Flame Retardants for Cotton Using APO- and APS-THPC Resins

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Abstract

A new group of polymers made by reacting tris(1-aziridinyl)phosphine oxide, referred to as APO, or tris(1-aziridinyl)phosphine sulfide, referred to as APS, with tetrakis-(hydroxymethyl)phosphonium chloride, referred to as THPC, are good permanent-type flame retardants for cotton. All three of the compounds are water-soluble crystalline materials. The application of APO- or APS-THPC resins to textiles consists of padding fabric in an aqueous solution of the compounds, drying the fabric, curing it at about 140° C. for about 5 min. to polymerize the compounds, and then rinsing the fabric to remove any unpolymerized material.

About 8% of the resins in 8-oz. cotton twill or sateen is adequate to make the fabric pass the vertical flame test before or after 15 launderings with synthetic detergents, followed by an acid fluoride sour after each laundering. The flame resistance is also very durable to boiling alkaline soap solutions.

The properties of fabric treated with these new polymers are, in general, excellent. The hand and strength of the fabric is only slightly different from that of untreated fabric. The flame-resistant fabrics are resistant to rot and mildew.

SEVERAL permanent-type flame retardants for cotton have been developed at the Southern Regional Research Laboratory [2, 4, 5, 6, 8, 10]. Although it is believed that all of these represented improvements over those currently available for commercial use, none of our flame retardants are completely satisfactory. Because of the importance of this problem from a military and civilian point of view, our studies on flame-retardant finishes for cotton are being continued.

One of the flame retardants reported recently is based upon a THPC resin [8]. It is formed by the copolymerization of tetrakis(hydroxymethyl)phosphonium chloride, THPC, with a methylolmelamine and urea. It has received attention from a number of textile finishers and is now being used for finishing both cotton and viscose rayon. Finishing fabrics with the THPC resin is reasonably simple: it consists in padding fabric through an aqueous solution of the monomers, then drying and curing to polymerize the flame retardant inside the cotton fiber.

Two flame retardants which contain bromine have been reported by members of Southern Regional Research Laboratory. These are formed by making a telomer of triallylphosphate and bromoform in one case [4] and a telomer of allylphosphonitrilate and bromoform in the other case [5]. The polymers are prepared in aqueous emulsion. They are applied to fabric in essentially the same manner as THPC resins.

Two additional flame retardants were reported that are formed by combining about one part of either of the aqueous emulsions of the telomers with about three parts of THPC resin-forming monomers [6, 10]. The resulting emulsions are also applied to fabric by the same technique used to apply the THPC resin.

The purpose of the present paper is to present our most recent and interesting flame retardants which are based upon resins made by reacting THPC with aziridinyl compounds. These compounds are tris-(1-aziridinyl)phosphine oxide, $(\overline{\text{CH}_2\text{CH}_2\text{N}})_3\text{P} = \text{O}$, which we refer to as APO and tris(1-aziridinyl)-phosphine sulfide, $(\overline{\text{CH}_2\text{CH}_2\text{N}})_3\text{P} = \text{S}$, which we refer to as APS. These aziridinyl compounds may also be named NN′N″ triethylenephosphoramide and NN′N″ triethylenethiophosphoramide respectively. These APO-THPC and APS-THPC flame retardants are not mere modifications of THPC-amine resins and are not a combination of two existing flame retardants. Instead, they are new thermosetting resins.

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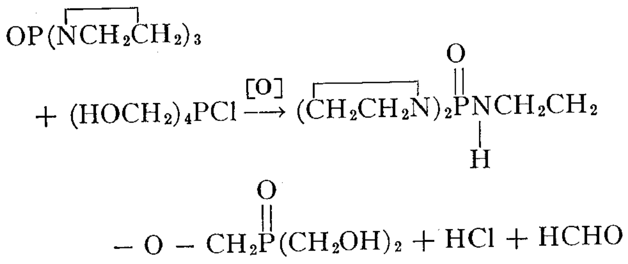
APO and APS are prepared by reacting ethylenimine with $POCl_3$ and $PSCl_3$, respectively. The reaction may be represented as follows:

$$POCl_3 + 3H\overline{NCH_2CH_2} + 3R_3N \rightarrow OP(\overline{NCH_2CH_2})_3 + 3R_3N \cdot HCl$$

