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OUSA NLABS TPMR 64-6-II

INVESTIGATION OF ORGANIC COMPOUNDS FOR THERMAL PROTECTION

Part II

ANNUAL SUMMARY REPORT 19 April 1963 - 18 June 1964

Thermal Protective Materials Research Section Clothing and Organic Materials Division U. S. Army Natick Laboratories Natick, Massachusetts

Project Officer: Dr. Wm. E. C. Yelland Project No. 1002 4401 All3

Prepared under Contract No. DA-19-129-QM-1773

by J. M. Butler J. A. Ellard Monsanto Research Corporation Dayton Laboratory

Dayton, Ohio

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FOREWORD

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This is an annual summary report on Contract DA-19-129-QM-1773(X) (0.I.5081), covering the period 19 April 1963 to 18 June 1964. This contract is under the administration of U.S. Army Natick Laboratory with Dr. William E. C. Yelland as project officer.

Various aspects of thermal protection are being investigated under this contract. Section I involves a study of endothermic materials and is being conducted at the Monsanto Research Corporation, Boston Laboratory. This has been reported separately by Dr. A. W. Berger and Dr. R. H. Jackson in USA NLABS TPMR 64-6-I. Work on Section II, a continuation of studies of smoke attenuation on thermal decomposition of fluoropolymers, was done at Monsanto Research Corporation, Dayton Laboratory, with Dr. John Mann Butler as project leader. Contributors to this part of the studies were Dr. J. A. Ellard, Dr. W. H. Hedley, Dr. G. B. Skinner and Mr. R. G. Olt.

Section III covers synthesis of special fluoro compounds requested by the Army. This work was performed at Monsanto Research Corporation, Dayton Laboratory by Dr. W. E. Weesner.

This report covers work on Sections II and III.

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SECTION II - SMOKE ATTENUATION

Authors

J. M. Butler, J. A. Ellard

Contributors

G. B. Skinner, L. E. Erbaugh, W. H. Hedley

I. INTRODUCTION

This is a continuation of previous studies (Ref. 1) on polymers for protection from thermal radiation, and on the factors responsible for such protection. From the previous work we concluded that attenuation of incident radiation by smoke formed on thermal decomposition of a polymer could be an important contribution to protection provided the smoke could be formed sufficiently rapidly. Thus to afford protection against thermal radiation by smoke formation it is necessary that the smoke be formed within time intervals significantly less than the time of the thermal pulse against which protection is desired. The hot filament technique used in previous studies did not heat the polymer sufficiently rapidly to study smoke formation in the time intervals of interest.

This report describes equipment developed for rapidly heating polymer samples by radiant energy and studies on the attenuation of this radiant energy by the products of thermal decomposition.

II. SUMMARY AND CONCLUSIONS

A high-intensity light source for simulation of the thermal pulse from nuclear explosions has been constructed, calibrated and used for testing of 12 polymer systems at 19.2 cal/sq cm/sec.

The following polymers, filled with 5% Cr2O3, were tested: polyethylene, polystyrene, 6,6-nylon; polyvinyl fluoride, polyacrylonitrile, polyvinyl chloride, polytetrafluoroethylene, chlorinated polyvinyl chloride, polymethyl methacrylate, polyvinylidene fluoride, and a polyurethane foam. In addition, two coded samples from U. S. Army Natick Laboratory (NLAB) were tested.

Polystyrene, polyvinyl chloride, polyurethane foam, and the NLAB samples gave the most rapid production of smoke, light attenuation being detected in less than 0.2 seconds. These materials also gave the greatest reduction (>60%) in transmission over a total four-second exposure. Consistent with our results with the hot filament pyrolysis technique, polymethyl methacrylate and polytetrafluoroethylene gave considerably less smoke on exposure to the high intensity light source.

It is concluded that smoke formation by radiant thermal degradation of a polymer can occur sufficiently rapidly to offer thermal protection by attenuation of further incident radiant energy.

Preliminary data obtained indicate: the possible enhancement of smoke generation by additives; the beneficial effects of low film thickness on reducing smoke generation time; and the potentially increased efficiency of polymers in form of foams.

The speed, versatility, and simplicity of this method suggest its use as a rapid screening method for testing of polymers, pigments, fillers, and physical configurations for smoke generation, thermal protection, and ablation.

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III. EXPERIMENTAL

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A. APPARATUS

The design of the apparatus shown in Figure 1 is essentially that suggested by W. H. Hedley in an earlier communication (Ref. 2). Light is furnished by five tubular tungsten filament lamps of 1200 watts nominal output each, mounted in a goldplated reflector. Each lamp is about 6 inches long and 1/2 inch in diameter. The lamps are mounted in two rows of three and two lamps each (Figure 2).

Power for the lamps is furnished by the unit shown on the left in Figure 1. The lamp voltage may be controlled between 0 and 250 volts, while heating time intervals up to 20 seconds, accurate to 0.05 seconds, can be used. The lamps can be run above their rated power level for short periods, and the power supply has sufficient capacity to provide 2400 watts per lamp, or 12,000 watts in all.

