monitored by a rotameter at the exit of the trapping system.

Initially, the helium flow rate was adjusted to 40 cc/min. As soon as pyrolysis began, the evolution of volatile materials from the polymer tended to increase the flow rate considerably. Therefore the helium stream was shut off temporarily. The volume of volatile products caused the flow rate to vary between 88 cc/min and 110 cc/min for about five minutes. Then the flow rate decreased markedly. Helium was again allowed to flow into the system and continued until all the volatile degradation products had been swept out of the ovens into the trapping systems.

NOTE 2. V_{pyr} and V_{hf} Trap

The V_{pyr} and V_{hf} trap consisted of standard polyethylene tubing, 1/2 inch OD x 3/8-inch ID, and about 8-1/2 feet long. It contained no packing. During a pyrolysis, this trap was kept at 0°C by means of an ice water bath. Hydrogen fluoride (b.p. 19°C) condensed with the V_{pyr} fraction. With heaters of the pyrolysis oven off and helium still flowing through the system, this trap was gradually allowed to warm to room temperature, approximately 25°C. This permitted the HF to volatilize slowly and to be carried by the helium stream into the next trap without entraining any appreciable amount of the V_{pyr} fraction.

NOTE 3. V_{hf} Trap

This trap consisted of a loop, approximately 24 inches long, and made from the same type of polyethylene as the previous trap. It was packed with 45g sodium fluoride (NaF) pellets*. Weight of the packed tube was approximately 50g. The NaF reacts with HF to form a complex $NaHF_2$ according to the reaction:

$$HF + NaF \longrightarrow NaHF_2$$

*Sodium Fluoride Tablets, No. 0202 T 1/8-inch, Lab No. 150, The Harshaw Chemical Co., Cleveland 6, Ohio.

This reaction is exothermic. Therefore, to avoid overheating and possible destruction of the trap, the rate of admission of HF into the trap was kept slow.

The remaining volatile materials passed through this trap. From the weights of the 25°C trap before and after the run, the weight of the V_{hf} fraction was calculated. The trap was then discarded because of the toxicity of the fluorine-containing materials.

NOTE 4. First Liquid Nitrogen Trap

This trap was designed to provide a means of catching the V_{25} fraction at liquid nitrogen temperature and monitoring the mixture in and out of the gas chromatograph. The essential components of the trap were a four-port switching valve and 3/64-inch wall stainless steel tubing of the following dimensions:

(1) inlet tube, large bore, 1/4-inch OD, 12 inches long;

(2) an inner tube, 1/2-inch OD, 8 inches long;

(3) an outer tube, taper welded to (2), 7/8-inch OD, 8 inches long;

(4) an outer tube from (3), 1/8-inch OD, 15 inches long.

The trap is shown schematically in Figure 1.

The trap was packed with stainless steel wool. When packed, the trap weighed 568.2g. Since the weights of V_{25} which collected in this trap were usually in the range of 5g or less, the large tare weight of the trap tended to make accurate determinations of the V_{25} fraction difficult.

NOTE 5. Second Liquid Nitrogen Trap

The second nitrogen trap consists of a four-port switching valve and 160 feet of 1/4-inch stainless steel tubing coiled to fit in a 4-liter Dewar flask. The internal volume of the trap was approximately 2 liters. Its weight was 5,821g.

NOTE 6. Copper Oxide Reactor

The purpose of this reactor was to confirm the presence in the V_{-190} fraction of materials, such as hydrogen and/or hydrocarbons,

whose presence had been indicated on the gas chromatographic records. The reactor itself was a quartz tube, 1/2-inch OD, 10 inches long. Copper oxide* was used as the oxidizing agent and was held in place by quartz wool plugs. The quartz tube was mounted in a ceramic tube, 1 inch OD, 5/8-inch ID and 3-3/4 inches long. The ceramic tube, in turn, was mounted in a perforated galvanized cylinder, 6 inches long and 2-1/4 inches OD. Glass wool was used as insulating layers. Heating was accomplished by a conventional Variac-controlled heating coil, and the temperature measured by a chromel-alumel thermocouple mounted between the quartz tube and the ceramic tube.

Products of the oxidation of the V_{-190} fraction by the hot copper oxide were water and carbon dioxide. These were caught in conventional calcium chloride and Ascarite** traps which had previously been tared.

