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HEADQUARTERS
QUARTERMASTER RESEARCH & ENGINEERING COMMAND
U S ARMY

TEXTILE SERIES
REPORT NO. 100

INVESTIGATION OF NEW FLAME RETARDANTS

FC

QUARTERMASTER RESEARCH & ENGINEERING CENTER
TEXTILE, CLOTHING & FOOTWEAR DIVISION

JULY 1957

NATICK, MASSACHUSETTS

HEADQUARTERS
QUARTERMASTER RESEARCH & ENGINEERING COMMAND, US ARMY
OFFICE OF THE COMMANDING GENERAL
NATICK, MASSACHUSETTS

1 July 1957

Major General Andrew T. McNamara
The Quartermaster General
Washington 25, D. C.

Dear General McNamara:

This study, "Investigation of Silicon Compounds and Dibromopropylphosphates as Flame Retardants for Cotton," reports research made under contract with the Southern Regional Research Laboratory, U.S. Department of Agriculture, and is part of the Quartermaster effort to give the combat soldier maximum protection against thermal-type weapons.

The possibility that silicon compounds would make cotton fabrics flame resistant was investigated. The laboratory data indicate that these compounds have only limited value as flame retardants. However, publication of the data will be useful to the chemical industry as reference for future studies, and should prevent duplication of investigations already made.

Sincerely yours,

C G Calloway

1 Incl
TS-100

C. G. CALLOWAY
Brigadier General, USA
Commanding

HEADQUARTERS QUARTERMASTER RESEARCH & ENGINEERING COMMAND, US ARMY
Quartermaster Research & Engineering Center
Natick, Massachusetts

TEXTILE, CLOTHING & FOOTWEAR DIVISION

Textile Series
Report No. 100

AN INVESTIGATION OF SILICON COMPOUNDS AND DIBROMOPROPYL PHOSPHATES AS FLAME RETARDANTS FOR COTTON.

PART I:
THE USE OF DIBROMOPROPYL PHOSPHATES AS FLAME RETARDANTS FOR COTTON.

J. David Reid
Robert M. Reinhardt George C. Daul

PART II:
AN INVESTIGATION OF SILICON COMPOUNDS AS FLAME RETARDANTS FOR COTTON FABRICS

J. G. Frick, Jr.
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SOUTHERN REGIONAL RESEARCH LABORATORY
NEW ORLEANS, LOUISIANA

Project Reference:
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Foreword

To provide the combat soldier with the maximum degree of protection during exposure to thermal-type weapons, the Quartermaster Corps has been investigating means of making cotton fabric flame resistant. This report summarizes laboratory work aimed at determining whether certain new compounds might be effective as flame retardants. The recent introduction and widespread use of silicon compounds in a variety of items from transistors to water repellents warranted an investigation of their possible use as flame retardants. The results indicate limited usefulness of these compounds as flame retardants. However, in view of the interest by the chemical industry in this type of compound, this exploratory work is being published as a guide and background material for other laboratories investigating these compounds

STEPHEN J. KENNEDY
Chief
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Approved:

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Commanding Officer
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Scientific Director
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ABSTRACT

Part I. The preparation and some of the properties of mono-, bis-, and tris-dibromopropyl esters of phosphoric acid have been described. The ammonium salts of mono- and bis-(dibromopropyl) phosphoric acid apparently form polymers with trimethylolmelamine having definite phosphorus-to-bromine ratios which change after curing on cotton cloth.

These polymers have been formed on cotton fabric by application of the monomers to confer excellent flame- and glow-resistance properties to the cloth. Cloth treated with these compounds will withstand solvent extraction and from 6 to 9 severe launderings. Crease-resistance is also imparted to the cloth and changes in hand, tear resistance, and other physical properties are of the same order as those obtained when trimethylol-melamine is used alone, as in commercial crease-proofing and dimensional stability treatments.

The tris (dibromopropyl) ester of phosphoric acid was applied by two methods in conjunction with trimethylolmelamine. One method consisted of applying the ester in organic solvent solution, followed by treatment with trimethylolmelamine; the other method involved making an emulsion of the ester with triethanolamine oleate and mixing the emulsion with a solution of trimethylolmelamine prior to its application to cloth.

Cloth treated by either of these latter methods is flame and glow resistant and will withstand about 9 launderings but not organic solvent extraction. Hand and tear strength are not materially affected by these treatments.

Part II. Several silicon compounds, potentially capable of making durable finishes, were investigated as flame retardants for cotton. The compounds studied included polysiloxanes, acetoxysilanes, and silyloxy-phosphorus polymers. None was effective enough to be a practical flame retardant for cotton fabrics. Compared to existing durable finishes, the add-ons required for flame resistance were excessive.

Part I

THE USE OF DIBROMOPROPYL PHOSPHATES AS FLAME RETARDANTS FOR COTTON

1. Introduction

The research described in this report was performed as part of an intensive program for the development of new and improved, launder-resistant treatments for imparting flame resistance to military-type cotton fabrics. The process described here was developed and patented(1) as part of this program and gave cotton fabrics which were flame-resistant and moderately resistant to laundering. However, other processes resulting from the program of this Laboratory showed so much greater promise that it was necessary to shift emphasis of work to provide sufficient personnel to develop them. Two of these processes, known as the BAP and THPC treatments, are now in pilot-plant and semi-commercial development.(2-7)

Among the investigations which were curtailed was one which involved the use of dibromopropyl esters of phosphoric acid. Although the treatment is described in the patent mentioned above, the present publication supplies further details of the preparation of the esters and their application to cotton fabrics. Because of the curtailment mentioned above, complete studies have not been carried out on the polymers formed. However, the information given may prevent duplication of effort and the compounds described may be of value to other workers in the field.

