

Calorimetric Study of Flammable Fabrics. II. Analysis of Flame Retardant-Treated Cotton*

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Synopsis

Efficiencies of three flame retardants for cellulose, phosphoric acid, diammonium phosphate, and THPOH ammonia finish, have been evaluated based on the heat release value and the rate of heat release of treated fabrics burning in air measured with the isoperibol calorimeter. The results were compared and correlated with those obtained previously with the bomb-calorimetric technique. Complete heat balances were obtained for the systems studied by correlation of the calorimetric data and the measurement of combustible gases evolved from the fabric burning in air. The rate of heat release was found to correlate with the flame propagation rate measured at a 45° angle. The results from the heat, rate, and combustible gas measurements were interpretable in terms of existing mechanisms of flame-retardant action.

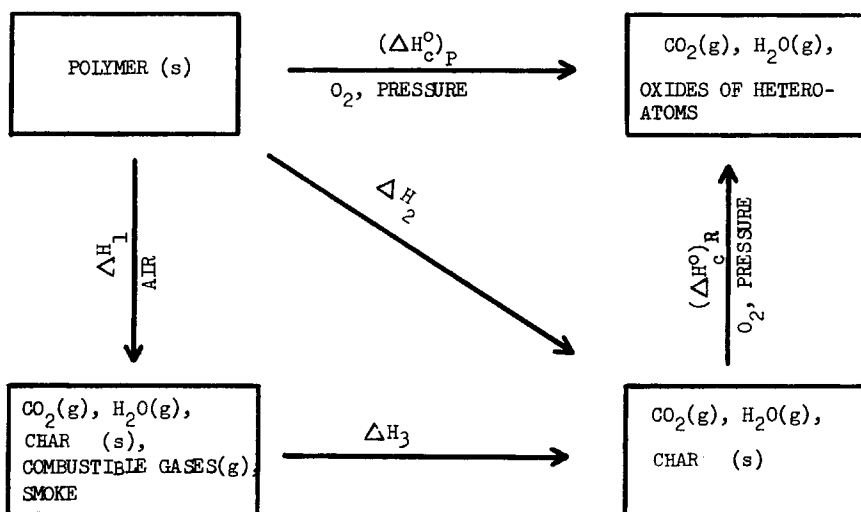
INTRODUCTION

Efficiency of a flame retardant for flammable fabrics is evaluated on the basis of the ability of the retardant to reduce hazards inherent in the use of these fabrics. Logically, a testing technique which gives quantitative measurements of the hazards posed by flammable fabrics can be used to obtain proper evaluation for a flame retardant. However, virtually all currently used flammability testing procedures are unsuitable for the collection of quantitative data related to the hazards of flammable fabrics.

Previous study,¹ employing a bomb-calorimetric technique to obtain heat release values of fabrics burning in the normal atmosphere, has shown that the technique can be used as an effective experimental tool to evaluate the efficiency of flame retardants for cellulose. It further demonstrated that some information on the mechanistic nature of retardant action can also be obtained. However, this technique, based on the assumption that all materials consumed in atmospheric burning are converted to their highest oxidation states (CO₂, H₂O, etc.), cannot predict accurate heat release values when the amount of incomplete combustion in the gaseous phase becomes substantial in normal atmospheric burning. It tends to

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$$(\Delta H_c^0)_P = \Delta H_2 + R \cdot (\Delta H_c^0)_R$$

$$\Delta H_2 = \Delta H_1 + \Delta H_3$$

where

$(\Delta H_c^0)_P$ = Heat of Combustion of Polymer, oxygen bomb

$(\Delta H_c^0)_R$ = Heat of Combustion of Char, oxygen bomb

ΔH_1 = Actual Heat-Release in Air, isoperibol

ΔH_2 = Heat, theoretical (assuming complete combustion of gaseous fuels)

ΔH_3 = Heat of Combustion of Combustible Gases, theoretical

R = Weight Fraction of Char from Burning in Air

Fig. 1. Diagram of combustion.

overestimate heat release values for most synthetic fabrics, and would fail to give correct evaluation for some flame retardants whose retardant action occurs predominately in the gaseous phase.

