

Organoboron Compounds as Durable Flame Retardants for Cotton Fabric

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Synopsis

Twenty-five organoboron compounds were evaluated for their ability to impart flame retardancy properties to a cotton twill fabric. Only those organoboron compounds in which the carbon-to-boron atom ratio was 4 or less imparted flame retardancy at an approximate 20% add-on level; if a halogen atom was also present in the molecule this ratio could be higher than 4. Washfast finishes with six different compounds were developed by either γ -radiation grafting of a vinyl organoboron compound or by chemical curing with hexamethylenediisocyanate, trimethylolmelamine or urea-formaldehyde.

INTRODUCTION

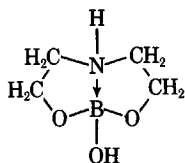
Several inorganic boron compounds are well known for their fire-retarding properties. On the other hand, the reported work on organoboron compounds in fire-retarding applications is limited.^{1,2} In the patent by Posner, the use of the reaction product between boric acid and triethanolamine as a fire retardant for textiles is described, and in the report by Liggett and Bosmajian, some 50 organoboron compounds as flame-resistant finishes for cotton fabric were evaluated. The latter authors concluded that although some compositions were effective flame retardants initially, none was effective even after a mild laundering. The well-known hydrolytic instability of many organoboron compounds, including simple esters, was responsible for these results.

Our efforts in the use of organoboron compounds as fire retardants involved, first, the synthesis or securing of hydrolytically stable organoboron compounds and, second, their development into durable fire-retarding finishes for cotton fabric. In this paper we report our initial results of these studies. The maximum durability of the developed finishes has not been established yet.

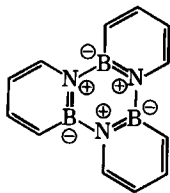
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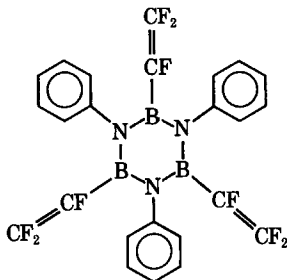
Five different classes of hydrolytically stable organoboron compounds were investigated: (1) compounds with coordinated boron–nitrogen bonding,^{3–5} for example, diethanolamine ester of boric acid,



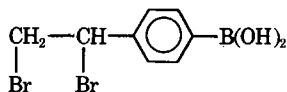
(2) compounds with aromatic boron–nitrogen bonding,^{6,7} for example, 14,16,18-tribora-13,15,17-triazarotriphenylene,



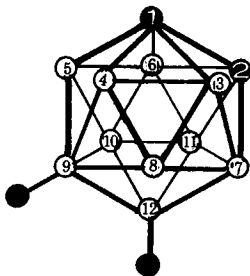
(3) borazines with bulky substituents on nitrogen,⁸ for example, 2,4,6-tris(trifluorovinyl)-1,3,5-triphenylborazine,



(4) boronic acids,^{9,10} for example, *p*-(1,2-dibromoethyl)benzeneboronic acid,



(5) carboranes (icosahedral boron compounds comprising a nucleus of ten atoms of boron bridged by two atoms of carbon),¹¹ for example, 9,12-dichloro-*o*-carborane,



Fire-retarding finishes durable to numerous home launderings (19 in one case) were developed with materials from the "aromatic boron-nitrogen bonding," "borazines," and "boronic acids" classes of compounds. Firm fixing of the compounds was accomplished by two means: (1) γ -radiation grafting and (2) chemical cure, using the following curing agents: hexamethylenediisocyanate, urea-formaldehyde, and trimethylol melamine.

EXPERIMENTAL

Materials

Fabric. The cotton fabric used in this work was 7.5 oz./y² S/423 Twill obtained from Test Fabrics, Inc., New York, New York.

Compounds with Coordinated Boron-Nitrogen Bonding. The ethanolamine and diethanolamine esters of boric acid were prepared according to the literature procedures^{12,13} and were obtained as viscous oils in a better than 80% yield. The triethanolamine ester of boric acid was obtained from Aldrich Chemical Company, Inc., and was used as received.

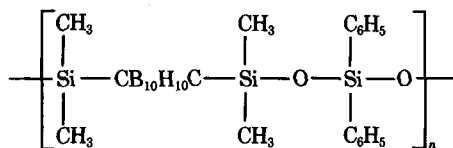
Compounds With Aromatic Boron-Nitrogen Bonding. 14,16,18-Tribora-13,15,17-triazarotriphenylene was prepared according to the literature procedures^{14,15} with the following modifications: 4-aminobutene-1 was best prepared by aluminum hydride¹⁶ reduction of 3-butenitrile. Instead of NaBH₄ in diglyme and BF₃-etherate in diglyme, we used diborane-tetrahydrofuran complex directly, resulting in much better yield (35%) of the product; the title compound was best obtained by *o*-chloranil dehydrogenation in refluxing *p*-xylene. The recrystallized product was obtained as light-tan colored needles in a 20% yield.