2. Background

The flame resistance of cotton has been a research problem for several decades and successful treatments have fallen into two classifications: durable and non-durable.(8) Clothing materials which are laundered frequently and tentage and tarpaulin fabrics which are exposed to rain require treatments of the durable type. Several methods of treatment to obtain durable flame resistance have been developed; most of them have one or more disadvantages which make them unsuitable for severe use.

An ideal treatment would impart to cotton the ability to resist flame and after-glow without impairing the other valuable properties of cotton as a textile material, e.g., breaking strength, tearing strength, elongation, abrasion resistance and hand or feel. Such a treatment also must be easily applied with existing textile machinery, preferably from aqueous solution or emulsion, and must not be excessively costly.

One of the more successful durable treatments was developed by Walter et al.(9) The treatment, which consists of the application of partially polymerized and brominated triallyl phosphate to cloth, gives excellent flame resistance and glow resistance without damaging the physical properties of cotton. However, the process is of limited practicability because of: (a) the cost of the reagents used, (b) the number of steps involved in the partial polymerization and bromination of the triallyl phosphate, and (c) the potential hazards and precautions required in using an organic solvent for applying the compound.

Because of the excellent flame resistance obtained with brominated polytriallyl phosphate on cotton, a search was made for less expensive compounds of a similar chemical nature but which could be applied from aqueous solution or emulsion. Three such compounds were investigated: the mono-, di-, and tri-esters of 2,3 dibromopropanol and phosphoric acid. The first two compounds are simply prepared from 2,3 dibromopropanol and phosphorus pentoxide (10) or phosphorus oxychloride (11) and the latter compound is prepared by the bromination of triallyl phosphate.(12) These esters would be less expensive than partially polymerized, brominated triallyl phosphate and obviate some of the hazards involved in the application to fabrics.

It was found that the ammonium salts of the mono- and di-esters are water soluble and that a stable emulsion of the tri-ester could be prepared. The mono- and di-esters were applied to cotton with amino resins particularly trimethylolmelamine. As will be described below, excellent flame resistance and glow resistance which is durable to dry-cleaning and will withstand from 6 to 9 Army Mobile Launderings (13) may be obtained by this method.

Walter and Hornstein (12) describe the preparation of tris-(dibromopropyl) phosphate and its application in benzene solution to cloth. However, cloth treated in this manner will not withstand laundering. When the tri-ester is applied in conjunction with a resinous binder such as trimethylolmelamine, the combination will remain on the cloth through at least 9 severe launderings. Furthermore, the trimethylolmelamine apparently also contributes to the flame resistance.

3. Experimental and Results

a. Preparation of phosphates

(1) Preparation of mono- and bis-(dibromopropyl) phosphoric acids. Mono- and bis-(dibromopropyl) phosphoric acids were easily prepared from 2,3 dibromopropanol and phosphorus pentoxide. The 2,3 dibromopropanol was obtained by adding an excess of bromine to allyl alcohol in chloroform and

washing the product with water to remove any unreacted allyl alcohol and bromine. A practically pure product in almost theoretical yield was obtained.

Four moles (872 g.) of the 2,3 dibromopropanol, dissolved in an equal weight of benzene, was added gradually and with cooling to 1 mole (142 g.) of phosphorus pentoxide. The mixture was shaken until the pentoxide went into solution, and was allowed to stand with intermittent shaking for 3 hours. The benzene was evaporated and the product extracted with water to dissolve the mono-dibromopropyl phosphoric acid. (A small amount of additional material, presumably bis-(dibromopropyl) phosphoric acid, also dissolved.) The water was removed by azeotropic distillation in benzene and the benzene evaporated. The product was dissolved in a minimum amount of chloroform, and carbon tetrachloride was added to the cloud point. Crystals of mono-(dibromopropyl) phosphoric acid formed which were filtered off and then dried under vacuum. The crystals were flat plates which melted at 84° C. (uncorr.) and had a neutral equivalent of 296 (theoretical, 298). Yield was 338.7 grams.

The residue remaining after the water extraction of mono-(dibromopropyl) phosphoric acid was neutralized with 10% potassium hydroxide which dissolved the bis-(dibromopropyl) phosphoric acid. A small residue of unreacted 2,3 dibromopropanol settled out. The solution was decanted and excess hydrochloric acid added to precipitate the bis-(dibromopropyl) phosphoric acid. After separation, the product was dried under vacuum to a thick brown syrup. Yield of the di-ester was 561.8 g. The total yield of both products was 88.8% of theory, of which 37.6% was mono-(dibromopropyl) phosphoric acid and 62.4% was bis-(dibromopropyl) phosphoric acid.

It was shown that in commercial practice it would not be necessary to separate and purify these compounds, since they perform almost equally well as flame retardant compounds.

(2) Preparation of tris-(dibromopropyl) phosphate. The tris-(dibromopropyl) phosphate was prepared similarly to the method of Walter and Hornstein (12) by adding 6 moles of bromine in chloroform, slowly and with stirring, to 1 mole of triallyl phosphate in chloroform at 0° to 5° C. After the addition was completed, the chloroform was distilled off on a steam bath. Approximately the theoretical yield was obtained.

This ester was a yellow oil, soluble in organic solvents but practically insoluble in water.

b. Application to Cotton Cloth

(1) Application of mono-(dibromopropyl) phosphoric acid. The mono-ester, which is strongly acidic, was converted to the ammonium salt prior to its application to cotton cloth as a flame retardant agent. Resloom HP* which corresponds approximately to a trimethylolmelamine, was used as a binding agent.