Samples to be tested are mounted immediately behind a 3/8 inch hole in a 12-inch square aluminum plate. The hole is bevelled, to give a nearly uniform radiation intensity over the exposed surface. A schematic drawing of the pyrolysis unit is shown in Figure 3 and a photograph of the sample cell is shown in Figure 4.

A photoelectric cell on the side of the aluminum plate opposite the lamps is used to detect the radiation that penetrates a 0.10 inch orifice behind the sample. A type 917 cell is used, the wave length sensitivity of this cell matching the output of the lamps better than most other available tubes. The photomultiplier output is recorded on a Sanborn recorder which can follow changes occurring at a frequency of 10 cycles/second or less.

Many of the samples produce large volumes of smoke. In order to protect the lamps and reflector from damage by this smoke, the front of the sample was covered by a quartz hemisphere of one inch in radius (Figure 3). The volume of this hemisphere was only 30 ml, and the bulk of the smoke was ejected through the viewing port of the sample support assembly into a one liter Kimax flask which provided an additional 7-inch light path for light attenuation.



Figure 1. Overall View of Thermal Radiation Facility



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Figure 2. Close-up of Tungsten Lamps in Reflector Housing



Figure 3. Schematic Drawing of Pyrolysis Unit

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Figure 4. Window Support, Mask, Cavity, Thermocouple, and Orifice As shown in Figure 3, each sample had a 1/8-inch diameter opening concentric with the 1/10-inch diameter opening of the sample support assembly. The light beam to the phototube was thus limited by the 1/10-inch orifice which was unaffected by changes in sample configuration. The sample was supported at its edges between the rim of the 3/8-inch diameter mask opening and the rim of a 7/16-inch diameter cavity in the face of the sample support assembly. This cavity was in the form of a 1/16-inch deep cylinder surmounted by a 1/8-inch deep cone. Its purpose was to isolate the sample from conductive cooling except at the edge of the mask. I

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A 5 mil (36 gauge) chromel-alumel thermocouple mounted in a 30 mil refractory support was inserted protruding just above the conical wall of the cavity. Its position was 0.11-inches behind the rear face of the sample, 1/8-inch from the center line of the assembly (midway between the edge of the mask and the edge of the sample orifice). The time constant of the thermocouple was such that a square wave radiation pulse produced 67% of peak deflection in 0.25 seconds. Cooling was equally rapid, so that the thermocouple measured primarily the heating rate rather than accumulated exposure. The recorded temperature profile then provided information as to all heating and cooling processes taking place during the irradiation pulse.

The calorimeters (Figure 5) used to calibrate the lamps consisted of 3/8-inch diameter curved copper cups coated with platinum black, suspended by .005-inch copper and constantan thermocouple wires behind a gold-plated silver mask. The masks were quite thin, allowing the calorimeters to view essentially the same included angle as the sample. Masks with 1/16-inch, 1/8-inch, and 1/4-inch apertures permitted accurate measurement of a wide range of exposure levels.

Integrated exposure was found to be a linear function of exposure time at each voltage tested (Figure 6). The average flux being 19.2, 15.4, 11.3 and 7.0 calories/sq cm/sec at 250, 217.6, 184.3 and 144 volts, respectively. However, the light output was not a square wave function. Instead, the "tail" exposure, after the excitation of the lamp had ceased, compensated for a heating interval of some two seconds required to reach full power (Figure 7).



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Figure 7. Light Output (Without Shutter). Marks on Baseline Represent 1-second Intervals

Since a 2-second rise time was incompatible with study of smoke generation times of a few tenths of a second, a copper plate hinged at one end was used as a falling shutter after a 2-second warm-up interval. This technique produced a rise time of 0.1 second or less as measured by the phototube, and made the irradiation pulses essentially square waves, since the "tail" exposure did no harm (Figure 8).

B. PROCEDURE

All polymer samples, except the NLABS samples which were already black, were filled with 5% Cr₂O₃. This made the samples at least 99% opaque from 4000-7000 Å and from 1 to 7 microns in a 0.0016-inch film. A 1/8-inch hole was punched or drilled in each sample and the thickness of the samples was measured with a micrometer. Film thicknesses from 0.0013 to 0.070 inch were used.

Samples were positioned in the apparatus as shown in Figure 3. Since removal of smoke and other decomposition products required dismantling the apparatus after each run considerable care was taken to replace the mask exactly one inch from the reflector and to clean the window and smoke chamber well. To reduce effects of minor changes sensitivity of the apparatus (photocell aging and replacement, changes in thermocouple caused by cleaning,

11

etc.) a check irradiation run without a sample was made each time the system was cleaned or altered.

In order to prevent destruction of the lamps by the initial surge of current, the filaments were preheated to a red glow before the start of each irradiation. Thirty seconds were allowed for this preheating, during which the sample was protected by holding the copper shutter in place. After this preheat of the filaments, the appropriate voltage to give the desired flux was applied. The shutter was manually released two seconds after applying the full voltage. This gave time for the filaments to come to temperature and give a square wave to the energy incident on the samples. The lamps were turned off automatically after a preset time. Usually an exposure of four seconds was used.

