

Protection Against Intense Light.

I. Discussion of the Usual Mechanisms of Energy Dissipation

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Synopsis

The relative thermal protection offered by a series of halogenated vinyl polymers is discussed in terms of the usual modes of energy attenuation and dissipation, such as reflection, endothermic decomposition, etc. It is shown that none of these modes is so overwhelming that it alone can account for the relative thermal protection offered by these polymers.

INTRODUCTION

Of the energy emitted from a thermonuclear air-burst, about one third is radiated in the form of light and heat rays. Although this intense energy is distributed over a wide area, it is still sufficient, in the case of a 1-megaton weapon, for example, to inflict first- and second-degree burns at slant ranges of 14 and 11 miles, respectively, and to ignite newspapers at a slant range of 9 miles.¹ In contrast, the lethal radii of gamma and neutron radiation and blast overpressure are about 2 miles. Since the area threatened by the thermal radiation is about 30 times larger than the area threatened by high-energy radiation and blast overpressure, a system which could provide significant protection against thermal radiation alone is certainly worthwhile. Of course, burns will not be eliminated entirely, but burn severity and ignition of property throughout the area would be considerably reduced. The mass and expense factors involved should be so low that the system can be applied liberally to just about anything, i.e., as a finish on clothing, as a coating or paint on buildings, as a cosmetic on the skin, etc.

The search for such a system has gone on for many years and much data have been accumulated. From studies of this information and from observations made during the tests in the arc-image furnace, it was felt that (a) since some materials provide markedly better thermal protection than others, a particular mechanism of energy dissipation may exist which is exceptionally efficient, and (b) since good thermal protection is usually accompanied by the emission of quantities of smoke and/or gaseous decomposition products during the test, energy attenuation by smokes and/or gaseous decomposition products may be an important route.² Of all the data, observations, deductions, conclusions, and suggestions amassed, these

two appear to be the best premises on which to base further reasoning. The converse of (b), that copious quantities of smokes and gaseous decomposition products necessarily provide good thermal protection was observed to be false (see 5 below). It was hoped that if an exceptionally good mechanism of thermal protection exists, it might provide a high degree of protection against the intense light energy of a thermonuclear explosion—and also meet the weight and cost requirements which would permit its practical use.

Certainly, if one is trying to establish the cause for a difference in performance, it will be easier to detect this cause if materials at the extremes of behavior are included in the comparison. Of the numerous materials tested, some halogenated vinyl polymers have shown excellent and some quite poor thermal protection. In fact, it was established by Barnes and Yelland³ that of the polymers poly(tetrafluoroethylene) (Teflon), poly(trifluoroethylene) (PVF₃), poly(vinylidene fluoride) (PVF₂), poly(vinyl fluoride) (PVF), polyethylene (PE), poly(chlorotrifluoroethylene) (Kel-F), and poly(vinyl chloride) (PVC), PVF₂ gave the best thermal protection and Teflon the poorest. The thermal protection provided by each polymer was determined by preparing 10 discs, 0.060 in. thick and 2 in. in diameter, containing 5% powdered Cr₂O₃ (Cr₂O₃ is green; several of these polymers after molding are transparent when pure), exposing them to a single elliptical, carbon arc-image furnace at an irradiance level of 23 cal/cm² for 1 sec, and measuring the maximum temperature rise (ΔT in °C) above ambient by means of a thermocouple placed on the rear surface (opposite to the surface exposed to the carbon arc) of the disc. The average ΔT value as well as additional information to which reference will be made later are given in Table I. The frequency of ignition was obtained by dividing the number of discs which ignited during exposure by 10 and then multiplying by 100.

The carbon arc-image furnace was a modified U.S. Navy searchlight.⁴ The parabolic mirror was replaced with an elliptical mirror with the carbon electrodes at one focus and the sample disc held vertically in the other. The major axis of the ellipse was horizontal, with shutters situated between the foci and close to the sample. The shutters were opened and closed with a timing device. The sample holder included a thermocouple connected to a strip-chart recorder which registered not only the output of the thermocouple but indicated the precise times at which the shutters opened and closed.

