CLOTHING AND ORGANIC MATERIALS DIVISION

Materials Research and Engineering Report
No. 65-4

DEGRADATION OF HALOPOLYMERS BY EXPOSURE
TO HIGH-INTENSITY THERMAL PULSES

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Project Reference:
1C024401A113

May 1965

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SUMMARY

Four series of halopolymers were exposed to
high-intensity thermal energy pulses in a carbon
arc-image furnace. By means of a "closed-cell" technique,
the thermal degradation products were collected and then
analyzed by gas chromatographic procedures. Data were
also obtained on the ignition and energy-dissipating
characteristics of the halopolymers.

The results indicate that: 1) the ignition
characteristics can be qualitatively predicted from the
ratio of halogen to hydrogen atoms in the polymer; 2) the
energy-dissipating characteristics do not depend entirely
on the halogen content of the polymers and are not
related to their halogen/hydrogen ratios; 3) copolymers
can be synthesized to have low ignition frequencies and
also good energy-dissipating characteristics; and, 4) as
the time of exposure to the thermal energy pulse increases,
the nature of the mixture of gaseous thermal degradation
products changes and new products appear in the mixture.

DEGRADATION OF HALOPOLYMERS BY EXPOSURE TO HIGH-INTENSITY THERMAL PULSES

I. Introduction

The purpose of this research was to investigate the behavior of halopolymers when exposed to high-intensity thermal pulses. The research was directed toward the ultimate development of new organic polymeric materials which will withstand and dissipate the intense radiant thermal energy emitted during the detonation of nuclear weapons. Such materials should be capable of affording protection to personnel and materiel exposed to the threat of nuclear warfare. Also, such energy-dissipating materials might find use in other applications, such as in heat shields for nose cones of rockets and re-entry vehicles.

Halopolymers were chosen for this study for the following reasons: a) some of the fluorinated polymers, e.g. Teflon, were well known to have high thermal resistance; b) a previous study[1] indicated that some of the halogenated materials showed good thermal energy-dissipating characteristics; and c) series of polymers and copolymers could be readily obtained for investigation of the effects of halogen content and type of halogen on the thermal behavior of the polymers.

Two characteristics of the polymers were evaluated: 1) their energy-dissipating characteristics, and 2) their tendency to ignite and burn during exposure.

Good thermal energy dissipators allow only minimal heat transfer through their mass. As a measure of this heat transfer, the maximum temperature rise (ΔT in $^{\circ}C$) behind the mass was used. The value ΔT is composite and depends on factors such as radiation intensity, reradiation, nature of the irradiated substance, thickness of sample, exposure time, and on secondary processes that occur as a result of the thermolysis started by the exposure.

Since flaming presents a hazard and a possible source of additional heat, non-flammability is an important requirement for a good heat-dissipating polymer. Research by Warner et al[2] of the Battelle Memorial Institute

established a general rule that a compound can be expected
to be non-flammable when the ratio of halogen to hydrogen
atoms in the molecule is approximately as follows: 2F/1H,
1Cl/1H, 1Br/7H, or 1I/7H. In other words, so far as
flammability is concerned, the order of the halogens in
decreasing effectiveness is iodine, bromine, chlorine and
fluorine. This order is attributed to two facts: 1) the
iodo- and bromo- compounds dissociate thermally more
readily than the chloro- and fluoro- compounds, and 2) the
bromine and iodine radicals are better chain-stoppers in
the free-radical flame propagation process than fluorine
and chlorine radicals.

II.   Background

There is a voluminous literature dealing with the
phenomena encountered in flame extinguishing and flame
inhibiting by halogenated compounds. G. B. Skinner
(3,4), in a comprehensive literature survey that includes
96 references, points out the necessity of a full under-
standing of the nature of uninhibited flames, e.g. their
reaction kinetics, heat transfer, diffusion, radiation,
convection, and other processes, before the influence of
flame inhibitors on these processes can be interpreted.

For the sake of simplicity, many earlier flame
theories were formulated mainly on the basis of a few
special factors, such as heat transfer and chemical
kinetics. This narrowed the field of application of these
theories and prevented their use in interpreting the more
complex flame systems.

More recent work has attempted to take into
account as many factors in flame propagation as possible,
e.g. diathermancy, boundary conditions, and chemical
degradation. This increased the mathematical complexity
of the theories and led to a requirement for more back-
ground information. Much of this background information
is still not available, although the amount of data about
flame propagation is increasing daily. Within the next
few years it is probable that extremely complex flame
theories and mathematical flame propagation models will be

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developed for electronic computer solution and that it
will be possible to calculate parameters for a number of
important flame systems.

At present there are two basic theories concerning
flame propagation: one is the ionic flame propagation
theory, and the other is the free radical theory. However,
there are many phenomena in a number of flame systems which
cannot be interpreted convincingly by these or any other
theory established to date.

In the ionic theory, E. C. Creitz[5] has postulated
that O_2^- ions are formed by electron capture from ionized
hydrocarbons during normal uninhibited combustion. Flame
inhibition in halogen compounds is then caused by halogens
removing the electrons, which are needed for oxygen
activation. However, in a recent personal communication
to one of the authors, Creitz states that this concept is
now being revised and the results will be published later.

In the free radical theory of flame propagation and
flame inhibition by halogens, W. A.Rosser et al[6] explain
the reaction mechanism as follows: hydrocarbon combustion
is propagated mainly by active species, that is, free
radicals such as H, OH, and O. Therefore, removal of these
radicals causes flame inhibition. At the high temperature
of flaming, the halogen compounds dissociate with the
formation of halogen atoms--bromine, for instance. These
halogen atoms react with a hydrocarbon (RH) to form HBr:

$$(Br + RH \longrightarrow R + HBr) \qquad\qquad (I)$$

Then HBr reacts with an active radical, such as OH:

$$(HBr + OH \longrightarrow H_2O + Br) \qquad\qquad (II)$$
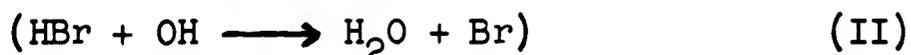
The bromine now reacts again as in equation (I), and so on.
This results in the removal of the active radicals H, OH,
and O, and their replacement by less reactive alkyl
radicals. However, this proposed mechanism is open to
question because, according to Rosser[6], the reaction:

$$(OH + RH \longrightarrow H_2O + R) \qquad\qquad (III)$$
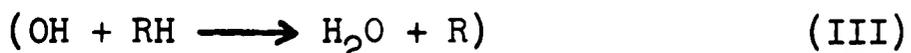
without any halogen present, is even more likely to occur.
Thus, it becomes obvious that the mechanisms of the
chemical reactions responsible for the behavior of
halogenated compounds must be explored and better under-
stood before an exact theory, encompassing many flame
processes, can be established.