Borazines. 2,4,6-Trichloro-1,3,5-triphenylborazine was obtained from Aldrich Chemical Company, Inc., and was used as received. 2,4,6-Trihydroxy-1,3,5-triphenylborazine was prepared essentially according to the procedure of Jones and Kinney.¹⁷ 2,4,6-Triamino-1,3,5-triphenylborazine was prepared according to the procedure of Toeniskoettler and Hall.¹⁸ 2,4,6-Tris(trifluorovinyl)borazine was prepared under conditions to exclude oxygen and moisture and utilizing the Barbier procedure^{19,20} to form the trifluorovinyl Grignard reagent which was then reacted with 2,4,6-trichloroborazine freshly sublimed at 25°C/0.0004 torr. Quantitative yield of a dark-colored product, mp ~80°C (sealed tube in vacuum), was obtained. Infrared spectra of the product contained absorptions at 1735 cm⁻¹, CF₂=CF—,^{19,21} and 1400 cm⁻¹, B=N ring. 2,4,6-Tris(trifluorovinyl)-1,3,5-triphenylborazine was prepared according to the procedure used in the preparation of 2,4,6-tris(trifluorovinyl)borazine. The product was isolated as an oil in a 44% yield. Infrared spectra contained absorptions at 3030 cm⁻¹, aromatic C—H; 1735 cm⁻¹, CF₂=CF—; 1595 cm⁻¹, benzene ring; and 1480–1295 cm⁻¹, C=N ring.

Boronic Acids and Their Derivatives. *p*-Vinylbenzeneboronic acid was prepared according to the literature procedures^{22,23} from *p*-chlorostyrene in a 29% yield. Because of the ease with which *p*-vinylbenzeneboronic

acid dehydrates,^{23,24} its anhydrides (trimeric as well as polymeric) were also obtained. *p*-(1,2-Dibromoethyl)benzeneboronic acid was obtained in a 58% yield by brominating *p*-vinylbenzeneboronic acid in carbon tetrachloride. The product was obtained as white needles with a mp 194–7°C, (lit.²⁵ mp 198–200°C). *p*-Vinylbenzeneboronic acid anhydride was brominated in a 3:2 molar ratio of the anhydride to bromine to yield a product with one out of every three double bonds unbrominated. A white solid of indefinite softening point was obtained. Hexachlorocyclopentadiene adduct of *p*-vinylbenzeneboronic acid anhydride was prepared in a typical Diels-Alder reaction²⁶ in a 67% yield. The product was isolated as a light tan-colored solid with a decomposition point around 247°C. Infrared spectra contained absorptions at: 2930 cm⁻¹, C—H; 1608 cm⁻¹, benzene ring; 1400–1325 cm⁻¹, B—O; and 800 cm⁻¹, C—Cl. Elemental analysis for chlorine calculated for C₆₅H₃₇B₅Cl₃₀O₈ (5 monomer units in the anhydride): 52.31% Cl; found 52.83%.

Carboranes. 9,12-Dichloro-*o*-carborane, B-decachloro-*m*-carborane, 9,10,12-tribromo-*o*-carborane, and a polymeric silylcarborane, Dexsil 202,



were all courtesy of Dr. H. A. Schroeder of Olin Chemical Corporation.

Curing Agents. Hexamethylenediisocyanate was obtained from Chemical Procurement Labs., Inc., and was used as received. Urea-formaldehyde, Resimenen U-901, and trimethylolmelamine, Resloom HP, were courtesy of the Plastics Division of Monsanto Company.

Other Chemicals. All other materials, except for 2,4,6-trichloroborazine, which was sublimed, were used as received. Ethanolamine, diethanolamine, benzeneboronic acid, *p*-bromobenzeneboronic acid, trimethyl borate, triethyl borate, tri-*n*-butyl borate, *p*-chlorostyrene, and diborane-tetrahydrofuran complex from Aldrich Chemical Company; boric acid, magnesium turnings, and bromine from Fisher Scientific Company; 2,4,6-trichloroborazine and *n*-butylboronic acid from Alfa Products of Ventron Corporation; bromotrifluoroethylene from PCR, Inc., 3-butenenitrile from Eastman Organic Chemicals; hexachlorocyclopentadiene and pentabromoethane from K & K Laboratories, Inc., methylamine and Flame Resistance of Cloth Test Gas (55% H₂, 24% CH₄, 18% CO, and 3% C₂H₆) from Matheson Gas Products; lithium aluminum hydride, sodium borohydride, and boron trifluoride from Research Organic/Inorganic Chem. Corp.

