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A DURABLE FLAME-RETARDANT TREATMENT FOR COTTON FABRICS

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ABSTRACT

The use of titanium tetrachloride and antimony oxide as flame-retarding agents for cotton was investigated. Cotton fabrics which had been treated with titanium tetrachloride and antimony oxide passed the vertical flame-resistant test, even after having been washed for 600 minutes in a domestic washing machine. The effect of the flame-retarding treatment on some mechanical properties of the cotton fabrics was studied. A DMDHEU resin had no effect on the flame-retardancy of fabrics which had been treated with titanium tetrachloride and antimony oxide, but certain other durable press resins had an adverse effect on the flame-retardancy.

KEY WORDS

Cotton – vertical flame-resistant test – flame-retardant treatment – titanium tetrachloride – antimony oxide.

INTRODUCTION

The dangers involved in the ignition of cellulosic materials such as clothing, household textiles and paper have been known for ages. Man has continuously been struggling to solve this problem and the first patent describing the flame-proofing of paper and textiles was granted to Obadiah Wyld[1] in 1735. Since then much work has been done on the flame-retarding of textiles but despite this many people still die annually because of their clothing having caught fire. Some 363 persons died in England[2] in 1963 as a result of clothing burns, while an average of 80 fatal cases per annum were reported in California[3] during the period 1951–1957. The mortality due to textile fires (ranging from 2 per million inhabitants in Switzerland to 13 per million in the U.S.A.) is very low, compared with the mortality caused by, for instance, traffic accidents[4].

Authorities have been slow in passing legislation which is aimed at eliminating the source of fabric flammability injuries and the first law[5] prohibiting the use of certain flammable textiles for clothing purposes was passed as recently as 1954 in the U.S.A. In spite of this people were still being burnt in accidents involving clothing which had passed the standard and this led to an amendment[6] of the Flammable Fabrics Act in 1967. This amendment authorized the Secretary for Commerce to develop and promulgate new standards or regulations, including labelling, "to protect the public against unreasonable risk of the occurrence of fire leading to death, injury or significant property damage". Furthermore it expanded

the scope of the act to include "interior furnishings". The standards DOC FF 1–70 and 2–70 for carpets and rugs came into effect on April 15th, 1971 and DOC FF 3–71 for children's sleepwear on July 1st, 1972. The flammability standard DOC FF 4–72 for mattresses is due to come into effect on May 31st, 1973.

In Britain the so-called "children's nightdress regulations"[7] were passed in 1964 and since then legislation has also been passed in other countries such as Switzerland. There is, at present, no law prohibiting the distribution and use of flammable textiles in South Africa, but legislation will probably be introduced in the near future.

There are many commercial textile flame-retarding agents available. In a directory of flame-retarding agents which was published recently, more than 60 products manufactured by 44 companies are listed[8]. The majority of the flame-retarding agents are classified as being non-durable or semi-durable and may withstand up to 15 mild washing cycles[9]. A durable finish, however, must be unaffected by at least 50 washing cycles[10].

Most of the durable flame-retarding agents available for the treatment of apparel and household textiles consist of organic phosphorus compounds which are fairly expensive and which are frequently adversely affected by metal ions picked up during laundering[11]. This prompted SAWTRI to survey compounds other than phosphorus which may be suitable as flame-retarding agents. Such a compound is titanium, which was recently shown to be a very effective flame-retarding agent for wool[12]. The first patent describing the use of titanium as a flame-retarding agent for textiles was granted in 1900 and since then a large number of patents and publications describing the use of various titanium derivatives as flame-retarding agents have been published[13, 14]. Cotton fabrics which had been treated with titanium derivatives only, showed a fair measure of flame-retardancy but the treatment was, however, only moderately resistant to laundering and furthermore the fabric exhibited little or no afterglow retardancy. The addition of compounds such as antimony oxide proved the most suitable for correcting these deficiencies. In the early fifties several authors[13–17] reported that titanium/antimony compositions could be used for the flame-retardancy of cotton. Since then very little has been published on the efficiency of these compounds as flame-retarding agents and they are apparently considered to be suitable for industrial textiles only[9]. Their application to apparel and household textiles can, however, be of practical importance and consequently it was decided to re-investigate some of the processes described in earlier publications.

