K = activity distribution function defined by Eq. 2
k_e = effective thermal conductivity of catalyst pellet
r = radius of catalyst pellet
R = rate of reaction
S = selectivity towards the desired reaction
T = temperature
X = dimensionless pellet radius
Y = dimensionless temperature

Greek Letters

α = parameter defining activity profile according to Eq. 2
β = heat of reaction parameter defined by Eq. 14
γ = dimensionless activation energy
ΔH = standard enthalpy change of reaction
η = effectiveness factor
σ = starvation parameter defined by Eq. 10
ϕ_A = modified Thiele modulus defined by Eq. 8
ψ = dimensionless surface rate constant defined by Eq. 7

Subscripts

1,2 = designate desired and undesired reactions
s = designates surface conditions

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Kinetics of Pyrolysis of Some Fire Retardants and Treated Fabrics

Intermediate phases and reactions occurring on decomposing diammonium hydrogen phosphate, ammonium para molybdate, sodium tungstate dihydrate and ammonium meta vanadate were established by thermal analysis and X-ray examination.

These salts promote fabric degradation at low temperatures but are effective at high temperatures. Diammonium hydrogen phosphate produced maximum amount of gases, absorbed the highest amount of heat and gave the highest fire retardation above 350°C.

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SCOPE

Some soluble salts can be easily applied for the protection of fabrics against incendiary agents and can be easily removed by washing. Conflicting data exist in the literature regarding their decomposition and the mechanism of fire retardation. The objective of this paper is to understand the reactions taking place on heating these salts and the behavior of treated cotton fabrics.

Combined thermal analysis in which DTA, TG and DTG can

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be obtained simultaneously for the same specimen when heated with a constant rate, characterizes the occurring reactions. Thermal curves obtained using different heating rates accompanied by X-ray examination determine the dissociation steps and the intermediate phases. TG curves obtained at different rates can fix the activation energy even if the kinetic equation is unknown. The role of the type and amount of salt absorbed by the fabric can be also obtained by comparing the thermal curves.

CONCLUSIONS AND SIGNIFICANCE

1. Diammonium hydrogen phosphate dissociated to the monophosphate at about 180°C and the activation energy is 65.1 kJ/mol. The latter dissociated to $(NH_4)_2H_2P_2O_7$ then to the metaphosphate which dissociated at 750°C to P_2O_5, NH_3 and water.

2. Ammonium molybdate heptahydrate dissociated to the pentahydrate below 100°C. Three intermediate compounds were formed before dissociating to MoO_3. The X-ray patterns for two of them were established.

3. Sodium tungstate dihydrate lost its water of crystallization in one step when low heating rates were used. The activation energy for this step is 25.6 kJ/mol. With high heating rates the rate of evaporation was less than the rate of evolution of water and two steps were observed.

4. Three intermediate compounds were formed when ammonium vanadate dissociated to V_2O_5. The compounds are $2NH_3 \cdot 3V_2O_5 \cdot H_2O$, $2NH_3 \cdot 4V_2O_5 \cdot H_2O$ and $2NH_3 \cdot 6V_2O_5 \cdot H_2O$.

5. At low temperature the salts were found to promote fabric degradation but at high temperatures, which are of interest in combating fire, a reduction in weight loss occurred.

6. In addition to the low price, diammonium hydrogen phosphate produced maximum amount of gases, absorbed the highest amount of heat and gave the highest fire retardation above 350°C.

INTRODUCTION

Temporary treatment of clothes with some salts protect them against incendiary agents by retarding the rate of burning. Some salts absorb the heat and perform a phase change while others melt or dissociate forming insulating coat on the fabrics or exhibiting a bubbling or foaming action forming an insulating barrier.

The commercial salts selected for this investigation are diammonium hydrogen phosphate, ammonium para molybdate, sodium tungstate dihydrate and ammonium meta vanadate. They are water soluble and are the most easily applied of the textile flame retardants.