Treatment Procedure

Two procedures, (1) radiation grafting and (2) curing with hexamethylenediisocyanate, urea-formaldehyde, or trimethylolmelamine were investigated.

TABLE I
Flame Retardancy of Organoboron Compound Treated Cotton Fabric

Compound	Add-on, %	Flame retardancy, angular degree
Ethanolamine ester of H ₃ BO ₃	18	180°
Diethanolamine ester of H ₃ BO ₃	14	0°
14,16,18-Tribora-13,15,17-triazarotriphenylene	16	180°
2,4,6-Trichloro-1,3,5-triphenylborazine	10	180°
2,4,6-Trihydroxy-1,3,5-triphenylborazine	10	180°
2,4,6-Triamino-1,3,5-triphenylborazine	10	0°
2,4,6-Tris(trifluorovinyl)borazine	18	180°
2,4,6-Tris(trifluorovinyl)-1,3,5-triphenylborazine	18	180°
<i>p</i> -Bromobenzenboronic acid	15	180°
<i>p</i> -Vinylbenzenboronic acid	15	none ^a
<i>p</i> -(1,2-Dibromoethyl)benzenboronic acid	17	180°
<i>p</i> -Vinylbenzenboronic acid anhydride	18	none ^a
Brominated <i>p</i> -vinylbenzenboronic acid anhydride	25	180°
Hexachlorocyclopentadiene adduct of <i>p</i> -vinylbenzenboronic acid anhydride	23	180°
9,12-Dichloro- <i>o</i> -carborane	15	none ^a
B-Decachloro- <i>m</i> -carborane	16	none ^a
9,10,12-Tribromo- <i>o</i> -carborane	18	none ^a
"Dexsil 202"	27	0°

^a Burned in a 0° position.

Radiation Grafting. Samples (0.5 × 2 in.) of the cotton twill fabric in glass ampoules were degassed before and after combining with 7–10% solutions (methanol or perchlorocyclopentadiene) of the various organoboron compounds. The grafting was done by means of a γ -radiation source (⁶⁰Co) at a dose rate of 0.1 Mrad/hr at 25°C to total doses of 4.8 to 6.4 megarads. Add-ons of 20% and higher were realized under these conditions. Following grafting, the samples were extracted with methanol, dried, and conditioned at 65% relative humidity and 70°F for 16 hr before testing for flammability characteristics.

Chemical Curing. Samples (2 × 5 in.) of the cotton twill fabric were first suspended in methylamine at –10°C for 30 min to decrystallize the cellulose.²⁷ Following a solvent exchange with methanol, acetone, and hexane, the fabric samples were padded with dimethylformamide solutions of the various organoboron compounds through squeeze rolls to the percent add-ons indicated in Tables I and II. The per cent add-on was calculated from the wet pickup of the fabric and the per cent solids in the bath. This procedure was followed, rather than weighing the conditioned samples, in order to eliminate any complications due to possible differential moisture sensitivity of the various boron compounds. The samples were then predried in a forced-air oven at 100°C for 15 min before padding to 10–15% add-on with one of the three curing agents through squeeze rolls. The hexamethylenediisocyanate curing agent was used as

TABLE II
Washfastness of Organoboron Compound Treated Cotton Fabric^a

Compound	Add-on, %	No. of machine washes	Flame retardancy, angular degrees
14,16,18-Tribora-13,15,17-triazarotriphenylene ^{b,c}	16	2	135°
2,4,6-Trichloro-1,3,5-triphenylborazine ^{b,c}	20	2	135°
<i>p</i> -Bromobenzeneboronic acid ^{e,d}	18	19	90°
<i>p</i> -(1,2-Dibromoethyl)benzeneboronic acid ^{e,g}	19	3	180°
Brominated <i>p</i> -vinylbenzeneboronic acid anhydride ^{e,g}	25	6	90°
Hexachlorocyclopentadiene adduct of <i>p</i> -vinylbenzeneboronic acid anhydride ^f	23	7	135°

^a Washed according to the AATCC Test Method 124-1967.

^b Padded from a 20% dimethylformamide solution.