The radiation passing through the 1/10-inch orifice back of the sample and falling on the photocell 16 1/2-inches back of the sample is automatically recorded as a function of temperature. In those cases where the temperature behind the sample was measured, this temperature was also recorded as a function of time.

C. DATA

The prime data obtained from the experiments was a recording of the transmission as a function of exposure time. Typical recordings are shown in Figure 8. In each case the trace on the left is without a sample and the right hand trace is with the designated material in place. Information that can be derived from these curves are: (a) time for initial smoke formation, (b) mean transmission over the 4-second period, and (c) minimum transmission during the exposure. These data are recorded in Tables 1-9, for the various polymers studied. Different thicknesses were investigated and some materials were studied at different radiant heat flux levels. All samples except the NLABS samples contained 5% Cr₂O₃. Some contained Thermolite RS-31, a stabilizer marketed by Metal and Thermite Company and believed to be dibutyltin mercaptide. The samples designated as irradiated were prepared by exposure to the electron beam from Van de Graaff electron accelerator.

In addition to the radiant energy transmission data, some information on the thermal history back of the sample was obtained by



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Figure 8. Typical Traces from Thermal Radiation Tests

Relative intensity of transmitted light without (at left) and with (right) samples specified. All exposures at 19.2 cal/sq cm/sec. Time marks on lower line represent 1 second intervals.



Polyvinylchloride, 2% Thermolite, 0.0071" Thick

Figure 8 (Cont'd). Typical Traces from Thermal Radiation Tests

Relative intensity of transmitted light without (at left) and with (right) samples specified. All exposures at 19.2 cal/sq cm/sec. Time marks on lower line represent 1 second intervals.

Flux cal/cm ^c /sec	Film Thickness in.	Time for Smoke Formation, sec.	4 Sec.Mean Trans. % of Incident	Min. Trans. % of Incident
15.4	• 0020	-61	64	46
15.4	• 0039	.83	19	77
15.4	.0058	16.	54	33
15.4	.0064	96-	747	. 30
15.4	.0108	1.16	56	38
15.4	-0187	1.27	60	1 1 6
7.0	.0019	1.9	11	45
0.7	0600.	2.1	72	39
0.7	1900.	2.5	87	65
0.7	6110.	3.13	87	38
19.2	-0027	0.51	52	37
19.2	9600-	0.54	62	50
19.2	· 0045	0.62	59	45
19.2	.0080	0.53	59	911
19.2	5110.	0-95	62	50
19.2	.0166	0.83	56	38
19.2	150.	1.00	59	45
19.2	.0527	1.10	59	24
19.2	.0524	1.06	63	49

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Thermal Radiation of Polyvinylidene Fluoride

Table 1

	Flux cal/cm ² /sec	Film Thickness in.	Time for Smoke Formation, sec.	4 Sec. Mean Trans. Ø of Incident	Min. Trans. % of Incident
	19.2	• JO15	0.52	61	40
	19. ∂	. 0027	0.54	59	50
	19.2	• 0039	:0.50	448	38
	19.2	• 3063	01.0	54	45
	19.2	.0100	0.77	58	946
	19.2	.0160	0.75	60	48
	19.2	• 0209	6.0	56	40
	19.2	+tt	6•0	25	777
*	15.4	• 074	1.03	52	35
*	۲.0	020.	3.1	86	35
*	19.2	-0702	0.72	59	45
*	19.2	.0604	0.87	53	41
*	19.2	4170.	.71	51	39

Table 2

Thermal Radiation of Polyvinyl Fluoride

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* Sample contains 1% Thermolite RS-31

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Flux cal/cm ² /sec	Film Thickness in.	Time for Smoke Formation, sec.	4 Sec. Mean Trans. % of Incldent	Min. Trans. ズ of Incident
19. 2	. 1700	0.18	39	Ci ge.
19.2	.0100	0*10	45	37
19.2	44IC.	0.50	48	38
19.2	.0678	0.55	48.5	38
19.2	• 0032	0.27	49	7: 7
19.2	• 0028	0.41	47	1;1
19.2	• 0057	0.41	45.5	<u> 3</u> 0
19.2	.0083	0.51	56	49

Thermal Radiation of Polyvinyl Chloride*

Table 3

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* All samples contain 2% Thermolite RS-31

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Polytetraflucroethylene
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Radiation
Thermal