EXPERIMENTAL

The following cotton fabrics were used in the present investigation:–

Fabric A : plain weave, bleached, mercerised (density 169 g/m^2)
Fabric B : netting (density 40 g/m^2)

Fabric C	:	poplin	(density 182 g/m^2)
Fabric D	:	calico	(density 172 g/m^2)
Fabric E	:	bleached calico	(density 127 g/m^2)
Fabric F	:	brushed cotton	(density 181 g/m^2)
Fabric G	:	printed	(density 140 g/m^2)
Fabric H	:	printed	(density 145 g/m^2)
Fabric I	:	plain weave, dyed	(density 191 g/m^2)
Fabric J	:	plain weave, bleached	(density 73 g/m^2)

Fabric A was obtained from a cotton mill while the rest of the fabrics were bought from local draperies. All chemicals used were of laboratory grade.

Several compositions of binary mixtures containing titanium and antimony have been mentioned as flame-retarding agents for cellulosic materials. In most cases titanium tetrachloride and either antimony trichloride or antimony oxide were used for treating cellulose. The flame-retarding composition described by the National Lead Company[17] contains antimony oxide and is fairly easy to prepare and after some preliminary trials it was decided to use this composition in the present investigation. The following solution was prepared: 80,5 g of hydrochloric acid (36%); 37,4 g of phosphoric acid (85,5%) and 925 g of water were mixed and 450 g antimony oxide was added while stirring. Titanium tetrachloride (850 g) was

TABLE I

COMPOSITION OF VARIOUS FLAME-RETARDING SOLUTIONS

Solution	Specific Gravity	CONCENTRATION (g/l)		PERCENTAGE SOLIDS PRESENT ON FABRIC AFTER TREATMENT	
		$TiCl_4$	Sb_2O_3	$TiCl_4$	Sb_2O_3
I	1,048	39,6	21,0	3,8	2,0
II	1,081	79,2	42,0	7,3	3,9
III	1,158	158,4	84,0	13,7	7,3
IV	1,236	237,6	126,0	19,2	10,2
V	1,363	356,4	189,0	26,1	13,9
VI	1,467	475,2	252,0	32,4	17,2

The ratio (molecular) of $TiCl_4$: Sb_2O_3 was 2,9:1 in all cases. The percentages of $TiCl_4$ and Sb_2O_3 were calculated for a wet "pick-up" of 100%. These percentages are probably higher than what was actually present on the fabrics, since some of the reagents must have been removed during the alkali rinsing process.

added slowly while cooling in ice. The solution was subsequently diluted with water to produce solutions* containing various concentrations of titanium tetrachloride and antimony oxide, which were used for treating the fabrics. The compositions of the various solutions are given in Table I. The fabric was immersed in the solution at room temperature and passed through squeeze rollers to effect a wet "pick-up" of 100%. The operation was repeated once to obtain thorough soaking of the cotton. The fabric was left at room temperature for 90 minutes and immersed for 10 minutes in a solution containing sodium carbonate (150 g/*l*) and sodium silicate (16 g/*l*). The fabric was then passed through squeeze rollers, washed in water until the pH of the aqeuous solution had decreased to 8,0 and dried at room temperature.

To investigate the effect of durable press treatments on the flame-resistance of the fabrics, some of the flame-retardant fabrics (prepared from fabric A), were treated with commercial aminoplast resins and a polyurethane resin containing free isocyanate groups. Some of the fabrics were padded in aqueous solutions of the aminoplast resins, containing 10% zinc nitrate catalyst (on mass of resin) and 1% polyethylene softening agent (on mass of cotton). The fabrics were then squeezed through squeeze-rollers (wet pick-up approximately 70%), dried in air, steam-pressed on a Hoffman Press and subsequently cured for 5 minutes at 160°C. Some fabrics were treated with a solution of the polyurethane resin dissolved in perchlorethylene, dried in air and then autoclave-steamed. (Two minutes evacuation, 2 minutes steaming, 2 minutes evacuation). In those cases where the mechanical properties of the fabrics were to be studied, resin-treated samples which had not been pre-treated with the flame-retarding compounds were also prepared for comparison.