An isoperibol calorimeter designed for measuring heat release and rate of heat release of burning fabrics in air has been reported previously.² The accuracy and reliability of this calorimeter for measuring directly the rate and amount of heat released from fabrics burned in the normal atmosphere were discussed. The difference between the two approaches for measuring the quantity of released heat is best illustrated diagrammatically in Figure 1. In the previous study which applied the Law of Constant Heat Summation and the oxygen bomb-calorimetric technique, the heat released during the burning in air, $-\Delta H_2$, was measured indirectly

as the difference of the heat of combustion of the fabric measured in the oxygen bomb calorimeter and that of the residue resulting from atmospheric burning. This value, $-\Delta H_2$, can be regarded as the maximum heat which can be liberated during burning in air, since an assumption of complete combustion in the vapor phase was followed. In the present study, the heat release value, $-\Delta H_1$, was obtained directly with the isoperibol calorimeter and is the value of actual heat released. The difference of these two heat values, $(-\Delta H_3) = (-\Delta H_2) - (-\Delta H_1)$, is the sum of the heat of combustion of combustible gases and smoke resulting from incomplete combustion in atmospheric burning, provided that the solid-phase residues (char) are the same in both studies. In this study, $-\Delta H_3$ was also measured directly with a combustible gas detector attached to the gaseous exhaust of the isoperibol calorimeter. The study reported herein is the comparison and correlation of the results obtained by both calorimetric techniques in the evaluation of three flame retardants for cellulose, phosphoric acid, diammonium phosphate, and THPOH.

EXPERIMENTAL

Materials. All chemicals used were reagent-grade chemicals. Tetrakis(hydroxymethyl)phosphonium hydroxide (THPOH) was obtained by adjusting an aqueous solution of tetrakis(hydroxymethyl)phosphonium chloride (THPC) to a pH 7.5–8.0 to convert THPC to THPOH. The fabric used was an 80 × 80 bleached and mercerized 100% cotton print-cloth.

Fabric Treatments. The treatment of cotton fabric with flame-retardant agents was carried out in the same manner as described previously.¹ Phosphorus contents of phosphoric acid- and diammonium phosphate-treated samples were obtained with wet chemical analysis, and those of THPOH-NH₃-treated samples were obtained with x-ray fluorescence analysis. All fabric samples were preconditioned at room temperature and 65% relative humidity prior to measurement in the calorimeter.

Equipments. Description and operation of the isoperibol calorimeter, as well as the theories and calculations involved in the measurement of the amount and rate of heat release, have been described in detail previously.²

A commercial combustible gas detector was attached to the gaseous exhaust of the calorimeter, as shown in Figure 2. The gas flow exhausted from the calorimeter was divided into two streams. The ratio of flow rates in the two streams was kept constant with two critical flow orifices. The combustible gas detector was connected upstream of the smaller orifice. The two streams were then recombined and connected to a vacuum pump. The pressure drop across the orifices was maintained at about 450 mm Hg, with the detector (upstream) operating essentially at atmospheric pressure. This large pressure drop provided by the vacuum pump assured constant flow in each stream, unaffected by slight upstream pressure change during the burning.

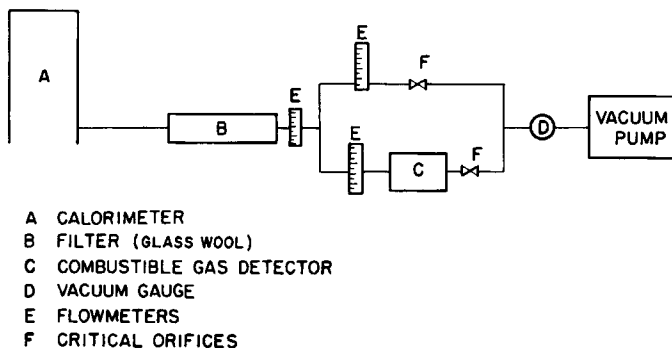


Fig. 2. Schematic setup for combustible gas measurement.

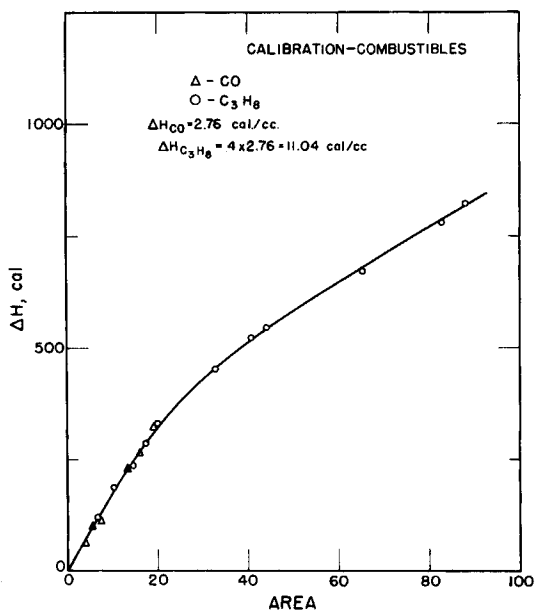


Fig. 3. Calibration curve of combustible gas measurement.