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A new and interesting approach to the problem of obtaining information on flame and flame inhibition processes is outlined by Line and King(7). They suggest that concentrations of radicals formed in a flame be measured quantitatively by passing a flame zone across the entrance slit of a Bendix Time-of-Flight mass spectrometer. They further suggest that experiments with molecular beams, which intersect in the ionization chamber, be carried out in such a mass spectrometer. At the low pressure of the beams, most molecules involved would undergo no more than one collision. Thus, only the simplest kind of reaction products would be produced, which would exclude reactions chains. For instance, H_2 and O would produce only products of the reaction $H_2 + O$——— and not those of that reaction plus several subsequent reactions. Such experiments would contribute materially to the understanding of combustion and inhibition mechanisms.

The approach presented in this report on the thermal degradation of halopolymers is not as sophisticated as that suggested by Line and King for the ultimate determination of reaction mechanisms. Rather, this work is an attempt, by use of some special equipment and techniques (carbon arc furnace and gas chromatograph; infrared spectroscopy and mass spectrometry), to find answers to the following questions:

1) Can halopolymers be designed to have low flammability or ignition characteristics and yet have good energy-dissipating characteristics?

2) Is there a relation between the ignition frequency and the energy-dissipating characteristics of halopolymers?

3) How closely can one predict the flammability or ignition characteristics of a halopolymer from its halogen/hydrogen ratio?

4) What are the characteristics which a halopolymer must possess to make it an effective energy dissipator?

5) Does the time interval of exposure of a halopolymer to a high-intensity thermal pulse have a measurable effect on the thermal degradation products of the polymer?

It is pointed out that the results of this report are preliminary and qualitative. This is because the analytical work was restricted to the separation and identification of as many as possible of the gaseous products of thermal degradation; no effort was made to analyze the solid, semi-solid (waxes), and liquid products of degradation. As a result, any postulations of thermal degradation mechanisms are highly speculative.

It is also pointed out that, while the terms "ignition" and "flammability" are not identical, they are so closely interrelated that they are often used interchangeably. Ignition, as used in this report in reference to the test results, includes all appearances of flaming, from a hardly discernible flame to a large and substantial flame, without any reference to size or duration.

III. Experimental Details

A. Materials

In this investigation approximately forty fluoropolymers were screened by thermal exposure tests. Only the results which were obtained on nineteen of the materials and which were considered the most important are presented here. Five of the nineteen compounds represent a sequence of homopolymers that proceeds, stepwise, from a fully hydrogenated material $(-CH_2-CH_2-)_n$ to a fully fluorinated one $(-CF_2-CF_2-)_n$. A second group consists of six homopolymers which contain different halogens in the same molecule, such as $(-CClF-CFBr-)_n$ or $(-CClF-CF_2-)_n$. The eight remaining materials ware copolymers that are grouped so as to show the influence of variations in monomer-weight ratios on ignitability and energy-dissipating characteristics. Finally, the first group of homopolymers was studied using different disk thicknesses to determine possible variations in the subsequent ΔT values.

The polymers had been synthesized in small batches by Pennsalt Chemical Corporation. Several batches were combined into a single shipment for testing. Therefore, slight differences in the thermal behavior of various shipments of the same polymer were encountered.

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B. Equipment and Techniques

1. Closed-Cell Method

The closed-cell method of exposing polymer disks to thermal pulses in the carbon arc-image furnace is an improvement over the open-cell method described previously ([1]). The closed-cell method makes it possible to collect pyrolyzates quantitatively, and therefore creates a basis for exact analytical determinations. The "Closed Cell" used by the Natick Laboratories is a modified version of a device which originated with the U.S. Naval Radiological Defense Laboratory, San Francisco, California ([8]). This modified cell is of Pyrex glass and has a volume of 15 ml (see Figure 1). The disk carrier is shown at the lower left of Figure 1. The hollow part of the carrier is equipped with a male standard taper joint which fits into the other half of the cell, shown at the upper left. This latter half has two side arms for the passage of the helium carrier gas stream. The disk carrier is interchangeable with a correspondingly sized rubber septum carrier (lower center), which is used when a gas sample is to be injected into the cell. A disk of the test material, 60 mils thick and 5/8 inch in diameter, is supported inside the cell by three tungsten needles on
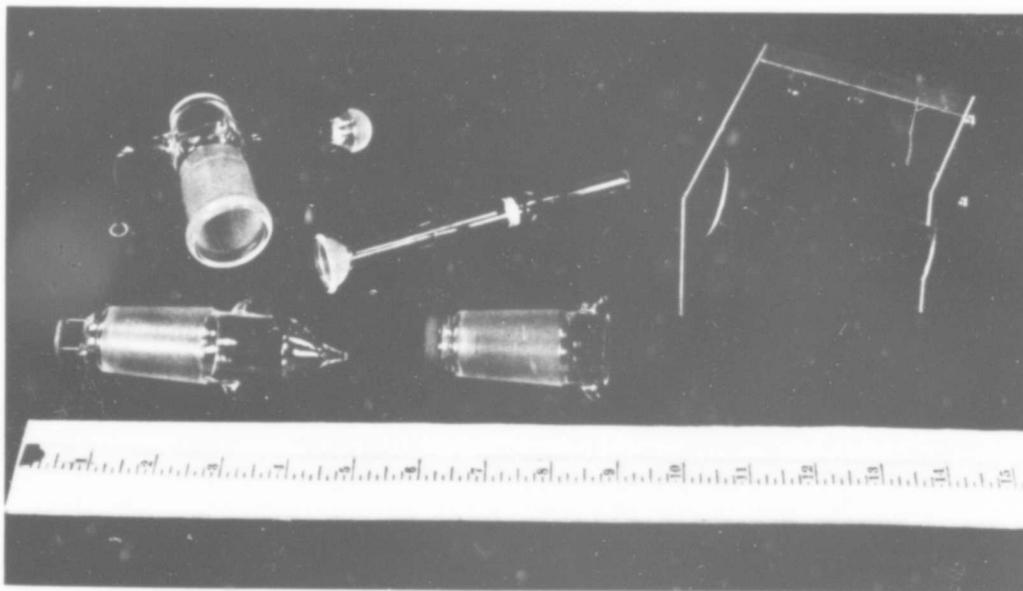

Figure 1. Closed cell (exploded view)

which the disk is impaled in a vertical position. The cell is connected directly with the gas chromatograph by a glass tube equipped with an extra-coarse fritted glass filter to retain solid particles.

The test samples are exposed by placing them, inside the cell, in the focal area of the QM Arc(9). The radiant energy enters and passes through the frontal glass wall of the cell and a continuous helium stream sweeps through the combined system of closed cell and gas chromatograph. Air is completely excluded. Immediately after their formation, the pyrolyzates are carried by the helium gas directly into the gas chromatograph.

Figure 2 shows the closed cell (at arrows) mounted on the QM Arc and ready for exposure. The connecting tube with fritted glass filter and the metal cell holder can be seen at the right, leading out from the closed cell.

Figure 3 gives a wider view of the closed cell mounted on the QM Arc, also the gas chromatograph at the right.

Figure 4 shows the closed cell at the moment of sample exposure.

2. Gas Chromatographic Procedures

A schematic diagram of the gas chromatograph and a description of its components, columns and sensing device. have been presented previously.(1). The same apparatus was used for the determinations described in this report. The experimental conditions were in all cases: thermal conductivity cell temperature—70°C; column temperature—21°C; and gas flow—60 ml/min.