PREVIOUS WORK

Diammonium Hydrogen Phosphate

In view of thermal analysis carried out at 10°C/min in vaccuum on 200 mg, specimens having average particle size 0.045 mm (Erdey et al., 1964) suggested the following reactions:

at 150°C $(NH_4)_2HPO_4 = NH_4H_2PO_4 + NH_3$ (1)

at 170°C $2NH_4H_2PO_4 = (NH_4)_2H_2P_2O_7 + H_2O$ (2)

at 280°C $(NH_4)_2H_2P_2O_2 = 2NH_4PO_3 + H_2O$ (3)

The metaphosphate melts and forms a water insoluble glassy phase that decomposes at 660°C giving P_2O_5, NH_3 and H_2O.

Menlibaev et al. (1976) supported the above first two reactions and stated that the activation energy for the first step is 34 kJ/mol.

Ammonium Molybdate

Conflicting data exists in the literature regarding the decomposition of $6NH_3 \cdot 7MoO_3 \cdot 7H_2O$. Three steps were suggested for its dissociation to MoO_3 with the formation of two intermediate compounds. Table 1 was constructed to show the compositions proposed by various authors and their operating conditions. It should be noted that these compositions were based on the observed weight loss.

Sodium Tungstate Dihydrate

Okada et al. (1974) reported that the orthorhombic dihydrate dissociates to the anhydrous salt at 100°C. Erdey et al. (1966) indicated that the anhydrous salt has three allotropic forms with reversible transitions at 580 and 620°C. It was reported to melt at 690°C.

Ammonium Vanadate

Several intermediate compounds were reported to appear on dissociating ammonium vanadate to V_2O_5 in air. Kuneev et al. (1974) reported that the bivanadate $(NH_4)_2O \cdot 2V_2O_5$ was formed at about 170°C and dissociated to the trivanadate at about 230°C. Brown et al. (1973) reported the existence of tetravanadate $(NH_4)_2O \cdot 4V_2O_5$. On the other hand, using a heating rate of

TABLE 1. INTERMEDIATE COMPOUNDS DEVELOPED ON HEATING AMMONIUM MOLYBDATE

	Composition (Molar Ratio)			Conditions		Heating Rate	
	NH_3	MoO_3	H_2O	Atm.	Temp., °C	°C/min	Authors
First Intermediate Compound	4	5	1	Vac	150–200	6	Bhatnager et al. and Eiko
	2	4	2	?	106–120	?	Rode & Tvedcklebov
	6	7	5	Vac	40–50	?	Eiko
Second Intermediate Compound	6	7	0	Vac	160–260	10	Erdey et al.
	2	4	1	?	220–250	?	Rode & Tvedcklebov

5°C/min Shimizu et al. (1975) reported the possibility of having five intermediate compounds but nothing was reported regarding their compositions or characteristics.

EXPERIMENTAL TECHNIQUES

Thermal Analysis

To throw light on the successive reactions taking place and the role of the retardants, pure salts and cotton fabrics (treated and untreated) were heated in a "Derivatograph" using constant heating rates. By obtaining curves for differential thermal analysis (DTA), thermogravimetric changes (TG), and differential thermogravimetric analysis (DTG) simultaneously for the same specimen, we could determine whether the reaction is exothermic or endothermic, or if it is accompanied by a change in weight. It determines also the amount of change and exactly fixes the beginning and ending of the thermal process.

For the thermal analysis of salts 500 mg of powdered specimens passing through a 200 mesh screen were used in a platinum crucible with calcined alumina as a reference material. In view of preliminary investigations it was found that the finer the particle the lower is the decomposition temperature and the higher is the oxidation temperature. It was also found that when the weight of the sample was raised from 0.2 to 1 g the results were not affected appreciably.