When a solution of the ammonium salt of mono-(dibromopropyl) phosphoric acid was added to a solution of trimethylolmelamine and warmed, formaldehyde was evolved and precipitation occurred at about 80 to 90° C. A relatively insoluble polymeric material was formed which had a bromine-to-phosphorus ratio of about 5.2 to 1 which is the same as the ratio in the ester. The ratio varied somewhat, from 4.5 to 6.0, in a series of polymers formed from mono-(dibromopropyl) phosphoric acid and trimethylolmelamine in weight ratios of from 4:3 to 1:7. Analyses are shown in Table I.

TABLE I. ANALYSES OF POLYMERIC MATERIAL OBTAINED FROM MONO-(DIBROMOPROPYL) PHOSPHORIC ACID AND METHYLOLMELAMINE.

Ratio ester/ methylolmelamine resin	N (%)	Br (%)	P (%)	Ratio	
				Br/P	N/Br
4:3	38.3	13.3	2.6	5.1	2.9
1:1	37.3	14.9	2.9	5.1	2.5
3:4	39.1	12.7	2.6	4.9	1.5
1:2	38.8	13.3	2.7	4.9	2.9
1:3	40.6	10.9	2.4	4.5	3.7
1:4	41.4	9.0	1.5	6.0	4.6
1:5	42.2	7.9	1.6	4.9	5.3
1:6	42.6	7.5	1.4	5.4	5.7
1:7	42.9	6.6	1.2	5.5	6.5

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* The mention of trade products and firms does not imply their endorsement over similar products or firms not mentioned.

Solutions of 30% concentration, in these same ratios, were applied to 12 in. squares of 8.2 oz. cotton twill, by padding to about 75% wet add-on, drying at 60° C. for 10 min., and curing at 150° C. for 6 min. After the treatment, the samples were laundered and analyzed and tested. The bromine-to-phosphorus ratios varied from about 1.4 to 3.8 indicating a loss of about half of the bromine as compared with the ratios of Table I.

Add-on and char lengths obtained on these samples are listed in Table II. After one laundering, resin retentions were poor on treatment with solution ratios (ester/methylolmelamine) up to about 1:3; however, good flame resistance and glow resistance, determined by the standard vertical test, was obtained with only 9.2% resin on the cloth.

TABLE II. APPLICATION OF MONO-(DIBROMOPROPYL) PHOSPHORIC ACID AND METHYLOLMELAMINE TO COTTON CLOTH.

Ratio ester/methylolmelamine resin	Cured Add-on (%)	Laundered Add-on (%)	Retention after Laundering (%)	Char Length* (in)	Br/P Ratio
4:3	19.8	5.4	27.3	B.E.**	1.4
1:1	19.3	6.9	35.8	9.0	2.0
3:4	18.8	9.2	48.9	4.1	2.2
1:2	17.4	9.2	52.9	4.4	3.0
1:3	16.9	13.6	80.5	4.2	2.8
1:4	16.5	13.0	78.8	4.6	2.5
1:5	16.4	12.3	75.0	4.0	3.1
1:6	16.3	12.6	77.3	4.5	2.5
1:7	16.1	12.8	79.5	4.0	2.6
1:8	16.2	15.2	93.8	4.0	3.8
1:10	16.0	15.3	95.6	4.0	3.8

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* Vertical Flame Test after one laundering.

** Burned to end.

The char obtained when the treated cloth is exposed to a flame is strong and bulky and has high heat-insulating properties which would protect underlying material against the heat of a flame. Also, the thickness of the char would tend to exclude the air and thus retard flame propagation to the inner layers.

Tear strength reductions and changes in hand were of the same order as those obtained when equivalent amounts of methylolmelamine resin alone are used, as, for example, in creaseproofing. That is, the loss averaged about 35 to 60% of the original tear strengths. Losses are not considered excessive when from 10 to 12% add-on is obtained. Crease-resistance is also obtained with the flame-retardant formulation. Recovery angles of from 110° to 130° were obtained as compared with an angle of 53° for the untreated fabrics.

(2) Application of bis-(dibromopropyl) phosphoric acid. The di-ester is insoluble in water. However, the soluble ammonium salt was used with trimethylolmelamine in aqueous solution for its application to cotton cloth.

The reaction of the ammonium salt of bis-(dibromopropyl) phosphoric acid and trimethylolmelamine also results in the formation of a polymeric material. Heating a solution of the two compounds gives a polymer with a bromine-to-phosphorus ratio of about 7.5 to 1. The di-ester has a theoretical bromine-phosphorus ratio of 10.3 to 1. The lower figure for the reaction product indicates a loss of one of the bromine atoms. When cloth is treated with a mixture of the two compounds and is cured, ratios varying from 4.9:1 to 7.2:1 are obtained, indicating further loss of bromine. Analyses of the polymeric reaction products from solutions containing the components in ratios of from 4:3 to 1:3 are shown in Table III. They may be compared with similar data for the polymers of mono-ester and trimethylolmelamine.

TABLE III. POLYMERIC MATERIAL OBTAINED FROM BIS-(DIBROMOPROPYL) PHOSPHORIC ACID AND METHYLOLMELAMINE.