The usual routes or mechanisms of attenuation and/or dissipation of impinging light energy are as follows:

1. Reflection at the surface of the polymer and, since many of the molded polymers are transparent when pure, at the interface between the polymer and a powdered additive (with a different refractive index).
2. Absorption causing the temperature of the polymer disc to rise.
3. Absorption and dissipation of heat: (a) endothermic decomposition; (b) loss of high temperature material (pyrolysis products); (c) change in phase; (d) cooling via convection.

4. Absorption and reradiation.

5. Scattering by particulate matter, usually dark in color (smoke).

The object of this report is to show that none of these avenues of energy attenuation can, singly, account for the relative ΔT values listed in Table I and hence that none dominates the others or combinations thereof. To establish this, three more criteria besides the known properties of the polymers are used. These are: (a) the discs of each polymer have the same reflectance at the start of each pyrolysis experiment; (b) as the temperature of the Cr_2O_3 rises, it is assumed that the surfaces of the discs degrade and blacken in the order of their decomposition temperatures (20%) (see Table I); and (c) it is also assumed that the surfaces of the charred polymers are predominantly carbon and, since these are all halogenated vinyl polymers, that all the charred materials have substantially the same physical properties, e.g., reflectance, thermal conductivity, heat capacity, and emissivity. The charring was thickest at the centers of the discs.

TABLE I
Polymers and Their Performance in the Carbon Arc-Image Furnace
Arranged in the Order of Their Temperatures of Decomposition (20%)

Polymer	Repeating unit	Av. ΔT , °C	Freq. of Ign., %	Temp. at which decomp. is 20%, °C
Poly(vinyl chloride) (PVC)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$	22.3	100	230
Poly(chlorotrifluoroethylene) (Kel-F)	$\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$	13.0	0	360
Poly(vinyl fluoride) (PVF)	$\begin{array}{c} \text{F} \quad \text{Cl} \\ \quad \\ \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$	16.8	100	375
Polyethylene (PE)	$\begin{array}{c} \text{H} \quad \text{F} \\ \quad \\ \text{H} \quad \text{H} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$	19.2	100	394
Poly(trifluoroethylene) (PVF ₃)	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$	11.3	0	398
Poly(vinylidene fluoride) (PVF ₂)	$\begin{array}{c} \text{H} \quad \text{F} \\ \quad \\ \text{H} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \end{array}$	10.8	50	434
Teflon (PVF ₄)	$\begin{array}{c} \text{H} \quad \text{F} \\ \quad \\ \text{F} \quad \text{F} \\ \quad \\ -\text{C}-\text{C}- \\ \quad \\ \text{F} \quad \text{F} \end{array}$	36.3	0	496

ENERGY DISSIPATION BY THE POLYMER DISCS

The dissipation of the energy from the carbon arc-image furnace by the polymer discs according to the routes listed above will now be discussed. It may be that one of these routes, perhaps endothermic decomposition, overwhelms the remaining routes of energy dissipation or attenuation, so that the relative ΔT values of the various polymers can be explained as resulting from variations in the degree of the endotherm. To check this possibility, each route in turn will be assumed to overwhelm the others. The consequences of this assumption will then be compared with the ΔT values in Table I, and the assumption will be accepted or rejected.

Of course, most if not all of the avenues of energy dissipation will be simultaneously operative, and their simultaneous consideration may be required to clarify the ΔT values. This approach is scarcely feasible, however. In the first place, it would require a quantitative evaluation for which the data are not available, and in the second place, if one of the routes is preponderant, then there is no need for the simultaneous consideration of all the factors. For seven polymers, there are 7!, or 5040, different orders into which their ΔT values can be arranged, one of which is given, of course, in Table I.

Reflection of the Light

Since all of the polymer discs were compounded with 5% Cr_2O_3 and were therefore green, their reflectances (400–700 $m\mu$) were substantially the same at the start of each pyrolysis experiment, about 35%. When carbonaceous material formed on the surface, the reflectance decreased from 35% to about 7% in all cases except Teflon. If reflectance were a major factor, then PVC should have had the highest ΔT value and Teflon the lowest; the remaining polymers should be in much the same order as in Table I, since the PVC surface blackens first and Teflon last. Since the surface of the Teflon was only "slightly blackened"⁵ whereas the central region of the surfaces of the other polymer discs were quite black at the end of the test, it is obvious that reflectance is not a major factor.

