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EFFECT OF ENERGETIC MATERIALS ON THE THERMAL STABILITY OF POLYMERS

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ABSTRACT

The effect that energetic additives, such as ammonium perchlorate, ammonium persulfate, cyclotetramethylenetetranitramine, triaminoguanidine nitrate, plastisol nitrocellulose, and a nitrate lacquer at the 5% level, had on the thermal stability of polyacetals, aliphatic and aromatic polyesters, and polyamides was investigated by isothermal and dynamic thermogravimetry in a nitrogen and air atmosphere. Activation energies were determined for some of the admixtures; the additives were found to lower the activation energy by 30–88%. The effect of a series of ammonium and potassium salts on the thermal degradation of polyacetals was determined. It was found that the more acid character the cation and anion moieties had, the more effective the substance was in decreasing the thermal stability of polyacetals. Thermal instability of an admixture of polymer and additive was observed as a shift of the thermogravimetry curve to a lower temperature or by an increase in the rate of volatilization. Dynamic thermogravimetry studies of polyacetal admixtures offered a novel method for distinguishing between the acid strengths of the additives.

INTRODUCTION

The objective of this study was the development of thermally decomposable structural materials and the effect of energetic additives on the thermal stability of these materials. Such polymeric materials should decompose at temperatures somewhat above their processing temperatures, which should not be too high, and leave little or no residue. The materials should be dimensionally stable in humid environments and should be sufficiently rigid so that thin-walled containers can be prepared from them. The additives should significantly lower the decomposition temperature and reduce the amount of residue, if any, from the structural material. The practical addition of these additives to polymeric systems that may be used in the fabrication of consumable cartridge cases, would not occur during the melt process because of the potential occurrence of degradation; rather, it could be applied to the finished product in the form of an aerosol spray after the surface to be coated is abraded, which would increase the surface area and thereby decrease the burning time.

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EXPERIMENTAL

Commercial polymers investigated included polyacetals (Delrin, Celcon), polyester (Hytrel, Valox, Lucite), and polyamides (Nylons 4, 612). Energetic additives included ammonium persulfate (APS), ammonium perchlorate (AP), cyclotetramethylenetetranitramine (HMX), triaminoguanidine nitrate (TAGN), plastisol nitrocellulose (PNC), and a black lacquer coating (BLC) which contained cellulose nitrate. Non-energetic additives included ammonium and potassium inorganic salts, and eleven organic compounds which yielded free radicals of carbon, nitrogen, oxygen, sulfur and halogen.

From 4 to 5 mg of additive was added to 90 to 100 mg of powdered polymer and the mixture was ground in a Wig-L-Bug for one minute to insure uniform distribution. Aliquots of about 5 mg were used. Isothermal thermogravimetry (TG) was carried out at 305°, 355°, and 424°C in a nitrogen and air atmosphere on a DuPont 990 thermal analyzer with a 951 thermogravimetric module. Dynamic thermogravimetry studies were run at a heating rate of 5 or 15°C min^{-1}. Dynamic differential scanning calorimetry (DSC) studies were carried out in a sealed pan with a pinhole in the cover at a heating rate of 5°C min^{-1}.

DISCUSSION

The effect of metal catalysts on the oxidative degradation of rubbers has been investigated by many workers and has been reviewed by Dunn [1]. Reich [2] studied the compatibility of polymers with highly energetic materials in the ratio of nearly 1 : 1 by weight, using DSC. Cagliostro et al. [3] studied the effect of citric acid on Delrin using TG. Swanson and Madsen [4] evaluated the compatibility of three popellants with a variety of plastic adhesives and foams using DSC.

Thus thermoanalytical techniques such as TG and DSC have been shown to be powerful tools for investigating the thermal stability of mixtures of polymeric materials and energetic additives.

A very useful thermal analytical technique for following the degradation of polymers is isothermal thermogravimetric analysis. The fraction of material remaining at a given temperature as a function of time is determined. The data are analyzed by plotting the rate of volatilization (% per min) as a function of the volatilization. Theoretical analysis of these isothermal curves for polymer degradation studies [5,6] show: (1) a maximum rate at ca. 25% volatilization is found for pure random depolymerization or for depolymerization of moderate zip length involving considerable molecular transfer; (2) a maximum at ca. 50% volatilization is representative of depolymerizations in which the initiation occurs at chain ends, the zip length is moderate and either a slight amount of transfer or random initiation takes place; (3) the

TABLE 1

Activation energies for thermal decomposition of polymers with/without additives in a nitrogen atmosphere

Sample	Activation energy (kcal mole^{-1})	% Change in E_a
Celcon	37.8	
Celcon + APS [a]	4.5	88
Celcon + PNC [b]	9.4	75
Lucite	25.2	
Lucite + AP [c]	7.4	71
Lucite + NH_4Cl	17.9	30
AP [c]	25.8	

[a] APS = ammonium persulfate
[b] PNC = plastisol nitrocellulose
[c] AP = ammonium perchlorate

maxima of the isothermal curves may be taken as the rate constants for the calculation of activation energies for the reactions involved in the degradation; (4) a straight line parallel to the abscissa means that the degradation reaction follows zero order kinetics, and may be observed when depolymerization is initiated at chain ends and the zip length is much shorter than the

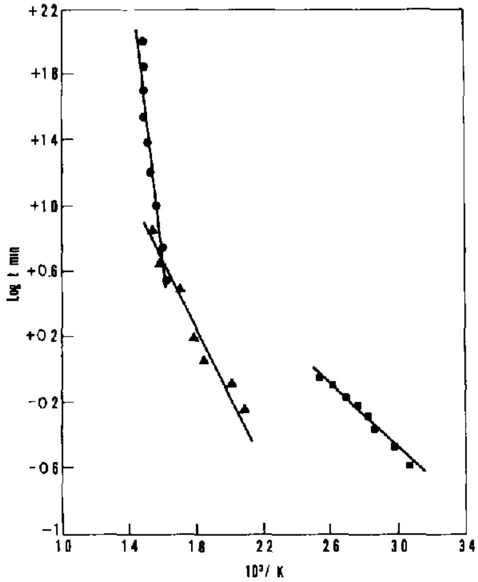

Fig. 1. Activation energy plots for Celcon and Celcon + additives. ●, Celcon, E_a = 37.8 kcal mole^{-1}; ▲, Celcon + PNC, E_a = 9.4 kcal mole^{-1}; ■, Celcon + APS, E_a = 4.5 kcal mole^{-1}.

polymer chain length; (5) a straight line inclined to the abscissa indicates a first order reaction and may be observed when the zip length is much larger than the polymer chain length; and (6) the maximum rate shifts towards lower conversion as the reaction order increases.

Activation energies were calculated for the thermal decomposition of Celcon and Lucite and for some of their admixtures (Table 1). The additives were found to lower the activation energy by 30–88%. Doyle's [7] relationship between isothermal and dynamic TG was used by plotting $\Delta(\log t)_{\text{iso}}$ vs. $\Delta(1/T)_{\text{dyn}}$ at fixed conversion values (α), and a slope of 0.457 E/R was obtained (Fig. 1). The method of Wall et al. [8] for isothermal TG was used by plotting $\Delta(\log t)_{\text{iso}}$ vs. $\Delta(1/T)_{\text{iso}}$ at constant α values, giving a slope of 0.457 E/R.