X-Ray Examination

In the absence of simultaneous reactions or the existence of an overlap, thermal curves can be used to suggest the dissociation mechanism and the reaction can be tentatively deduced. To identify the phases produced and to write the exact reaction occurring, the powder patterns were obtained using copper radiation with nickel as a filter. The *d*-spacings were calculated using Bragg's law and were compared with ASTM cards.

If overlap occurs more than one phase coexist together and can be identified if all phases were previously reported. Otherwise, phase identification is difficult and the deductions may not be absolutely correct.

Calculation of Activation Energy

Thermogravimetric curves were used to calculate the activation energy since they give more reliable results that DTA. Carroll and Manche's technique (1972) was selected since in deducing their methods the reaction rates were not considered to be proportional to the *n*th power of the undecomposed solid as in the case of homogeneous reactions. It should be noted that the latter assumption was adopted by various other authors but the equations developed can have theoretical significance only in the cases where the values of n are 0, ½, ⅔ or 1 as indicated by Criado-Morales (1977), Reich-Stivala (1979) and Beer-Oswald (1980).

According to Carroll and Manch's method, $-dw/dt = kf(w)$. The constant rate k is related to the temperature by the Arrhenius equation $k = Z \exp(-E/RT)$.

If the heating rate

$$\phi = \frac{dT}{dt} \therefore -\frac{dw}{dT} = \frac{Z}{\phi} \exp\left(-\frac{E}{RT}\right) f(w)$$

$$\therefore \ln\left[\phi\left(-\frac{dw}{dT}\right)\right] = \ln\left[Zf(w)\right] - \frac{E}{RT}$$

A plot of $\ln[\phi(-dw/dt)]$ vs. $1/T$ for a given value of w obtained at different heating rates will lead to a value of E.

Impregnation Technique

Cotton fabric having a bulk density of 290 g/m^2 and containing 183 mesh/in.^{2} was used for thermal analysis before and after impregnation. The fabrics were dipped for various periods in solutions containing different concentrations to achieve various salt contents. The weight determined after drying determines the amount of add-on. The treated and untreated fabrics were heated in the Derivatograph in air using a constant heating rate of 10°C/min.

RESULTS AND DISCUSSION

The four salts used were analytical grade diammonium hydrogen phosphate $(NH_4)_2HPO_4$, ammonium molybdate $(NH_4)_6O_3 \cdot Mo_7O_{24} \cdot 4H_2O$, ammonium vanadate NH_4VO_3 and sodium tungstate $Na_2WO_4 \cdot 2H_2O$.

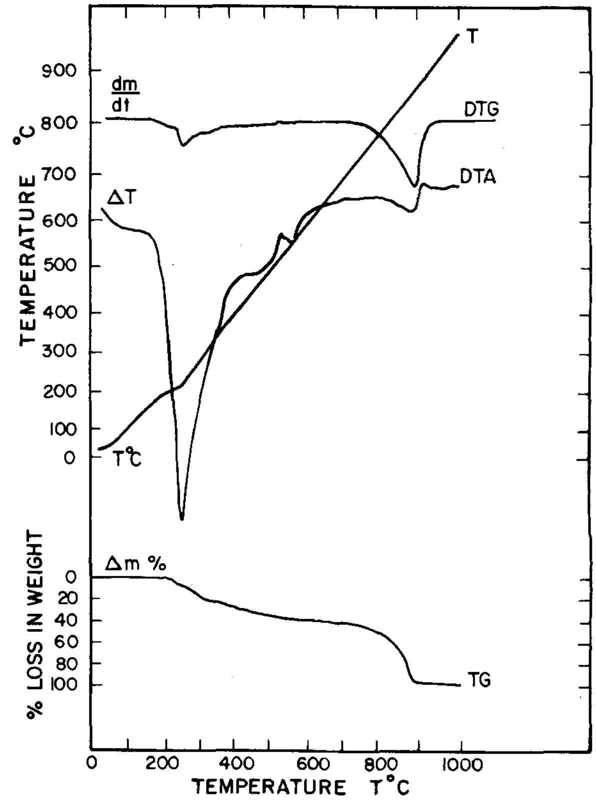

Figure 1. Thermal analysis curves for diammonium monohydrogen phosphate (rate of heating, 6°C/min).

