THERMOANALYTICAL STUDIES OF FLAME-RETARDANT POLYESTER/ COTTON TEXTILE BLENDS: A COMPARISON OF THPC-urea-PVBr AND THPOH AMMONIA TREATMENTS*

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ABSTRACT

Flame-retardant polyester/cotton fabrics are increasing in importance in the apparel and household fabrics market. Phosphorus-nitrogen flame-retardant systems developed for 100% cotton are not necessarily effective for polyester/cotton blends. Bromine effectively imparts flame-retardant properties to polyester resins. It has been theorized that systems containing both bromine and phosphorus should be suitable for polyester/cotton blends. A thermoanalytical study was undertaken to elucidate the effect of bromine in flame-retardant polyester/cotton blend fabrics. Fabrics having various ratios of polyester to cotton were treated with THPOH-NII₃, which is particularly effective on 100% cotton, and with THPC-urea-PVBr, which was designed for 50/50 polyester/cotton blends. For comparison, data are also presented on a 50/50 polyester blend fabric treated with THPOH-NH, and with THPC-urea flame retardants plus tris(2,3-dibromopropyl) phosphate in a two-step application. TG and DSC data were obtained in atmospheres of either nitrogen or air, using a DuPont 990 Thermal Analysis System ***. The thermal changes are assigned to decompositions of cotton, polyester, char, and resin finish. A comparison is made of the effects caused by the different flame-retardant finishes. OI values and FF 3-71 data are reported.

INTRODUCTION

The thermogravimetric study by Neumeyer et al.¹ and the differential thermal analysis by Hobart et al.² of polyester/cotton fabrics were undertaken to determine the interaction of the blend components on thermal degradation of the fabric. The

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THPC-urea-PVBr flame-retardant finish described by Donaldson et al.³ was chosen because it provides a phosphorus-nitrogen compound and a bromine compound for treating both the cotton and polyester blend components, respectively. In this sequel to those earlier studies, a comparison is made between THPC-urea-PVBr (FR-1) and THPOH-NH₃, a finish for 100% cotton fabrics that has aroused widespread interest in the textile industry.

Thermal analysis data are also presented for 50/50 polyester/cotton fabrics treated with tris(2,3-dibromopropyl) phosphate (DBPP) alone, and in combination with THPC-urea or THPOH-NH₃. DBPP was chosen to gain further information on interactions of this particular bromine compound with thermal degradation of polyester/cotton blend fabrics. Flame retardancy data resulting from measurements by Oxygen Index (OI) and FF 3-71 were correlated with observations from thermal analysis.

EXPERIMENTAL

A series of polyester/cotton sheeting fabrics with blend ratios of 0/100, 11/89, 20/80, 30/70, and 50/50 were treated with THPOH-NH₃ flame retardant^{*, 5}. These blend fabrics treated with THPC-urez-PVBr flame retardant were described by Donaldson and Knoepfler⁶. The five fabrics were sewn together to form one roll for treatment. This roll was padded through a 35% THPOH solution, dried at 160°F for 1½ min, ammoniated for 5 min, and oxidized with H₂O₂. The phosphorus add-ons ranged from 4.6% for the 100% cotton fabric to 3.9% for the 50/50 blend.

A 50/50 polyester/cotton basketweave fabric was treated with tris(2,3-dibromopropyl) phosphate via a Thermosol process. Portions of the same treated fabric were treated in a second application with either THPC-urea⁷ or THPOH-NH₃. The solution concentrations of THPC-urea were 25% and of THPOH, 20, 25, or 30%.

A DuPont 990 Thermal Analysis System was used for performing thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses. Sample preparation and analysis procedures were the same as those described by Neumeyer et al. and Hobart et al. Flame resistance was measured by the Children's Sleepwear Flammability Standard, FF 3-71⁸ or by the vertical flame test⁹. Nitrogen was determined by the Kjeldahl method; phosphorus by a gravimetric procedure as the phosphomolybdate following a Kjeldahl digestion; and bromine by a volumetric procedure using oxygen flask combustion. The OI values were determined with a Michigan Chemical oxygen index apparatus according to ASTM procedure¹⁰.