The separation and identification, when possible, of the single components of the gas mixtures produced by thermal degradation were made by using a 2-column system on the gas chromatograph. One column contained a liquid stationary phase, fluoroalkylcamphorate(1), and the other a solid stationary phase, silica gel (Burrel's Kromo-tog). The separations were carried out first on the fluoro-alkylcamphorate column and then on the silica gel column. In this way, two retention-time sets were obtained for the same gas mixture. For identification of the single
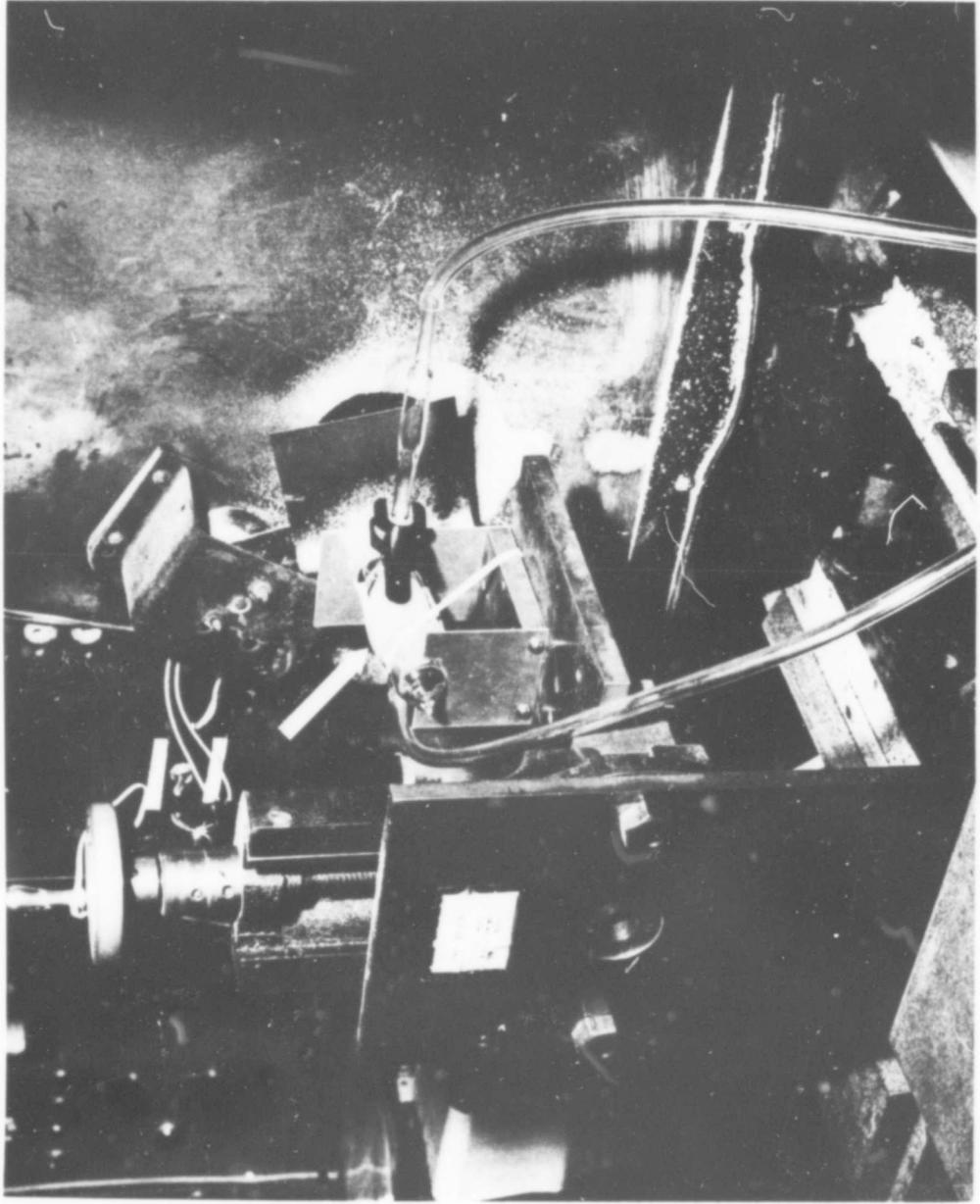
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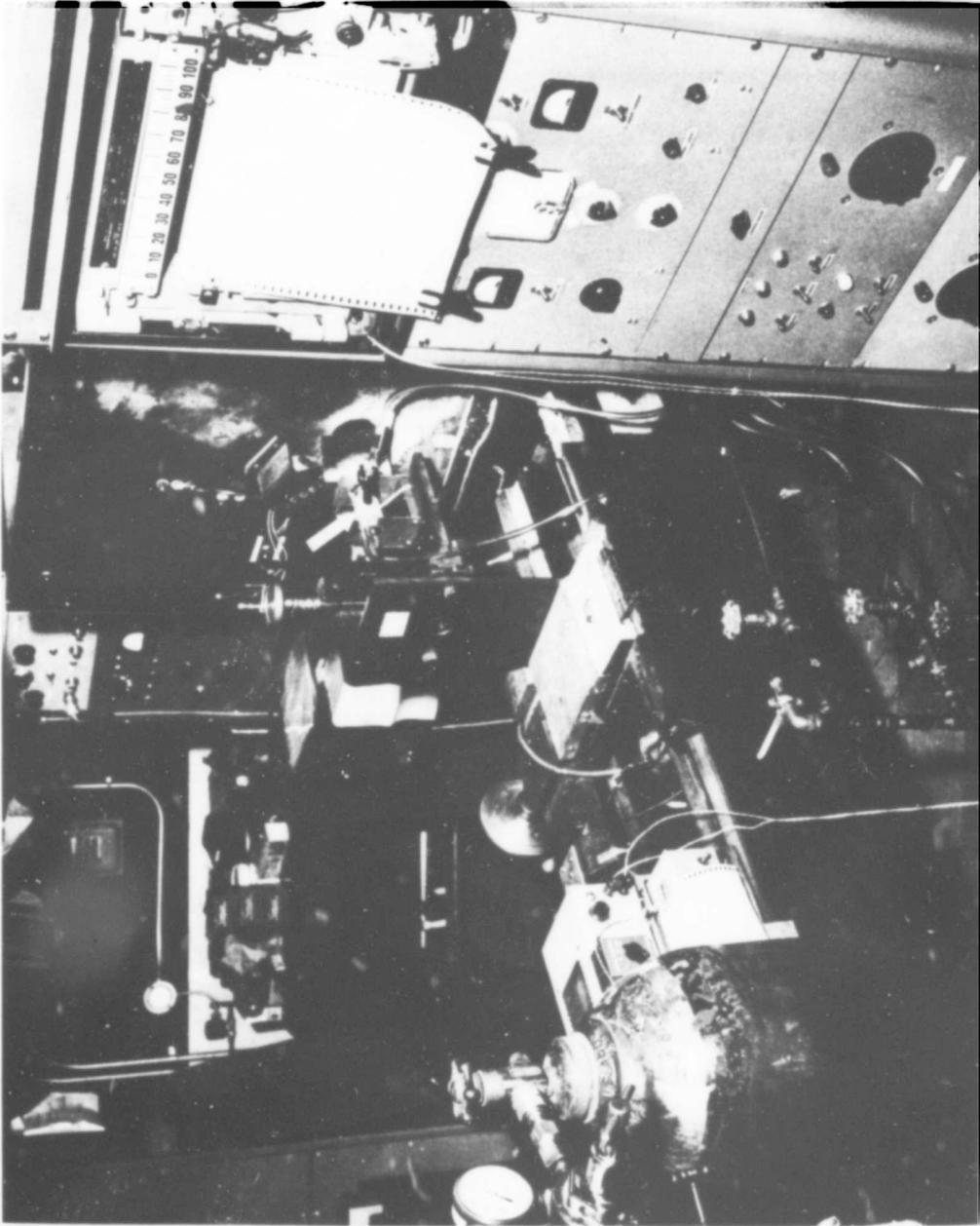Figure 2. Closed cell mounted on QM Arc, ready for exposure