Absorption Causing the Temperature to Rise

The final temperature of the discs, and their ΔT values, will depend on the product of the specific heat and density of each disc, since all the discs have the same volume. These values and thermal conductivities are given in Table II.

Since the amounts of energy absorbed by these polymers should be in the same order as that in which their surfaces blacken, Kel-F > PE > Teflon, and the heat required to raise the temperature of 1 cc of each polymer 1°C is in the order Kel-F < PE < Teflon, their ΔT values should be in the order Kel-F > PE > Teflon, but they are not. The specific heat of the polymer is, therefore, not a dominant factor in the dissipation of the impinging energy.

TABLE II
Heat Required to Raise the Temperature of 1 cc of Polymer 1°C
(in cal/°C-cc)

Polymer	Specific heat ^a cal/°C-g	Density, ^a g/cc	Heat required, cal/°C-cc	Thermal conductivity ^a cal/sec/cm ² /(°c/cm)
PVC	0.4	1.2	0.48	$3-7 \times 10^{-4}$
Kel-F	0.22	2.1	0.46	$5-6 \times 10^{-4}$
PVF
PE	0.55	0.91-0.97	0.51	$8-12 \times 10^{-4}$
PVF ₃
PVF ₂	0.33	1.77	0.58	3×10^{-4}
Teflon	0.25	2.13-2.22	0.54	6×10^{-4}
Graphite ^b				$4.4-31 \times 10^{-4}$
Charcoal ^b				1.3×10^{-4}

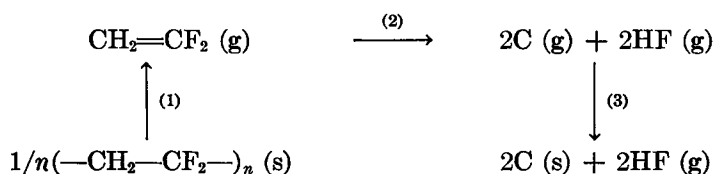
^a Plastics Properties Chart, *Modern Plastics Encyclopedia*, 1963-64, Modern Plastics, New York, 1963.

^b *American Inst. of Physics Handbook*, McGraw-Hill, New York, 1957, pp. 4-68, 69.

Absorption and Dissipation of Heat

Endothermic Decomposition

The primary degradation process for PVF₂ is decomposition to char (primarily carbon) and HF. Certainly much carbonaceous material and HF are produced.⁶ Stepwise, this process can be represented as



The enthalpy changes are as follows:

Step 1: Heat of formation of the monomer (-77.5 kcal/mole)⁷ minus heat of formation of the polymer (-113.3 kcal/mole)⁸ = +35.8 kcal/mole.

Step 2:

$$\begin{array}{r}
 2 \text{ C-H} = 197.4^9 \\
 1 \text{ C=C} = 145.8 \\
 2 \text{ C-F} = \underline{232.0} \\
 + 575.2 \text{ kcal/mole} \\
 2\text{HF} = -269.2^9 \text{ kcal/mole}
 \end{array}$$

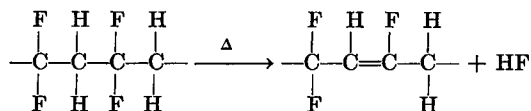
Step 3: Twice the heat of condensation of carbon = -343.4 kcal/mole.¹⁰ The overall enthalpy change is:

$$35.8 + 575.2 - 269.2 - 343.4 = -1.6 \text{ kcal/mole.}$$

The reaction is slightly exothermic. However, since the errors in some of the values used are probably several kcal/mole and since the enthalpy changes

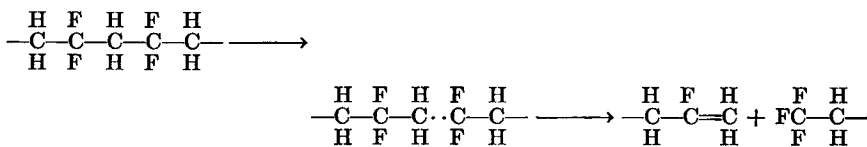
to be computed next are much larger, degradation solely to C and HF will be considered energetically neutral.