RESULTS AND DISCUSSION

THPOH-NH₃-treated polyester/cotton sheeting

Differential thermogravimetric analysis (DTG) and DSC curves for the treated blend fabrics analyzed in nitrogen are shown in Fig. 1. Two maximum rates of weight loss are apparent in the thermogravimetric data. The first indicates volatilization of



Fig. 1. Normalized DTG and DSC curves for THPOH-NH₃ treated polyester/cotton blend fabrics. Heating rate -- 5"C min⁻¹; 100% nitrogen atm.



Fig. 2. Normalized DTG and DSC curves for untreated polyester/cotton blend fabrics. Heating rate $= 5^{\circ}$ C min⁻¹; 100% nitrogen atm.

the sample due to decomposition of the cotton portion. The second results from decomposition of the polyester. In each case, the area under the peaks is proportional to the amount of component in the blend.

In comparison to the DTG data for the untreated fabrics reported by Neu-

meyer et al. and reproduced here in Fig. 2, it is apparent that the mechanism of cotton decomposition is altered considerably by the flame retardant. This is evidenced in the 100% cotton sample by a shift in the temperature corresponding to the maximum rate of weight loss (hereafter referred to as peak temperature) from 347 to 278°C.

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Fig. 3. Normalized DTG and DSC curves for THPOH-NH₃ treated polyester/cotton blend fabrics. Heating rate = 5 'C min⁻¹; air atm.



Fig. 4. Normalized DTG and DSC curves for untreated polyester/cotton blend fabrics. Heating rate = 5° C min⁻¹; air atm.

TAULE 1

DTO DATA FOR UNTREATED AND ILAME-RETARDANT TREATED FOLVESTIR/COTTON SHIEFTNO

Healing rate = 5°C min⁻¹.

	Virogen.	atm.					Oxygen/n	ltrogen atm.				
	Carton p.	prolysis		PE pyrol)	5/2		Cotton p)	rolysis		PE pyroly	sis	
PECM	Temp.	Raten	Restitue	Temp."	Rate	Cliard	Temp.	Rateb	Residuee	Temp.*	Rate''	Chard
Untreated							2		ę			
0/100	347	0.15	20	I	ł	80	. /15		5	1]	2
50/50	345	8.	50	410	0.0	0	318	.08	5	396	0.03	0
100/0	I	I	I	416	11.	2	I	ł	1	405	8	0
THPOH-NH	-treated								;			:
0/100	278	0.09	8	ł	ł	48	278	0.11	64]	ļ	2
50/50	268	.06	79	403	0.03	31	266	90.	8	397	0.03	<u>م</u>
TupC-mea-F	VBr-treated ('F.R.1)°							ł			:
0/100	289	0.09	46	I	I	4	279	0.10	53	l	1	= '
50/50	288	8	73	412	0.03	34 3	283	0	74	403	0.04	6
T			the love (90)	h Normalia	initriana por	m 1.5 6. 61 53	nnle wriaht	וח מנח) אחן י	o (l-um l-ui	Residue af	lier cotton 1	vrolvsis

, ì 5 Ŷ Temperature at maximum rate of weight loss ("C)." Normalized munimum rate of sample weight loss (mg (%). " Residue at 600°C (%). " 30% THPC-urea (1:1 molar ratio) and 6% PVBr in padding solution. The DSC data (Fig. 1) show the cotton degradation for treated fabrics to be exothermic, rather than endothermic, as was observed by Hobart et al. for samples which had no treatment (also reproduced in Fig. 2).

Examination of the polyester weight loss and thermal activity during pyrolysis show little differences from those measured in the untreated series. The melting point endotherm of the polyester peaks at 250 °C, its peak temperature of decomposition occurs at about 400 °C, and its rate of decomposition weight loss is approximately the same as when untreated. Its decomposition remains endothermic, as evidenced by the slight depression of the DSC curve at about 417 °C. It is thus concluded that addition of the THPOH-NH₃ flame retardant does not measurably alter the polyester decomposition.

Figure 3 shows DTG and DSC curves for the same samples analyzed in 80% nitrogen-20% oxygen atmosphere (hereafter referred to as air). The presence of oxygen increases the weight-loss activity in comparison to that obtained in nitrogen. Both cotton and polyester decompositions are exothermic; oxidation of the residual chars remaining after pyrolysis occurs. As in nitrogen, the action of the flame retardant lowers both decomposition temperature and rate of decomposition weight loss for the cotton portion. Auto-ignition of the char is observed in the untreated fabrics.