Isothermal polymer degradation

Table 2 gives the rate of volatilization of the polymers at 355°C in nitrogen and air. The order in air is Celcon > Delrin > Lucite ≫ Nylon 4 ≫ Hytrel > Valox > Nylon-612. Rate of volatilization plots are shown in Figs. 2 and 3. In Fig. 2, Delrin shows only a plateau at 305°C in nitrogen and a straight line plot in air, a maxima at about 60–70% at 355°C, and a shift in the maxima to a higher percent volatilization as the temperature is raised to 424°C. These results indicate that different processes are occurring at different temperatures in nitrogen and air. In Fig. 3, it is seen that Celcon and Lucite have their rate of volatilization maxima at about 20–40% while for Hytrel it is at 50% volatilization.

The effect of energetic additives on the thermal degradation of polymers at 355°C in nitrogen and air is given in Tables 3–9. Dynamic TG in Figs. 4 and 5 show the effect of these additives on Delrin and Celcon, respectively.

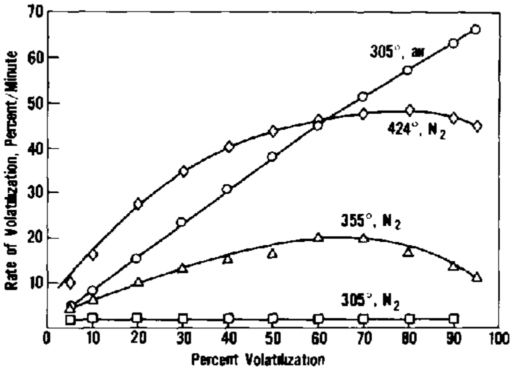

Fig. 2. Rate of volatilization of Delrin in nitrogen and air.

TABLE 2

Comparison of the rate of volatilization of polymers at 355°C in N_2 and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Delrin	Celcon	Hytrel	Valox	Lucite	Nylon 4	Nylon 612
Nitrogen							
5	3.8	1.4	0.7	0.7	3.5	3.4	0.1
10	6.1	1.7	0.9	1.0	4.5	6.2	0.1
20	10.0	1.8	1.1	1.4	5.6	11.1	
30	12.7	1.8	1.2	1.6	5.9	15.1	
40	14.8	1.6	1.3	1.7	5.9	18.5	
50	16.4	1.4	1.4	1.8	5.7	21.4	
60	17.5	1.2	1.3	1.7	5.2	23.5	
70	17.7	1.0	1.2	1.6	4.5	25.4	
80	16.6	0.8	1.1	1.4	3.7	26.1	
90	13.8		0.8	1.0	2.6	25.4	
95	10.8				1.8	23.8	
Air							
5	5.8	6.9	2.9	1.3	4.3	3.7	0.2
10	11.4	13.5	5.4	1.8	8.5	6.7	0.2
20	22.2	26.7	5.5	2.4	16.5	11.7	
30	32.6	39.5	11.5	2.8	24.8	15.7	
40	42.6	51.2	9.2	3.1	32.8	19.0	
50	52.1	61.7	7.1	3.2	40.3	21.5	
60	61.2	71.4	4.9	3.2	48.0	23.3	
70	70.0	80.5	3.5	3.1	55.1	24.6	
80	76.9	89.4	2.4	2.7	62.0	25.2	
90	84.1	97.8		1.5	68.2	24.7	
95	86.4	101.1			70.9	23.3	

Polyethers: Delrin and Celcon

Delrin is an acetal homopolymer and Celcon is an acetal copolymer. The data in Tables 3 and 4 show that the rate of volatilization is greater in air

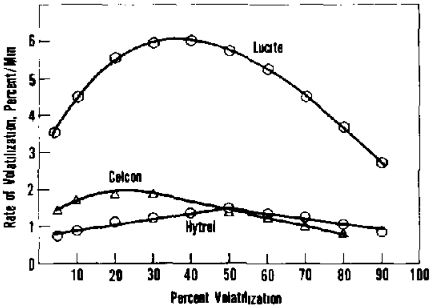

Fig. 3. Rate of volatilization of polymers in nitrogen at 355°C.

TABLE 3

Effect of additives on the rate of volatilization of Delrin at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Delrin	Delrin +					
		5.1% APS [a]	4.4% AP [b]	4.7% HMX [c]	4.6% TAGN [d]	4.5% PNC [e]	~ 4% BLC [f]
Nitrogen							
5	3.8	15.6	14.3	6.0	9.3	21.7	7.1
10	6.1	25.0	25.0	10.5	10.2	34.5	11.8
20	10.0	38.5	42.6	17.1	18.4	51.3	17.4
30	12.7	48.4	54.6	21.9	20.6	60.0	20.8
40	14.8	56.3	66.7	25.2	21.7	66.7	22.9
50	16.4	63.3	71.4	27.2	22.1	71.4	23.3
60	17.5	68.2	80.0	28.3	21.6	75.9	21.7
70	17.7	72.9	82.4	29.2	20.2	79.6	18.2
80	16.6	76.2	88.9	30.1	17.7	82.5	13.9
90	13.8	76.3	90.0	25.6	14.1	83.3	8.2
Air							
5	5.8	20.8	25.0	8.9	6.4	12.5	7.1
10	11.4	30.3	45.4	15.2	10.2	21.7	12.8
20	22.2	51.3	80.0	25.0	17.0	39.2	22.5
30	32.6	62.5	103.4	32.6	24.4	56.6	31.9
40	42.6	72.7	117.6	41.2	32.0	74.1	42.1
50	52.1	82.0	119.1	51.0	39.4	89.3	51.5
60	61.2	93.8	115.4	58.8	46.5	103.4	60.0
70	70.0	104.5	112.9	66.7	53.4	114.8	68.0
80	76.9	114.3	111.1	73.4	59.3	125.0	75.5
90	84.1	123.3	107.1	79.0	49.4	132.4	81.8

[a] APS = ammonium persulfate

[b] AP = ammonium perchlorate

[c] HMX = cyclotetramethylenetetranitramine

[d] TAGN = triaminoguanidine nitrate

[e] PNC = plastisol nitrocellulose

[f] BLC = black lacquer coating

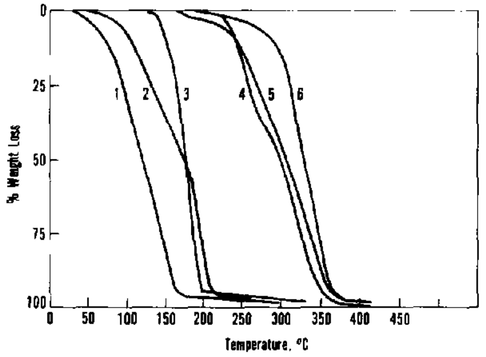

Fig. 4. Effect of additives on the degradation of Delrin in nitrogen at a heating rate of 5°C min^{-1}. 1, Delrin + 5.1% APS; 2, Delrin + 4.5% PNC; 3, Delrin + 4.4% AP; 4, Delrin + 4.6% TAGN; 5, Delrin + 4.7% HMX; 6, Delrin.