The copper oxide reactor is shown schematically in Figure 1.

NOTE 7. Gas Chromatograph

Conventional gas chromatography was employed in attempts to separate the components of the highly complex mixtures of the V_{25} and V_{-190} fractions. To avoid losses associated with the use of syringes to inject samples into the gas chromatograph, the latter was connected directly to either one or the other of the two liquid nitrogen traps which served to concentrate the samples (see Appendix A Notes 4 and 5). In the gas chromatograph two thermal conductivity cells were used, one to indicate the total volume of sample entering the chromatograph column, the other to record the individual fractions eluted from the column. The column oven temperature was kept constant at 125°C. Three columns were located in the instrument and any one column could be selected at will. Each column consisted of copper tubing, 1/4 inch outside diameter, packed with 60-80 mesh firebrick which served as the substrate for the three liquid phases. Column characteristics are given below:

	Length	Liquid Phase
a.	30 feet	Di-n-decylphthalate, 20% liquid phase
b.	50 feet	1,2,3,tris-(2-cyanoethoxy)-propane 25% liquid phase
c.	50 feet	Silicone oil, DC-200, 33.3% liquid phase

*Copper oxide - Cupric Oxide, Wire, Special for Microanalytical Analysis Lot K119, City Chemical Corp., New York, N. Y.
**Ascarite - 20-30 Mesh, Lot 5206. Arthur H. Thomas Co., Philadelphia, Pa.

Details of the gas chromatography investigations on the V_{25} and V_{-190} fractions are given in Reference 3.

APPENDIX B

Calculations of Energy Values for Formation of Hydrogen Fluoride from Fluorine-Containing Compounds

The energy involved in the elimination of hydrogen and fluorine from a fluorinated compound and their combination to form HF may be calculated from the bond energies given by Pauling[9] as follows:

(a) Rupture of a C-F bond absorbs 105.4 Kcal/mole

(b) Rupture of a C-H bond absorbs 98.8 Kcal/mole

(c) Total energy absorbed = (a) + (b) = 204.2 Kcal/mole

(d) Formation of a H-F bond emits 134.6 Kcal/mole

(e) Total energy change = (c) - (d) = 69.6 Kcal/mole absorbed.

Thus, the overall reaction of splitting HF out of a fluorine-containing compound is endothermic.

For long pyrolysis times, the amounts of HF obtained from PVF_2 and PVF were practically the same (Table II). For short pyrolysis times, slightly more HF was obtained from PVF_2 than from PVF (Table III). However, since the differences were small, any differences in endotherms would be expected to be very small and would not explain the difference in energy-attenuating capabilities of these polymers.

The foregoing calculations are based solely on the formation of HF. Because of the complexity of the other thermal degradation products, no effort has been made to calculate the possible energies involved in formation of fluorocarbons and/or hydrocarbons formed during degradation.

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13. ABSTRACT

The purpose of this study was to determine differences in the major thermal degradation products of polyvinylidene fluoride (PVF_2) and polyvinyl fluoride (PVF). Such differences might help explain the greater ability of PVF_2 to attenuate radiant energy from high-intensity thermal sources. The study comprised degradation of the polymers by oven pyrolysis, separation of the degradation products into major fractions, elemental analyses of the fractions, and identification of a number of the components of the volatile fractions.

During pyrolysis, both PVF_2 and PVF yielded hydrogen fluoride, complex mixtures of other volatile products, and residual char. The main differences were in the nature of the volatile products and the amounts of char formed. The volatile products from PVF_2 consisted largely of highly fluorinated nonflammable materials; those from PVF contained much less fluorine and were flammable. The amount of char formed from PVF_2 was approximately twice as great as that formed from PVF. Although the amounts of HF yielded by each polymer were large, differences between them were small and were not considered significant.

It is therefore inferred that the greater ability of PVF_2 to attenuate energy from high-intensity thermal sources, as compared to PVF, may be attributed in part to its ability to produce nonflammable smoke. This would tend to scatter the radiant thermal energy and keep it from reaching the polymer surface, whereas the smoke from PVF would ignite and thus create an additional heat source. Another

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High intensity	0					
Mechanism			8			
Protection	4		9			
Arc-image furnaces	10					
Energy					8	
Attenuation					8	