It is carried out by adding the oxy- or thiochloride to a cold solution of ethylenimine and an acid acceptor like triethylamine in some inert solvent such as benzene [1]. Then the amine hydrochloride is filtered off, and the organic solvent is distilled. The residue consists mainly of the crude aziridinyl compound which can be purified by crystallization from benzene. APO and APS have been prepared several times and the yields have averaged about 90%. APO melts at 41° C. and APS at 51° C. Both compounds are soluble in water and a number of organic solvents. These compounds have been studied recently as agents for retarding cancer growth. Both compounds were found to be useful in this respect [3, 7].

APO and APS react with THPC to form highly flame-resistant thermosetting resins. Aqueous solutions of APO or APS and THPC are stable for many hours at about 25° C., but when heated to about 100° C. or higher, reaction and subsequent resinification occur rapidly. The initial reaction of APO with THPC may be indicated as shown here.



$$OP(\overline{NCH_2CH_2})_3 + (HOCH_2)_4PCl \xrightarrow{[O]} (\overline{CH_2CH_2N})_2\overset{O}{\overset{\|}{P}}\underset{H}{\underset{|}{N}}CH_2CH_2 - O - CH_2\overset{O}{\overset{\|}{P}}(CH_2OH)_2 + HCl + HCHO$$

Note that the phosphonium structure shown in THPC has been converted to a phosphine oxide structure. It is indicated in this manner because it has been found that THPC is converted to tris-(hydroxymethyl)phosphine oxide by heat, either in alkaline or acid conditions. With respect to the addition reaction, one of the aziridinyl rings was opened by one of the methylol groups of THPC to form a stable ether-type bond. In the initial reaction product there still exists two aziridinyl rings and two methylol groups which may also react. Therefore, extensive reaction leads to highly cross-linked polymers. And to add further to the complexity of the reaction, the hydrogen atom attached to the nitrogen as a result of ring opening is reactive toward both aziridinyl rings and methylol groups.

Fortunately the textile finisher does not have to be too much concerned with the various reactions. For him the reaction is simple. He merely impregnates fabric with an aqueous solution of the reagents, dries it at a relatively low temperature, and then cures it at about 140° C. to produce the flame-resistant polymer in the fabric.

Experimental

Preliminary experimentation indicated that useful flame retardants might be made by polymerizing APO or APS with THPC in cotton fibers. But the preferred mole ratio of monomers, the amount of resin, and the curing temperature had to be established.

Influence of Mole Ratio of APS to THPC upon Resin Add-On and Tear Strength

According to theoretical considerations APS and THPC should form highly cross-linked polymers over a rather broad mole ratio range. This is no doubt the case under drastic conditions. Since it is preferred to process cotton under just as mild conditions as possible, the amounts of these reagents should be selected so that as much of the compounds can be polymerized in cotton as possible under mild conditions. In order to establish the preferred amount of the reagents, aqueous solutions made up to contain various mole ratios of the reagents were used to treat an 8-oz. sateen under a selected set of conditions. In each case, the solution contained some APS, THPC and an amount of triethanolamine equivalent to one quarter of the weight of THPC used. The primary purpose of the triethanolamine was to neutralize free hydrochloric acid which is usually present in THPC. The combined weight of APS and THPC in each solution amounted to 20% of the total solution. The composition of the solutions used is shown in Table I.

Samples of 8-oz. sateen were padded through various solutions using a tight nip so that the wet pickup was 53% (± 1%). The samples were dried 4 min. at 80° to 90° C. and cured 5 min. at 140° C., then washed 30 min. in hot tap water containing a detergent, rinsed, and dried. The increase in weight of the resin-treated fabrics is termed resin add-on.