TABLE 4

Effect of additives on the rate of volatilization of Celcon at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Celcon	Celcon +					
		4.8% APS [a]	5.0% AP [b]	4.6% HMX [c]	4.6% TAGN [d]	4.1% PNC [e]	~ 4% BLC [f]
Nitrogen							
5	1.4	19.2	23.8	6.0	12.5	8.3	8.3
10	1.7	29.4	40.0	10.0	10.5	12.5	16.1
20	1.8	45.4	64.5	13.3	6.7	17.4	24.7
30	1.8	55.6	83.3	13.8	4.0	18.9	25.0
40	1.6	65.6	93.0	11.1	2.8	18.6	22.9
50	1.4	73.5	102.0	5.2	2.1	16.7	17.5
60	1.2	79.0	109.1	3.1	1.7	13.1	11.8
70	1.0	85.4	112.9	2.1	1.4	9.5	7.6
80	0.8	88.9	117.6	1.5	1.1		4.6
90		92.8	118.4				2.2
Air							
5	6.9	29.4	10.9	9.3	8.3	7.6	10.0
10	13.5	45.4	21.8	16.1	10.6	12.2	17.5
20	26.7	64.5	40.8	26.3	16.1	21.5	22.2
30	39.5	79.0	58.8	35.7	23.1	30.6	25.0
40	51.2	87.0	75.5	45.4	29.8	39.2	26.7
50	61.7	94.3	89.3	55.6	37.0	48.1	32.5
60	71.4	100.0	96.8	65.2	44.1	56.6	36.4
70	80.6	104.5	100.0	73.7	50.7	64.8	41.7
80	89.4	108.1	101.3	82.5	56.7	72.1	45.2
90	97.8	109.8	100.0	90.0	62.9	79.0	

[a] APS = ammonium persulfate
[b] AP = ammonium perchlorate
[c] HMX = cyclotetramethylenetetranitramine
[d] TAGN = triaminoguanidine nitrate
[e] PNC = plastisol nitrocellulose
[f] BLC = black lacquer coating

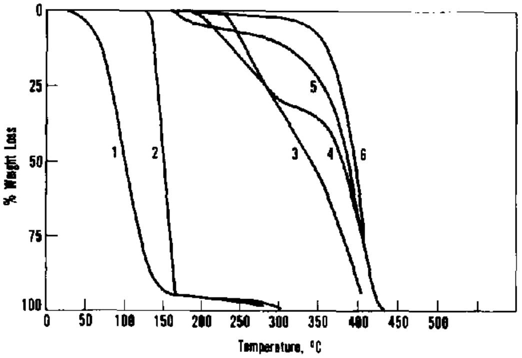

Fig. 5. Effect of additives on the degradation of Celcon in nitrogen at a heating rate of 5°C min^{-1}. 1, Celcon + 4.2% APS; 2, Celcon + 5.0% AP; 3, Celcon + 4.1% PNC; 4, Celcon + 4.6% HMX; 5, Celcon + 4.6% TAGN; 6, Celcon.

TABLE 5

Effect of additives on the rate of volatilization of Hytrel at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Hytrel	Hytrel +					
		4.3% APS[a]	4.9% AP[b]	4.4% HMX[c]	4.6% TAGN[d]	4.7% PNC[e]	~ 4% BLC[f]
Nitrogen							
5	0.7	6.2	4.5	5.3	1.3	2.5	10.4
10	0.9	10.0	8.2	1.8	1.0	1.5	20.0
20	1.1	14.3	16.7	1.6	1.2	1.6	35.7
30	1.2	4.4	10.0	1.7	1.4	1.7	8.7
40	1.3	3.3	3.8	1.7	1.45	1.7	4.3
50	1.4	2.8	2.9	1.6	1.4	1.6	2.3
60	1.3	2.5	2.4	1.5	1.3	1.5	1.7
70	1.2	2.1	2.0	1.4	1.2	1.4	1.2
80	1.1	1.8	1.6			1.2	
90	0.8						
Air							
5	2.9	5.6	6.7	7.1	5.2	4.5	10.2
10	5.4	10.5	12.2	8.4	5.7	6.9	20.0
20	5.5	20.0	20.0	10.0	6.4	11.9	39.2
30	11.5	15.0	15.0	9.1	5.5	13.6	25.0
40	9.2	10.3	7.8	7.7	4.8	9.5	14.3
50	7.1	7.6	6.0	6.3	4.2	7.0	1.7
60	4.9	5.9	5.0	5.2	3.7	6.5	
70	3.5	4.7	4.2	4.1	3.1	4.3	
80	2.4	3.5	3.2	2.8	2.3	3.0	
90							

[a] APS = ammonium persulfate

[b] AP = ammonium perchlorate

[c] HMX = cyclotetramethylenetetranitramine

[d] TAGN = triaminoguanidine nitrate

[e] PNC = plastisol nitrocellulose

[f] BLC = black lacquer coating

than in nitrogen. Some observations regarding Delrin are made; (1) the order for the effect of additives in increasing the rate of volatilization in nitrogen or air is: AP > PNC > APS ≫ HMX > TAGN = BLC; (2) in nitrogen there are maxima in the rate of volatilization only with BLC, TAGN, and Delrin by itself; and (3) in air there is a monotonic increase in the rate of volatilization for Delrin with/without additives. With Celcon it is seen that (1) in nitrogen the order is AP > APS ≫ BLC > PNC > HMX > TAGN; (2) in air the order is APS > AP > HMX > PNC > TAGN ≫ BLC; (3) in nitrogen there are peak maxima in the rate of volatilization with HMX,

TABLE 6

Effect of additives on the rate of volatilization of Valox at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Valox	Valox +					
		5.1% APS[a]	4.6% AP[b]	4.8% HMX[c]	4.7% TAGN[d]	4.5% PNC[e]	4% BLC[f]
Nitrogen							
5	0.7	1.7	2.6	1.3	1.3	1.3	8.6
10	1.0	1.6	2.5	1.2	1.2	1.2	16.4
20	1.4	1.8	2.2	1.4	1.6	1.3	8.3
30	1.6	1.9	2.4	1.6	1.7	1.4	3.8
40	1.7	1.9	2.5	1.65	1.75	1.5	2.8
50	1.8	1.9	2.4	1.6	1.8	1.55	2.2
60	1.7	1.8	2.3	1.5	1.7	1.5	1.8
70	1.6	1.7	2.0		1.6	1.4	1.3
80	1.4	1.5	1.7		1.3		
90	1.0						
Air							
5	1.3	1.8	2.6	2.8	2.1	2.2	10.0
10	1.8	2.2	2.7	2.5	2.3	2.3	14.9
20	2.4	2.8	2.8	2.9	2.9	2.8	6.8
30	2.8	3.2	3.1	3.3	3.4	3.1	4.2
40	3.1	3.25	3.3	3.5	3.6	3.3	4.0
50	3.2	3.35	3.35	3.6	3.7	3.35	3.7
60	3.2	3.3	3.2	3.6	3.6	3.3	3.0
70	3.1	3.1	3.0	3.4	3.5	3.1	
80	2.7	2.8	2.6	3.1	3.0	2.7	
90	1.5	1.7		2.5		1.5	

[a] APS = ammonium persulfate

[b] AP = ammonium perchlorate

[c] HMX = cyclotetramethylenetetranitramine

[d] TAGN = triaminoguanidine nitrate

[e] PNC = plastisol nitrocellulose

[f] BLC = black lacquer coating

TAGN, PNC, BLC, and Celcon by itself; and (4) in air there is a monotonic increase in the rate of volatilization for Celcon with/without additives. The dynamic TG curves in Figs. 4 and 5 show the same order for the effectiveness of the additives except that APS > AP with Delrin.