Ratio ester/methylol-melamine resin	N (%)	Br (%)	P (%)	Ratio Br/P	Ratio N/P
4:3	40.2	13.1	1.8	7.3	22.3
1:1	35.9	18.0	2.3	7.8	15.6
3:4	38.8	14.5	1.9	7.6	20.4
1:2	40.2	12.6	1.8	7.0	22.3
1:3	41.6	10.9	1.4	7.8	29.7

When the ammonium salt of bis-(dibromopropyl) phosphoric acid and trimethylolmelamine in ratios of 4:3 to 1:10 were applied to cloth, good flame resistances (indicated by char-length) were obtained with the ratio of 3:4; increasing amounts of trimethylolmelamine did not decrease significantly the flame resistance (Table IV).

TABLE IV. APPLICATION OF BIS-(DIBROMOPROPYL) PHOSPHORIC ACID AND METHYLOLMELAMINE TO COTTON CLOTH

Ratio ester/methylolmelamine resin	Cured Add-on (%)	Laundered Add-on (%)	Retention after Laundering (%)	Char Length* (in.)	Br/P Ratio
4:3	16.8	7.1	42.3	BE **	4.9
1:1	16.1	7.9	49.1	BE **	5.7
3:4	16.1	9.3	57.8	4.6	5.9
1:2	16.0	11.3	70.6	4.2	6.5
1:3	15.5	12.0	77.4	4.2	6.9
1:4	16.1	14.8	91.9	3.2	6.2
1:5	16.2	14.8	91.4	4.2	6.8
1:6	16.3	15.3	93.9	4.8	7.1
1:7	15.8	15.0	94.9	4.5	6.9
1:8	16.3	15.8	96.9	5.1	6.6
1:9	16.1	15.3	95.0	4.3	7.2
1:10	16.2	15.3	94.4	5.0	6.2

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* Vertical flame test after one laundering.

** BE = burned to end.

Launder-fastness, as indicated by resin retention, was obtained beginning at the ratio of 1:4. Other properties such as crease-resistance, hand, and tearing strength, were the same as observed with treatment with the mono-ester.

The effect of varying the curing time and temperature was observed (Table V). Two sets of samples were padded with a 30% solution of the di-ester and trimethylolmelamine in a ratio of 1:2. Curing was for from 3 to 8 minutes at 130° or 150° C. All of the samples cured at the lower temperature burned, whereas samples cured at 150° C. were flame resistant. The latter samples contained more bromine and had higher resin retentions on laundering. Adequate curing was judged to be obtained on heating for 6 minutes at 150° C.

TABLE V. EFFECT OF TIME AND TEMPERATURE OF CURING OF BIS-(DIBROMOPROPYL) PHOSPHORIC ACID AND METHYLOLMELAMINE ON COTTON CLOTH.

Time (min)	Cured Add-on (%)	Laundered Add-on (%)	Retention After Laundering (%)	Char Length* (in.)	Br (%)
			130° C. Cure		
3	17.7	9.7	54.8	BE**	0.17
4	17.2	9.7	56.4	BE**	0.16
5	17.0	10.0	58.8	BE**	0.17
6	16.8	10.1	60.1	BE**	0.24
7	17.1	10.5	61.4	BE**	0.30
8	16.7	10.5	62.9	BE**	0.37
			150° C. Cure		
3	16.5	12.0	72.7	5.3	0.66
4	16.3	11.9	73.0	4.2	0.83
5	16.3	12.0	73.6	4.6	0.99
6	15.9	12.1	76.1	4.8	0.99
7	15.9	12.0	75.5	4.3	0.79
8	16.1	12.4	77.0	4.0	0.92

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* Vertical flame test after one laundering.

** BE = Burned to end.

(3) Application of a crude mixture of mono- and di-esters.

The similar results obtained on the application of the mono- and di-esters to cotton cloth indicated that it might be possible to apply a mixture of the two esters to cloth and still obtain satisfactory results. This would eliminate the necessity of separating and purifying the compounds and could cut the cost of the treatment considerably.

The feasibility of using such a mixture was confirmed by the following experiment. A crude mixture of the mono- and di-ester, neutralized with ammonium hydroxide, was used with 3 parts of trimethylolmelamine to make a solution of 30% concentration. This was padded to a 75% wet add-on on 8.2 oz. cotton twill, and dried and cured as before. Results were similar to those obtained with the individual esters: char-length, 4.5 in.; add-on, 12.4%; bromine/phosphorus ratio, 4.5 to 1.

(4) Application of tris-(dibromopropyl) phosphate. As previously mentioned, the tri-ester is practically insoluble in water but is soluble in a number of organic solvents. Therefore, alternative methods of application of the ester and trimethylolmelamine were used. In one, the ester was dissolved in alcohol, padded onto the cloth, dried at 60° C. and then treated with aqueous trimethylolmelamine solution and dried and cured in the usual manner. The ratio of ester to methylol resin was varied from 1:1 to 3:1 by weight. Concentration of the reagents was kept at 30% total in each case. Table VI shows the results of such treatment. This treatment,

TABLE VI. APPLICATION OF ALCOHOLIC TRIS-(DIBROMOPROPYL) PHOSPHATE TO COTTON FOLLOWED BY TREATMENT WITH METHYLOLMELAMINE.

Ratio ester/methylol-melamine resin	Cured Add-on (%)	Laundered Add-on (%)	Retention After Laundering (%)	Char Length* (in.)
1:1	20.3	13.4	66	3.9
1.5:1	20.2	16.6	82	3.9
2:1	21.3	17.3	81	3.9
2.5:1	22.6	18.5	82	3.9
3:1	23.9	19.4	81	3.9

* Vertical flame test after one laundering.

involving an organic solvent and requiring two steps in application, was considered impractical from a textile finishing viewpoint.