^c Hexamethylenediisocyanate was used as a curing agent and was padded from a 50% dimethylformamide solution to an add-on of about 10%. The samples were cured at 100°C for 1 hr.

^d Padded from a 20% dimethylformamide solution also containing 2% pentaboromethane.

^e Padded from a 20% dimethylformamide solution also containing 4% pentaboromethane.

^f Radiation grafted to a total dose of 4.8 Mrads from a 10% perchlorocyclopentadiene solution.

a 50% dimethylformamide solution. This was followed by curing in a forced-air oven at 100°C for 1 hr and then conditioning at 65% relative humidity and 70°F for at least 16 hr before checking for the flammability characteristics.

Washing Procedure

The samples were washed according to the AATCC Test Method 124-1967 in a Sears Kenmore 600 washer, normal cycle, low water level, 4 lb dummy load, water at 140°F, 12-min washing cycle, 90 g AATCC Standard Detergent used only in the first washing cycle.

Flame Retardance Evaluation

Except for a few samples for which the AATCC Test Method 34-1966 was used, all the other evaluations were conducted on a 0.5×2 in. samples in the angular match test of Reeves, McMillan, and Guthrie.²⁸

Analysis for Boron

A technique for a fast quantitative boron analysis, involving radio frequency-discharged oxygen plasma, was developed for an independent check of the treated fabric samples.²⁹ In general, the per cent boron found by

this technique was in agreement with that calculated from the percent add-on data.

RESULTS AND DISCUSSION

Although hydrolytically stable organoboron compounds have been described in the literature, only a few are available commercially. Thus, the major effort in this work consisted of synthesizing hydrolytically stable compounds which in turn dictated that the initial evaluation be done on a small scale utilizing the angular match test rather than the standard vertical char test (AATCC Test Method 34-1966).

As there was nothing in the literature to guide one in the selection of appropriate flame-retarding organoboron compounds, a preliminary examination of a series of structurally different, commercially available compounds was conducted. Hydrolytic stability was not considered in this preliminary evaluation. The following compounds were evaluated in the standard vertical char test: trimethyl borate, triethyl borate, tributyl borate, *n*-butylboronic acid, triethanolamine ester of boric acid, benzeneboronic acid, *p*-bromobenzeneboronic acid, 2,4,6-trichloroborazine, and 2,4,6-trichloro-1,3,5-triphenylborazine. When the above compounds were padded directly or from a dimethylformamide solution to an add-on of at least 20%, only trimethyl borate, *n*-butylboronic acid, *p*-bromobenzeneboronic acid, 2,4,6-trichloroborazine, and 2,4,6-trichloro-1,3,5-triphenylborazine imparted flame retardance to the cotton fabric. Thus, this brief list of compounds indicated that only those organoboron compounds in which the carbon-to-boron atom ratio was 4 or less would impart flame retardancy. If a halogen atom was also present (2,4,6-trichloro-1,3,5-triphenylborazine) in the molecule, this ratio could be greater than 4 and the compound would still impart flame retardancy.

Monomer Synthesis

The general synthetic effort was guided by the relationships found in the preliminary examination. The ethanolamine and diethanolamine esters of boric acid were prepared by refluxing a 1:1 molar mixture of boric acid and the alcohols, and benzene was used to remove the water formed in the reaction as a benzene azeotrope. The esters were obtained as very viscous syrupy materials which could not be induced to crystallize. Although the esterification was continued only until one mole of the water was collected, the easy dehydration of boronic and boric acids in general, to yield the anhydrides, could have also taken place. Infrared spectroscopic analysis, however, was not conclusive on this point.

In the preparation of 14,16,18-tribora-13,15,17-triazarotriphenylene, we started with the commercially available 3-butenenitrile which was best reduced to the corresponding amine with a 1:1 molar complex of aluminum hydride and aluminum trichloride. Direct use of the diborane-tetrahydrofuran complex in the next reaction step yielded 1,2,3,4,5,6,7,8,9-,10,11,12-dodecahydro-14,16,18-tribora-13,15,17-triazarotriphenylene in a 38% yield. Dehydrogenation of this compound was accomplished with

o-chloranil in refluxing *p*-xylene. The twice-chromatographed (activated alumina) and recrystallized (1-hexene) material was obtained as white needles in a 20% yield.

Preparation of the *p*-vinylbenzeneboronic acid also always yielded its anhydride (trimeric or polymeric) as a byproduct. Bromination of *p*-vinylbenzeneboronic acid was best done in carbon tetrachloride. The hexachlorocyclopentadiene adduct of *p*-vinylbenzeneboronic acid anhydride was prepared in refluxing excess hexachlorocyclopentadiene in a 67% yield.