Thus Delrin by itself has a greater rate of volatilization in nitrogen than Celcon by itself, while in air they are nearly the same. The most effective additives in increasing the rate of volatilization of Delrin and Celcon are APS and AP; the effect is about the same in air while in nitrogen it is

TABLE 7

Effect of additives on the rate of volatilization of Lucite at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Lucite	Lucite +					
		5.0% APS[a]	4.5% AP[b]	4.9% HMX[c]	5.4% TAGN[d]	5.2% PNC[e]	~ 4% BLC[f]
5	3.5	3.6	6.6	4.9	7.6	5.8	5.2
10	4.5	4.4	11.6	8.5	10.2	5.4	7.1
20	5.6	5.0	20.0	14.3	14.1	4.5	6.1
30	5.9	5.0	27.0	16.7	12.5	4.3	5.2
40	5.9	4.9	32.8	16.5	9.1	4.0	4.3
50	5.7	4.4	37.0	11.9	6.8	3.6	3.7
60	5.2	3.9	39.7	7.9	5.2	3.2	3.2
70	4.5	3.3	40.7	5.0	4.0	2.7	2.9
80	3.7	2.5	38.6	3.0	2.8	2.2	2.5
90	2.6	1.5	20.9	1.6	1.6	1.5	2.2
Air							
5	4.3	61	77	60	93	46.7	8.5
10	8.5	105	141	105	132	86.2	12.0
20	16.5	194	247	189	208	167	18.2
30	24.8	275	333	273	291	248	26.5
40	32.8	354	404	354	364	317	34.8
50	40.3	417	472	427	439	385	43.1
60	48.0	476	536	500	504	451	50.8
70	55.1	522	582	569	574	504	58.3
80	62.0	559	667	635	635	559	65.6
90	68.2	600	714	692	692	604	72.6

[a] APS = ammonium persulfate
[b] AP = ammonium perchlorate
[c] HMX = cyclotetramethylenetetranitramine
[d] TAGN = triaminoguanidine nitrate
[e] PNC = plastisol nitrocellulose
[f] BLC = black lacquer coating

slightly greater for Delrin. Table 1 shows that APS and PNC decreased the activation energy for the thermal decomposition of Celcon by 88 and 75% respectively.

Polyesters: Hytrel, Valox, and Lucite

Hytrel is a terephthalate copolymer, Valox a terephthalate polymer, and Lucite an aliphatic polymethylmethacrylate. Tables 5–7 show that energetic additives have an insignificant effect on the rate of volatilization of Hytrel and Valox whether in a nitrogen or air atmosphere, but have a great effect

TABLE 8

Effect of additives on the rate of volatilization of Nylon-4 at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Nylon-4	Nylon-4+					
		4.6% APS[a]	5.0% AP[b]	4.6% HMX[c]	4.7% TAGN[d]	4.5% PNC[e]	~ 4% BLC[f]
5	3.4	4.0	6.2	6.1	6.2	6.7	7.1
10	6.2	6.9	11.0	8.5	8.5	6.8	12.2
20	11.1	12.7	19.4	13.9	13.5	11.7	13.8
30	15.1	16.6	26.8	18.2	17.5	15.8	17.1
40	18.5	20.5	33.3	21.5	20.6	19.0	19.8
50	21.4	23.8	38.8	23.9	23.1	21.6	21.7
60	23.5	26.7	43.5	26.0	25.0	23.5	23.0
70	25.4	29.0	47.3	27.2	26.3	25.0	23.1
80	26.1	30.2	49.1	27.6	26.9	25.8	26.4
90	25.4	29.3	45.0	26.5	26.4	25.4	
Air							
5	3.7	6.2	5.4	5.2	6.7	8.3	8.3
10	6.7	10.0	9.8	7.6	8.9	8.3	13.3
20	11.7	16.7	18.0	12.9	14.3	13.8	14.8
30	15.7	22.4	25.0	17.1	18.8	18.2	18.1
40	19.0	27.6	31.5	20.6	22.2	21.7	20.8
50	21.5	31.8	37.0	23.3	25.0	24.6	22.8
60	23.3	35.3	41.7	25.4	27.0	26.9	24.4
70	24.6	37.8	45.2	26.8	28.6	28.6	25.0
80	25.2	38.5	45.7	27.4	29.6	29.5	18.8
90	24.7	36.0	31.0	26.5	29.1	29.0	

[a] APS = ammonium persulfate
[b] AP = ammonium perchlorate
[c] HMX = cyclotetramethylenetetranitramine
[d] TAGN = triaminoguanidine nitrate
[e] PNC = plastisol nitrocellulose
[f] BLC = black lacquer coating

on Lucite, especially in an air atmosphere. Hytrel and Valox show peak maxima in their rate of volatilization. Hytrel has a slightly higher volatilization in air than in nitrogen, and it is a little more than that for Valox. The order for the additives in increasing the rate of volatilization for Hytrel is: (1) in nitrogen, BLC > AP > APS ≫ HMX = PNC > TAGN, (2) in air, BLC > AP = APS > PNC > HMX > TAGN; for Valox in nitrogen or air, it is BLC > AP = APS = HMX = TAGN = PNC. However, for Hytrel or Valox with/without additives their rate of volatilization at 355°C in nitrogen or air is very low compared to that for Delrin, Celcon, and Lucite.

TABLE 9

Comparison of rate of volatilization of polymers coated with black lacquer at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})						
	Delrin	Celcon	Hytrel	Valox	Lucite	Nylon 4	Nylon 612
Nitrogen							
5	7.1	8.3	10.4	8.6	5.2	7.1	9.1
10	11.8	16.1	20.0	16.4	7.1	12.2	17.9
20	17.4	24.7	35.7	8.3	6.1	13.8	33.9
30	20.8	25.0	8.7	3.8	5.2	17.1	20.7
40	22.9	22.9	4.3	2.8	4.3	19.8	8.3
50	23.3	17.5	2.3	2.2	3.8	21.7	3.0
60	21.7	11.8	1.7	1.8	3.2	23.0	0.7
70	18.2	7.6	1.2	1.3	2.9	23.1	
80	13.9	4.6			2.5	26.4	
90	8.2	2.2			2.2		
Air							
5	7.1	10.0	10.2	10.0	8.5	8.3	10.0
10	12.8	17.5	20.0	14.9	12.0	13.3	18.2
20	22.5	22.2	39.2	6.8	18.2	14.8	33.3
30	31.9	25.0	25.0	4.2	26.6	18.1	23.1
40	42.1	26.7	14.3	4.0	34.8	20.8	15.1
50	51.5	32.5	1.7	3.7	43.1	22.8	2.1
60	60.0	36.4		3.0	50.8	24.4	1.1
70	68.0	41.7			58.3	25.0	1.0
80	75.5	45.2			65.6	18.8	0.9
90	81.8				72.6		0.7

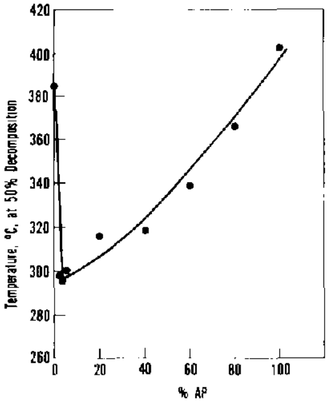

Fig. 6 Effect of AP concentration on the thermal decomposition of a mixture of Lucite+AP.