Accordingly, the second method was tried: an emulsion of the tri-ester was prepared, using ethanolamine and oleic acid. The emulsion was applied to cloth with trimethylolmelamine in ratios of from 1:1 to 3:1 with total concentration of reactants maintained at 30%. The samples were dried at 60° C., cured at 150° C., and laundered, yielding the results listed in Table VII.

TABLE VII. APPLICATION OF TRIS-(DIBROMOPROPYL) PHOSPHATE EMULSION AND METHYLOLMELAMINE TO COTTON CLOTH

Ratio ester/methylol-melamine resin	Cured Add-on (%)	Laundered Add-on (%)	Retention After Laundering (%)	Char Length* (in.)
1:1	24.2	19.2	79	2.2
1.5:1	23.3	18.8	81	3.4
2:1	25.2	20.8	90	3.9
2.5:1	22.6	18.1	80	3.8
3:1	23.8	18.9	79	4.9

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* Vertical flame test after one laundering.

There was no polymer formation with the tri-ester and trimethylolmelamine. Thus it is assumed that the ester remains on cloth by virtue of its relative insolubility and the binding action of the trimethylolmelamine polymer.

Samples treated with the tri-ester and methylol resin had considerably better tearing strength and hand than those treated with the mono- and di-ester and resin.

4. Launderability and extraction of treated samples.

a. Launderability. Treated samples were tested for launderfastness by a modification of the Army Standard Mobile Laundering Test.(13) Laundering was identical with the standard method with respect to concentration of detergent, number of rinses, etc., except that a table top agitator-type washer was used instead of a washwheel. Consequently, samples were probably washed more severely than with the standard procedure.

Samples treated with the mono- and di-esters, and the tri-ester by the two methods of treatment, were laundered for 1 and 6 cycles by the standard method and gave the results shown in Table VIII. Tests on other samples have indicated that good flame resistance may be retained through 9 laundry cycles. However, after 12 cycles all the samples burned.

TABLE VIII. LAUNDERABILITY OF COTTON CLOTH TREATED WITH THE DIBROMOPROPYL ESTERS OF PHOSPHORIC ACID AND METHYLOLMELAMINE.

Treatment	Cured Add-on (%)	Number of Launderings	Retention After Laundering (%)	Char Length* (in.)
Mono ester/methylolmelamine 1:3	23.9	1	74	4.9
	23.8	6	65	5.2
Di-ester/methylolmelamine 1:3	25.1	1	85	3.9
	24.0	6	71	4.6
Tri-ester/methylolmelamine 2:1 (emulsion)	22.6	1	80	3.8
	23.0	6	60	4.8
Tri-ester/methylolmelamine 2.5:1 (solution)	22.6	1	82	3.9
	22.6	6	57	4.9

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* Vertical flame test after laundering.

b. <u>Extraction</u>. The effect of organic solvent extraction on samples treated with the three esters was investigated. Treated cloth samples were extracted with ethanol in a Soxhlet extractor for 3, 6, and 12 passes of the solvent (Table IX). The mono- and di-ester treated samples lost very little weight and none of their flame resistance. Samples treated with the tri-ester, however, lost from 75 to 80% of the original add-on and were consequently no longer flame resistant. This would tend to indicate that the mono- and di-ester treatment would probably be resistant to ordinary dry-cleaning while the tri-ester would not.

TABLE IX. ALCOHOL EXTRACTION OF COTTON CLOTH TREATED WITH THE ESTERS OF DIBROMOPROPYL PHOSPHORIC ACID AND METHYLOLMELAMINE

Treatment	Cured Add-on (%)	No. of Extractions	Retention after Extraction (%)	Char Length* (in.)
Mono-ester/methylolmelamine 1:3	23.2	3	96	3.9
	23.6	6	93	3.4
	23.2	12	89	3.4
Di-ester/methylolmelamine 1:3	23.6	3	95	3.5
	24.3	6	91	3.6
	24.3	12	85	3.1
Tri-ester/methylolmelamine 2:1	23.8	3	26	BE**
	23.6	6	23	BE**
	24.1	12	21	BE**

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* Vertical flame test after alcohol extraction.
** BE = Burned to end.

5. Summary and Conclusions.

The dibromopropyl esters of phosphoric acid have been shown to be applicable for imparting flame resistance and glow resistance to cotton textiles when used with a resin-former such as trimethylolmelamine. Cloth may be treated with these flame-retarding compounds on existing textile machinery which is used for creaseproofing treatments. The treated cloth has essentially the same properties as cloth treated with creaseproofing resins but, in addition, is flame resistant and glow resistant. When a flame is brought in contact with the treated cloth, a thick, strong char is formed which has good insulating properties and would protect underlying materials.

Trimethylolmelamine combines with diammonium mono-(dibromopropyl) phosphate to produce a polymeric material which has a bromine-to-phosphorus ratio of about 5.2 to 1. When a solution of the ammonium salt of the mono-ester is mixed with a solution of trimethylolmelamine and applied to cloth with subsequent drying and curing, the bromine-to-phosphorus ratio dropped, indicating loss of about half of the bromine.

Reaction of the water soluble ammonium salt of bis-(dibromopropyl) phosphoric acid with trimethylolmelamine results in a polymeric material which has a bromine-to-phosphorus ratio of about 7.5 to 1. Apparently one atom of bromine is lost from each molecule of the ester, since its bromine-to-phosphorus ratio is 10.3 to 1. When a mixture of the di-ester and trimethylolmelamine is applied to cloth, there is further loss of bromine as the ratio drops to 4.9-7.2 to 1.