If HF splits off the chain with the formation of a double bond,⁶ the enthalpy change for the second mechanism of decomposition is as follows:



$$\Delta H = +16.9 \text{ kcal/mole of HF formed}$$

The third mode of degradation is to low molecular weight species by homolytic dissociation and disproportionation⁶:



$$\Delta H = +19.4 \text{ kcal/mole of decomposition products.}$$

Note that the number of C—H and C—F bonds have not changed, and hence the third mode of degradation will be endothermic by 19.4 kcal/mole, irrespective of the polymer involved. If the overall degradation were exothermic, the ΔT value of PVF₂ should be greater than that of Teflon, because the surface of the PVF₂ disc blackens first and should thereby absorb more energy than the Teflon disc, and because energy is released during the exotherm. The overall decomposition of PVF₂ is, therefore, endothermic.

Since the front surface of the PVF₂ disc must reach 430°C, and since the ΔT 's for PVF₃ and PE are higher, the front surfaces of discs of PVF₃ and PE also should reach this temperature (based on the similarity in surface properties before and after decomposition). At about 430°C, 94% of a sample of PE volatilizes, of which 97% is lower molecular weight material.⁶ Decomposition of PE is then primarily by the third mode and is endothermic by 19.4 kcal/mole of decomposition products. A mole in this case simply amounts to 6.023×10^{23} molecules of any and all kinds that are formed by the third mode of degradation. At about 430°C, 98% of a sample of PVF₃ volatilizes, of which 94% is lower molecular weight material.⁶ Hence, PVF₃ decomposes primarily by the third mode. PVF₃ does yield some HF, indicating that there is some degradation by the first and second modes of decomposition; however, these can be ignored because the amount of material decomposed by the second mode is less than 6% and decomposition by the first mode is energetically neutral. As stated earlier, the primary mode of decomposition of PVF₂ is to C and HF, which is energetically neutral. Hence, if the enthalpy change during degradation is a major factor, the ΔT for PVF₂ should be above those of PVF₃ and PE and the ΔT 's for PVF₃ and PE should be close, but neither is the case. However, the ΔT 's for PE, PVF₂, and PVF₃ should all be less than that of Teflon, and this is

true. Hence, endothermic decomposition is probably a factor, even though it does not explain the sequence of the ΔT values in Table I.

If the heat derived from the burning of the decomposition products of PE and PVF₂ were a major factor, then PVF₃, Teflon, and Kel-F would have the lowest ΔT 's; this is not the case. If reaction between HF and Cr₂O₃ were a major factor, the ΔT of PVF₂ would be among the highest, since PVF₂ yields by far the most HF.

Chromium trioxide may have a catalytic effect on, react with, and react with the decomposition products of some polymers during pyrolysis.¹⁵ These effects could seriously affect the rates of decomposition and should be taken into consideration. Since the energy removed by many mechanisms is equal to the product of the energy removed per gram of decomposition products times the rate of decomposition in grams per second (exposure time is 1 sec in all cases), comparison among the different polymers of the energy attenuated via each mechanism does include the rate factor where applicable. It is not enough to compare the rates alone, since the rate may be quite high, whereas the energy attenuated by the various mechanisms operating could be quite low.

Loss of Material at High Temperatures

During irradiation of the discs by the carbon arc-image furnace, quantities of material "erupt" from the surface of the discs (except Teflon). Particulate matter carries away heat energy. As the gaseous decomposition products expand, they perform work against the atmosphere. For PVF₂, the volume of gas is estimated to be almost $\frac{1}{2}$ liter, and hence the energy involved is somewhat less than $\frac{1}{2}$ liter-atm (12.1 cal). This amount is hardly negligible compared to the energy received, 23 cal, during the 1-sec exposure. If this energy (heat) loss plus the loss of hot fragments were a major factor, one would expect that all of the polymers which behave similarly, i.e., all except Teflon, would have lower ΔT 's than Teflon, which is the case. The order of the ΔT values would be clarified if the weight losses of the various polymer discs used in these tests were inversely proportional to the ΔT values, but the weight losses were not reported.³ However, since the decomposition temperatures and weight losses of PVF₃ and PE are close,⁶ their energy losses and hence ΔT values should also be close. This is not so.

PVF₃, PE, and PVF all show much greater weight losses than does PVF₂⁶ and should therefore have lower ΔT values than PVF₂; however, the opposite occurred. The loss of energy via expelled decomposition products is a factor; from the evidence available, however, it does not appear to explain the relative ΔT values, and hence it is not a determining factor.