Pyrolysis of Diammonium Hydrogen Phosphate

Three heating rates were used to investigate the dissociation mechanism of $(NH_4)_2HPO_4$; 6, 11 and 14.5°C/min. Figure 1 shows the set of thermal curves obtained using a heating rate of 6°C/min. Similar curves were obtained using other heating rates indicating that dissociation occurred over four steps as expected by previous work but the reactions took place at higher temperatures since the present results were obtained in air whereas previous work was obtained in vacuum.

A sample was heated with a rate of 6°C/min up to 210°C before quenching in air. X-ray analysis showed the existence of $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ confirming that the first step is governed by reaction 1.

TG curves were used, as explained above, to calcualte the activation energy for this step which was found to be 65 kJ/mol. This value is almost twice that calculated by Menlibaev et al. (1976). The present value is more accurate since it was deduced from more than one curve with no assumption for an operating mechanism or a kinetic equation. When one TG curve is used to calcualte the activation energy each mechanism produces a straight line with a different slope. The ratio between the slopes is equal to the ratios between the powers (n). This point was discussed in details by Criado-Morales (1977) and Reich-Stivala (1979).

The sequence of decomposition after this step could not be followed by X-rays because of the overlap due to the successive reactions. The compositions reached on TG diagram at the end of each peak on DTG are nearly the same as those proposed by Erdey et al. (1966).

Pyrolysis of Ammonium Paramolybdate

The salt was stated by the supplier to consist of pure $6NH_3 \cdot 7MoO_3 \cdot 7H_2O$ and was heated with constant heating rates of 5.5, 10 and 12.5°C/min. Figure 2 shows the set of curves obtained with

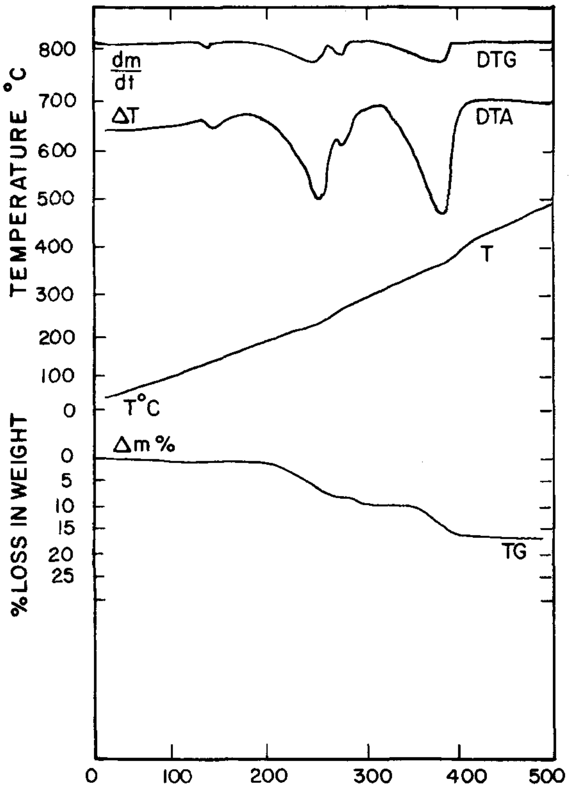

Figure 2. Thermal analysis curves for ammonium molybdate tetrahydrate (rate of heating, 5.5°C/min).