For Lucite the order for the additives in increasing the rate of volatilization in nitrogen is AP $\gg$ HMX > TAGN > APS > PNC = BLC. In air the rate of volatilization is much greater and the order is AP = HMX = TAGN > APS = PNC $\gg$ BLC $\gg$ Lucite. Lucite by itself has a greater rate of volatilization in air than in nitrogen. In nitrogen, Lucite with/without additives shows a peak maxima in the rate of volatilization while in air there is a monotonic increase in the rate. Table 1 shows that the activation energy required for the thermal decomposition of Lucite is decreased by 71 and 30% by AP and NH_4Cl, respectively. Figure 6 shows the effect of the AP concentration on the thermal decomposition of a mixture of Lucite + AP. The limiting effect is at about 2% AP.

Polyamides: Nylon 4 and Nylon 612

Table 8 shows the effect of additives on the rate of volatilization of Nylon 4 at 355°C in nitrogen and air. A peak maxima in the rate of volatilization was not observed in nitrogen or air. The rate of volatilization is about the same in nitrogen or air for Nylon 4 with/without additives except for AP. The order for the additives is: AP > APS = HMX = TAGN = PNC = BLC = Nylon 4. Nylon 612 had a much lower rate of volatilization at 355°C; it was lower than that for Hytrel or Valox.

Volatilization order for additives

In nitrogen at 355°C, the volatilization order for the energetic additives was: PNC > TAGN > HMX > APS > AP. The first three volatilized in less than 0.8 min, APS in 10.6 min, and AP in 46 min. In air, PNC and HMX volatilized faster, APS and TAGN a little slower, and AP about the same as in nitrogen. Thus one of the advantages of APS and AP as additives was the longer time that they are effective in promoting the breakdown of polymers, especially polyacetals.

The effect of free radical initiators on the thermal decomposition of Delrin

The effect of eleven additives, yielding free radicals of carbon, nitrogen, oxygen, sulfur and halogen, on the thermal degradation of Delrin was investigated. The following order of effect on lowering the decomposition temperature was observed: *N*-bromosuccinimide $\gg$ peracetic acid- 40% > *N*-chlorosuccinimide > dicumyl peroxide > azo-*iso*butyronitrile > dimethylbenzylamine > benzoylperoxide > 1,3-diphenyltriazene > paramethane hydroperoxide > *tertiary* butyl hydroperoxide-70% > tetramethyl thiuram disulfide. The more effective additives had exotherms in the melting region (170–190°C) of Delrin. Combination of free radical initiators with ammonium persulfate or ammonium perchlorate had only a small synergistic effect; it was greater with ammonium persulfate. The order among the additives is summarized in Table 10 by listing the temperatures at which 80% decomposition by weight occurs. The most effective organic free radical initiator was found to be *N*-bromosuccinimide ($C_4H_4O_2NBr$). It caused a two-step TG curve with the first step complete at 152°C after a 35% weight loss (Fig. 7). The substitution of bromine for a chlorine atom in *N*-halo-substituted succinimide causes a large, dramatic effect on the decomposition of Delrin. Perhaps, it should not be too surprising that *N*-bromosuccinimide reacts differently since it is known from kinetic studies in the gas phase between hydrogen and halogen that with chlorine a simple second order

TABLE 10

Temperature at which 80% decomposition by weight occurs for Delrin + additives

Temperature (°C)	Additive
Delrin + 2% additive	
200	Ammonium persulfate
211	Ammonium perchlorate
230	Potassium persulfate
264	*N*-Bromosuccinimide [a]
330	Peracetic acid, 40%
341	Potassium perchlorate
351	*N*-Chlorosuccinimide [a]
353	Dicumyl peroxide
355	Azo-*iso*butyronitrile
366	Dimethyl benzylamine
374	Benzoyl peroxide
380	1,3-Diphenyltriazene [a]
382	Paramethane hydroperoxide
388	Delrin alone
398	*Tertiary* butyl hydroperoxide, 70%
403	Tetramethyl thiuram disulfide [a]
Delrin + 2% $(NH_4)_2S_2O_8$ *+ 2% additive*	
178	*N*-Chlorosuccinimide
185	Azo-*iso*butyronitrile
197	Dicumyl peroxide
200	Benzoyl peroxide
202	Tetramethyl thiuram disulfide
Delrin + 2% NH_4ClO_4 *+ 2% additive*	
203	*N*-Chlorosuccinimide
216	Azo-*iso*butyronitrile
218	Benzoyl peroxide
231	Dicumyl peroxide
231	Tetramethyl thiuram disulfide

[a] Two step TGA curve and two DSC decomposition peaks.

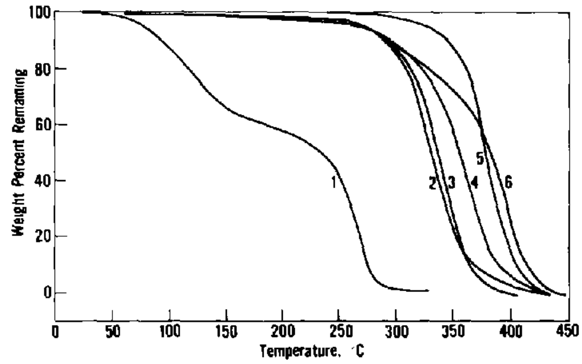

Fig. 7. Effect of free radical initiators on the thermal decomposition of Delrin. 1, Delrin + 2% *N*-bromosuccinimide; 2, Delrin + 2% *N*-chlorosuccinimide; 3, Delrin + 2% azo*iso*butyronitrile; 4, Delrin + 2% benzoyl peroxide; 5, Delrin alone; 6, Delrin + 2% tetramethylthiuram disulfide.

reaction is found, while with bromine a complex reaction order expression is obtained. The dynamic TG curves in Fig. 7 show the effect of some of the additives on the thermal decomposition of Delrin.

Ammonium persulfate and *N*-bromosuccinimide are the most effective free radical initiators studied so far in lowering the decomposition temperature of Delrin. This may be because their exotherms come in the melting range of Delrin, and consequently, because of the liquid phase a greater interaction can occur. However, 1, 3 diphenyltriazene also has an exotherm in the 180°–200°C region and it is not an effective additive. Perhaps, because of its low melting point and consequently, possible mass losses due to vaporization, its effective concentration may be low in the processing range of Delrin. DSC curves are shown in Fig. 8.

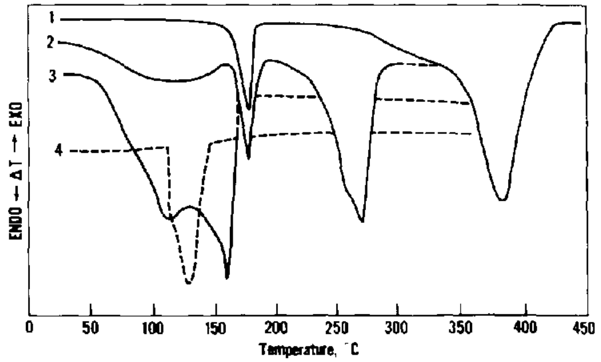

Fig. 8. DSC of Delrin and Delrin + additives. 1, Delrin; 2, Delrin + 2% *N*-bromosuccinimide; 3, Delrin + 2% ammonium persulfate; 4, Delrin + 2% ammonium perchlorate.

Effect of halide salts on Delrin

Figure 9 shows the effectiveness of ammonium and potassium halides on lowering the decomposition temperature of Delrin. The order is $NH_4I >$ $NH_4Br > NH_4Cl > KI > KBr$. This trend among the halides may be correlated with the increase in covalent character, ionic radius, acidity, and atomic number of the halogen as you go down Group VIIA. In comparing cations with non-metal and metal properties, $NH_4 > K$ because the nitrogen atom in ammonium is more electronegative than potassium and therefore is less basic or has more acidic character.