The combustible gas detector was calibrated with carbon monoxide and propane gases. The combustible gas was introduced into the calorimeter through a solenoid valve, and the volume was measured by a volume meter. The heat of combustion of carbon monoxide was used as the reference standard, since infrared and gas chromatography analyses indicated that CO was the only combustible gas present in significant amount in the gaseous combustion products of the fabrics studied. Propane gas was also used to obtain a wider range of calibration, and the conversion factor provided with the detector was used. Output from the detector was fed to a recorder equipped with an integrator. The area under the response curve was integrated, and a calibration curve of heat versus area under curve was constructed, as shown in Figure 3.

Measurements. Fabric samples were cut into a size of 2 in. \times 5 in. with a cutting die. At least three measurements were made for each treated sample, and the averaged values for the char yield, the rate of heat release, and the amount of heat release were reported. Standard deviation was also calculated for the char yield and the rate of heat release, based on each set of measurements. The standard deviation for the heat release value was taken to be $\pm 3\%$ in the previous study,² based on errors estimated from calibration. Char yield was obtained as the ratio of the residue weight after burning in the calorimeter to the original weight of the fabric.

RESULTS AND DISCUSSION

Char yields, the rate of heat release, and the amount of heat release obtained with the isoperibol calorimeter for three retardant-treated systems are tabulated in Table I.

TABLE I
Char Yields, Heats and Rates of Flame Retardant-Treated Cotton as Measured in Isoperibol Calorimeter

Retardant	P, %	Char, %	Rate, cal/sec cm	$-\Delta H_1$, ^a cal/g
H_3PO_4	0.56	19.7 \pm 0.4	66.7 \pm 2.0	2069
	0.77	24.8 \pm 0.6	60.2 \pm 1.0	1764
	1.03	29.7 \pm 0.7	53.5 \pm 1.0	1655
	1.38	34.9 \pm 0.4	50.0 \pm 2.0	1421
$(NH_4)_2HPO_4$	0.49	19.5 \pm 0.6	67.5 \pm 2.0	2047
	0.81	25.7 \pm 0.6	60.2 \pm 2.4	1626
	0.93	28.9 \pm 0.4	56.9 \pm 0.6	1559
	1.11	31.9 \pm 0.9	53.5 \pm 0.6	1403
THPOH-NH ₃	0.15	7.5 \pm 0.8	71.9 \pm 1.6	2866
	0.53	21.3 \pm 0.8	66.1 \pm 1.6	2116
	0.98	30.1 \pm 0.4	55.1 \pm 1.6	1765
	2.23	41.2 \pm 0.8	44.9 \pm 3.0	1330

^a 1 Calorie = 4.184 joules.

Char Yields

Char yields from each of the treated samples are listed in column 3 of Table I, in terms of per cent of the original sample weight. Per cent char yields are also shown graphically in Figure 4, as a function of per cent phosphorus content. Values obtained by the previous method¹ are also included for comparison. Char yields from the two studies are in good agreement.

In order to provide a basis for a meaningful comparison of the results from the two methods, it is essential that char yields from both studies are the same. Since the amount of heat release depends on the mass consumed in burning, char yields determine the amount of fuels generated