The flame resistance of the fabrics was determined according to the vertical AATCC Test Method 34-1969[18], using propane gas, instead of Matheson Gas B, which was not available. The AATCC test method is an extremely severe test and is conducted by exposing the fabric to a flame for 12 seconds. The residual flame times, afterglow times and the char lengths were determined as described in the test. A fabric passed the test when the char length was less than 17,8 cm and when the residual flame time was less then 10 seconds. At present no criterion has been laid down for the afterglow time.

The fabrics were washed at 60°C in an automatic domestic washing machine. A washing cycle lasted 30 minutes, and was followed by three rinses in cold water, (the total rinsing time being 30 minutes) and spin drying for 5 minutes. A commercial washing powder recommended for automatic washing machines, was used in this investigation.

*All the concentrations given in this publication refer to the concentrations of titanium tetrachloride and antimony oxide which were used to prepare the various solutions. It must be pointed out, however, that some of the titanium tetrachloride could have been hydrolysed to titanium oxychlorides, and some of it might have reacted with the antimony oxide. The actual concentration of titanium tetrachloride and antimony oxide present in the solution was therefore not known.

TABLE II

THE FLAME-RETARDANCY OF COTTON (FABRIC A) TREATED WITH VARIOUS CONCENTRATIONS OF TITANIUM TETRACHLORIDE AND ANTIMONY OXIDE

Solution	TREATMENTS: Percentage solids on fabric		CHAR LENGTH (CM) AFTER WASHING CYCLES							AFTERGLOW (SECONDS) AFTER WASHING CYCLES						
	$TiCl_4$	Sb_2O_3	0	1	5	10	15	20	30	0	1	5	10	15	20	30
I	3,8	2,0	BEL*							BEL						
II	7,3	3,9	BEL							BEL						
III	13,7	7,3	10	10	BEL					26	37	BEL				
IV	19,2	10,2	4	5	6	10	12	12	BEL	5	6	10	20	30	120	BEL
V	26,1	13,9	3	5	4	6	8	8	11	8	10	7	10	19	12	25
VI	32,4	17,2	4	4	4	9	6	7	9	11	11	8	10	11	13	26

* Burned entire length

TABLE III

THE FLAME-RETARDANCY OF SOME COMMERCIAL COTTON FABRICS

FABRIC	CHAR LENGTH (CM) AFTER WASHING CYCLES						AFTERGLOW (SECONDS) AFTER WASHING CYCLES					
	0	1	5	10	15	20	0	1	5	10	15	20
B	7	7	–	8	17	BEL	2	1	2	3	6	BEL
C	6	4	4	6	6	11	7	5	7	4	12	15
D	4	5	5	6	6	8	21	10	9	10	16	18
E	5	4	4	5	7	10	5	6	3	5	7	16
F	6	6	4	9	9	12	20	12	16	16	170	113
G	5	5	4	5	7	10	7	5	5	6	8	11
H	7	5	6	5	12	–	–	6	4	5	8	–
I	5	5	5	6	6	8	21	11	18	10	21	18
J	6	5	5	BEL	–	–	1	0	2	BEL		

The mechanical properties of the fabrics were determined in the usual manner, after having been washed once.

RESULTS AND DISCUSSION

A durable flame-retardant finish must pass the vertical flame-test after having been washed for 50 cycles of 12 minutes each, as described under washing procedure 6,2 (III), in AATCC Test Method 124-1969[10]. This gives a total washing time of 600 minutes at 60°C. The washing machine specified in the test method was, unfortunately, not available in South Africa and consequently a domestic washing machine with a washing cycle of 30 minutes was used in this investigation. It has been assumed that 20 washing cycles (each cycle lasting 30 minutes, the total washing time being 600 minutes) in the local washing machine is more or less equal to 50 washing cycles in the machine described in AATCC Test Method 124-1969. A flame-retardant finish which passed the vertical flame test after having been washed for 20 washing cycles in the washing machine used in this study, was therefore regarded as being *durable* to laundering.