TABLE 2

DSC DATA FOR UNTREATED AND FLAME-PETARDANT TREATED POLYESTER/COTTON SHEETING

Nitrogen	aim.			•	$O_2 N_2$ atm	r.
Collor py	rolysis		PE pyrolys	sis -	Collon py	olysis
·	Temp.*	Rate	Temp.*	Raic	Temp.+	Raie
Untreplet	/					
0/100	348	-0.26		~~~	334	1.90
50/50	347	~ 0.09	417	-0.02	333	0.62
100,0	~		426	0.09		
THPOH-	NHrucated					
	277	0.94			1 774	0.98
0;100	283	0.34	-		281	0.68
60:60	260	077	417	0.01	273	0.71
JU <u>i</u> U	280	0,27	-117	~0.04	277	0.81
THPC-w	n-PVEs-treate	·d (FR-1)*			-	•
0/1/0	10-1	0.17			285	0.93
vj 100	£8.3	0.17		~	302	0.88
50/50	283	.10	413	~0.02	1 280	0.36

Heating rate - 5°C min-1,

* Temperature at maximum rate of energy change (*C). * Normalized maximum rate of energy change (meal sec⁻¹ mg⁻¹). * 30% THPC-urea (1:1 molar ratio and 6% PVBr in padding solution.

Auto-ignition is indicated by the large energy release associated with complete and rapid consumption of the residual materials at about 450-500°C, as shown in Fig. 4. Samples treated with flame retardants do not auto-ignite.

Tables 1 and 2 summarize data presented in Fig. 1 through 4. The peak temperature and decomposition rates of the 100% cotton and the 50/50 polyester/ cotton samples analyzed in both nitrogen and air atmospheres are presented in Table 1. It is apparent in the cotton decomposition that not only peak temperature but also maximum rate of weight loss is decreased by the presence of the flame retardant. In nitrogen, THPOH-NH₃ reduces the maximum rate of weight loss of the 100% cotton fabric from 0.15 to 0.09 mg min⁻¹ mg⁻¹. A reduction in both peak temperature (from 317 to 278°C) and decomposition rate (from 0.25 to 0.11 mg min⁻¹ mg⁻¹) are found by analysis in the air atmosphere. Similar decreases are measured for the 50/50 polyester/cotton fabric. In comparison with the untreated sample there are no significant differences in the rate of weight loss and temperature at which polyester decomposition occurs that can be attributed to the addition of THPOH-NH₃. This is true in both nitrogen and air atmospheres.

The percent char remaining after pyrolysis greatly increases when flame retardant is added to the fabrics. The char remaining at 600 °C after pyrolysis in nitrogen is 48% for the treated 100% cotton fabric. In the air atmosphere, 32% char remained at 600 °C. In comparison, the untreated fabrics yielded about 8% char in nitrogen and zero char in air atmosphere. The 600 °C residual char of the 50/50 THPOH-NH₃ treated fabric is 31% in nitrogen and 19% in air, compared with 10 and 0% for untreated fabric in the same atmosphere. As the cotton content decreases in treated fabrics, the char remaining at 600 °C decreases as expected. These changes in thermal stability and increased char production have been observed previously and were attributed to acid catalysis of the dehydration reaction in the cellulosic decomposition mechanism¹¹.

Table 2 presents DSC data for samples analyzed in both nitrogen and air atmospheres. The peak temperature of thermal activity for cotton pyrolysis in nitrogen is lowered by addition of the flame retardant. However, the rate of energy release increases significantly from -0.26 mcal sec⁻¹ mg⁻¹ for the untreated 100% cotton sample to 0.94 mcal sec⁻¹ mg⁻¹ for the sample treated with THPOH-NH₃. Char formation is exothermic², and since the flame retardant increases the amount of char, it is reasonable to expect this change to exothermic activity. In air, the decomposition of the untreated sample released 1.90 mcal sec⁻¹ mg⁻¹; the flame retardant decreased this rate to 0.98 mcal sec⁻¹ mg⁻¹. Apparently the flame retardant controls the heat released during cotton decomposition regardless of the atmosphere. Similar energy changes are noted for the 50/50 blend fabrics.