Sec. Mean Trans. Min. Trans. % of Incident % of Incident	ć 17 62	73 60	83 . 5	76 5.7
Time for Smoke 4 Formation, sec.	2.15	0.5	ı	1.78
Film Thickness in.	. 261	0.0613	.061	• 2590
Flux cm/cm ² /sec	15.4	19.2	19.2	19.2

cm/cm/ bc/	Film Thickness In.	Time for Junke Formation, sec.	T of Inclunt	f of Inclies
19.5	+ 3015		1.34	UL I
19.2	1400.	0.61	75	
19.5	6500.	2.45	5	đ
19.2	.0085	0.45	35	1
1	10101	0.40	44	36
19.5	0850.	0.60	15	u) C
19.2	0980.	0.42	58	1-1
19.2	ST20.	0-85	78	CU •
2.61	.0013	71.0	4.	trt7
19.2	1200.	0.40	40	55
19.2	5400.	0.25	52	39
19.2	.0070	0.27	34	39
3.61 .	.0057	0-27	54	35
19.2	.0016	0.10	75	61
19.2	.0022	0.10	29	52
19.2	.0032	0.70	76	€Ţ
19.2	.0055	0.46	59	Ιt
19.2	.0080	0.57	09	£1
. 19.2	-0575	0.70	7	742
. 19.2	.0552	0.60	\$	34
. 19.2	6100.	0.10	Q.	38
• 19.2	4600.	0.10	65	£4
. 19.2	\$500.	01.0	50	37
. 19.2	1100.	01.0	14	35

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Table 6

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15.4 .0698 0.7 19.2 .0603 0.7 19.2 .060 0.8 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0057 0.4 19.2 .0138 0.4 19.2 .0133 0.4 19.2 .0150 0.4 19.2 .0173 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0052 0.4 19.2 .0052 0.4 19.2 .0052 0.4 19.2 .0050 0.4	rmation, sec.	4 Sec. Mean Trans.	Min. Trans.
19.2 .0603 0.7 19.2 .060 0.8 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0057 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0595 0.4 19.2 .0595 0.4 19.2 .0595 0.4 19.2 .0595 0.4 19.2 .0057 0.4 19.2 .0050 0.4 19.2 .0150 0.4 19.2 .0150 0.4	0.93	57	44
19.2 .060 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0082 0.4 19.2 .0118 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0150 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0150 0.4 19.2 .0057 0.4 19.2 .0052 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4	0.7	25	43
19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0041 0.4 19.2 .0057 0.4 19.2 .0082 0.4 19.2 .0118 0.4 19.2 .0118 0.4 19.2 .0150 0.4 19.2 .0173 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0150 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0056 0.4 19.2 .0056 0.4	0.80	64	53
19.2 .0041 0.8 19.2 .0057 0.4 19.2 .0082 0.4 19.2 .0082 0.4 19.2 .0150 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0056 0.4 19.2 .0150 0.4	0.46	11	56
19.2 .0057 0.4 19.2 .0082 0.4 19.2 .0118 0.4 19.2 .0150 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0173 0.4 19.2 .0057 0.4 19.2 .0057 0.4 19.2 .0052 0.4 19.2 .0052 0.4 19.2 .0150 0.4	0.85	99	74
19.2 .0082 0. 19.2 .0118 0. 19.2 .0150 0. 19.2 .0173 0. 19.2 .0173 0. 19.2 .0173 0. 19.2 .0173 0. 19.2 .0173 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0.	0.43	99	45
19.2 .0118 0. 19.2 .0150 0. 19.2 .0173 0. 19.2 .0173 0. 19.2 .0595 0. 19.2 .0595 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0.	0.48	62	0#
19.2 .0150 0. 19.2 .0173 0. 19.2 .0595 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0056 0.	0.58	63	51
19.2 .0173 0. 19.2 .0595 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0057 0. 19.2 .0056 0.	0.61	60	45
19.2 .0595 0. 19.2 .0057 0. 19.2 .0092 0. 19.2 .0150 0.	0.69	11	59
19.2 .0057 0. 19.2 .0092 0. 19.2 .0150 0.	0.70	61	52
19.2 .0092 0. 19.2 .0150 0.	0.48	59	44
19.2 .0150 0. 19.2 .0606 0.	0.50	52	01
19.2 .0606 0.	0-50	53	38
	0.68	60	84
19.2 .0608 1 0.	0.60	50	54

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* Irradiated, 2.5 x 107 Rads

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Table	

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Thermal Radiation of 6,6-Nylon

Flux cal/cm ^c /sec	Film Thickness in.	Time for Smoke Formation, sec.	4 Sec. Mean Trans.	Min. Frans. % of Incident
19.2	.0088	0.50	68	36
1 CJ 6T	.0108	0.57	48	CI M
19.2	.0166	0.67	53	36 8
19.2	.0206	1.01	54	3.7
19.2	.0227	06.	611	33
19.2	• 013	-82	52	37
+ 19.2 • 19.2	0010.	0.72 0.72	58 58	41 37

* Irradiated, 2.5 x 107 Rads

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Table 8

Thermal Radiation of Polymethyl Methacrylate

Flux cal/cm ^c /sec	Film Thickness in.	Time for Smoke Formation, sec.	4 Sec. Mean Trans. \$ of Incident	Min. Trans.
19.2	.0566	0.85	76	58
19.2	.0020	0.43	87	84
19.2	.0033	0.60	96	95
19.2	1800.	0.52	62	61
19.2	-0102	.58	п	611
19.2	1610.	-56	44	61
19.2	1910.	.78	76	56
19.2	-0202	.68	11	57
19.2	-0557	-75	69	44
19.2	.0567	.58	87	73