Figure 10 shows the effect of chloride salts of zinc, aluminum and ammonium on the decomposition of Delrin and Celcon. The observed order is $Zn \gg NH_4 > Al$. Zinc chloride has the most deleterious effect on the stability of Delrin and Celcon. Over 50% decomposition occurs before the melting point, with degradation starting at ~ 40°C. It leaves a 4.8% residue at 300°C in a nitrogen atmosphere, while in air there is a 7.5% residue at 300°C which decreased to 2% at 500°C. Zinc chloride has a synergistic effect on the decomposition of polyacetals since zinc acetylacetonate or other chloride salts do not have such a dramatic effect. It affects Celcon and Delrin to approximately the same extent. Hybart and Rowley [9] found that zinc stearate and zinc chloride accelerated the degradation of polyvinyl chloride because of the catalytic action of zinc chloride. Grassic and McGuchan [10] observed that zinc chloride appears to be more efficient than strong acids in the catalytic degradation of polyacrylonitrile.

Effect of perchlorates on Celcon

Figure 11 shows the effect of perchlorates on the decomposition of Celcon. The decomposition order is $NH_4 > Mg > Li > K > Cs$. In an overly

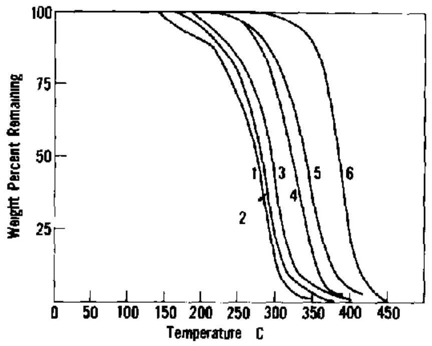

Fig. 9. Effect of ammonium and potassium halides on the thermal decomposition of Delrin. 1, Delrin + 2% NH_4I; 2, Delrin + 2% NH_4Br; 3, Delrin + 2% NH_4Cl; 4, Delrin + 2% KI; 5, Delrin + 2% KBr; 6, Delrin.

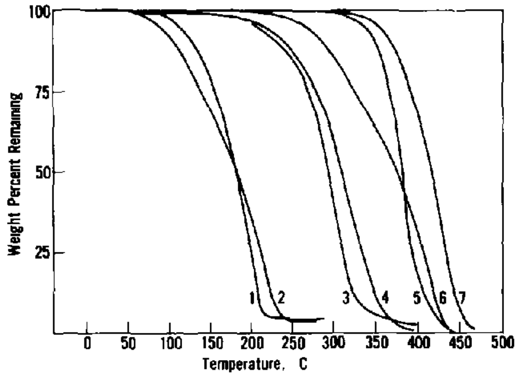

Fig. 10. Effect of chlorides on the decomposition of Delrin and Celcon in a nitrogen atmosphere. 1, Celcon + 2% $ZnCl_2$; 2, Delrin + 2% $ZnCl_2$; 3, Delrin + 2% NH_4Cl; 4, Delrin + 2% $AlCl_3$; 5, Delrin; 6, Celcon + 1% NH_4Cl; 7, Celcon.

simplified manner, this trend may be correlated with changes in the values of ionic potential (charge/radius), oxidation potentials and acidity as you go down and across the Periodic Table. Decreasing covalent character is predicted with increasing atomic number in groups containing metals and the opposite in groups containing non-metals.

In Group 1a, the smaller cation (Li), because of its greater concentration of positive charge, has a greater polarizing effect upon an anion than a larger cation (Cs) and thus favors increasing covalent character with increasing ionic potential (Mg > Li > K > Cs). In addition, as the size of the cation decreases, its oxidation potential decreases (Mg < K < Cs; Li is anomalous) and its acidity increases. Thus the decomposition order of perchlorates may be explained on the basis of increasing acidity and covalent character of the

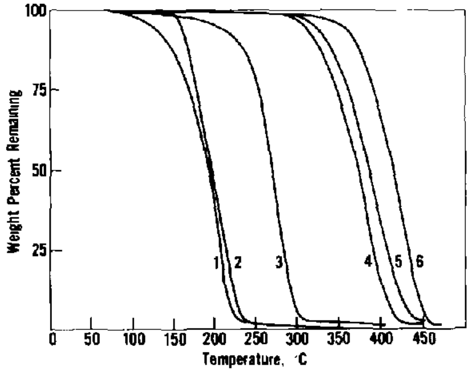

Fig. 11. Effect of perchlorates on the decomposition of Celcon in a nitrogen atmosphere. 1, Celcon + 1.4% AP; 2, Celcon + 1.9% $Mg(ClO_4)_2$; 3, Celcon + 2.1% $LiClO_4$; 4, Celcon + 2.2% $KClO_4$; 5, Celcon + 2.0% $CsClO_4$; 6, Celcon.

cations ($NH_4 > Mg > Li > K > Cs$) as you go up a group (Ia) and across a period in the Periodic Table. Osawa et al. [11] postulated that the more ionic character there is in a metallic salt, the more effective it is for the catalyzed thermal oxidative degradation of isotactic polypropylene.

Effect of ammonium perchlorate concentration on Celcon and Delrin

Figure 12 shows the effect of NH_4ClO_4 concentration on the decomposition of Celcon and Delrin. The addition of only 0.2% AP causes a dramatic decrease in the thermal stability of polyacetals. Increasing the AP concentration beyond 0.4% has only a negligible effect on the decomposition of Delrin and Celcon, both of which are affected to the same extent. This is surprising, since in the absence of additives, Celcon is more thermally stable. The temperatures at which 90% volatilization has occurred for Celcon and Delrin are 442°C and 412°C, respectively, in a nitrogen atmosphere at a 15°C min^{-1} heating rate. It will be shown later than some additives have a more pronounced effect on Delrin than Celcon.

Effect of oxidizing agents on Delrin and Celcon

Figure 13 shows the effects of permanganate, perchlorate and dichromate salts of potassium on the thermal decomposition of Delrin and Celcon. The decomposition order is $MnO_4^- > ClO_4^- > Cr_2O_7$. This is the order of decreasing oxidation potential and consequently, the order of decreasing acidity. Thus, as the acidity of the anion and cation increases, the more effective the salt is for the thermal degradation of polyacetals. The oxidation potentials in acidic solutions are -1.5, -1.37, and -1.33 V for the couples Mn(II)–Mn(VII), Cl(I)–Cl(VII) and Cr(III)–Cr(VII), respectively. Potassium permanganate leaves the largest residue (5% at 400°C) and has a much greater effect on the decomposition of Delrin than on Celcon.

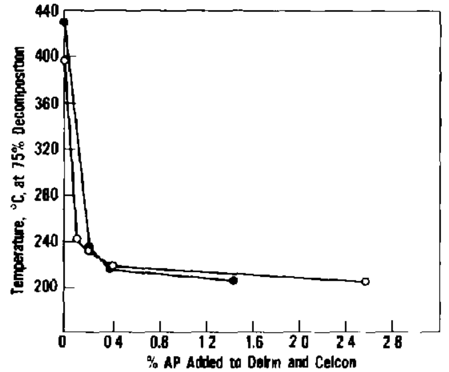

Fig. 12. Limiting effect of AP concentration on the decomposition of Delrin and Celcon in a nitrogen atmosphere. ○, Delrin; ●, Celcon.