It is shown in Table I that the resin add-on was

TABLE I. The Influence of Mole Ratio of APS to THPC upon Resin Add-On and Tear Strength

Treating solution						Tear strength, Elmendorf, lb.	
THPC		APS			Resin add-on		
%	Moles	%	Moles	TEA,* %	%	W	F
16.0	4	4.0	1	4.0	2.3	6.3	5.4
15.0	3	5.0	1	3.7	2.9	7.3	5.6
13.3	2	6.7	1	3.3	4.4	8.5	9.2
10.0	1	10.0	1	2.5	6.7	10.1	12.5
6.7	1	13.3	2	1.7	7.2	10.3	—
5.0	1	15.0	3	1.2	6.2	10.2	—
4.0	1	16.0	4	1.0	6.6	9.8	—

* TEA = triethanolamine.

low in each case where the mole ratio of APS to THPC was less than 1:1. That is, the add-on increased as the concentration of THPC in the treating solutions decreased until a maximum was reached at about 1 mole of APS per mole of THPC. The mole ratio of APS to THPC had a similar influence upon the Elmendorf tear strength; the tear strength reached a maximum and leveled off when the molar concentration of APS was at least equal to that of THPC. Therefore, for the greatest efficiency of resin formation and best tear strength, under the limiting conditions of this experiment, the APS should be present in at least a 1:1 molar ratio to THPC.

Influence of Cure Temperature upon Resin Add-On and Tear Strength

Experiments were run in which two 8-oz. fabrics of different construction were padded with aqueous resin-forming solutions, dried 4 min. at 85° C., and then cured 5 min. at various temperatures. In these experiments APS-THPC and APO-THPC solutions were used as the resin-forming solutions. In both cases the concentration (by weight) of the aziridinyl compound was equal to the THPC concentration (this is about a 1:1 molar ratio). The total concentration of aziridinyl compound plus THPC was 33 and 25%, respectively, for APS-THPC and APO-THPC solutions. The APS-THPC solutions were used to treat 8-oz. sateen and APO-THPC solutions were used to treat 8-oz. twill. The wet pickup of the fabrics was 60% (± 1%) for the sateen and 57% (± 1%) for the twill. It can be seen in Table II that the resin add-on increased as the curing temperature increased, but the tear strength decreased as cure temperature increased. It is intresting to see that the tear strength of the treated twill is substantially better than untreated control fabric even at the 140° C. cure temperature, whereas the sateen retained essentially all of its original tear strength up to only 130° C. cure. According to these data, the preferred curing temperature would be dependent upon whether a good tear strength or good efficiency of reagents was desired. A good compromise might be 135° C.

Minimum Amount of Resin Needed in 8 Oz. Fabric

A number of samples of 8-oz. twill treated with APO-THPC resin were examined to determine the minimum amount of flame retardant needed in these materials as measured by the Vertical Flame Test. The fabrics were all treated with solutions containing an equal weight of THPC and aziridinyl compound. The amount of resin put into the fabric samples was varied by altering the concentration of resin-forming reagents in the treating solutions. Flame resistance was determined by the vertical flame test [11]. The test was made on fabrics that contained as little as 3.6% resin. It is shown in Table III that 8-oz. fabrics containing 6.8% resin passed the flame test before an alkaline boil. About 10.2% or more was needed for the fabric to pass the flame test after a 3-hr. boil in a solution containing ½% soap and 0.2% sodium carbonate.

A sample of 8-oz. sateen containing 7.8% resin was given 15 launderings according to Federal Specifications [11], method 5556, using Igepon T * as the detergent and an acid fluoride sour following washing. This sample passed the Vertical Flame Test after the 15 washes. Therefore it appears that

TABLE II. Influence of Cure Temperature upon Resin Add-On and Tear Strength

Cure temp., °C	Resin add-on, %		Tear strength, lb. Elmendorf (w)	
	APO-THPC on twill	APS-THPC on sateen	APO-THPC on twill*	APS-THPC on sateen†
110	6.7	6.7	8.1	13.0
120	8.8	10.5	7.2	10.2
130	10.2	11.1	7.0	11.6
140	11.3	11.9	5.4	8.0
150	11.6	—	4.0	—

* Tear strength of untreated twill was 4.9 lb.

† Tear strength of untreated sateen was 11.9 lb.

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* Mention of trade names is for information and convenience only and does not imply their endorsement over materials not mentioned.