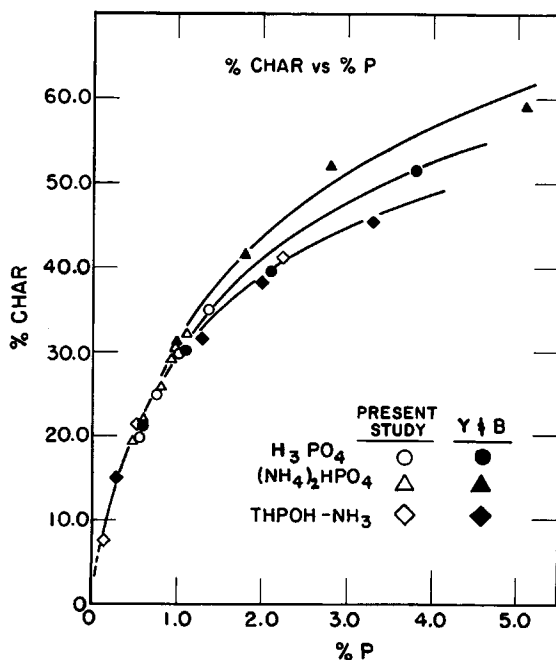
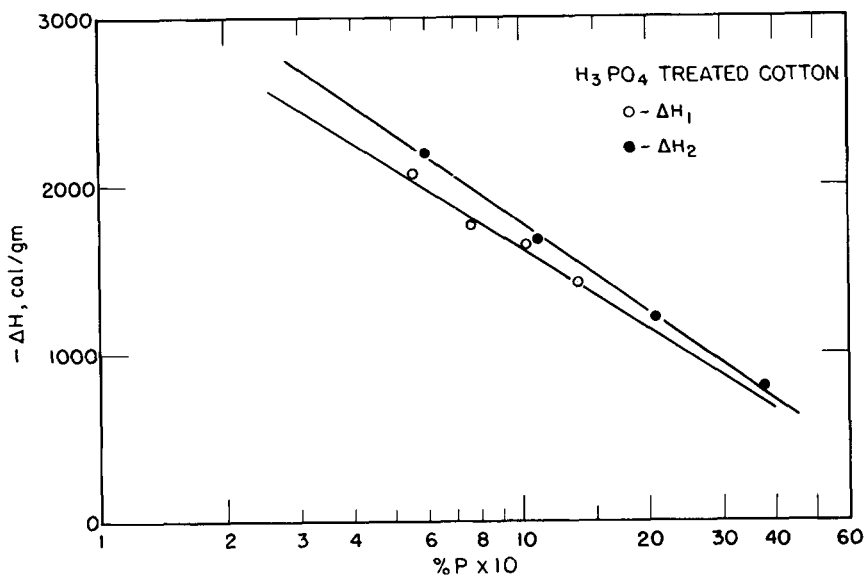
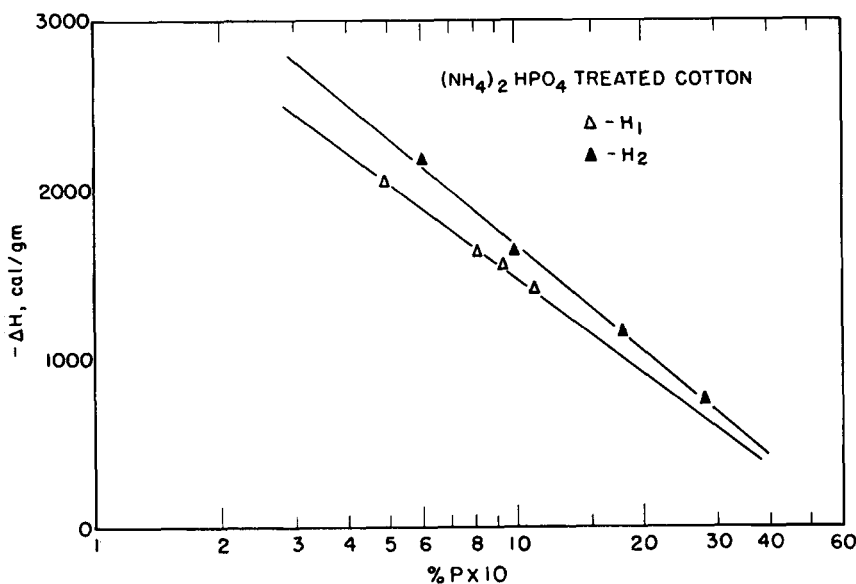


Fig. 4. Char yields of flame retardant-treated cotton as function of phosphorus content.

from solid-phase pyrolysis and thus affect the amount of heat evolved from the oxidation of these fuels in the vapor phase. So long as the char yield can be held constant, independent of experimental condition, the relationship $(-\Delta H_2) = (-\Delta H_1) + (-\Delta H_3)$ is established. While $(-\Delta H_2)$ is the maximum heat evolved when complete combustion of fuels takes place in the vapor phase, the ratios $\Delta H_1/\Delta H_2$ and $\Delta H_3/\Delta H_2$ represent fractions of complete and incomplete combustions, respectively, in the vapor phase.