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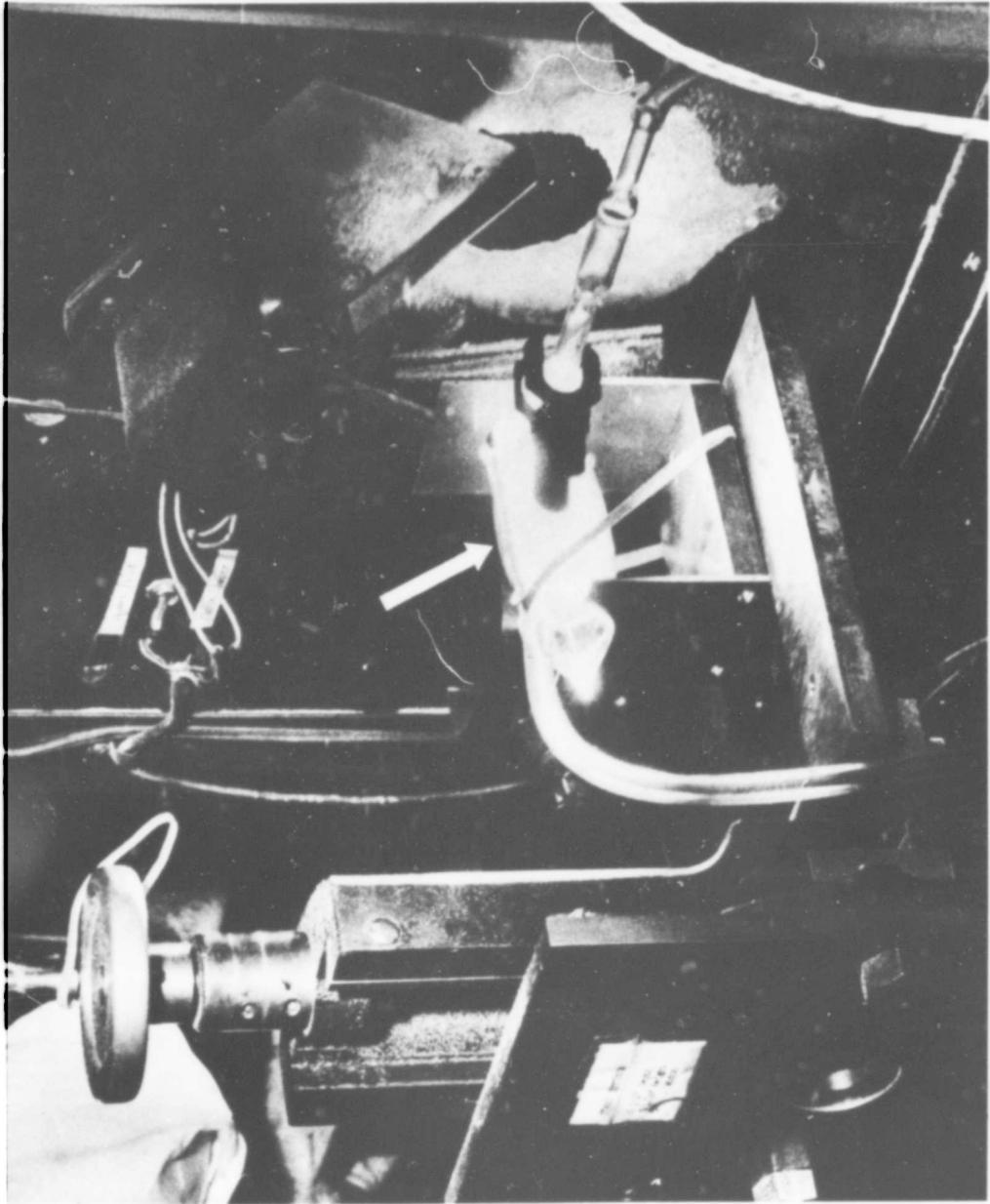Figure 3. QM Arc (from rear) showing mounted closed cell

Figure 4. Closed cell (mounted on QM Arc) at moment of exposure

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constituents, several methods were used. One consisted of running standard single gases on the two columns, determining their retention times, and then trying to find the corresponding retention times from the peaks of the unknown gas mixtures. Another consisted of systematically freezing out the single components of the separated gas mixtures after they emerged from the exit of the gas chromatograph and then submitting them to infrared or mass spectrometry analysis.

IV. Results and Discussion

A. Thermal Behavior of Homopolymers

1. Effect of Fluorine

The thermal behavior of the series of homopolymers containing only one type of halogen (fluorine) is shown in Table I. There is no apparent relationship between the fluorine/hydrogen ratio of the polymers and their energy-attenuating capabilities as measured by ΔT values. The completely fluorinated polymer (Teflon) and the polymer (polyethylene) containing no fluorine show the highest ΔT values and thus appear to have the poorest energy-attenuating capabilities. However, there is a relationship between the fluorine content of the polymers and their ignition characteristics. With a fluorine/hydrogen ratio of 1/1, ignition occurred in 50 percent of the samples; with a ratio of 3/1 or greater, ignition did not occur; and with a ratio of less than 1/1, ignition invariably occurred. These results are in agreement with those reported by Warner et al of Battelle Memorial Institute[2], i.e. that a minimum ratio of fluorine to hydrogen atoms of 2/1 is required for nonflammability.

2. Effect of Different Halogens

Table II shows the thermal behavior of the series of homopolymers having one or more different halogens in the polymer molecule. The materials are listed in the order of decreasing ΔT values. As in Table I, there is no relationship between halogen/hydrogen ratios and ΔT values. However, the polymers which have a low effective halogen/hydrogen ratio (0.6/1 and 0.66/1) ignited at the irradiance level of 23 cal cm^{-2} sec^{-1} and the polymers which have an effective halogen/hydrogen ratio of 2/1 or greater did not ignite.