Table II shows the effect of the concentration of the titanium tetrachloride/antimony oxide on the flame-retardancy of cotton fabric A before and after washing. No residual flame was observed when the fabrics were tested and consequently no residual flame times are given. The results show that the fabric must contain at least 19,2% titanium tetrachloride and 10,2% antimony oxide (on mass of fabric) to qualify as a *durable* flame-retardant finish. Cotton fabrics requiring no laundering can be rendered flame-retardant with as little as 13,7% titanium tetrachloride and 7,3% antimony oxide present on the fabrics. Increasing the concentration of the titanium tetrachloride and antimony oxide to 26,1% and 13,9% respectively, or more, improved the durability of the finish so that it withstood 30 washing cycles, the total washing time being 900 minutes. The afterglow times increased with increasing reaction times and varied between 5 seconds and 30 seconds in most of the cases.

In a further study some light-weight and medium-weight cotton fabrics which had been bought from local stores were treated with flame-retarding solution IV, which yielded fabrics containing 19,2% titanium tetrachloride and 10,2% antimony oxide. After treatment the flame-retardancy of the fabrics, as well as the durability of the flame-retarding finish to washing, were determined. The results obtained, are given in Table III, and once again illustrate the efficiency of the flame-retarding treatment. It was found that all the fabrics could be rendered flame-retardant, even the extremely light ones. It was furthermore found that only two of the fabrics failed the vertical flame test after having been washed for 20 cycles. Fabric B, a cotton netting with density 40 g/m^2 passed the vertical flame test after having been washed for 15 cycles while fabric J, with density 73 g/m^2 only passed the test when washed for 5 cycles, or less.

TABLE IV

THE EFFECT OF THE FLAME-RETARDANT TREATMENT ON SOME MECHANICAL PROPERTIES OF COTTON FABRICS

Fabric	Treatment	Fabric density (g/m^2)	Flat Abrasion (Stoll) (cycles to endpoint)	Flat Abrasion (Martindale) (% mass loss after 10 000 cycles)	Flex* Abrasion (cycles to rupture)	Flexural Rigidity (mg cm^2 per cm)		Fabric Breaking Strength (Kgf)	
						Warp	Filling	Warp	Filling
C	19,2% $TiCl_4$ and 10,2% Sb_2O_3	202	239	3,44	199	233	109	94	28
	5% Methylolmelamine	189	205	3,44	412	205	89	85	30
	5% DMDHEU	184	189	3,14	462	204	86	102	36
	Untreated	182	226	3,67	553	200	86	97	36
E	19,2% $TiCl_4$ and 10,2% Sb_2O_3	154	105	14,25	139	62	34	40	22
	5% Methylolmelamine	124	87	12,11	153	89	32	41	22
	5% DMDHEU	125	93	12,83	233	79	27	42	23
	Untreated	127	83	13,25	271	62	31	39	25
F	19,2% $TiCl_4$ and 10,2% Sb_2O_3	205	275	7,32	182	151	106	40	36
	5% Methylolmelamine	182	191	10,33	452	105	89	32	30
	5% DMDHEU	178	164	8,47	558	101	82	39	28
	Untreated	181	180	8,93	564	105	94	41	31
J	19,2% $TiCl_4$ and 10,2% Sb_2O_3	88	105	6,81	70	45	19	33	23
	5% Methylolmelamine	74	61	4,57**	213	34	17	27	20
	5% DMDHEU	73	77	5,36**	93	33	40	31	25
	Untreated	73	89	5,39	77	33	16	32	23