Table 2. *d*-Spacings for M_I and M_{II}

M_I		M_{II}	
d	I/I_o	d	I/I_o
9.09	58	10.38	63
7.12	100	8.62	76
5.49	10	7.58	60
4.79	24	6.89	35
4.01	16	6.55	100
3.60	29	6.33	80
3.44	21	5.84	48
3.31	17	5.31	27
3.16	10	3.27	61
3.05	12		
2.95	36		

a heating rate of 5.5°C/min. At 450°C the product was found by X-rays to be MoO_3. In all cases, the loss in weight was less than the theoretical amount calculated and corresponds to the formula $6NH_3 \cdot 7MoO_3 \cdot 5H_2O$ which is not the highest state of hydration. Accordingly the salt was saturated with water vapor and kept at 10°C. The fully hydrated specimen gave two extra endothermic peaks below 160°C with a loss of two molecules of water in the liquid state (40–100°C) and evaporation of the evolved water in the range 100–160°C. Accordingly, the first step in dehydration is governed by the equation:

$$6NH_3 \cdot 7MoO_3 \cdot 7H_2O \rightleftarrows 6NH_3 \cdot 7MoO_3 \cdot 5H_2O + 2H_2O$$

The behavior of the produced pentahydrate is clear from Figure 2 which shows the existence of three endothermic peaks (after excluding the first one which is due to the equilibrium moisture content). This implies the existence of two intermediate compounds. It should be noted that with a heating rate of 12.5°C/min a small peak appeared at 420°C in the DTG curve indicating the existence of a third intermediate compound.

During each step gaseous H_2O and NH_3 may evolve simultaneously and accordingly no attempt was made to assign specific

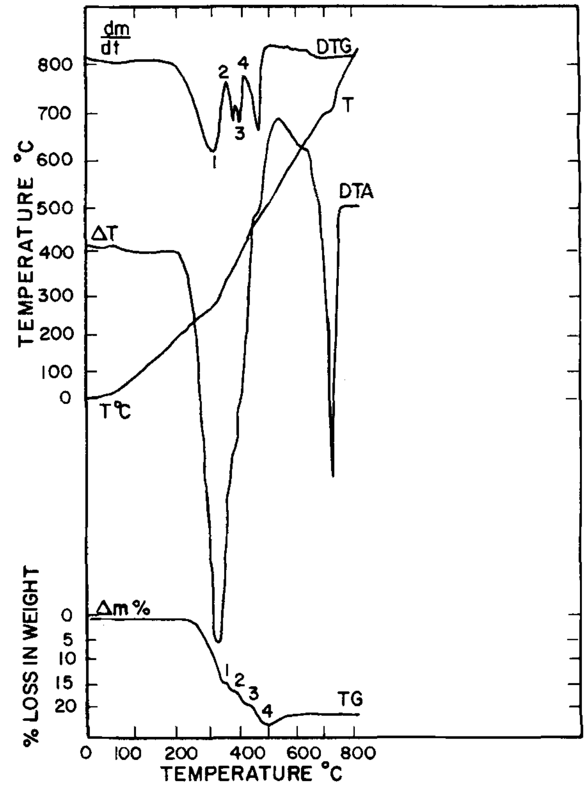

Figure 3. Thermal analysis curves for ammonium meta vanadate.

chemical formulas from the TG curve but the following sequence is suggested

$$6NH_3 \cdot 7MoO_3 \cdot 7H_2O \rightarrow 6NH_3 \cdot 7MoO_3 \cdot 5H_2O$$
$$\rightarrow M_I \rightarrow M_{II} \rightarrow M_{III} \rightarrow MoO_3$$

From Figure 2 it is clear that M_{II} can be isolated since it exists over a relatively wide temperature range. It was prepared by heating the salt with a rate of 10°C/min up to 310°C before quenching in air. The calculated d-spacings are shown in Table 2. Complete separation of M_I and M_{II} is extremely difficult but after heating up to 230°C the pattern consisted of pentahydrate and new lines which were considered to correspond to M_I (Table 2). Trials to isolate M_{III} failed since it appeared only with a rate of 12.5°C/min and was stable over a range of 15°C.

In air MoO_3 melted at about 800°C with an endothermic peak.