TABLE III. Minimum Amount of APO-THPC Resin Needed in 8-Oz. Cotton Twill

Resin add-on, %	Flame resistance, char length: Original, in.	Flame resistance, char length: After 3-hr. alkaline boil, in.
5.6	BEL*	BEL
6.5	BEL; 4.4	BEL
6.8	4.5	BEL
8.0	4.4	BEL
8.8	4.2	BEL
10.0	3.6	BEL; 4.3
10.2	4.0	4.6
11.2	4.4	5.1
11.6	4.3	4.4

* BEL means that both of the test samples burned the entire length of the strip.

about 8% resin is adequate in fabric to be laundered with neutral detergents, whereas slightly more than 10% is needed if the goods are to be given strongly alkaline washes.

Flame Retardancy of APO- and APS-THPC Resins on Other Fibers

A qualitative experiment was run in which APO- and APS-THPC resins were put on a number of fabrics, some consisting of hydrophobic fibers, some of hydrophilic, and one consisting of a blend of the two types of fibers. In most cases a rather high resin add-on was obtained. The flame resistance was determined by the Strip Flame Test [9]. That is, the angle was determined at which a 1-cm. strip of the fabric failed to support combustion when held at the angle indicated and ignited at the end with a match or other source of flame. The treated fabrics fell into two categories. They were either highly flame-resistant or had no flame resistance. It is clearly shown in Table IV that the resins do not contribute flame resistance to the hydrophobic fibers which are orlon, nylon, or acetate rayon, but do make viscose rayon, fortisan, and cotton flame resistant. The blended fabric which contained about 75% cotton with 25% nylon was also made flame-resistant.

Processing of Fabric

There are additional details that still need to be studied before the best method of applying APO- and APS-THPC resin to fabric will be known. Therefore, we have tentatively adopted a very simple procedure for processing based upon experimental data and experience with other resin finishes. The procedure presented below describes a typical run on pilot plant equipment.

Procedure

A treating solution was made by dissolving 350 g. THPC, 87 g. triethanolamine, 350 g. APS, and 20 g. Triton X-100* in 1193 g. water in the order given. The temperature of the solution was 30°–35° C. and pH was 6.1. The concentration of the resin-forming constituents, THPC plus APS, was 35%. Fourteen yards of half-width 8-oz. sateen were padded through the solution using two dips and two nips. The wet pickup was 65%. The wet fabric was immediately dried 4 min. at 85° C. and then cured 5 min. at 140° C. Salts and unused reagents were removed by a jig wash consisting of a cold rinse, a hot wash using 0.01% Igepon T,* a hot rinse, and a cold rinse using 5 ends in each step. After drying on a tenter, the fabric was softened by padding it through a 3% solution of Triton X-400* to a 50% wet pickup and drying again. The fabric contained 16% resin.

A piece of fabric containing 10.5% of the APS-THPC resin was made by using the procedure, as described above, except that the aqueous treating solution contained 12.5% THPC, 12.5% APS, 3.1% triethanolamine, and 1% Triton X-100.*

TABLE IV. Flame Retardancy of APO- and APS-THPC Resins on Other Fibers

Fabric description	Resin used	Resin add-on, %	Flame resistance, angle
Viscose rayon	APO-THPC	27	180
	APS-THPC	12	170
Orlon	APO-THPC	34	0
	APS-THPC	25	0
Nylon	APO-THPC	29	0
	APS-THPC	21	0
Acetate rayon	APO-THPC	12	0
	APS-THPC	10	0
Fortisan	APO-THPC	26	180
	APS-THPC	11	135
Cotton	APO-THPC	22	180
	APS-THPC	15	180
Cotton-Fortisan	APO-THPC	20	180
	APS-THPC	17	170
Cotton-Nylon	APO-THPC	25	180
	APS-THPC	17	135

Fabric Properties

A number of small samples of 8-oz. twill and sateen have been processed essentially according to the procedure given just above. Most of the earlier samples were tested only for flame resistance, durability, and tear strength. The most recent samples, shown in Table V, were examined more thoroughly. Therefore, emphasis has been placed upon test data from these samples, although some of the earlier samples had somewhat better tear strength.

Test data is given in Table V for 8-oz. twill and sateen treated with APO-THPC and APS-THPC resins, and for twill treated with APO-APS-THPC resin. The last fabric was obtained by treating twill with an aqueous solution containing 8.5% APO, 8.5% APS, 17% THPC, 4% triethanolamine, and 1% Triton X-100.*

Durability

A sample of sateen treated with APS-THPC resin and containing 1.55% nitrogen and 1.45% phosphorus was soxhlet extracted 3 hr. with tetrachloroethylene. The flame resistance was unchanged by the extraction. After extraction the fabric contained 1.54% nitrogen and 1.50% phosphorus.