*Average of warp and filling

** One test only, after 5 000 cycles

The effect of the flame-retarding treatment on some mechanical properties of cotton fabrics is given in Table IV. The flat abrasion test results show that the titanium tetrachloride/antimony oxide treatment compared well with some conventional aminoplast resins, as well as with the results obtained on the untreated control samples. It must be pointed out, however, that the densities of the fabrics treated with titanium tetrachloride/antimony oxide were higher than those of the other fabrics. In the case of the flex abrasion test results, a significant decrease was observed in the case of the fabrics treated with titanium tetrachloride/antimony oxide, compared with the resin-treated or untreated samples. This could have been due to acid tenderising of the fabrics during the flame-retarding treatment and attempts will be made to shorten the fairly long reaction period of 90 minutes. The flexural rigidity test results show that the fabrics treated with titanium tetrachloride/antimony oxide were more stiff than were the control samples. The handle of the fabrics treated with titanium tetrachloride/antimony oxide was, however, still acceptable. Finally, it can be seen that the flame-retarding treatment had no adverse effect on the breaking strength of the fabrics.

The effect of certain resin treatments on the flame-retardancy of cotton which had been treated with flame-retarding solution IV, was also investigated. The results obtained, are given in Table V. It can be seen that the DMDHEU treatment had no adverse effect on the flame-retardancy of the cotton. Fabrics which had been treated with 5% and 10% resin (on mass of fabric) passed the vertical flame test after having been washed for 20 cycles. Substituting half of the DMDHEU by an alkylated methylolmelamine resin resulted in a deterioration in the flame-retardancy,

TABLE V

THE EFFECT OF CERTAIN RESIN TREATMENTS ON THE FLAME-RETARDANCY OF COTTON TREATED WITH TITANIUM TETRACHLORIDE AND ANTIMONY OXIDE

RESIN	CHAR LENGTH (CM) AFTER WASHING CYCLES					
	0	1	5	10	15	20
5% DMDHEU	5	5	6	14	11	17
10% DMDHEU	5	6	6	8	10	14
2,5% DMDHEU + 2,5% METHYLOLMELAMINE	5	6	7	11	BEL	
5% POLYURETHANE	7	7	8	17	BEL	

with the fabric failing the vertical flame test after 15 washing cycles. Cotton which had been treated with a polyurethane resin containing free isocyanate groups also failed the vertical flame test after 15 washing cycles.

CONCLUSIONS

It was found that cotton fabrics passed the vertical flame-resistant test after treatment with a solution of titanium tetrachloride and antimony oxide containing as little as 158,4 g/*l* titanium tetrachloride and 84,0 g/*l*, antimony oxide. This solution yielded fabrics containing 13,7% titanium tetrachloride and 7,3% antimony oxide. When the concentration of the flame-retarding solution was increased to produce fabrics containing 19,2% titanium tetrachloride and 10,2% antimony oxide, a durable flame-retardant finish was obtained, even in the case of lightweight cotton fabrics. The treatment of the flame-retardant cotton fabrics with a DMDHEU resin had no adverse effect on the flame-retardancy, but when some of the DMDHEU was replaced by a melamine resin, a deterioration in the durability of the flame-retardant finish was observed. The treatment of flame-retardant cotton with a polyurethane resin also decreased the durability of the flame-retardant finish.

The treatment of cotton fabrics with titanium tetrachloride and antimony oxide had no adverse effect on the resistance of the fabrics to flat abrasion, but decreased the resistance to flex abrasion. Fabric breaking strength was not affected by the flame-retarding treatment. The flame-retardant fabrics were more stiff than the untreated samples, but the handle of the fabrics was still acceptable.

Preliminary results showed that the titanium tetrachloride/antimony oxide flame-retardant treatment affected the lightfastness of certain dyes, but quite a few dyes were found to be unaffected by the treatment. This will be reported on in a future publication.

The cost of the chemicals used in the flame-retarding treatment is of the order of 40c per Kg of cotton treated and compares favourably with other commercially available durable flame-retarding agents which cost approximately R1,20 per Kg of treated cotton.

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