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Table I

EFFECT OF HIGH-INTENSITY THERMAL RADIATION
ON HOMOPOLYMERS CONTAINING FLUORINE

Irradiance Level - 23 cal cm^{-2} sec^{-1}
Ten specimens tested per polymer
Exposure Time - 1 sec

Homopolymer	Ratio Fluor/Hyd	Avg $\Delta T(°C)$	Freq of Ign (%)
Polyethylene ($-CH_2-CH_2-)_n$	-	19.2	100
Polyvinyl Fluoride ($-CH_2-CHF-)_n$	0.33/1	16.8	100
Polyvinylidene Fluoride ($-CH_2-CF_2-)_n$	1/1	10.8	50
Polytrifluoroethylene ($-CHF-CF_2-)_n$	3/1	11.3	0
Teflon ($-CF_2-CF_2-)_n$	4/0	36.3	0

Tables III and IV recapitulate some of the data from Tables I and II in order that a comparison can be made of the effect of different halogen atoms in the polymer molecule.

In Table III, both polymers are only partially halogenated and both have a very low halogen/hydrogen ratio. Consequently, both materials ignited. The fluoropolymer has a lower ΔT value than the chloropolymer and thus appears to have a greater energy-dissipating capability.

In Table IV, all the polymers are completely halogenated and do not ignite. However, as fluorine is progressively replaced by chlorine, the ΔT values decrease. This is not consistent with the results noted in Table III, where the fluoropolymer has a lower ΔT value than the chloropolymer. It implies that the behavior of fluorine versus chlorine in a completely halogenated polymer is different from that in a polymer containing some hydrogen atoms. It is likely that the explanation lies in the relative ease of the degradation of the polymers and in the mechanisms by which the degradation takes place.

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In Table IV, it will also be noted that a further decrease in ΔT occurs when an additional fluorine is replaced by bromine.

Table II

EFFECT OF HIGH-INTENSITY THERMAL RADIATION ON HOMOPOLYMERS CONTAINING DIFFERENT HALOGENS

Irradiance Level - 23 cal cm^{-2} sec^{-1}
Ten specimens tested per polymer
Exposure Time - 1 sec

Homopolymer	Hal/Hyd Ratio Actual	Effective*	Avg $\Delta T(^\circ C)$	Freq of Ign (%)
$(-CH_2-CHCl-)_n$	0.33/1	0.66/1	22.3	100
$(-CF_2-CF=CF-CH_2-)_n$	2/1	2/1	13.9	0
$(-CFCl-CF_2-)_n$	4/0	5/0	13.0	0
$(-CCl_2-CF_2)_n$	4/0	6/0	11.6	0
$(-CH_2-CH-)_n$ OCH_2-CF_3	0.6/1	0.6/1	10.7	80
$(-CCl_2-CFBr-)_n$	4/0	19/0	8.9	0

*Calculated on basis that 1 Br = 7 Cl = 14 F (2)

Table III

THERMAL BEHAVIOR OF PARTIALLY HALOGENATED HOMOPOLYMERS: COMPARISON OF EFFECT OF FLUORINE VERSUS CHLORINE

Irradiance Level - 23 cal cm^{-2} sec^{-1}
Ten specimens tested per polymer
Exposure Time - 1 sec

Homopolymer	Effective Ratio* Halogen/Hydrogen	Avg $\Delta T(^\circ C)$	Frequency of Ignition (%)
$(-CH_2-CHF-)_n$	0.33/1	16.8	100
$(-CH_2-CHCl-)_n$	0.66/1	22.3	100

*Calculated on the basis that 1 Cl = 2 F (2)

Table IV

THERMAL BEHAVIOR OF COMPLETELY HALOGENATED
HOMOPOLYMERS: COMPARISON OF EFFECTS OF
DIFFERENT HALOGENS

Irradiance Level - 23 cal cm^{-2} sec^{-1}
Ten specimens tested per polymer
Exposure Time - 1 sec

Homopolymer	Effective Ratio* Halogen/Hydrogen	Avg $\Delta T(^{o}C)$	Frequency of Ignition (%)
$(-CF_2-CF_2-)_n$	4/0	36.3	0
$(-CFCl-CF_2-)_n$	5/0	13.0	0
$(-CCl_2-CF_2-)_n$	6/0	11.6	0
$(-CCl_2-CFBr-)_n$	19/0	8.9	0

*Calculated on the basis that: 1 Br $\rightleftharpoons$ 7 Cl $\rightleftharpoons$ 14 F [2]

B. Thermal Behavior of Copolymers

In an attempt to synthesize materials which would
have high energy-attenuating capabilities (low ΔT values)
and would not ignite under high-intensity thermal energy
pulses, several series of compounds were made by
copolymerizing vinylidene fluoride $(CH_2=CF_2)$ in various
percentages by weight with the following monomers:
perfluoropropene (C_3F_6); chlorotrifluoroethylene
$(CFCl=CF_2)$; symmetrical difluorodichloroethylene
$(CFCl=CFCl)$; trifluoroethylene $(CHF=CF_2)$; and 2,2,
2-trifluoroethyl acrylate $(CH_2=CH$
$|$
$COOCH_2CF_3)$.
The results of exposure to thermal radiation are presented
in Table V.

It shows that when the halogen/hydrogen ratio is
4.8/1 or greater, no ignition occurs. When this ratio
is 2.3/1 or less, ignition occurs in every case but
one and the frequency of ignition was usually (but not
always) greater with the lower ratio. This is in
qualitative agreement with the work by Warner et al[2].

The ΔT values for the copolymers are all low (under
$13^{o}C$). It is interesting that, as in the homopolymers,

there is no direct relationship between the ΔT value and the tendency of the copolymer to ignite. Of the two copolymers which have the lowest ΔT value (6.5°C), one did not ignite and the other ignited 40 percent of the time. The one which did not ignite ($CH_2=CF_2/C_3F_6$: 40/60) has a high halogen/hydrogen ratio (5.5/1); the other ($CH=CF_2/CFCl=CFCl$: 70/30), which showed considerable ignition frequency, has a low halogen/hydrogen ratio (2.3/1).

Table V

EFFECT OF HIGH-INTENSITY THERMAL RADIATION ON COPOLYMERS OF POLYVINYLIDENE FLUORIDE WITH OTHER HALOGENATED MONOMERS

Irradiance Level - 23 cal cm^{-2} sec^{-1}
Ten specimens tested per polymer
Exposure Time - 1 sec

Copolymer Composition
(% by weight of monomer)

$CH_2=CF_2$	C_3F_6	Ratio* Hal/Hyd	Avg $\Delta T(°C)$	Freq of Ign (%)
100	0	1/1	10.8	50
70	30	2.3/1	8.6	80
40	60	5.5/1	6.5	0

$CH_2=CF_2$	$CFCl=CF_2$			
100	0	1/1	10.8	50
90	10	1.3/1	11.9	100
40	60	4.8/1	9.5	0
20	80	11/1	11.6	0
0	100	5/0	13.0	0

$CH_2=CF_2$	$CFCl=CFCl$			
100	0	1/1	10.8	50
70	30	2.3/1	6.5	40

$CH_2=CF_2$	$CHF=CF_2$			
100	0	1/1	10.8	50
36	64	2/1	9.6	0

$CH_2=CF_2$	$CH_2=CH$ | $COOCH_2CF_3$			
100	0	1/1	10.8	50
30	70	0.65/1	9.2	100

*Calculated on the basis that 1 Cl =○= 2 F (2)