There are no measurable effects of the THPOH-NH₃ flame retardant on polyester pyrolysis in the nitrogen atmosphere. In air, the large exothermic char oxidation masked the polyester decomposition, thus data in this temperature range were not included in Table 2. Comparison of THPOH-NH3 with THPC-urea-PVBr (FR-1) polyester/cotton sheeting

Pyrolysis data of samples treated with FR-1 are similar to those of the THPOH-NH₃-treated fabrics as can be seen in Figs. 5 and 6. Both the cotton and the polyester decomposition temperatures for the FR-1 samples are close to those measured for the THPOH-NH₃-treated samples. Referring back to Table 1, we note the percent char at 600°C in nitrogen is about the same for fabrics treated with either flame retardant. In the air atmosphere, there is more char from THPOH-NH₃ samples than from FR-1-treated samples. The maximum rate of cotton weight loss for the THPOH-NH₃ samples appears slightly higher than for the FR-1 samples in either atmosphere.

The cotton thermal changes are exothermic in both atmospheres. Referring back to Table 2, we note that there is little activity in the region of the polyester decomposition in nitrogen. In nitrogen atmosphere the rates of energy release during



Fig. 5. Normalized DTG and DSC curves for FR-1 treated polyester/cotton blend fabrics. Heating rate = 5° C min⁻¹; 100% nitrogen atm. and air atm.

THPOH-NH3 TREATED POLYESTER/COTTON



Fig. 6. Normalized DTG and DSC curves for THPOH-NH₃ treated polyester/cotton blend fabrics. Heating rate -5° C min⁻¹; 100% nitrogen atm. and air atm.

cotton pyrolysis of THPOH-NH₃-treated samples are roughly 5-7 times greater than for FR-1 samples. An oxidation step after ammoniation is an essential part of the THPOH-NH₃ process¹². Perhaps the greater activity is caused by the liberation of oxygen during pyrolysis of the THPOH-NH₃ fabrics¹³.

In Table 3 are results of elemental analyses and measurements of flame retardancy of the treated sheeting fabrics. The OI values of the FR-1 fabrics are higher than those of the THPOH-NH₃ fabrics. The 100% cotton FR-1 fabric has an OI of 0.37, and the THPOH-NH₃ of 0.32. As the amount of polyester in the blend fabric increases, the OI values decrease down to 0.30 for the FR-1 and 0.28 for the THPOH-NH₃. All of the treated fabrics initially passed FF 3-71. After 50 launderings, all samples again passed FF 3-71 with the exception of the 50/50 blend fabric treated with THPOH-NH₃. This sample had lost 15% nitrogen after 25 launderings and 24% after 50 launderings, which is higher than with the FR-1 finish.

		Nitrogen	(%)		.1.		FF 3-71	!
PE¦Ctn	Phos. (%)	Initial	SO Wa	shes Br. (%)	Initial	SO Washes	Initial	50 Washes
тнрон	-NH_Treate	i.						
0/100	4.6	23	2.2		0_32	0.30	Рь	Р
11/89	4_5	2.3	20		0.30	0.28	P	Р
20/80	4.4	2.2	1.9		0.29	0.27	P	Р
30,70	42	2.0	1.7		0.28	0.25	P	P
50/50	3.9	1.9	1.4		0.28	0.24	P	BEL
THPC-u	rea-PVBr-tre	ated (FR	-1)ª					
0/100	25	2.8	-	3.0	0.37		P	e
11/89	2.4	29		3.0	0.35		P	e
20/80	2.4	2.8		2.9	0.32		Р	e
30j70	2.3	2.7		2.9	0.32		Р	e
50/50	2.4	29		2.9	0.30		Р	•

FLAME RETARDANT POLYESTIC COTTON SHEETING

* 35% THPOH in padding solution. $^{\circ}$ P = passed. $^{\circ}$ BEL \rightarrow burned entire length. $^{\circ}$ 30% THPCurea (1:1 molar ratio) and 6% PVBr in padding solution. $^{\circ}$ This set not laundered, but would be excepted to pass, based on other data.