Heat Release

Values of heat release obtained with the isoperibol calorimeter for the three treated systems are tabulated in Table I. In each treated system, the heat values showed a steady decrease with increasing flame retardant add-on (phosphorus content), as was observed in the previous study.² Furthermore, the present study, on the basis of heat values, gave a similar evaluation of the relative efficiencies of the three retardants, $(\text{NH}_4)_2\text{HPO}_4 > \text{H}_3\text{PO}_4 > \text{THPOH-NH}_3$, although actual differences among the three are rather small. Figures 5, 6, and 7 show comparisons of heat values from the present study $(-\Delta H_1)$ and those from the previous study $(-\Delta H_2)$ for the three treated systems. The $-\Delta H_2$ value was obtained from previously reported values¹ (designated Δ in the previous study) by correction for the heat of vaporization of water. Values of $-\Delta H_1$ are consistently smaller than those of $-\Delta H_2$. As defined, $-\Delta H_2$ represents the

Fig. 5. Heat release values of H₃PO₄-treated cotton.Fig. 6. Heat release values of (NH₄)₂HPO₄-treated cotton.

maximum heat liberation that could be obtained when all fuels in the gaseous phase are completely combusted. Thus, $-\Delta H_1$, the actual heat evolved, would be expected to be smaller, since maximum oxidation of gaseous fuels is normally not achieved in atmospheric burning.

In Figures 5, 6, and 7, heat values ($-\Delta H_1$ and $-\Delta H_2$) are shown plotted versus the logarithms of phosphorus contents, since both heat values ap-

peared to be linearly dependent on the logarithms of phosphorus contents within the range studied. Unfortunately, the kinetic significance of the linearity cannot be established with these measurements, because the values obtained are the net heats measured and the determinations of these values do not allow an unambiguous resolution of heterogeneous kinetics involved in these systems. However, the practical significance of the linearity provides an effective means for the comparison and correlation of the two studies.

Since the samples used in the present study were prepared separately from those used previously, it was not possible to obtain samples having

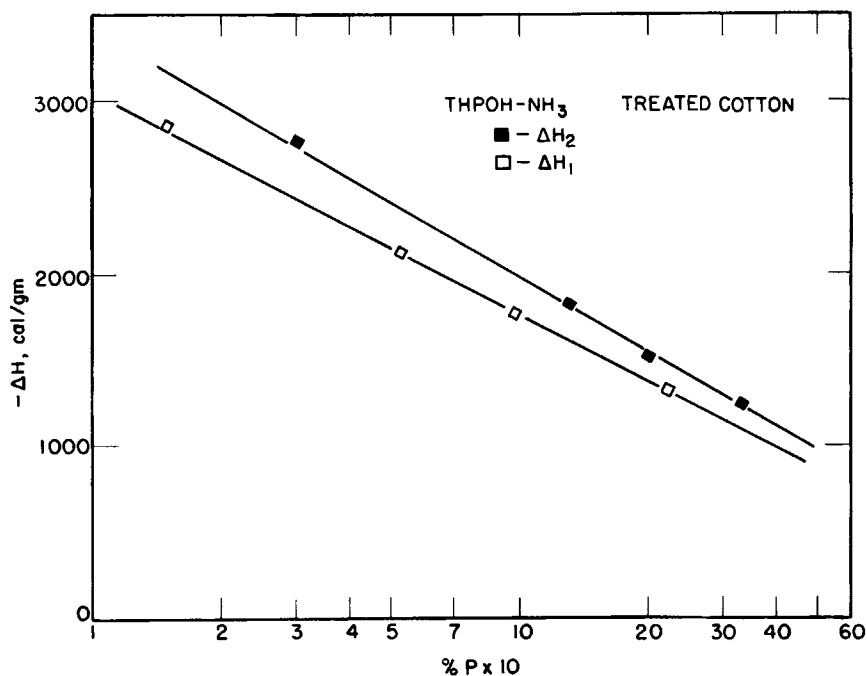


Fig. 7. Heat release values of THPOH-NH₃-treated cotton.

identical levels of retardant add-on as those previously used. The raw experimental heat values ($-\Delta H_1$) shown in column 5 of Table I could not be used to correlate with those of the previous study. It was necessary to interpolate results from both studies in order that comparison and correlation could be made at the same level of retardant add-on. At the same time, it is more desirable statistically to correlate the results after each has been smoothed. Both goals can be achieved by treating $-\Delta H$ in each system as linearly dependent on the logarithm of the per cent phosphorus content, within the range studied:

$$-\Delta H = A + B \log (\%P) \quad (1)$$

TABLE II
Linear Regression Constants of Heat Release Values of
Flame Retardant-Treated Cotton