C. **Effect of Polymer Disk Thickness on Energy Atten-
    uation**

The ΔT values reported in the previous tables
were measured behind polymer disks having a uniform thick-
ness of 60 mils. The effects of different disk thick-
nesses on the ΔT values of the same series of polymers
shown in Table I were measured and are given in Table VI.
Three of the materials showed that, as the thickness of
the polymer disk was increased, the ΔT values erratically
decreased. This general trend might be expected.
However, the two homopolymers at each end of the fluor-
ination series behaved in an anomalous fashion: poly-
tetrafluoroethylene (Teflon) showed no significant change
in ΔT as the thickness increased; polyethylene showed an
unexpected increase in ΔT values as thickness increased.
No explanation for this behavior is obvious at the present
time.

Table VI

EFFECT OF POLYMER DISK THICKNESS
ON THERMAL ENERGY ATTENUATION

Irradiance - 20 cal cm^{-2} sec^{-1}
Exposure Time - 1 sec

Homopolymer		ΔT (°C) at Disk Thickness of			
		30	40	50	60
			(mils)		
Polyethylene	$(-CH_2-CH_2-)_n$	15.2	18.8	24.9	19.2
Polyvinyl Fluoride	$(-CH_2-CHF-)_n$	20.4	21.3	14.0	16.8
Polyvinylidene Fluoride (KYNAR)	$(-CH_2-CF_2-)_n$	16.4	12.5	10.9	10.8
Polytrifluoro-ethylene	$(-CHF-CF_2-)_n$	17.4	16.7	17.7	12.3
Teflon	$(-CF_2-CF_2-)_n$	37.6	33.7	37.7	36.3

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D. Gaseous Degradation Products Analyzed by Gas Chromatography

Typical chromatograms of the gaseous degradation products of two polymers exposed to high intensity thermal radiation by the closed-cell technique are shown in Figure 5 (polyethylene) and Figure 6 (polytrifluoroethylene). The polyethylene gives a relatively simple chromatogram, the five gaseous products consisting of three saturated hydrocarbons (containing one, two, and three carbon atoms) and two unsaturated hydrocarbons (ethylene, the monomer, and propylene). The polytrifluoroethylene gives a much more complex chromatogram consisting of eight peaks including two unidentified peaks (B and G) and a CO_2 peak.

The presence of small amounts of CO_2 in the chromatogram of polytrifluoroethylene (Figure 6) was definitely established. This is rather disturbing since the thermolysis of the polymers had been carried out, as mentioned before, in a helium atmosphere with complete exclusion of oxygen. However, other workers have also found CO_2 when O_2 was not expected to be present. White and Rice (10) stated that, at elevated temperatures, a reaction occurred between their fluoro compound, C_2F_6, and the SiO_2 of the glass vessel and led to the formation of CO_2 ($2C_2F_6 + 3SiO_2 \longrightarrow 2CO + 2CO_2 + 3SiF_4$). On the other hand, Madorsky and his coworkers (11) assumed that polytrifluoroethylene contains some oxygen as part of its structure and that CO_2 can be formed by a reaction of this oxygen with the carbon in the polymer chain.

Table VII summarizes the results of the chromatographic analysis of the gaseous thermal degradation products of four of these homopolymers. The following generalizations appear evident:

1) In every case, the monomer was formed to an appreciable extent with saturated and unsaturated 2-carbon compounds.

2) Compounds containing only one carbon atom were also formed.

3) In polyethylene, saturated and unsaturated 3-carbon compounds were formed; in the fluorinated polymers, no 3-carbon compounds were identified as such, however, they may be concealed among the unidentified peaks observed for polyvinylidene fluoride and polytrifluoroethylene.
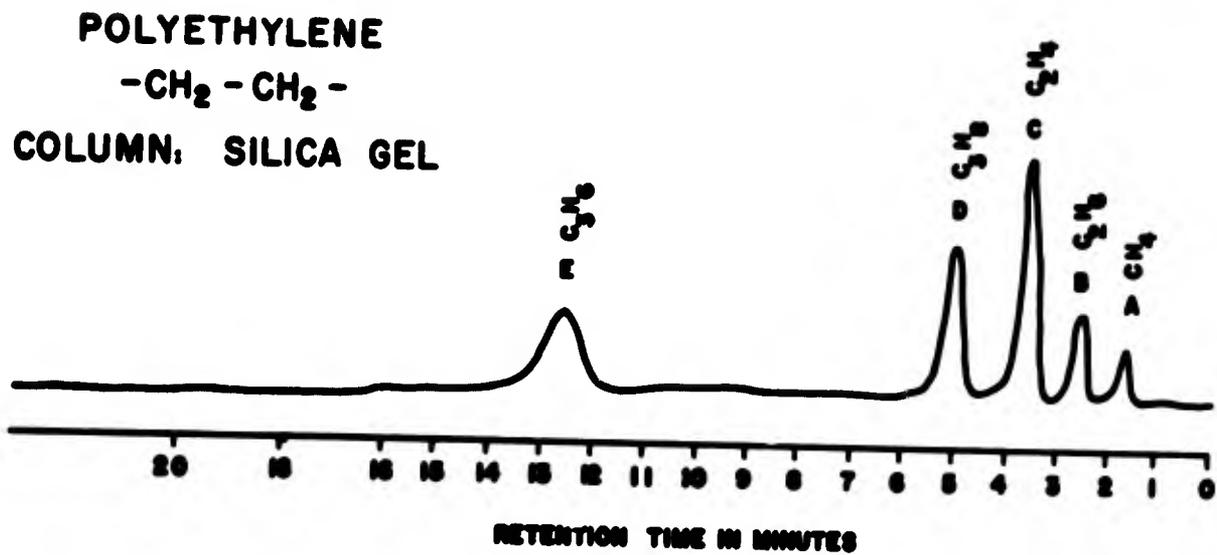
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Figure 5.   Chromatogram of gaseous fraction
of polyethylene pyrolyzates
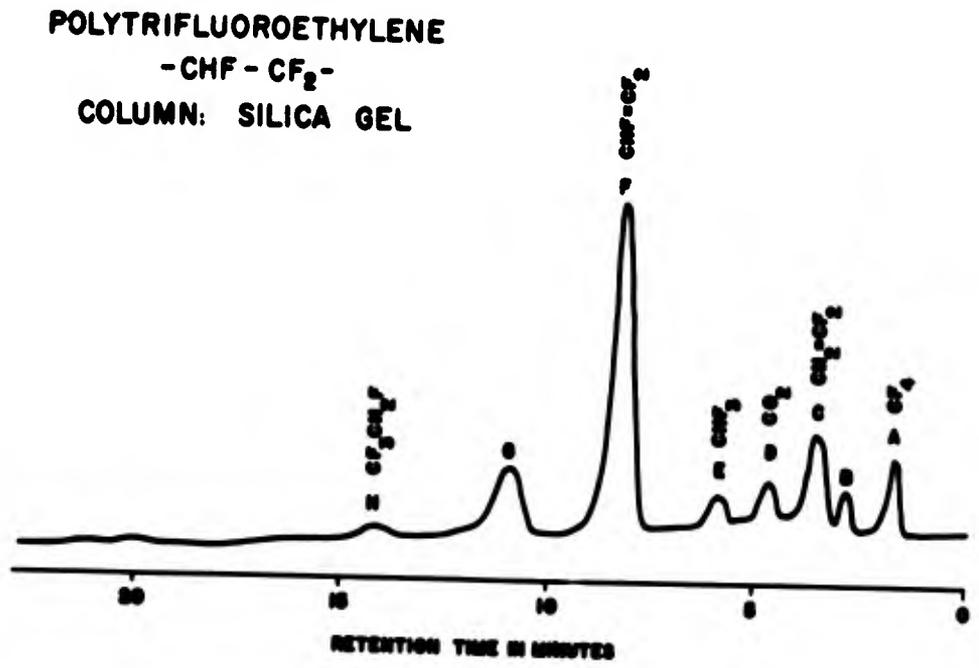
Exposure Time - 1 sec
Irradiance - 23 cal/cm^2/sec