Pyrolysis of Sodium Tungstate Dihydrate

Using low heating rates gave one endothermic peak corresponding to complete dehydration in one step giving Na_2WO_4 as reported by earlier workers. High heating rates (10 and 13°C/min) gave TG and DTG curves showing that the process occurred on two steps. At the end of the second step X-rays showed no change in the state of oxidation of W indicating that with high heating rates, the rate of evaporation is less than the rate of evolution of water. The activation energy was calculated for the low heating rates and was found to be 25.6 kJ/mol.

It should be noted that allotropic transitions reported earlier were found to be completely reversible.

Pyrolysis of Ammonium Vanadate NH_4VO_3

While curves obtained using low heating rates (up to 10°C/min) indicates the presence of two intermediate compounds, curves obtained using high heating rates (Figure 3) indicates the presence of three intermediate compounds corresponding to points 1, 2 and 3. In view of the TG curves obtained these three compounds are:

TABLE 3. THERMAL BEHAVIOR OF FOUR SALTS

	Phosphate	Vanadate	Molybdate	Tungstate
Wt. of Gases Evolved (%)	100	22	17	11.5
Heat Abs. per Unit Mass (Rel. to Phosphate)	100	46	21	20
M.pt. of Residual Oxide, °C		700	800	690

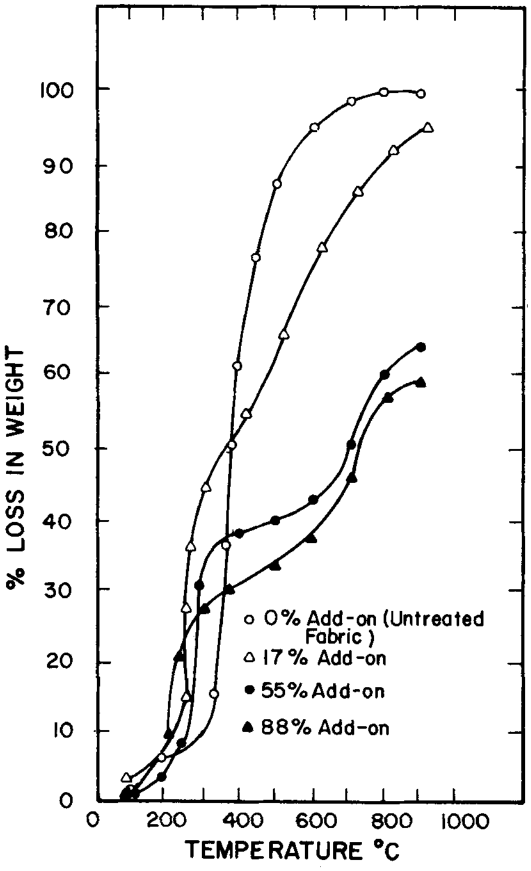

Figure 4. Behavior of fabric before and after impregnation with different amounts of diammonium hydrogen phosphate.

$2NH_3 \cdot 3V_2O_5 \cdot H_2O - 2NH_3 \cdot 4V_2O_4 \cdot H_2O$ and $2NH_3 \cdot 6V_2O_5 \cdot H_2O$. Apart from the last compound the present results are in agreement with those published by Brown et al. (1973). The bivanadate was not detected and direct formation of trivanadate was confirmed by X-rays.

Another interesting feature appearing in the curves is the formation of vanadium oxide with $O/V < 2.5$ followed by oxidation to V_2O_5. X-rays showed that point 4 in Figure 3 corresponds to a mixture of V_2O_5 and V_4O_5. Such partial reduction may be due to cracking of the evolved ammonia.

Assessing Salts as Fire Retardants

The above thermal changes were established using heating from 5.5 to 14.5°C/min. Higher rates will generally allow the thermal changes to occur at higher temperatures and some reactions may overlap. The gaseous products will be produced in large amounts and will change the partial pressure of the constituents of the surrounding atmosphere. Relevant reactions may be retarded. Highly endothermic reactions will cause the temperature to drop and the heating rate will decrease.