Retardant	A	B	S.D.*
I. Isoperibol Calorimetric Values, $-\Delta H_1 = A + B \log (\% P)$			
H ₃ PO ₄	+1643	-1582	±42
(NH ₄) ₂ HPO ₄	+1484	-1800	±17
THPOH-NH ₃	+1769	-1315	±19
II. Bomb Calorimetric Values, $-\Delta H_2 = A + B \log (\% P)$			
H ₃ PO ₄	+1784	-1725	±28
(NH ₄) ₂ HPO ₄	+1675	-2095	±26
THPOH-NH ₃	+1987	-1469	±20

* S.D. = Standard deviation.

TABLE III
Heat Balance in Flame Retardant-Treated Cotton Systems

P, %	$-\Delta H_1^a$	$-\Delta H_2^a$	$\frac{\Delta H_1}{\Delta H_2}, \%$	$-\Delta H_3$	$\frac{\Delta H_3}{\Delta H_2}, \%$
0	3324	3688	90.1	436	11.8
H ₃ PO ₄					
.56	2041	2218	92.0	301	13.6
.77	1823	1980	92.1	273	13.8
1.03	1623	1762	92.1	219	12.4
1.38	1422	1543	92.2	177	11.5
			Ave. 92.1		Ave. 12.8
(NH ₄) ₂ HPO ₄					
.49	2042	2324	87.9	337	14.5
.81	1649	1867	88.3	277	14.8
.93	1541	1741	88.5	265	15.2
1.11	1403	1580	88.8	246	15.6
			Ave. 88.4		Ave. 15.0
THPOH-NH ₃					
.15	2852	3197	89.2	394	12.3
.53	2132	2392	89.1	297	12.4
.98	1781	2000	89.0	244	12.2
2.23	1311	1475	88.9	174	11.8
			Ave. 89.0		Ave. 12.3

* Smoothed values except for untreated cotton (0% P).

where A and B are fitted constants obtained by least-squares regression analysis. These constants together with standard deviation from the regression for each system were listed in Table II.

Smoothed values of $-\Delta H_1$ and $-\Delta H_2$ were calculated at each level of phosphorus content investigated in the present study and tabulated, respectively, in columns 2 and 3 of Table III. The ratio $\Delta H_1/\Delta H_2$ was defined as the fraction of heat released, or the fraction of complete combus-

tion in the gaseous phase. These values were listed in column 4 of Table III. Within each of the three treated systems, the fraction of heat released is essentially constant, independent of flame retardant add-on. Furthermore, of perhaps more significance, the value from each system is essentially the same as the value for untreated cotton.

While these values cannot be considered quantitative, the consistency of the results strongly suggests that combustion of the fuels in the gaseous phase in these systems is not significantly affected by the flame retardant. This agrees with the general belief that the action of these phosphorus-containing retardants occurs predominately in the solid phase. This is also in agreement with the previously proposed model¹ that these retardants, acting as catalysts, alter the normal decomposition course of the cellulose substrate in the solid phase, and thus result in increasing amounts of char formed and decreasing amounts of fuels released into the vapor phase.

Combustible Gases

The above-observed vapor-phase behavior in these systems was further confirmed with direct measurement of the combustible gases evolved during the burning in the isoperibol calorimeter. As defined in Figure 1, $-\Delta H_3$ is the heat of combustion of the combustible gases and smoke resulting from incomplete combustion in the open air. In all samples investigated in the present study, only a small amount of smoke has been observed during the burning. Thus, in this study, the heat contribution from the smoke was neglected, and $-\Delta H_3$ was treated as equal to the heat of combustion of the combustible gases only. Values of $-\Delta H_3$ obtained from the combustible gas detector are listed in column 5 of Table III. In column 6, these values are shown as per cent incomplete combustion in the gaseous phase.

Values of per cent incomplete combustion in the vapor phase, $\%(\Delta H_3/\Delta H_2)$, listed in column 6 of Table III, show that the fraction of incomplete combustion is not affected by the flame retardant add-on. This is parallel to that observed with the value of the per cent heat released, $\%(\Delta H_1/\Delta H_2)$, listed in column 4 of the same table. The sum of the two values, $\%(\Delta H_1/\Delta H_2)$ and $\%(\Delta H_3/\Delta H_2)$, is larger than 100% in all cases, although the errors involved are relatively small for these types of measurements. And the significance of the vapor-phase behavior, consistently demonstrated by both sets of data, is evident in these systems.