Figure 6.   Chromatogram of gaseous fraction
of polytrifluoroethylene pyrolyzates

Exposure Time - 1 sec
Irradiance - 23 cal/cm^2/sec

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It should be remembered that the products analyzed in the gas chromatograph include only the gaseous portion of the degradation fraction.

The ΔT values shown in Table VII indicate, as previously pointed out, that the three fluoropolymers, especially polyvinylidene fluoride, are better energy-dissipating materials than the polyethylene. The material with the lowest ΔT value (10.8°C—polyvinylidene fluoride) gave the fewest gaseous degradation products, but it is not known whether or not this has any significance.

Table VII

GASEOUS THERMAL DEGRADATION PRODUCTS OF HOMOPOLYMERS

Polymer	Monomer	No. of Peaks	Gaseous Degradation Products				Avg ΔT(°C)
Polyethylene	$CH_2=CH_2$	5	CH_4	CH_3-CH_3 $CH_2=CH_2$	$CH_3-CH_2-CH_3$ $CH_3-CH=CH_2$		19.2
Polyvinyl Fluoride	$CH_2=CHF$	5	CH_4 $CH_2=CF_2$	CH_3-CH_3 $CH_2=CH_2$ $CH_2=CHF$			16.8
Polyvinylidene Fluoride (KYNAR)	$CH_2=CF_2$	4	CF_4 $CH_2=CF_2$		2*		10.8
Polytrifluoro Ethylene	$CHF=CF_2$	8	CF_4 CHF_3	CF_3-CH_2F $CH_2=CF_2$ $CHF=CF_2$	2* CO_2**		12.3

2* - Two unidentified peaks
** - See text for possible explanation of CO_2

From the foregoing discussion, it is evident that the degradation products of fluoropolymers are complex mixtures. That the complexity of these mixtures is increased by increased time of exposure of the polymer to the thermal energy pulse is demonstrated by the four chromatograms
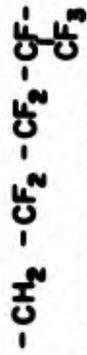
19
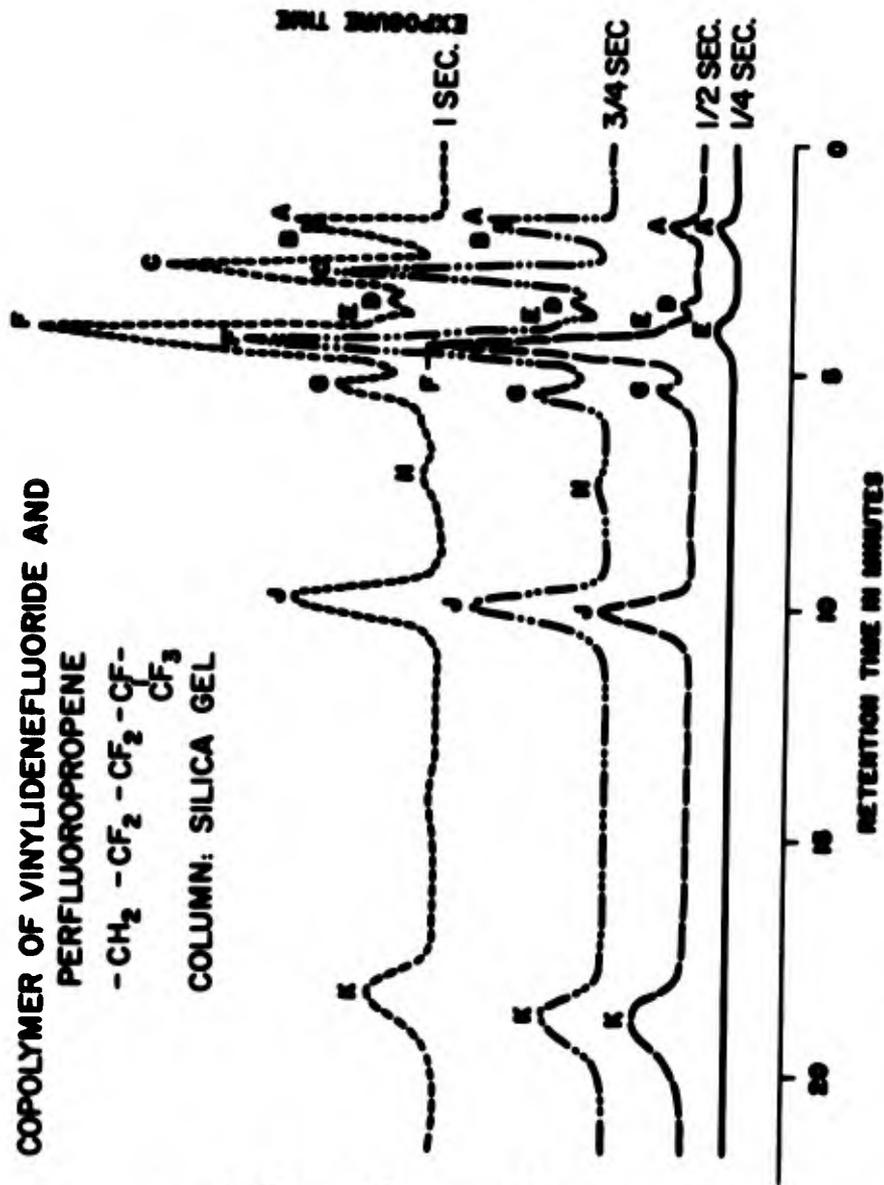
Figure 7. Four chromatograms, superimposed, showing effect of exposure time on thermal degradation

Irradiance - 23 cal/cm²/sec

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shown in Figure 7 and the results given in Table VIII.
In this experiment, four replicate disks of a copolymer
(vinylidene fluoride/perfluoroprene: 70/30) were exposed
for increasing periods of time, i.e., for 1/4, 1/2, 3/4,
and 1 second respectively. Samples of the gaseous
decomposition products were analyzed. The four chromato-
grams obtained are shown in Figure 7. It is evident that,
as the exposure time increased, the composition of the
mixture of gaseous products changed and became more
complicated. During the first 1/4 second, only CF_4 and
$CH_2=CF_2$ were formed. During the next 1/4-second interval,
more of these products were formed plus five new compounds,
three being identified as CHF_3, $CF_2=CF_2$ and $CF_2=CF-CF_3$ and
the other two being yet unidentified. During the third
1/4-second interval, trifluoroethylene ($CHF=CF_2$) appeared
along with two additional unidentified peaks, and at the
same time the previous peaks were intensified. During the
last 1/4-second interval, no new peaks appeared but the
earlier ones increased in size.