Mono- and bis-(dibromopropyl) phosphoric acid may be attractive for the treatment of flame-resistant cotton cloth because: (1) a mixture of the mono- and di-ester is easily prepared from dibromopropanol and phosphorus pentoxide, (2) the two esters function equally as well in optimum ratios of from 1:3 to 1:7 with trimethylolmelamine, (3) the treatment may be applied to cloth on existing textile machinery.

The tri-ester, tris-(dibromopropyl) phosphate does not form a polymer with trimethylolmelamine. Cloth treated with this ester would not be fast to dry-cleaning, but it gives products with greater tearing strength and softer hand than cloth treated with the other two esters. This treatment does not seem to have the possibilities of the other treatments.

6. Acknowledgment

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7. References

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Part II

AN INVESTIGATION OF SILICON COMPOUNDS AS FLAME RETARDANTS FOR COTTON FABRICS

1. Introduction

Although at least one silicon compound has been used in a flame retardant finish for cotton fabrics, to suppress after-glow in a commercial flame-retardant composition (1), no information could be found on the overall value of silicon compounds as flame retardants for cotton. Some preliminary work at the Southern Regional Research Laboratory (2) indicated that bromoalkyl acetoxysilanes were effective flame retardants although of poor durability. Following these initial experiments, it was decided to investigate more fully the possibility of using silicon compounds as durable flame retardants for cotton fabrics.

For this purpose the flame retardancy of a number of silicon compounds which were either polymeric or potentially capable of reaction with cellulose were tested. These two classes of compounds were the only ones considered likely to have the resistance to laundering that is necessary in a durable finishing agent for cotton. All the compounds tested contained bromine, which has been shown to assist the flame-retardant action of other elements or groups.(3,4)

The polymeric silicon compounds investigated were of the siloxane type, where silicon is bonded between oxygen atoms in the polymeric chain. Polymers consisting of an organic chain with silicon side groups were not investigated, since the unsaturated monomers were found to polymerize only poorly under the conditions tried.

The results obtained with the silicon compounds investigated were disappointing since add-on required was excessive and the cost of reagents would be high. It was felt that the expenditure of further effort would be uneconomical, particularly in view of the development of a number of more promising treatments at the Southern Regional Research Laboratory.(5) The present report, therefore, is necessarily less complete than is desirable from an academic viewpoint, but the information presented may be useful in preventing repetition of the work done and may serve as a basis for other studies in the investigation of silicon polymers.

2. Experimental

a. Preparation of a Monomeric Bromoalkyl Silane

In order to prepare a polysiloxane containing relatively stable bromine atoms, it was necessary to synthesize a bromoalkyl chlorosilane for a monomeric, starting material. Preferably, the beta-carbon atom in the alkyl group would be unbrominated, since the activity of halogen atoms in this position (6) would make the materials difficult to apply to cotton fabrics without extensive degradation, and would make the fabric finish very sensitive to moisture.

The addition of bromoform to vinyl trichlorosilane by free radical initiation would produce 1,3,3-tribromopropyl trichlorosilane (7) which has a highly brominated alkyl group of the desired structure. This compound was synthesized by the following procedure.

To 150 g. bromoform in a round-bottom flask, equipped with reflux condenser and protected from moisture with a drying tube, 24 g. of vinyl trichlorosilane and 2 g. benzoyl peroxide were added. The mixture was heated at 100° C for 2 hours. A reaction of moderate vigor occurred spontaneously, with refluxing which subsided in 10 to 15 minutes, and the reaction proceeded quietly for the rest of the 2-hour period. An additional 2 g. peroxide, added after the 2-hour reaction period with an additional hour at 100° C. increased the yield of crude adduct as high as 77%, whereas the 2-hour reaction period alone gave 65 to 70% yields. The crude product was obtained by distilling the excess bromoform at 30 to 40 mm. pressure. Recovered bromoform was used in subsequent preparations.

The crude product is distillable under vacuum; a 35% of theoretical yield of distilled product was collected at 100-110° at 3 mm. Analysis of the distilled product showed:

	% Silicon	% Chlorine	% Bromine
Found	6.09	22.96	59.93
Calculated for $C_3H_4Br_3SiCl_3$	6.78	25.67	57.87

The high bromine content and low silicon and chlorine contents indicate that the product is still contaminated with about 10% bromoform, possibly due to formation of an azeotrope.

A sample of the distilled product was hydrolyzed by addition to water during vigorous stirring. The polysiloxane formed was filtered off and dried in a vacuum oven. When sufficiently dry, it was ground to a powder and dried to constant weight under vacuum. Analysis of this polysiloxane showed: 8.04% silicon and 70.24% bromine. This is an atomic ratio of bromine-to-silicon close to 3, as calculated for a siloxane from tribromopropyl trichlorosilane.

A similar hydrolysis of the residue left in the still pot after distillation of the silane gave a product that analyzed: 12.41% silicon and 51.70% bromine. This is an atomic ratio of bromine-to-silicon slightly less than 1.5. The residue, then, is a telomer of bromoform and vinyl trichlorosilane consisting mainly of a product with two silane units:

$$CHBr_2-CH_2CH(SiCl_3)_2-Br$$

The distilled tribromopropyl trichlorosilane, containing the small amount of bromoform, was used throughout this investigation as the silicon-containing starting material. The bromoform should be inert in all the reactions performed.

b. Treatment of Fabric with Polysiloxanes

The preparation of a bromine-containing polysiloxane for treatment of cotton fabric was accomplished in the following manner. Tribromopropyl trichlorosilane was added slowly to excess ethanol. The resulting solution was heated to 80°C, whereupon hydrogen chloride was expelled. Toluene was added, and the solution vigorously stirred with an equal volume of water. The toluene layer was separated and used for impregnation of the fabric samples. By proper dilution of this solution, a range of add-on on the fabric was obtained.