A sample of 8-oz. twill containing 14.1% APS-THPC resin with 1.51% nitrogen and 1.47% phosphorus was boiled 3 hr. in a 0.5% soap solution containing 0.2% sodium carbonate. Analyses after the boil gave 1.3% nitrogen and 1.25% phosphorus. The char length of the boiled sample was 3.5 in. as compared with 4.0 in. before the boil.

The resins are also very resistant to laundering techniques described in Federal Specifications [11]. Table V shows that an 8-oz. fabric containing as little as 7.8% APO-THPC resin passed the Vertical Flame Test after 15 of the launderings. None of the fabrics described in Table V passed the Strip Flame Test after the 15 laundry cycles, but another sample (8-oz. sateen) containing 14.9% APS-THPC resin did pass the Strip Flame Test after the fifteenth laundering.

Strength

The strip breaking strength might be reduced but only slightly. Considering the values reported in Table V under strip breaking strength, four samples of sateen lost an average of 6% tensile strength. However, if one considers the strength values recorded under chlorine retention for untreated con-

TABLE V. Properties of Resin-Treated Twill and Sateen

Test	8-Oz. sateen					8-Oz. twill			
Resin and add-on, %	Untreated control	APS-THPC 14.3	APO-THPC 15.0	APS-THPC 10.2	APO-THPC 7.8	Untreated control	APS-THPC 15.7	APO-APS-THPC 14.3	APO-THPC 15.5
Strip breaking strength (w) lb.	115	112	108	108	109	134	126	116	123
Abrasion resistance									
1. Flex (w)	1578	749	728	819	1149	2498	891	1084	772
2. Flat	525	779	650	593	—	—	—	—	—
Elmendorf tear (w) lb.									
1. Original	A.C.*	10.0	8.2	11.0	11.4	10.7	5.7	6.6	6.4
2. After 15 washes	11.2	8.0	8.3	8.8	7.8	—	—	—	—
Stiffness (bending moment × 10^4 in. lb.)	10	12	12	11	9	16	26	16	21
Char length (in.)									
1. Original	—	3.0	2.8	3.6	2.8	—	3.1	2.9	2.7
2. After 5 washes	—	2.5	2.7	4.1	3.7	—	—	—	—
3. After 15 washes	—	3.2	3.6	4.6	6.1	—	—	—	—
Chlorine retention strength (lb.) after									
1. Wash (no bleach)	113	114	112	—	—	—	—	—	—
2. Wash with bleach	114	113	117	112	—	—	115	111	118
3. Wash with bleach and scorched	110	107	110	111	—	—	112	116	119

* A.C. = above capacity of machine which is about 13 to 14 lb.

trol and two samples of resin-treated sateen, the strength loss would be nil. But on the other hand, the resin-treated 8-oz. twill does show an average loss in strength of 9%.

The two most difficult objectives in the development of permanent-type flame retardants for cotton fabric are the maintenance of good hand and tear strength. In our present work, the Elmendorf tear test has been used to evaluate tear strength retention. These new resins do reduce tear strength but not as much as is usually obtained with other known permanent-type flame retardants. It seems that the strength retained should be adequate for most uses.

Samples of twill shown in Table II retained 100% tear strength. It appears from Table V that the tear strength decreases as the amount of resin put into the fabric increases. However, this decrease is only slight.

Hand

The hand of fabric treated with APO- and APS-THPC resins is altered only slightly. It feels a little fuller and is slightly springy due to a mild degree of crease resistance. Since the resin goes inside the fibers, the feel is still essentially that of untreated cotton. One factor influencing the hand is stiffness. The stiffness of several fabrics is shown in Table V. The differences in stiffness values for the untreated and treated sateen are all within experimental error. The differences in stiffness for the twill are slightly more than experimental error.

Abrasion Resistance

Two test methods have been used to determine abrasion resistance. It is doubtful if either method actually reflects use tests. According to the flex abrasion method, as shown in Table V, the resin treatments reduce abrasion resistance substantially, but according to the flat abrasion tests, the resin actually improves the abrasion resistance.