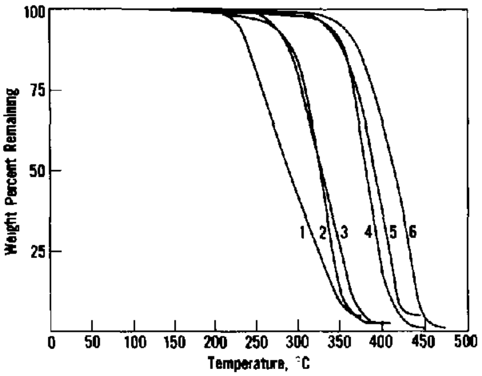

Fig. 13. Effect of oxidizing agents on the decomposition of Delrin and Celcon in a nitrogen atmosphere. 1, Delrin + 2% $KMnO_4$; 2, Delrin + 2% $KClO_4$; 3, Delrin + 2% $K_2Cr_2O_7$; 4, Delrin; 5, Celcon + 2% $KMnO_4$; 6, Celcon.

Effect of metal acetylacetonates on Delrin and Celcon

Figure 14 shows the effect of metal acetylacetonates on the decomposition of Delrin and Celcon. The decomposition order is $Fe^{3+} > Co^{2+} > Co^{3+} > Zn^{2+}$. These additives have a more pronounced effect on Delrin than Celcon. Osawa and Shibamiya [12] studied the effect of fourteen transition and alkaline earth metal salts of stearic acid on the oxidative degradation of isotactic polypropylene and found Co ≫ Al > Zn, and for the decomposition of *tert*-butyl hydroperoxide found Co ≫ Fe > Zn > Al.

Effect of ammonium salts of perchlorate, sulfate and phosphate on Delrin

Figure 15 shows the order $NH_4ClO_4 > (NH_4)_2SO_4 > (NH_4)_2HPO_4$ in lowering the thermal decomposition of Delrin. Phosphate, sulfate, and

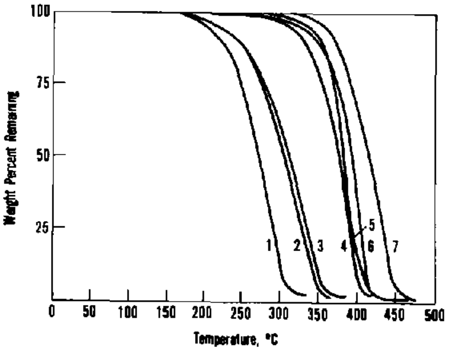

Fig. 14. Effect of metal acetylacetonates on the decomposition of Delrin and Celcon in a nitrogen atmosphere. 1, Delrin + 2% Fe(III) AA; 2, Delrin + 2% Co(II) AA; 3, Delrin + 2% Co(III) AA; 4, Celcon + 2% Co(III) AA; 5, Delrin; 6, Celcon + 2% Zn AA; 7, Celcon.

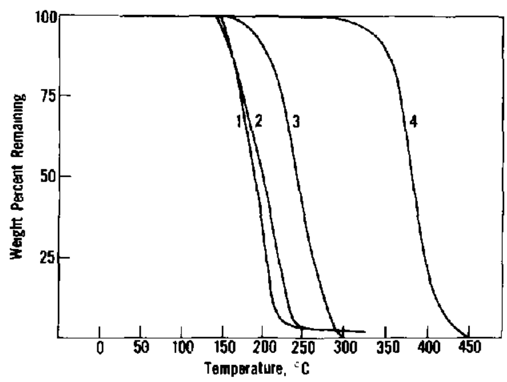

Fig. 15. Effect of ammonium perchlorate, ammonium sulfate and ammonium phosphate on the thermal decomposition of Delrin. 1, Delrin + 2% NH_4ClO_4; 2, Delrin + 2% $(NH_4)_2SO_4$; 3, Delrin + 2% $(NH_4)_2HPO_4$; 4, Delrin.

perchlorate are isosteric groups and are members of the third period. As you go across this period for this series, there is an increase in electronegativity of the non-metal and hence, an increase in acid strength of the anion and therefore, an increase in the effectiveness of the anion as an additive in decreasing the thermal stability of Delrin.

Effect of potassium salts on Delrin

Figure 16 shows the order $K_2S_2O_8 \gg KClO_4 > KClO_3 > K_2Cr_2O_7 > K_2SO_4$ in decreasing the thermal stability of Delrin. There are at least three observations that can be made: (1) perchlorate is more effective than chlorate because the presence of an additional oxygen atom causes chlorine

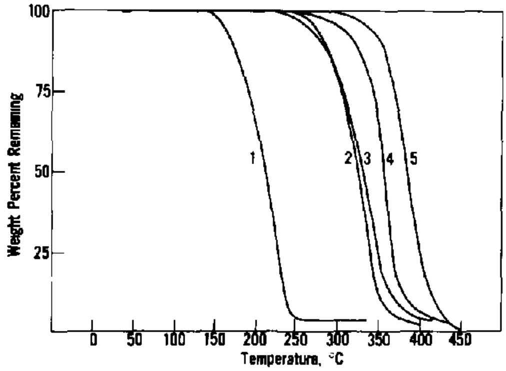

Fig. 16. Effect of potassium chlorate, potassium perchlorate, potassium sulfate and potassium peroxydisulfate on the thermal decomposition of Delrin. 1, Delrin + 2% $K_2S_2O_8$; 2, Delrin + 2% $KClO_4$; 3, Delrin + 2% $KClO_3$; 4, Delrin + 2% K_2SO_4; 5, Delrin.

to be more positive (i.e. higher oxidation state), thereby decreasing its ionic radius, and consequently increasing the acid strength of the anion; (2) perchlorate is more effective than sulfate because the chlorine is more electronegative and therefore increases the acid strength of the anion; and (3) peroxydisulfate is much more effective than sulfate or perchlorate, probably because when it is heated, the peroxide linkage between the sulfur atoms breaks and liberates free radicals and oxygen which has a large catalytic effect on the decomposition of acetals. In comparison, potassium dichromate with seven oxygen atoms is not as effective an additive as potassium peroxydisulfate with eight oxygen atoms because the chromium atoms are linked together with a single oxygen, and consequently do not liberate oxygen or free radicals when heated; potassium dichromate is about as effective as potassium chlorate.

Effect of persulfate and perchlorate salts on Delrin

Figure 17 shows the order $(NH_4)_2S_2O_8 > NH_4ClO_4 > K_2S_2O_8 \gg KClO_4$ on lowering the thermal decomposition of Delrin. This order indicates that (1) the more acid the character of the cation and anion, the more effective they are as additives, and (2) persulfates liberate free radicals and oxygen which can catalyze the decomposition reaction. It is evident that the effect on Delrin in going from $K_2S_2O_8$ to $(NH_4)_2S_2O_8$ is small compared to going from $KClO_4$ to NH_4ClO_4. DSC showed that the exothermic peak in $K_2S_2O_8$ corresponding to the exotherm in $(NH_4)_2S_2O_8$ came at a higher temperature (290°C).