Effect of tris(2,3-dibromopropyl) phosphate (DBPP) on 50/50 polyester/cotton basketweave

To gain further insight into the relative importance and interactions of phosphorus-nitrogen and bromine systems on the thermal degradation processes of polyester/cotton blends, the effects of DBPP were investigated. Bromine compounds can be introduced into the component fibers during manufacture, or they may be part of the chemical system used for finishing the fabric, in which case the halogen may be applied separately or simultaneously with the other flame-retardant chemicals. In the THPC-urea-PVBr finish the halogen compound and the phosphorus-nitrogen compounds were mixed together and applied in a single pad-dry-cure operation. In treatments containing DBPP the halogen was applied in a separate operation followed by application of the THPOH-NH₃ or THPC-urea finish.

DTG and DSC curves for 50/50 polyester/cotton fabrics treated by the latter method are shown in Figs. 7 and 8 and are summarized in Tables 4 and 5. The effects of DBPP on the thermal degradation of the blend components are most apparent in the nitrogen atmosphere (Fig. 7 and Table 4). The polyester degradation remains essentially the same as in the untreated sample; its decomposition rate was not altered and the process remained endothermic. Thus the bromine introduced with the DBPP does not react in the polyester solid phase; therefore, its effectiveness must be through alteration of the course of oxidation reactions in the gas phase. There is a decrease in both decomposition rate and peak temperature of the cotton portion of the fabric treated with DBPP. The rate after treatment is reduced to 0.04 from 0.08 mg min⁻¹ mg⁻¹ for the untreated, and the temperature goes from 343°C for the



Fig. 7. Normalized DTG and DSC curves for flame retardant polyester/cotton 50/50 blend fabrics. Heating rate $= 5^{\circ}$ C min⁻¹; 100% nitrogen atm.



Fig. 8. Normalized DTG and DSC curves for flame retardant polyester/cotton 50/50 blend fabrics. Heating rate = 5° C min⁻¹; air atm.

DEG DALA FOR 50/50 POLYER/COTFON HASKETWEAVE, UNTRIATED AND TREATED

Heating rate - 5°C min⁻¹.

	Niroge	n atmosphe	10				Oxygenli	ultrogen al	tinosphere			
	Catton	probals		PE p) rol.	y:1/1		Colton p.	yroly \k		PE pyroi	l):s/s	
50/50 PE/Cni	Temp	Rate"	Restelue	Temp.	Rateh	Char	Temp.	Rate	Residue	Temp.	Rate	Chard
Unireated	343	0.08	47	405	0.0	01	317	0.03	51	398	50	0
THPOH-NII,	277	0.06	78	407	0.04	26	277	0.06	62	3 99	<u>10</u> 0	1
THPOH-NH3 + CHN-HOTHT	279	0.05	75	406	0.04	26	273	0.06	72	320	0.04	*7
Dilph	315	0.04	53	406 804	0.04	~	297	0.06	S	398	0.06	0
TilPC-urea + DBPP	282	0.05	77	407	0.05	27	282	0.05	77	403	003	9
THPC-urea	291	0.06	76	4[4	0.04	28	286	0.05	11	405	004	0
and a second		and the last		and headles			manual and a local	in the second	the second se	and an and a set		

* Temperature at maximum rate of weight loss (*C). ¹ Normalized maximum rate of sample weight loss (mg min⁻¹ mg⁻¹). ^a Residue after cotion pyrolysis (%). ^a Residue at 600*C (%).

	P	N .	Br	0.1.	VFT=	
	(%)	(%)	(%)		W	F
THPOH-NH2	1.76	0.87		0.24	BEL	BEL
THPOH-NH ₃ + DBPP	0.76	0.83	1.31	0.25	BL	BL
THPOH-NH1°	2.20	1.13	_	0.24	P	Р
THPOH-NH2 + DBPP	2.11	1.04	1.34	0.26	P	P
THPOH_NH₄	2.75	1.34	—	0.25	Р	P
THPOH-NH1 + DBPP	2.58	. 1.25	1.32	0.26	Р	Р
DBPP	0.10	0.04	1.49	0.19	BEL	BEL
Untreated				0.18	BEL	BEL

SOME PROPERTIES OF 50/50 POLYESTER/COTTON BASKETWEAVE TREATED WITH THPOH-NH3 AND DBPP

* Vertical Flame Test; P == passed; BL == borderline (at least one specimen failed); BEL -- burned entire length or failed. b 20% THPOH in padding solution. c 25% THPOH in padding solution.
4 30% THPOH in padding solution.