The cotton fabric used throughout this investigation was khaki-dyed 8 oz. twill of the type used for military garments. The treatment of the fabric consisted in impregnation of samples, about 1-foot square, with the solution by passing the wet samples through squeeze rolls. Two dips and two nips were used. Toluene was allowed to evaporate from the samples at room temperature. Some of the samples were soaked in a 2% ammonium hydroxide solution after the above treatment, to further polymerize the siloxane, and then dried at 110°C before testing.

The methods used for testing the flame resistance of the treated fabric were the Vertical Flame Test (8) and the "match"test.(9) The latter test consists in suspending, in a draft-free space, a strip of fabric, 1/4 inch by 10 inches, and igniting the lower end with a match flame for about 6 seconds. If no flame persists after removal of the match, the flame resistance is classed as "excellent". If a flame persists only briefly, it is classed as "good". If the flame lasts long enought to char not more than 5 inches of the strip, it is classed as "fair". If more than 5 inches is charred, it is classed as "poor". If the strip is charred completely, it is classed as "fails". This test is considerably more rigorous than the Vertical Flame Test.

The results from the testing of the fabric samples treated with the polysiloxanes are shown in Table I. Chemical analysis of some of the samples was performed to confirm the silicon and bromine content of the fabric. The tabulated results show that an add-on of about 35% is required to give enough flame resistance to the 8 oz. twill to have a measurable char length in the Vertical Flame Test. Even at these add-ons, results in the Match Test are no better than "fair". The analytical values support the conclusions from measurement of weight add-ons regarding the high silicon and bromine contents that are required for flame resistance.

TABLE I - FLAME-RESISTANCE OF COTTON FABRIC TREATED WITH POLYSILOXANES

Weight Add-on (%)	Flame Resistance: Vertical Flame Test (in.)*	Flame Resistance: Match Test	Silicon Content (%)	Bromine Content (%)
		Air Dried Only		
44	4.7	poor	2.80	16.4
32	BEL**	fails	1.75	10.8
24	BEL**	fails	-	-
17	BEL**	fails	-	-
		Ammonia Washed		
36	6.3	fair	2.36	13.1
31	BEL**	fails	2.08	11.2
21	BEL**	fails	-	-
15	BEL**	fails	-	-

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* Length of char.

** BEL = Burned entire length, greater than 10 inches.

In order to raise the silicon content and lower the bromine-to-silicon ratio in the polysiloxane, a copolymer was prepared by hydrolysis of a mixture of diethyldichlorosilane and tribromopropyl trichlorosilane. A solution of 0.1 mole each of diethyldichlorosilane and tribromopropyl trichlorosilane in 200 ml. dioxane was prepared. Water, 0.5 mole, was added and the solution evaporated to dryness. The residue was redissolved in dioxane, and the solution again evaporated to remove the hydrogen chloride. Redissolving the residue in dioxane formed the treating solution for the fabric. The fabric samples were impregnated as before, rinsed in water, and oven dried before testing.

Results from the testing of these samples are tabulated in Table II. No higher than 19% add-on was obtained. At this add-on, no flame resistance was observed although the fabric contained 1.63% silicon.

TABLE II - FLAME RESISTANCE OF FABRIC TREATED WITH COPOLYMERIC SILOXANE

	Flame Resistance			
Weight Add-on (%)	Vertical Flame Test (in.)*	Match Test	Silicon Content (%)	Bromine Content (%)
19	BEL**	fails	1.63	8.4
14	BEL**	fails	-	-

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* Inches of Char.

** BEL = Burned entire length.

c. Acetoxy Silanes

The tribromopropyl trichlorosilane was converted to the acetoxy silane, where the chlorine atoms are partially or entirely replaced by acetoxy groups. These compounds are essentially mixed anhydrides of a silicic acid and acetic acid. They are capable of reacting with the cellulosic hydroxyl groups to form a silyl ester of cellulose and a relatively weak acid, acetic acid. This latter property prevents the extensive degradation that would occur on an attempt to treat cotton directly with the trichlorosilane.

Conversion of the trichlorosilane to the acetoxy silane was accomplished by the procedure of Schuyten, Weaver, and Reid.(10) In a 500 ml. gas washing bottle, equipped with a porous glass plate near the bottom, was placed a suspension of 40 g. anhydrous sodium acetate in 200 ml. dry toluene. Tribromopropyl trichlorosilane, 54.5 g., diluted with 50 ml. toluene, was added dropwise with continuous stirring. The speed of addition was so regulated as to maintain a gentle reflux. At the end of the addition, the solution was sucked through the glass plate. Toluene was distilled from the solution under vacuum, leaving 38.4 g. product. This product was not further purified but used directly in the treatment of fabric.

The complete yield of acetoxy silane was dissolved in 200 ml. toluene. A small quantity of pyridine was added to neutralize any acid remaining in the solution. The solution was applied to fabric samples in various dilutions in the same manner as the polysiloxanes had been applied. Samples were oven dried, rinsed in water, and redried before testing.

Results of the testing of these samples are shown in Table III. It is seen that 23% add-on still gives uncertain results in the Vertical Flame Test. Unfortunately 23% add-on was the highest obtained. Flame resistance in the Vertical Flame Test would probably be obtained at about 25% add-on, which is lower than required with the polysiloxanes but still rather high. A still higher add-on would be necessary for good results in the match test.