Chlorine Retention

Chlorine retention has been a fault of many resins used on cotton. In order for a flame retardant to be generally useful, it should be resistant to chlorine bleach. This is another property in which APO- and APS-THPC resin-treated fabrics are very satisfactory. It is somewhat unusual for a nitrogenous resin to be unaffected by chlorine bleach. According to Table V, the resin-treated fabrics did not lose strength when they were washed with a solution containing a chlorine bleach and then ironed. White sheeting treated with the resins were discolored somewhat by the chlorine bleach.

Rot Resistance

Another plus feature of these resin-treated fabrics is resistance to rot. For many uses, flame-resistant fabrics are given an additional processing to impart rot resistance. With APO- and APS-THPC resin-treated fabrics, the rot resistance is "built in." The amount of rot resistance obtained with these resins has not been fully established, but it has been determined in one soil burial experiment that 88% strength was retained after 25 days and 65% after 38 days in a rot bed where untreated control fabric lost essentially all of its tensile strength within 10 days.

Discussion

The experiments reported here are preliminary and have served to select a good set of processing conditions but are not necessarily the best. Additional experiments are being run to establish conditions which will produce flame-resistant fabrics with the best properties possible.

The pH of the resin-forming solutions used to prepare the fabrics described herein has been about 6.0. Just how the pH affects the resin-forming solutions is not fully known. It is known, however, that alkaline solutions cause the conversion of THPC to tris(hydroxymethyl)phosphine oxide which reacts with the aziridinyl compounds more slowly than THPC. Also at low pH values, the resin-forming solutions are less stable than at about 6.

A very important factor in the use of these new flame retardants is the stability of the resin-forming solutions. Some APO- and APS-THPC resin-forming solutions have been prepared and used immediately and then set aside at about 10°–15° C. for 24 hr. and then used again. There was a slight change in hand and tear strength due to aging of the solutions. The fabrics treated with the aged solutions were slightly stiffer and the tear strengths were about 25% less. Therefore, it appears that the solutions could be made up and used for 8 hr. without producing noticably adverse effects. It should be understood that heat should not be used in dissolving the reagents, nor should the resin-forming solutions be heated before or during use.

A flame-retardant finish satisfactory for military and civilian use must withstand the laundering techniques used by these groups. For example, for military use it must withstand washing with a neutral detergent and a fluoride sour. For industrial use, it must withstand strong alkali washes. Household laundering is usually less severe than either of these. In many cases the finish must also withstand chlorine bleach. According to the data obtained, fabric finished with APO- and APS-THPC resins should be satisfactory for all these uses.

It should be emphasized that the amount of these resins needed in 8-oz. cotton fabric (about 8%) to make it pass the Vertical Flame Test after 15 launderings is substantially less than that of any other known durable flame retardant. The only other flame retardant approaching this efficiency is the retardant made by combining one part of a telomer of bromoform and allylphosphonitrilate with three parts of THPC resin [6].

Substantially more of the APO- and APS-THPC resins are needed (about 15% for 8-oz. twill and sateen) in a fabric for it to pass the Strip Flame Test.

The cost of the new flame retardants is prohibitive considering the present price of ethylenimine which is used in making APO and APS. The cost of ethylenimine is probably largely due to the small-scale production of the compound because the process for making it is simple and the reagents used in the process are cheap. Phosphorylchloride is a cheap chemical and thiophosphoryl chloride should sell for about the same price if produced in large quantities.

Up to now we do not know which of the aziridinyl compounds is most suitable for use in a flame-retardant finish. However APS is more stable than APO when stored.

Summary

New flame retardants based upon resins made by reacting APO and APS with THPC have been developed. Fabrics are treated by padding them through an aqueous solution of either APO and THPC or APS and THPC, then drying and curing at an elevated temperature to form the insoluble resin inside the fibers.

The new flame retardants have the following outstanding features:

1. The treating solutions show good stability.
2. The amount of resin needed in a fabric is very low in comparison with other durable flame retardants.
3. The resin treatment alters the hand of fabric only slightly.
4. The tear and tensile strengths of treated fabric are good.
5. The strength of treated fabrics is not damaged by chlorine bleach.
6. The resin is very resistant to neutral and alkaline washes.

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