untreated to 315°C for the DBPP treated sample. There are also reductions in decomposition rate and peak temperature for the samples treated with THPC-urea or THPOH-NH₃, with an without DBPP. When DBPP was used alone, there was no increase in char formation as with THPOH-NH₃ or THPC-urea, and the cotton degradation remained endothermic, as in the untreated sample. These findings lend additional support to the theory that the exothermic activity associated with thermal degradation of cotton treated with phosphorus-nitrogen flame retardants results from exothermic char forming reactions. Once again we note the higher rate of energy release for the cotton thermal decomposition in nitrogen for the THPOH-NH₃ samples than for the THPC-urea samples, with and without DBPP.

DTG and DSC curves for these fabrics, pyrolyzed in air, are shown in Fig. 8, and DTG data are recorded in Table 4. There is some lowering of the cotton's decomposition peak temperature (from 317 to 297° C) with the DBPP treatment, but no increase in char formation. With the THPOH-NH₃ or the THPC-urca treatments, there is further lowering of the cotton decomposition temperatures, and a corresponding increase in char formation. Again, the large exothermic char oxidation masked the polyester decomposition.

Because the effect of the bromine occurs primarily in the vapor phase of the thermal decomposition, and thermal analysis examines the reactions in the solid phase, other measurements of the effectiveness of the DBPP on the flame retardancy were made. In Table 5, phosphorus, nitrogen, and bromine contents for three levels of treatment with THPOH-NH₃ are recorded, as well as OI values and results of the vertical flame test. The addition of the halogen increases the OI value at each level of flame retardant application, and at the lowest level (20%) increases the flame resistance so that the samples which failed the vertical flame test were raised to a borderline state, where some specimens passed.

CONCLUSIONS

A thermoanalytical study was undertaken to determine the influence of selected flame retardants on polyester/cotton blend fabrics. Treatment with THPOH-NH₃ or with THPC-urea-PVBr lowers the temperature at which the maximum rate of decomposition occurs and increases the char formation of the cotton component. Neither retardant significantly affected polyester decomposition. The decomposition of THPOH-NH₃-treated cotton in nitrogen was much more exothermic than was the THPC-urea-PVBr decomposition in nitrogen. It is proposed that oxygen liberated from the oxidized THPOH-NH₃ polymer by thermal stress contributed to the increased exothermic activity. The two treatments had about the same exothermic activity in the air atmosphere. Auto-ignition did not occur in samples treated with either cotton flame retardant.

The OI values of the THPC-urea-PVBr treated samples ranged from 0.37 for the 100% cotton to 0.30 for the 50/50 blend fabric. OI values varied from 0.32 for the 100% cotton to 0.28 for the 50/50 blend for fabrics treated with THPOH-NH₃. All treated fabrics passed FF 3-71 initially and after 50 launderings, except the 50/50 blend fabric treated with THPOH-NH₃. This sample had the lowest polymer add-on initially, as indicated by phosphorus and nitrogen contents, and after 50 launderings, had lost about 25% polymer (based on nitrogen values).

The addition of bromine increased the flame retardancy of the treated samples, as measured by OI values and the vertical flame test, for the polyester/cotton basketweave fabrics treated first with DBPP then by THPOH-NH₃ or THPC-urea. Thermoanalytical techniques could not differentiate the effects of the bromine in the presence of the cotton flame retardants. However, the blend fabric treated with DBPP alone exhibited a lower decomposition temperature of the cotton portion but no noticeable alteration of the polyester portion. The DBPP did not decrease the quantity of volatile products of couton or polyester degradation, and the amount of char residues was not increased, as was the case with the phosphorus-nitrogen flame retardants.

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RESULTS FROM THE LLS PROCEDURE FOR TRACE 1

f (x)	A (sec ⁻¹)	E (kcal mol ⁻¹)	п	<i>m</i>	P
(1-α) [*]	9.005×1015	55.623	1.656		· · ·
$\frac{\alpha}{1-1}$	1.157×10	-75.542		2.281	1016
$(1-\alpha)^{\alpha}\alpha^{\alpha}$	1.347×10 ⁶	25.570	1.281	0.525	4.710
$(1-\alpha)^{\mu} [-\ln (1-\alpha)]^{\mu}$	0.532	6.027	1_397		0.855