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Table 9

Thermal Radiation of Miscellaneous Polymers

m ² /sec	Film Thickness in.	Time for Smoke Formation, sec.	4 Sec. Mean Trans. % of Incident	Min. Trans. % of Incldent
		Polyacrylon1tr11	e	
	0.0165	06.0	51	04
	0.049	0.84	53	14
	0-025	0.90	53	14
	Polyacrylo	nitrile, Irradiated,	2.5 x 107 Rads	
	0.0156	0.77	54	37
, CI	0.0682	04.0	11	59
		Polyurethane Fo:	퇴	
	0.100	60.0	43	34
	0.100	0.12	50	38
		NLAB Sample No.	61	
01	0.016	0.07	1ħ	36
QI.	0.016	90.0	40	36
		NLAB Sample No.	0	
Ċ.	0-013	0.05	43	Ctt
CU	0.013	10.07	39	32

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recording the output from the thermocouple located behind and in the shadow of the sample but not touching the sample. This information is secondary to the light transmission data and was included primarily because it could be readily obtained simultaneously and hopefully could give further leads and insight into the complex picture of thermal protection. 1

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Typical temperature histories are shown in Figure 9 and additional data in Tables 10 and 11.



Teflon



Polyvinyl Fluoride



Polyethylene



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Polyvinylidine Fluoride



Irradiated Polyethylene



Irradiated Polystyrene



Polystyrene

Figure 9. Temperature Behind Thick (>0.05") Samples. All Exposures at 19.2 cal/sq cm/sec.

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Material	Thickness in.	Max.Temp. °C	Test Duration	Time for Max.Temp.
Teflon	• 059	68	18	18
PVF2	·052	80	18	18
_{PVF} (1)	.071	84	13	1.8
PE(2)	•060	63	8	8
PE	.060	120	13	8
_{PS} (2)	.060	62	8	8
PS	.058	110	13	9

Temperature Behind Thick Samples Exposed to 19.2 cal/cm²/sec

(1) Containing % "Thermolite RS-31"
(2) Irradiated, 2.5 x 107 Rads

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Temperatures	Behind	Exposed	(19.2 cal	/cm ² /sec) Samples

	Т	lime to Re	ach ΔT	
Material	Thickness in.	ΔT=30°C sec/mil	ΔT=60°C sec/mil	ΔT=90°C sec/mil
Polyethylene	0.0603	0.022	0.069	0.091
Polyethylene ⁽¹⁾	0.0606	0.098	0.125	0.136
Polystyrene ⁽¹⁾	0.0575	0.093	0.117	0.150
Polytetrafluoroethylene	0.0613	0.032	0.284	0.34
Chlorinated Polyvinyl Chloride	0.0682	0.029	0.341	0.51
Polymethyl Methacrylate	0.0557	0.094	0.111	0.107
6,6-Nylon ⁽¹⁾	0.011	0.111	0.126	0.159
6,6-Nylon	0.011	0.022	0.112	0.123
Polyacrylonitrile	0.017	0.077	0.122	0.140
Polyacrylonitrile ⁽¹⁾	0.016	0.045	0.093	0.125
Polystyrene	0.010	0.054	0.075	0.102
NLAB Sample 2	0.016	0.008	0.014	0.024

(1) Irradiated, 2.5 x 10⁷ Rads
(2) Contains 2% Thermolite RS-31

IV. DISCUSSION OF RESULTS

A. SMOKE GENERATION TIME

As pointed out previously one of the major objectives of this part of the work was to determine if smoke can form sufficiently rapidly on degradation of polymers by thermal radiant energy to give protection by attenuation of the incident radiation. The apparatus was designed primarily to measure the time for formation of the first detectable smoke. It can be seen from the typical recorder traces shown in Figure 8 and the data in Tables 1-9 that under a flux of 19.2 cal/cm²/sec smoke formation usually starts in less than a second and in some cases in less than 0.1 seconds. At the 19.2 cal/cm²/sec flux the NLAB samples produced smoke before the photocell registered the peak output of the incident beam. A polyurethane foam gave smoke in 0.09 sec. Polystyrene and polyvinyl chloride, each containing Thermolite RS-31 (believed to be dibutyltin mercaptide), showed attenuation in less than 0.20 sec.

The time required to produce smoke was found to be a function of both the thickness of the polymer film and the radiant flux level. The higher flux levels and the thinner films produce smoke more rapidly. This is shown for polyvinylidene fluoride in Figures 10 and 11. Figure 10 also shows that as the flux level increases, the influence of film thickness on smoke formation time decreases.

Thermolite RS-31, a commercial polyvinyl chloride stabilizer, was used to stabilize some of the halogen containing polymers during compounding and molding. It appeared that these samples had unusually short smoke formation times. This additive was then incorporated in polystyrene. Although the data are somewhat erratic the incorporation of the additive gave reduced smoke formation times.