TABLE III - FLAME RESISTANCE OF FABRIC TREATED WITH TRIBROMOPROPYL ACETOXY SILANES

	Flame Resistance			
Weight Add-on (%)	Vertical Flame Test (in)*	Match Test	Silicon Content (%)	Bromine Content (%)
23	7.7** BEL	fails	1.9	9.7
18	BEL	fails	-	-
11	-	fails	-	-

* Length of char.

** Two samples tested; one gave a 7.7 inch char length, the other burned the entire length; BEL= Burned entire length.

d. Silyloxy - Phosphorus Polymers

The discouraging results obtained with the polysiloxanes as flame retardants was thought to be due possibly to the high thermal stability of the siloxane chain. This would hinder the decomposition of the polymer into the silicic acids which are probably the active flame retardants. The possibility of introducing another atom, phosphorus, into the silicon-oxygen chain was investigated as a means of decreasing the thermal stability of the polymer chains and increasing their effectiveness as flame retardants.* The phosphorus in such polymers would also contribute toward flame retardancy.

To prepare a polymeric compound of the type desired, the reaction of tribromopropyl methoxy dichlorosilane with ethanephosphonic acid was used. The use of tribromopropyl methoxy dichlorosilane instead of tribromopropyl trichlorosilane gives polymers of greater solubility which

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* The use of phosphorus for this purpose was suggested by Dr. Gennady Kosolapoff of Alabama Polytechnic Institute, a collaborator of the Southern Utilization Research Branch.

are, therefore, easier to use in textile treatments. This reaction should give a polymer with a chain composed of silicon-oxygen-phosphorus-oxygen units. The repeating unit would be:

$$-[Si(C_3Br_3H_4)(OCH_3)-O-P(O)(C_2H_5)-O]-$$

Tribromopropyl methoxy dichlorosilane was prepared by the addition of an equimolar quantity of methanol to tribromopropyl trichlorosilane below 10°C with vigorous stirring. After standing one hour at room temperature, the hydrogen chloride remaining in the product was removed by placing the product under vacuum at 60°C for one hour. A 99% of theoretical yield was obtained. The product was then used without further purification.

To prepare the silyloxy-phosphorus polymer, equimolar quantities of tribromopropyl methoxy dichlorosilane and ethanephosphonic acid were mixed and heated at 100°C for 2 hours under vacuum. Hydrogen chloride was expelled during this period, and the mixture became homogeneous. The residue was equivalent to 92% of the theoretical yield of polymer. A 30% solution of the polymer in dioxane was prepared, and this was used for the treatment of fabric samples, after filtering to remove a trace of insoluble material.

Fabric samples were treated with the dioxane solution by padding, followed by drying in a blower oven. The solution was diluted to give a range of add-ons. For add-ons greater than 20%, two treatments were required. One series of samples was rinsed in water and dried before testing; another series was tested without the water rinse. The flame resistance of these samples is shown in Table IV.

The results obtained with the samples not submitted to the water rinse are good, approaching the best obtained with other flame retardants of higher phosphorus content.(9) The water rinse, however, reduces the phosphorus content and the flame resistance markedly. Even so, the flame resistance is superior to that obtained with the polysiloxane (Table I). For instance, the sample with 20% add-on and only 0.21% phosphorus is superior to the sample with 30% add-on of polysiloxane.

The reduction in phosphorus content on the water rinse can be due to hydrolysis of the silyloxy-phosphorus polymer or to removal of unreacted phosphonic acid. The latter possibility seems less likely, since the near theoretical yields of polymer indicate that little phosphonic acid remains unreacted.

In any event, the finish shows little practical value upon comparison with known finishes. Even before the water rinse, the polymer shows no advantage in flame resistance over known finishing agents.(5) The water rinse reduces the flame resistance to well below practical levels, and the results indicate poor durability can be expected.

TABLE IV - FLAME RESISTANCE OF FABRICS TREATED WITH SILYLOXY-PHOSPHORUS POLYMERS

	Flame Resistance			
Weight Add-on (%)	Vertical Flame Test (in.)*	Match Test	Silicon Content (%)	Phosphorus Content (%)
		Without Water Rinse		
31	5.1	excellent	1.45	3.10
14	6.3	excellent	1.40	0.66
11	7.0	fair	-	-
6	BEL**	fails	-	-
		With Water Rinse		
31	7.1	poor	1.96	0.17
20	7.0	fails	1.40	0.21
14	BEL**	fails	0.60	0.16

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* Inches of Char

** BEL= Burned entire length

3. Conclusions

The data obtained in this investigation indicate that silicon compounds that could be durable to laundering are not good flame retardants for cotton. Siloxane type polymers, even with a high bromine content, require add-ons of 35% to give flame resistance to 8 oz. cotton twill. (Phosphorus polymers, on the other hand, are effective at 20% or less add-on.(3,9) The silyloxy-phosphorus polymers are better than the polysiloxanes but are still less effective than some phosphorus polymers now used as flame retardants.

Although most of the silicon compounds tested were potentially capable of making a durable finish on cotton, no actual tests of durability were made. In view of the poor flame resistance obtained, it was considered that the expenditure of effort to develop a durable finishing agent was not justified.

The work reported cannot be said to include all possible silicon compounds that could be durable. The advances made in silicon chemistry in recent years have introduced a large number of compounds that could be considered for this use. Results of this investigation would indicate, however, that there is little chance of developing any practical flame retardant based primarily on silicon.

4. Acknowledgements

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