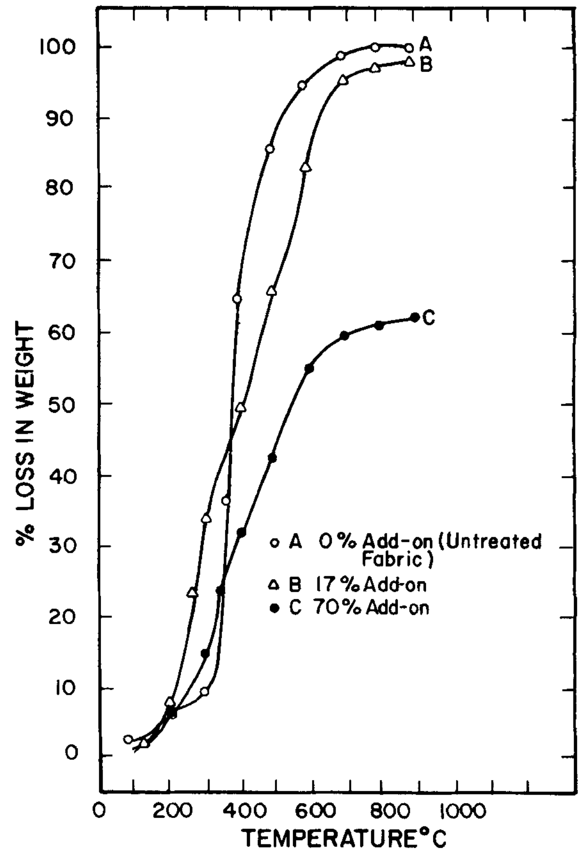

Figure 5. Behavior of fabric before and after impregnation with different amounts of ammonium molybdate.

The pyrolysis of the four salts is accompanied by absorption of heat which can be considered as a probable mechanism for fire retardation as mentioned above. Accordingly the areas under DTA peaks were measured per unit mass for each salt and is shown in Table 3 relative to the areas obtained with diammonium hydrogen phosphate.

During decomposition the gases evolved (water vapor and ammonia) are expected to dilute the combustion gases produced from cellulose degradation in such a way that a flame cannot be sustained. Accordingly the weight of gas evolved per 100 g of salt was calculated and the results are shown in Table 3. The melting point of the residual oxide is also shown for the three salts which give solid residue. The melting points are relatively high and accordingly an insulating coating that exclude oxygen and inhibit the escape of combustible gases from the fibres is not expected.

It should be noted that in case of diammonium hydrogen phosphate at about 550°C metaphosphate is formed and melts giving a water insoluble glassy phase that decomposes above 750°C in air. A lower temperature of 660°C was proposed by Erdey et al. (1966) since they carried their experiments in vacuum.

Thermal curves obtained for the untreated fabrics, the pure salts and fabrics treated with various amounts of retardants were compared. DTA curves could not be used to detect the mechanism of fire retardation.

The untreated fabric was found to lose weight continuously up to about 420°C. The sharp weight loss occurred at 370 and 415°C indicating that combustion took place on two steps. From 420 to 640°C only slight weight loss was detected for the residual ash. TG curves for the treated fabrics were used to construct Figures 4, 5, 6 and 7 which show the loss in the fabric weight against temperatures achieved by heating with a constant rate of 10°C/min. It should be noted that the loss in weight occurring in the salt was deduced from the observed loss for the treated fabrics. These figures indicate that while at low temperatures the salts promoted degradation, at higher temperatures (which are of interest in combating fire) a reduction in weight loss is observed. Figures 4