B. ATTENUATION OF RADIANT FLUX

Several factors are involved in effective protection by smoke formation. These include time to start of smoke formation, rate of smoke formation, opacity of the smoke and duration of the smoke. The 4-second mean transmission and minimum transmission



Smoke Generation Time vs Sample Thickness Figure 10. I

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data obtained are indirect measures of these factors. Using data from the 19.2 cal/cm²/sec exposures the materials tested can be placed in three general categories on the basis of this test. This is summarized in Table 12. The low level of smoke formation from polytetrafluoroethylene and polymethyl methacrylate is consistent with the data obtained (Ref. 1) by the hot filament technique and is consistent with the known mechanism of degradation of these polymers. Contributing to the low level of smoke from polytetrafluoroethylene is the thermal stability of this polymer and the relatively low extent of degradation that probably occurred at this flux level and duration. The low level of smoke from chlorinated polyvinyl chloride means that degradation of this polymer probably occurs primarily through loss of HCl leaving a carbonaceous residue. This is known to occur with polyvinylidene chloride (Ref. 3).

Since structurally the urethane is so similar to the nylon, the high efficiency of the urethane foam is attributed to the physical structure (foam) rather than the chemical nature.

C. THERMAL HISTORY BEHIND SAMPLES

A thermocouple was installed in the shadow of the sample but not touching the sample as shown in Figure 3. It was hoped that the temperature history would give additional information on the nature of the thermal protection obtained with different polymers. This back-side temperature measurement should not be confused with the ΔT measurements as run in previous studies by the Quartermaster Corp (Ref. 4). In the QM tests the thermocouple touched the back of the sample in the center and there was no hole in the sample. Gases from the decomposition of the polymer could not contact the thermocouple to cool or heat it. The results from the temperature measurements in the current study are difficult to interpret. Temperature can be influenced by heating or cooling by the gases of decomposition as mentioned above and also, with some polymers, by the enlargement of the hole on heating with resulting exposure of the thermocouple to the radiant source.

The order of effectiveness of various materials in preventing temperature rise behind the sample depends greatly on the level of temperature rise selected as a criteria. For example, some samples reach $\Delta T=30^{\circ}$ C slowly, apparently because of endothermic decomposition, but are consumed or melted rapidly and thus $\Delta T=60^{\circ}$ C

Table 12

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Effectiveness of Various Polymers

<u>Class 1</u>: 40-45% 4-sec mean transmission 30-40% minimum transmission

NLAB samples Polyurethane foam

Class 2: 45-70% 4-sec mean transmission

35-50% minimum transmission

Polyvinylidene fluoride Polyvinyl fluoride Polyvinyl chloride 6,6-Nylon Polyacrylonitrile Polyethylene Polystyrene

Class 3: 70-96% 4-sec mean transmission

50-70% minimum transmission

Polytetrafluoroethylene Polymethyl methacrylate Chlorinated polyvinyl chloride

and $\Delta T=90^{\circ}C$ are reached relatively quickly. Other samples, possibly by exothermic decomposition, result in a $\Delta T=30^{\circ}C$ quickly but may not decompose completely or melt and thus require sustained exposure to reach $\Delta T=90^{\circ}C$.

The order of decreasing performance at three different ΔT levels is shown below:

Δ T= 30°C	<u>ΔT=60°C</u>	<u>ΔT=90°C</u>
Irradiated nylon	Chlorinated polyvinyl chloride	Chlorinated poly- vinyl chloride
Irradiated polyethylene	Polytetrafluoro- ethylene	Polytetrafluoro- ethylene
Polymethyl methacrylate	Irradiated nylon	Polyvinyl fluoride
Irradiated polystyrene	Irradiated poly- ethylene	Irradiated nylon
Polyacrylonitrile	Polyacrylonitrile	Irradiated poly- styrene
Polyvinyl chloride	Irradiated polystyrene	

The materials with the best performance at $\Delta T=90^{\circ}C$ are those which, under the conditions used, leave the largest residue and thus probably do not expose the thermocouple to the incident radiation.

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V. RECOMMENDATIONS

Based on the present investigation the following two areas of study appear promising for further study:

Foams - Since smoke formation time was shown to decrease with decreasing film thickness, and since a foam can be considered as a self-supporting array of thin films, and also since a polyurethane foam showed rapid smoke generation on thermal radiation, it is recommended that further tests on foams for thermal protection by smoke attenuation be made. Foams offer the additional possible advantage of giving a self renewing surface of thin films and thus might operate over prolonged or repeated exposure. Foams also offer the advantage of low thermal conductivity and light weight.

Additives - It should be possible to increase the rate of smoke formation, the smoke density and smoke duration by use of chemical additives.

VI. REFERENCES

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Authors

J. M. Butler, W. E. Weesner

Preparation of Fluorinated Olefins

I. INTRODUCTION

A sample of 1,1,3,3,3-pentafluoropropene was requested by the U. S. Army Natick Laboratory for use in related in-house research.