Organoboron Compounds as Flame Retardants

Most of the flame retardancy data are reported in Table I. The general structure-flame retardancy relationship found in the preliminary examination of commercially available compounds was also found to hold true for all the subsequent compounds, except for 2,4,6-trihydroxy-1,3,5-triphenylborazine and 2,4,6-triamino-1,3,5-triphenylborazine. These compounds were found to be good flame retardants despite their higher than the carbon-boron atom ratio of 4. The presence of a small undetected amount of the starting material in the reaction products would explain their good flame-retarding properties. Of the three different ethanolamine esters of boric acid, only the ethanolamine and diethanolamine esters imparted flame retardancy. The triethanolamine ester that was available to us possessed no flame-retarding properties, which is in a disagreement with the claim in the patent by Posner.¹ As expected, the *p*-vinylbenzeneboronic acid possessed no flame-retarding properties. Of the four carborane derivatives evaluated, only the polymeric silylcarborane, Dexsil 202, imparted marginal flame retardancy. Interestingly, even the perchlorinated carborane possessed no flame-retarding properties whatever. Thus, as far as the flammability characteristics are concerned, the carboranes still resemble the boron hydrides rather closely. Pentabromoethane even in small amounts has been found to be an efficient flame-extinguishing agent, however, in our formulations it had little if any beneficial effect. This was probably so due to our inability to incorporate it in the cellulose because of its inert nature.

Washfast Finishes

We used two approaches in the development of washfast finishes. In one approach, the flame retardant was attached to the cellulose through a hydrolytically stable carbon-to-carbon bond. In the other approach, the flame retardant was first deposited throughout the fiber and then cross-linked in a polymeric form.

In the carbon-to-carbon bond formation approach, we used vinyl organoboron compounds in a γ -radiation grafting reaction. ESR spectroscopy studies of trapped radicals in methylamine decrystallized γ -irradiated cellulose showed the spectrum to consist of five lines.³⁰ The hyperfine splitting was very weak in agreement with the studies of Arthur, Hinojosa, and Tripp for decrystallized celluloses.³¹ According to Baugh, Hinojosa,

and Arthur,³² at least one of the long-lived free-radical sites present in cellulose I (containing regain moisture) was on C₆. Thus, grafting of vinyl monomers at this site will result in a stable C-C bond formation. We grafted the following compounds: hexachlorocyclopentadiene adduct of *p*-vinylbenzeneboronic acid anhydride, *p*-vinylbenzeneboronic acid, 2,4,6-tris(trifluorovinyl)borazine, and brominated *p*-vinylbenzeneboronic acid anhydride. However, only the hexachlorocyclopentadiene adduct (Table II) was fully evaluated.

In the other approach, the various organoboron compounds were deposited throughout the decrystallized fiber first and the fabric was then predried, followed with padding of the crosslinking agents. A two-step procedure had to be used as the combining of the crosslinking agents with the organoboron compounds gave an immediate precipitate. Of the three crosslinking agents investigated, the hexamethylenediisocyanate insolubilized the various compounds the most efficiently and was the one used for the five compounds reported in Table II. According to the literature,³²⁻³⁶ reactions between the isocyanate group and a borazine ring or boronic acid groups have been reported. Although a controversy still exists as to the exact structure of the product formed when a borazine or boronic acid is reacted with an isocyanate, an insoluble product formation was demonstrated.

The washfastness results of six different organoboron finishes are recorded in Table II. These results are not the maximum stability results, rather they are all the results that could be obtained with the limited amounts of the compounds that had been synthesized. The results of the *p*-bromobenzeneboronic acid especially indicate that a good washfastness of an organoboron finish is a possibility. The next objective in this area should be the development of a less complicated flame-retarding organoboron system such as, for example, the boron "ate" complexes.

CONCLUSIONS

A total of 25 organoboron compounds have been evaluated for their flame retardancy properties on a cotton fabric. Most of these compounds had to be synthesized, some by a rather elaborate procedure. From the list of compounds investigated, it was concluded that only those organoboron compounds in which the carbon-to-boron atom ratio is 4 or less are effective flame retardants. If a halogen atom was also present in the molecule, this ratio could be higher than 4. Washfast finishes were developed with six compounds by either γ -radiation grafting reaction of a vinyl organoboron compound or by chemical crosslinking with hexamethylenediisocyanate, trimethylolmelamine, or urea-formaldehyde. Maximum durability of the developed finishes has not been established yet because of the small amounts of the compounds available.

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