Table VIII

EFFECT OF EXPOSURE TIME ON THE NATURE
OF THE GASEOUS DEGRADATION PRODUCTS OF A COPOLYMER
OF VINYLIDENE FLUORIDE AND PERFLUOROPROPENE

Irradiance Level - 23 cal cm^{-2} sec^{-1}

Exposure Interval	New Peaks Formed After Exposure			
1/4 sec.	CF_4 $CH_2=CF_2$			
1/2 sec.	CHF_3 $CF_2=CF_2$	$CF_2=CF-CF_3$		2*
3/4 sec.	$CHF=CF_2$			2**
1 sec.	No new peaks appeared; old peaks intensified			

*Unidentified
**Additional unidentified peaks.

E. Some Possible Thermal Degradation Mechanisms

On the basis of this preliminary work, it is not possible to formulate an overall reaction mechanism for the thermal degradation of this copolymer. However, one can tentatively postulate as to the mechanisms that account for the formation of many of the individual products and perhaps indicate to some extent the sequence in which the reactions might occur. These are as follows for the copolymer of vinylidene fluoride and perfluoropropene:

1) CF_4 is formed immediately and continues to be formed in increasing amounts. This could be accounted for by the following mechanism:

$$
\begin{array}{ccccc}
H & F & F & F \\
| & | & | & | \\
-C - C - C - C - & \longrightarrow & -C - C - C = C -- & + CF_4 \\
| & | & | & | \\
H & F & F & F \\
& & CF_3 \\
\end{array}
\qquad
\begin{array}{cccc}
H & F & F & F \\
| & | & | & \\
-C - C - C = C -- \\
| & | \\
H & F \\
\end{array}
$$

2) CHF_3 is formed after the CF_4 and continues to be formed in increasing amounts, although apparently not to the same extent as CF_4. CHF_3 could be formed as follows:

$$
\begin{array}{cccccccccc}
F & H & F & F & F & H & F & F & F & H \\
| & | & | & | & | & | & | & | & | & | \\
-C - C - C - C - C - C - C - C - C - C - & \longrightarrow \\
| & | & | & | & | & | & | & | & | & | \\
CF_3 & H & F & F & CF_3 & H & F & F & CF_3 & H \\
\end{array}
$$

$$
\begin{array}{cccccccccc}
F & H & F & F & F & H & F & F & F & H \\
| & | & | & | & | & | & | & | & | & | \\
-C = C - C - C - C = C - C - C - C = C - & & + 3\ CHF_3 \\
& & | & | & & & | & | \\
& & F & F & & & F & F \\
\end{array}
$$

3) The monomers $CH_2 = CF_2$ and $CF_2 = CF - CF_3$ could be formed by simple depolymerization, i.e. by "unzipping" the copolymer chain. However, this would not explain why $CH_2 = CF_2$ appears before $CF_2 = CF - CF_3$ and in smaller amounts. Obviously, simple depolymerization is not the explanation.

4) It is difficult to visualize the formation of $CHF = CF_2$ directly from the original copolymer. Undoubtedly, a number of intermediate reactions and/or rearrangements take place, which would explain why this compound shows up relatively late in the sequence.

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The foregoing simple mechanistic pictures may be complicated by the fact that fluoropolymers often assume coiled-chain configurations. A -CF$_3$ group may be much closer to a hydrogen or fluorine atom farther along the polymer chain than is indicated by the conventional graphic organic-chemistry formulae. Thus, geometric configuration may play a considerable role in thermal degradation processes. A study of molecular models of fluoropolymers would undoubtedly be valuable in gaining further understanding of the degradation mechanisms.

It is obvious that considerably more information than is now available will be required in order to formulate degradation mechanisms for such a complex copolymer as the the one discussed above. The unknown degradation products must be identified, especially those whose peaks are labelled in Figure 7 as C, F and K, since these occur in relatively large amounts. It would also be desirable to identify B, although this product is apparently formed in considerably smaller amounts.

V.   Conclusions

Although the experimental results presented are highly preliminary, they point toward the following conclusions:

1)   Halopolymers can be designed or tailored to have very low ignition frequencies and yet good energy-dissipating characteristics (low ΔT values).

2)   There is no close relationship evident between the ignition frequency and energy-dissipating characteristics of a polymer.

3)   The rule of Warner et al[2] on the effect of the halogen/hydrogen content of polymers on their ignition characteristics holds true qualitatively, i.e., the higher the ratio, the less the tendency toward ignition. Halogen/hydrogen ratios of 4/1 or above definitely allow no ignition; ratios below 1/1 always produce ignition; ratios in the range of 1/1 to 4/1 may or may not produce ignition. In these cases, the structure of the polymer molecule appears to be the determining factor.

4)   The energy-dissipating characteristics of a polymer are not a function of its halogen content alone.

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Too high a halogen content in a polymer produces poor energy-dissipating characteristics, e.g. Teflon. It would appear that such a polymer is too stable, thermally. On the other hand, unhalogenated polymers, e.g. polyethylene, which are not stable thermally, are ineffective energy dissipators. This implies that an effective energy dissipator must be a polymer which degrades by such mechanisms as to either absorb much thermal energy or else to generate materials such as smoke to act as a barrier to prevent much of the thermal energy from impinging on the polymer. Insufficient data are available as yet to prove which set of mechanisms is the more effective.

5) The time interval of exposure of a polymer to high-intensity thermal radiation materially affects the nature of the degradation products. As the exposure time is increased, not only are the first-formed products increased in amount but also new products are formed. A more detailed study of this phenomenon would undoubtedly throw more light on the mechanisms of the thermal degradation of halopolymers exposed to intense thermal energy.

6) It is obvious that considerable further research is required in order to formulate reaction mechanisms for the thermal degradation of halopolymers. A knowledge of such mechanisms is essential to the development of ideal "tailor-made" halopolymers which will afford high levels of protection against high-intensity thermal pulses from nuclear weapon detonations.

7) Consideration should be given to the possibility that pyrolyses that proceed in an inert atmosphere such as helium may differ substantially from thermal degradation in air. Consequently, controlled atmospheric conditions may become necessary for the comparison of test results.

VI. Acknowledgments

VII. <u>References</u>

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