II. SUMMARY AND CONCLUSIONS

A procedure for the preparation of 1,1,3,3,3-pentafluoropropene was developed. It involves the non-catalytic addition of trifluoromethyl iodide (CF₃I) to 1,1-difluoroethylene (CF₂=CH₂) to form 1,1,3,3,3-pentafluoropropyl iodide. This intermediate is then dehydroiodinated by heating with lithium chloride in dimethylformamide to yield the desired clefin. The product obtained contained 9.1 more CF₃I as determined by mass spectroscopy.

Attempts to promote the addition of CF3I to $CF_2=CH_2$ catalytically were unsuccessful The ultraviolet light-induced reaction of these materials as atmometric pressure was also unsuccessful.

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III. RESULTS AND DISCUSSION

A. PREPARATION OF 1, 1, 3, 3, 3-PENTAFLUOROPROPIL LODIDE

The preparation of this material is described by Haszeldine and Steele, J. Chem. Soc. <u>1954</u>, 923-25. They reacted a 1:1 mole ratio of trifluoromethyl iodide and 1,1-difluoroethylene under pressure in silica glass in the presence of UV light for four days to get an 83% yield of the desired iodide. An attempt to duplicate these results at atmospheric pressure was unsuccessful.

Attempts to promote the free radical addition of trifluoromethyl iodide to 1,1-difluoroethylene catalytically are summarized in Table 13. In several of these runs, excessive amounts of 1,1difluoroethylene resulted in lower than desired ratios of iodide to olefin. Even in runs where the ratio reached 1 or over, however, the only product appeared to be polyvinylidine fluoride. This shows that, at the temperatures employed, the chain transfer constant of trifluoromethyl iodide for a vinylidine fluoride radical is low compared with the propagation rate constant. In other words, reaction (1) is highly favored over reaction (2).

$$R-CH_2-CF_2 + CH_2=CF_2 \rightarrow R-CH_2-CF_2-CH_2-CF_2 \cdot (1)$$

$$R-CH_2-CF_2 + CF_3I \rightarrow R-CH_2-CF_2I + CF_3$$
 (2)

The addition of trifluoromethyl iodide to 1,1-difluoroethylene by heating in the absence of catalysts was then studied and the results are summarized in Table 14. The reaction proceeds too slowly at 190°C, but at 200-220°C the rate is sufficient to react all of the olefin in about 24 hr. 1,1,3,3,3-Pentafluoropropyl iodide and higher boiling products are obtained in this reaction. The higher boiling materials are undoubtedly telomers containing more than one 1,1-difluoroethylene moiety for each trifluoromethyl iodide molecule. These telomers on dehydroiodination would lead to higher homologs of the fluoro-hydro olefins.

$$CF_3-CH_2-CF_2-CH_2-CF_2I \xrightarrow{-HI} CF_3-CH_2-CF_2-CH=CF_2$$

The ratio of residue to product and the yield of product are very dependent on the charge ratio of iodide to olefin. Large excesses of trifluoromethyl iodide are required for the lowest residues and best yield.

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	and CF2=CH2
	CF3I
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Table	Reaction
	Radical
	Free

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Results	
Reaction Conditions Temp. Fress. Time °C psi hr.	
Charge Catalyst Charge moles moles moles	

hr.	4.2 Trace of polyvinyidene fluoride	20 No reaction	20 5g viscous oil obtained	20 12.3g liquid recovered.Mostly heptane	ob could molywinvidence fluoride in water	
ps1	1000	500	650	003	2	100
Juo	70-80	75-30	100	0	00	70
moles	0.235	0.144	0.342		12.0	0.396
CF2=CH2 moles	1.46	0.36	0.422		0.251	0.36
Catalyst	AZHN(1)	NELY	ALLAN CONTRACTOR	Henzoyi peroviue	AZBN (1.0g)	K persulfate (0.1g)
JEN	of an		20622	26962	26907	26913
Run No.	.	-	C1	4	5(2)	6(3)

Azoblaisobutyronitrile 333

10 ml heptane solvent added

25 ml of aqueous sol'n containing $\mathrm{KH}_2\mathrm{PO}_4\mathrm{and}$ MaOH added

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Tab	Reaction
	Thermal

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Part of Re-10.1	Proluct	5.44	2.5		1.22	1.57	1.84	1.54	1.27
Results	(1)×	a.	17.4	re disk.	30*2	23-2	25.2	6*12	27.6
		† •[†	24.8	Pin hole leak in ruptu	30-0	25.1	47.9	، 13- د	53.0
	NT. Craundurat	7.6	e		24.6	16.0	26.0	28-3	16.5
Reaction Conditions	hr.	8 0 00	1 9	-1	30	59	27	'2 L	63 67
	Press ps1	8.68 8.68 8.68	150	1500	1300	1000	1550	1500	1100
	Temp.	220 220 220	190 200	002	200	5 00	200	200	200
Charge	Mole CF3I Ratio <u>CF2=CH2</u>	ن* 8ر	1.43	. 1.36	2.52	0.0	1.82	5 •3 6	2.7
	CF3I moles	0.398	0.29	0-90	0.79	0.53	0.82	3.32	0.633
	CF_=CH_ mõles	0.358	. 0• ≥03	0.47	0.313	0.255	0.45	0•39	0.234
	NBP	26903	21915	816-8	26919	26921	26922	2£927	62692
	Run No.	1	AI.	m	-1	5	י ני	2	αO