Rates of Heat Release

The rates of heat release obtained from the isoperibol calorimeter are tabulated in column 4 of Table I. These values are also plotted versus phosphorus contents in Figure 8. The identical dependence of the rate on phosphorus content observed for all three systems seems to be of some mechanistic significance. In the previous study,¹ the theoretical fuel yield generated from pyrolyzed cellulose substrate was calculated from the heat

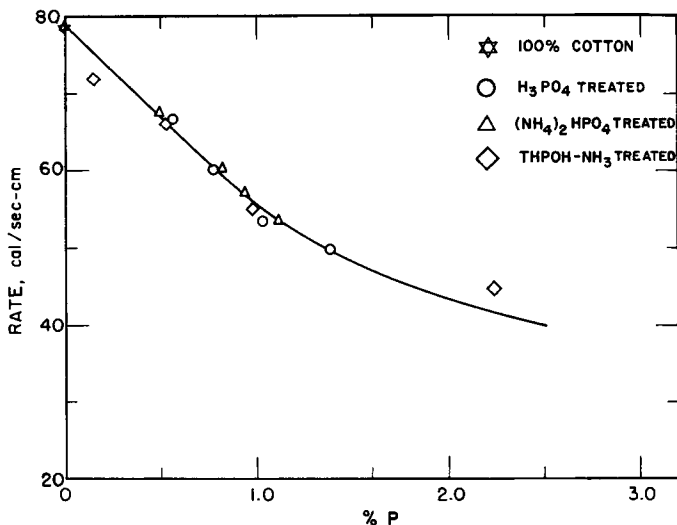


Fig. 8. Rates of heat release of flame retardant-treated cotton.

release value $-\Delta H_2$ by corrections of the heat contribution from the retardant and other extraneous heat terms involved in the burning process. This value, which was designated $y/(1-X)$ in the previous study (where y is the weight fraction of fuels generated from the fabric and X is the weight fraction of flame retardant on the fabric), represents the theoretical amount of fuels generated from unit mass of cellulose in each treated system during the burning process. The fuel values for all three treated systems also showed identical dependence on the phosphorus content. Thus it was concluded that these three retardants presumably operate through the same general mechanism. The correlation of this theoretical fuel yield with the rate of heat release is shown in Figure 9. Points in Figure 9 were obtained from the previous plot of $y/(1-X)$ versus $\log (\%P)$ and from Figure 6 at phosphorus contents ranging from 0.3% to 2.0% P. The remarkable correlation shown in Figure 9 would seem to indicate that this is somehow reflecting the kinetics of cellulose pyrolysis. However, due to the ambiguity of heterogeneous kinetics involved, further interpretation of the data would not be significant at the present time.

The rate of flame propagation measured at a 45° angle has been reported by Hendrix et al.³ for cotton fabrics treated with H_3PO_4 and $(NH_4)_2HPO_4$. The comparison of these burning rates with current obtained rates of heat release is shown in Figure 10. The burning rate data reported by Hendrix et al.³ were first screened; data for fabrics with phosphorus content above 2% were not used, because of the variation of data due to the self-extinguishing property posed by the fabrics. A total of four points, two each for H_3PO_4 and $(NH_4)_2HPO_4$, were used, ranging from 1.0% to 1.8% P. These values were plotted as burning rate versus % P, and the curve was then extrapolated to include the rate for untreated cotton. Burning rates

at various phosphorus contents from 0.25% to 1.50% P were read out from the plot. The rate of heat release at each level of phosphorus content was obtained from Figure 8. The direct relationship between these two rates seem to be evident within the range shown.