Change in Phase

Some of the polymers are partially crystalline, and a portion of these crystallites will melt. The expulsion of any monomer or telomer present would also require energy. Since the polymer discs were all quite hard, one would

expect the concentration of monomer and telomer to be quite low, certainly less than 10%. Although there is no reason to believe that any one polymer had an unduly high concentration of monomer or telomer compared to the others, let us make this assumption and determine the energy involved. The maximum loss in weight for any of the polymer discs during pyrolysis in the carbon arc-image furnace was less than 50 mg. The heat of vaporization of most organics is less than 200 cal/g. The energy involved is then about $0.05 \times 0.10 \times 200 = 1$ cal. The combined endotherm is then undoubtedly small compared to the energy received, 23 cal, and will be ignored.

Cooling Via Convection

Newton's law of cooling states that the rate of loss of heat is directly proportional to the difference between the temperature of the surface of the disc and the ambient temperature, which in this case is room temperature. At the end of the 1-sec exposure to the arc, assume that the temperatures at the front and at the rear surfaces of the discs were in the same order as in Table I. By Newton's law of cooling, at any later time the temperatures of all the surfaces would be lower; however, they would be still in the same order. (It is assumed that the amount of heat that must be removed to lower the temperature of 1 cc of each polymer one degree is the same which is essentially the case, Table II). Therefore, cooling by convection does not affect the relative ΔT values and hence cannot change them. As a result, since PVC blackens first, it will absorb the most energy, and its ΔT should be the highest and the ΔT values should decrease somewhat regularly with an increase in the decomposition temperature (20%). This is not the case.

Absorption and Reradiation

If only those polymers are considered which have approximately the same thermal conductivities, PVC, Kel-F, PVF₂, and Teflon (see Table II), it is to be expected that the ΔT value for PVC will be the lowest, since this polymer should blacken first, reach the highest temperature, and reradiate the most energy. If reradiation were a dominant factor, the ΔT values should rise somewhat regularly with the decomposition temperatures as listed in Table I; but this is not so.

Smoke Formation

Everyone who has observed the pyrolysis of the polymer discs listed in Table I in a carbon arc-image furnace has noted the expulsion of quantities of materials from the surface of all of the discs (except Teflon) in the direction of the light source. In many cases, such as PE or ferrocene,¹¹ the expelled material was black, particulate matter and was therefore termed smoke. The expulsion of smoke appears to commence instantaneously on irradiation and to continue during the 1-sec exposure at a steady rate. The smoke expands in front of the polymer disc and rises quickly. If smoke production is the controlling factor in thermal protection, then Kel-F, PFV₂,

and PVF_3 , which have the lowest ΔT 's, must have produced much more smoke than PVF and PE. The reverse is the case.

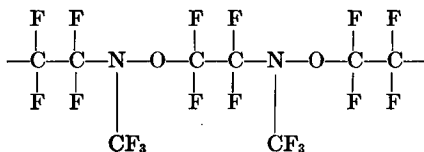
When a polymer produces quantities of smoke (excluding target materials that are sufficiently exothermic to sustain smoke production spontaneously), sufficient light must be penetrating the smoke to decompose enough polymer to provide more smoke. Hence the presence of smoke is evidence that light is getting through. An equilibrium between the rate of smoke formation and the rate at which energy strikes the surface of the polymer disc must be quickly reached. The temperature at which this equilibrium is reached must be at least the decomposition temperature, and the higher the polymer decomposition temperature the greater the amount of energy that must reach the polymer disc.

Since we are assuming that smoke is an effective screening agent, even small amounts should intercept a substantial portion, perhaps most of the incident light. All of the polymers produced some smoke. It follows that the temperatures of the various polymers should not rise much above their respective decomposition temperatures. The decomposition temperature of the polymer would then be the controlling factor and the ΔT values should be in much the same order as the decomposition temperatures listed in Table I. However, they are not. Smoke formation is undoubtedly a factor, and, by using other techniques,¹² sufficient smoke can be generated to intercept 95% or more of the light energy supplied. Under these experimental conditions, however, smoke formation is not an overwhelming factor.

All of the obvious factors or routes usually considered to be important in thermal protection have now been eliminated, i.e., none, individually, can explain the data in Table I. It is not stated, maintained, nor even implied that these factors or combinations thereof are insignificant and afford negligible thermal protection. On the contrary, several factors, e.g., endothermic decomposition and reflectance, in fact, probably all of them, operate simultaneously to dissipate a considerable amount of the impinging energy from the carbon arc-image furnace.