(1) Based on $CF_{c^2} = CH_2$

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B. PREPARATION OF 1,1,3,3,3-PENTAFLUOROPROPENE

The preparation of this material is also described by Haszeldine (op.cit.) who prepared it in 85% yield by dehydroiodination of 1,1,3,3,3-pentafluoropropyl iodide over powdered KOH. It is also described by Henne and Waalkes [J. Am. Chem. Soc. <u>68</u>, 496 (1946]7.

The procedure we chose for dehydroiodination /Hauptschein and Oesterling, J. Am. Chem. Soc. 82, 2868 (1960/ involves reaction of the iodide with lithium chloride in dimethylformamide. Much better yields are claimed for this novel elimination reaction than are generally obtained by the conventional treatment with alcoholic or aqueous potassium hydroxide. The reaction proceeded very smoothly and the yield of material obtained after washing with aqueous sodium carbonate and drying was 89% of theory.

Subsequent analysis by mass spectroscopy showed the material to contain 9.1% mole-% of trifluoromethyl iodide as impurity. It is difficult to explain the presence of this material, since distillation of the intermediate pentafluoropropyl iodide should have removed it completely. Separation of $CF_{3}I$ from $CF_{3}CH=CF_{2}$ may be difficult by conventional methods, since the boiling points are -22.5°C and -21°C respectively.

IV. EXPERIMENTAL

A. PREPARATION OF 1,1,3,3,3-PENTAFLUOROPROPYL IODIDE

$$CF_3I + CF_2=CH_2 \xrightarrow{\Delta} CF_3CH_2CF_2I$$

A 300 ml stainless steel Aminco autoclave was sealed and a valvegauge-rupture disk assembly (Aminco No. 20-4754) attached. The autoclave was evacuated, pressured to 1500 psi with nitrogen to test for leaks, evacuated again with an oil pump and cooled in dry ice. Trifluoromethyl iodide (155g., 0.79 moles) was then added from small lOOg cylinders. Then 1,1-difluoroethylene (20g., 0.313 moles) was pressured in. The autoclave was heated and rocked at 200°C for 30 hr as the pressure fell from 1300 psi to 760 psi.

After cooling to room temperature, the bomb was vented through a dry ice cold-trap where 107g of pink liquid collected. This was assumed to be recovered trifluoromethyl iodide. The autoclave was cooled slightly, opened, and a deep red liquid weighing 65.2g poured into a cooled distilling flask.

This crude liquid was distilled through a 2 ft Vigreux column to give 24.6g of pink liquid boiling at 71-73°C, N5⁵ 1.3715. This represents a 30.2% yield of 1,1,3,3,3-pentafluoropropyl iodide based on vinylidene fluoride. The higher boiling residue weighed 30g and 7.5g of additional CF₃I was collected in the cold-trap.

B. PREPARATION OF 1,1,3,3,3-PENTAFLUOROPROPENE

 $CF_3CH_2CF_2I + LiCl \xrightarrow{DMF} CF_3CH=CF_2 + HC1 + LiI$

The procedure followed is that of Hauptschein and Oesterling, J. Am. Chem. Soc. <u>82</u>, 2868-71 (1960).

A 500 ml, 4-necked flask was equipped with a stirrer, thermometer and 1-ft Vigreux column. The column was fitted with an icecooled condenser and the vapor line from the condenser ran to a dry-ice cooled cold-trap.

The flask was charged with 250 ml of dimethylformamide and then 28g (0.66 mole) of lithium chloride was added. Heat of solution raised the temperature to about 45°C. Then 100g (0.385 mole) of 1,1,3,3,3-pentafluoropropyl iodide was added over 5 min. The pale yellow solution (some LiCl not dissolved) was then heated slowly to 150°C. At 98°C (25 min after heating started), liquid began collecting in the dry-ice cold-trap and also refluxing from the ice cold condenser. At 115°C (1 hr reaction) the DMF solution was very dark brown and this color gradually faded to pale yellow as the temperature reached 143°C after 2.6hr. Most of the reaction was probably over by this time, but heating at 150-157°C was continued an additional hour.

The crude liquid in the dry-ice cold-trap (50.5g) was allowed to distill slowly through a fritted glass gas bubbler into 400 ml of 5% Na₂CO₃ to remove any HCl, HI, or HF present. Then the gas was passed through a Drierite drying tower and recondensed in a dry-ice cold-trap. The weight of purified product in the cold-trap was 45.3g, representing an 89% yield.

Analysis by mass spectroscope showed the product to contain 9.1 mole-% trifluoromethyl iodide and a trace of the pentafluoro-propyl iodide.

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