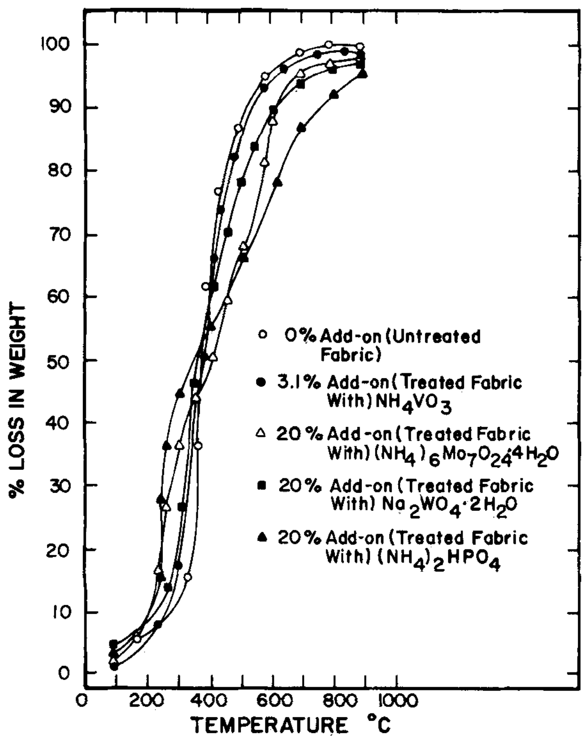

Figure 6. Behavior of fabric before and after impregnation with same amount of phosphate, molybdate and tungstate as well as with maximum amount of ammonium vanadate.

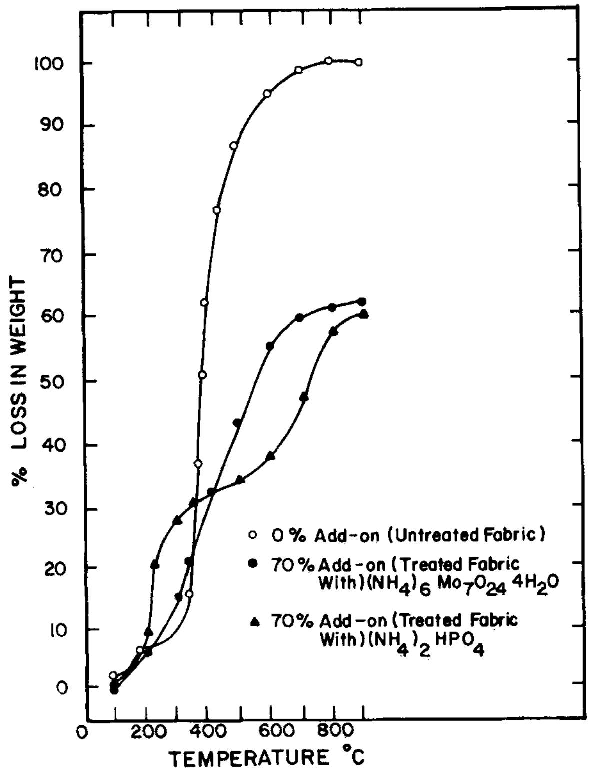

Figure 7. Behavior of fabric before and after treatment with 70% add-on ammonium phosphate and molybdate.

and 5 indicates that above 350°C higher retardation can be achieved by increasing the salt content of the fabric.

Figure 6 and 7 were constructed to compare the four salts. Fabrics containing 20% add-on phosphate, molybdate and tungstate as well as a fabric containing the maximum possible amount of ammonium vanadate were compared with the untreated fabric in Figure 6. Fabrics treated with phosphate or the molybdate gave high retardation. The behavior of fabrics treated with higher salt content is shown in Figure 7. In view of the present results and cost information provided by *Chemical Marketing Reporter* (1983), it could be concluded that diammonium hydrogen phosphate is the most effective and cheapest salt.

NOTATION

d = interplanar spacing
E = activation energy
I/I_o = relative intensity
R = universal gas constant
T = temperature
t = time
w = weight of unreacted portion of sample
Z = frequency factor
$\phi = \frac{dT}{dt}$ = heating rate

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