Effect of ammonium salts of perchlorate and chloride on Delrin

Figure 18 shows the order $NH_4ClO_4 > NH_4Cl > (CH_3)_4NClO_4 > (CH_3)_4NCl$ in decreasing the thermal stability of Delrin. This order provides

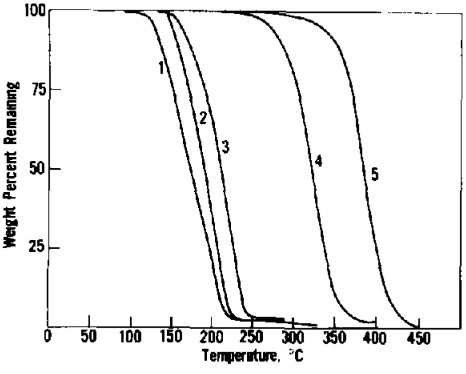

Fig. 17. Effect of ammonium and potassium persulfates and perchlorates on the thermal decomposition of Delrin. 1, Delrin + 2% $(NH_4)_2S_2O_8$; 2, Delrin + 2% NH_4ClO_4; 3, Delrin + 2% $K_2S_2O_8$; 4, Delrin + 2% $KClO_4$; 5, Delrin.

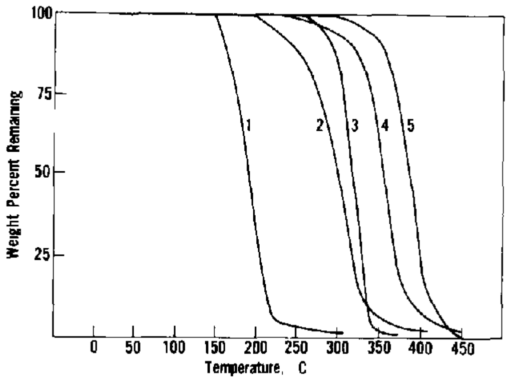

Fig. 18. Effect of two ammonium perchlorates and chlorides on the thermal decomposition of Delrin. 1. Delrin + 2% NH_4ClO_4; 2. Delrin + 2% NH_4Cl; 3. Delrin + 2% $(CH_3)_4NClO_4$; 4. Delrin + 2% $(CH_3)_4NCl$; 5. Delrin.

TABLE 11

Effect of ammonium salts on the rate of volatilization of Delrin at 355°C in nitrogen and air

Volatilization (%)	Rate of volatilization (% min^{-1})				
	Delrin	Delrin +			
		4.4% NH_4ClO_4	4.5% $(NH_4)_2SO_4$	4.5% NH_4Cl	4.6% NH_4NO_3
Nitrogen					
5	3.8	14.3	10.9	10.4	6.2
10	6.1	25.0	20.4	15.8	10.0
20	10.0	42.6	34.5	23.8	15.4
30	12.7	54.6	45.5	29.7	18.7
40	14.8	66.7	52.6	33.9	20.0
50	16.4	71.4	59.5	37.3	20.7
60	17.5	80.0	65.2	39.5	18.6
70	17.7	82.4	70.0	41.2	14.5
80	16.6	88.9	73.4	41.7	11.1
90	13.8	90.0	76.3	40.9	7.7
Air					
5	5.8	25.0	11.9	11.4	7.7
10	11.4	45.4	23.3	19.2	12.7
20	22.2	80.0	44.4	29.0	23.3
30	32.6	103.4	65.2	35.7	34.1
40	42.6	117.6	85.2	41.2	44.4
50	52.1	119.1	104.2	45.4	54.3
60	61.2	115.4	120.0	48.8	63.8
70	70.0	112.9	137.3	51.1	72.9
80	76.9	111.1	150.9	51.9	80.8
90	84.1	107.1	160.7	52.1	89.1

additional support for the conclusions drawn earlier; that the more acid character the cation and anion have, the more effective it is in decreasing the thermal stability of polyacetals. Perchlorate is more effective than chloride because the presence of oxygen atoms makes chlorine more positive and hence increases its acid strength. Methyl groups are base strengthening, consequently tetramethylammonium is more basic than ammonium and therefore less effective.

The admixture Delrin + NH_4NO_3 was also run. In comparing the effect of ammonium salts of perchlorate, sulfate, chloride, and nitrate on decreasing the thermal stability of Delrin, the order was $NH_4ClO_4 > (NH_4)_2SO_4 > NH_4Cl > NH_4NO_3$. This is the order of decreasing acidity; the acidity functions (H_0) for the corresponding acids are −2.84, −2.76, −2.12, and −1.79 respectively [13].

The rate of volatilization of these additives with Delrin at 355°C is given in Table 11. In nitrogen the order is the same as observed by dynamic TG in nitrogen. However, in air the order is different, namely $NH_4ClO_4 = (NH_4)_2SO_4 > NH_4NO_3 > NH_4Cl$.

CONCLUSIONS

The rate of volatilization of seven polymers with/without 2 to 5% energetic additives has been determined by isothermal and dynamic thermogravimetry in a nitrogen and air atmosphere. Activation energies were determined for the thermal decomposition of some of the admixtures; the additives were found to lower the activation energy by 30–88%. Based on thermal analysis data only, Delrin, Celcon, and Lucite showed promise as a possible consumable cartridge case.

The effect of a series of ammonium and potassium salts at the 2% level on the thermal decomposition of polyacetals was investigated by dynamic thermogravimetry. A general observation was that the more acid character the cation and anion had, then the more effective the additive was in lowering the decomposition temperature of the polyacetal. These observations were based on the series

$(NH_4 > Mg > Li > K > Cs)ClO_4$

$NH_4ClO_4 > (NH_4)_2SO_4 > (NH_4)_2HPO_4$

$NH_4I > NH_4Br > NH_4Cl > KI > KBr$

$(NH_4)_2S_2O_8 > NH_4ClO_4 > K_2S_2O_8 \gg KClO_4 > KClO_3 = K_2Cr_2O_7 > K_2SO_4$

$KMnO_4 > KClO_4 > K_2Cr_2O_7$

$NH_4ClO_4 > (NH_4)_2SO_4 > NH_4Cl > NH_4NO_3 > (CH_3)_4NClO_4 > (CH_3)_4NCl$

In addition, the effect that organic additives yielding radicals had on the thermal degradation of Delrin was determined. The more effective additives had exotherms in the melting region of Delrin.

Our studies indicated that dynamic thermogravimetry offers a novel method for distinguishing between the acid strength of many inorganic compounds by the measurement of the shift of the TG curve of the Delrin admixture to lower temperature.

REFERENCES

1 J.R. Dunn, Rubber Chemistry and Technology, 51 (1978) 686.
2 L. Reich, Thermochim. Acta, 8 (1974) 399.
3 D.E. Cagliostro, S. Riccitiello and J.A. Parker, J. Macromol. Sci. Chem., 3 (1969) 1601.
4 F.D. Swanson and J.L. Madsen, Honeywell Final Report, Contract No. 0174-72-C-0338, Honeywell Inc., Hopkins, MN, May 1973.
5 L.A. Wall and J.H. Flynn, Rubber Chem. Technol., 35 (1962) 1157.
6 J.H. Flynn and L.A. Wall, J. Res. Natl. Bur. Stand. Sect. A, 70 (1966) 487.
7 C D. Doyle, J. Appl. Polym. Sci., 6 (1962) 639.
8 L.A. Wall, J.H. Flynn and S. Straus, Polym. Eng. Sci., 10 (1970) 19.
9 F.J. Hybart and G.N. Rowley, J. Appl. Polym. Sci., 16 (1972) 715.
10 N. Grassie and R. McGuchan, Eur. Polym. J., 7 (1971) 1503.
11 Z. Osawa, T. Ishinzuka, M. Sorimachi and Y. Ogiwara, Polym. Lett., 9 (1971) 497.
12 Z. Osawa and T. Shibamiya, Polym. Lett., 6 (1988) 721.
13 Lange's Handbook of Chemistry, 11th edn., pp. 5–44.