Perhaps certain combinations of routes of energy attenuation or dissipation can explain the relative ΔT values; they certainly are not obvious. Char formation falls into this category, since it involves several of the above factors such as endothermic decomposition, reflectance, and loss of high-temperature material, etc. Correlation of chars and ΔT values would involve, therefore, the simultaneous consideration of a set of factors.

Char formation is not a prerequisite for good thermal protection, however. As an example, the nitroso rubber system, a copolymer of trifluoronitrosomethane and tetrafluoromethane shows good thermal protection:



When properly compounded with inert fillers that absorb light, the copolymer has a ΔT of about 5°C .¹³ On pyrolysis, this polymer decomposes primarily to $\text{CF}_2=\text{O}$ and $\text{CF}_2=\text{N}-\text{CF}_3$ ¹⁴ and leaves no char, i.e., the surface of the irradiated portion has exactly the same color as the rest of the material. Decomposition to the above two gases is exothermic.¹⁴

CONCLUSION

It appears that none of the usual routes of energy attenuation can be used to clarify the relative ΔT values of Table I. Since to our knowledge no one else has shown that the above routes, either singly or in combination, can clarify the relative thermal protection offered by test materials, there may be another route. It turns out that there are no combinations of the routes listed that will explain the ΔT values in Table I. As yet, we have not investigated the role in thermal protection of the gaseous decomposition products mentioned in the introduction. In a subsequent article it will be shown how the gaseous decomposition products control and hence can be used to explain the sequence of the ΔT values of Table I.

This paper reports research undertaken at the U.S. Army Natick Laboratories and has been assigned TP No. 840 in the series of papers approved for publication. The findings in this report are not to be construed as an official Department of the Army position.

References

1. S. Glasstone, *The Effects of Nuclear Weapons*, U.S. Government Printing Office Washington, D.C., 1964, pp. 333, 523.
2. T. Kapala and J. F. Oesterling, *Hand and Face Creams for Protection Against Thermal Radiation*, U.S. Army Quartermaster Research and Development Command, Natick, Massachusetts, April 26, 1957.
3. W. V. Barnes and W. E. C. Yelland, *Degradation of Halopolymers by Exposure to High-Intensity Thermal Pulses*, Materials Research and Engineering Report No. 65-4, Clothing and Organic Materials Division, U.S. Army Natick Laboratories, Natick, Massachusetts, 1965.
4. B. McQue, *The QM Arc*, Pioneering Research Division, Report T-6, U.S. Army Quartermaster Research and Development Command, Natick, Massachusetts, March 1956.
5. W. J. Barnes, C&P Division, Report #1, U.S. Army Natick Laboratories, Natick, Massachusetts, Feb. 1960, p. 6.
6. S. L. Madorsky, *Thermal Degradation of Organic Polymers*, Interscience, New York, 1964, Chaps. IV and V.
7. C. A. Neugebauer and V. L. Margrave, *J. Phys. Chem.*, **60**, 1318 (1956).
8. W. D. Good et al., *J. Phys. Chem.*, **68**, 579 (1964).
9. J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry*, W. A. Benjamin, New York, 1965, p. 77.
10. J. M. Klotz, *Chemical Thermodynamics*, Prentice-Hall, New York, 1950, p. 54.
11. A. D. Little, *Development of a Means to Neutralize Intense Thermal Radiation*, Final Report, Contract DA 19-129-QM-1087, 1960, p. 46.
12. D. V. Mahoney, D. D. Keogh, and D. T. Kilminater, *Thermal Attenuation by Chemical Smokes*, Army Chemical Center, Edgewood Arsenal, January 1960.

13. W. D. Barnes and W. E. C. Yelland, *Thermal Protective Materials Evaluation*, Report No. 11, U.S. Army Natick Laboratories, Natick, Massachusetts,
14. A. R. Schultz, N. Knoll, and G. A. Morneau, *J. Polym. Sci.*, **62**, 220 (1960).
15. R. A. Prosser, *Anal. Chem.*, **39**, 1125-1130 (1967).

Received August 7, 1970

Revised January 8, 1971