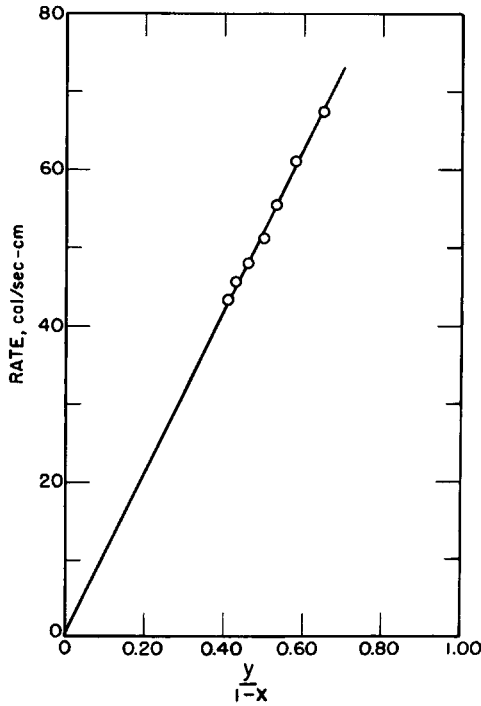


Fig. 9. Rates of heat release vs. theoretical fuel yields in flame retardant-treated cotton systems.

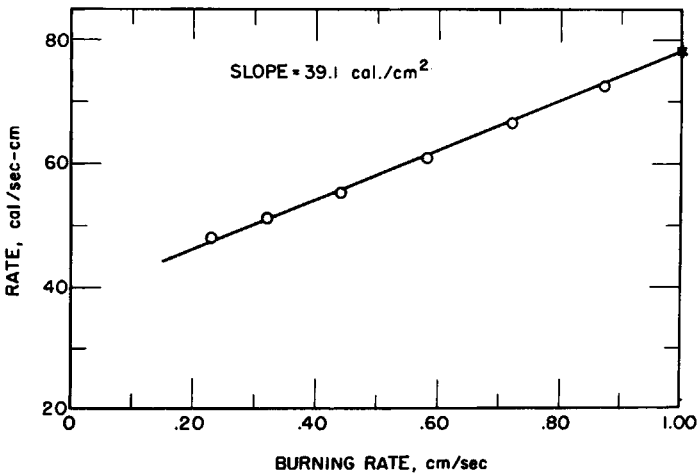


Fig. 10. Rates of heat release vs. 45° flame propagation rates for flame retardant-treated cotton.

The relationship between the two rates was stated by eq. (10) of the previous study²:

$$\dot{Q}/y = -\Delta H \delta \dot{x} \quad (2)$$

where \dot{Q}/y is the rate of heat release, in cal/sec cm; $-\Delta H$ is the heat of combustion of the vapor-phase fuel, in cal/g; δ is the fabric weight, 10.8 mg/cm² (3.2 oz/yd²) for the fabric used by Hendrix et al.; and \dot{x} is the burning rate, in cm/sec. It is obvious from eq. (2) that the linearity observed in Figure 10 can be true only up to a small range of retardant add-on, while the incorporation of retardant on the fabric does not significantly change the value of δ (δ increases by about 5% at 1.5% P). However, the fact that eq. (2) holds for untreated cotton as well as retardant-treated materials whose apparent heats of combustion¹ are different from that of untreated cotton tends to indicate that the nature of fuels generated from solid-phase pyrolysis is not drastically altered by the presence of the flame retardant. But the amount of fuel is reduced, since both calculated fuel yields and actual heat release values decrease with increasing retardant add-on.

These conclusions on the mechanistic nature of retardant action observed from correlations on the rate of heat release, as well as on the amount of heat released, are in agreement with those reported by Hofmann and Raschdorf⁴ in their study of the pyrolysis products of retardant-treated cotton. Their analyses showed that the major gaseous products from the pyrolysis of treated cotton are the same as those of untreated cotton, only the quantities are reduced. They further concluded that the action of phosphorus- and nitrogen-containing retardants is mainly a catalysis of the thermolysis and has little direct influence on the oxidation process. Of perhaps greater significance, $-\Delta H$ calculated from the slope of the fitted line in Figure 10 has a value of 3620 cal/g, which is very close to the actual heat of combustion of cellulose, 3688 cal/g.

CONCLUSIONS

The amount and rate of heat release for three series of flame retardant-treated cotton fabrics have been measured with the isoperibol calorimeter. The results are in agreement with the previous study, thus further supporting the conclusion that the heat release value correlates with the efficiency of the flame retardant and can be employed as an effective experimental parameter for the evaluation of flame retardants.

Correlation of present heat and rate values with heat values obtained previously by the bomb-calorimetric technique indicates that the action of these retardants is predominately in the solid phase and that the mode of action is to reduce the amount of fuel evolution into the gaseous phase. The oxidation process in the gaseous phase is not significantly influenced by the retardant. The measurement of combustible gases evolved during burning supports this observation.

The rate of heat release was found to correlate with the 45° flame propagation rate.

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