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Original Article

Improvements of natural rubber for flame resistance

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Abstract

The present invention provides a process for treating natural rubber to increase its flame retardant capability. The process comprises a mixture of a natural rubber with, (a) halogenated free flame retardant agent (zinc hydroxystannate; STORFLAM ZHS) and (b) halogenated flame retardant agent (decabromodiphenyl; Great Lake DE-83R and chlorinated paraffins; Plastoil 152) and another material like antimony trioxide and aluminium hydroxide in appropriate amount, with ratio of halogenated flame retardant agent: antimony trioxide 3:1. In the resulting product with halogen flame retardant showed a more efficient flame retardant property than halogen free flame retardant, i.e. brominated flame retardant provide higher efficiency than chlorinated and ZHS, respectively. The minimum requirement ratio for being flame retardant of antimony trioxide: brominated or chlorinated agent is 7:21 or 10:30 phr while aluminium hydroxide: ZHS is 10: 150 phr. It was found that burning rate was zero for brominated and chlorinated agent used but not for zinc hydroxyl stannate system. Average time of burning (ATB) was 135, 118 and 41 second for brominated, chlorinated and ZHS flame retardant, respectively. Average extent of burning (AEB) was 24, 19 and 14 millimeters, respectively. An advantage of this invention is that chemicals (antimony trioxide and either brominated or chlorinated agent) added to natural rubber have the effect of rendering the natural rubber flame-resistant like synthetic rubbers, chloroprene.

Keywords: halogen free, flame retardant, zinc hydroxyl stannate, natural rubber

1. Introduction

Flame retardants are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing them down or by inhibiting them. They can act in both physical and chemical ways. Many types of them are used in consumer products. They are mainly chlorides and bromides or antimony aluminium, phosphorous and boron-containing compounds, etc. (Seymour, 1978). The proposed mechanism is based on a charred layer acting as physical barrier, which slows down heat and mass transfer between the gas and the condensed phases (Bourbigot *et al.*, 1996). Natural rubber (NR) is widely used in various applications such as housing construction, transport and electrical engineering. This rubber is easily inflammable due to its chemical constitution. Its flammability could be reduced by several approaches, such as, firstly, blending with flame retardant monomer or polymer (Ramesan, 2004) which contains element that can impart a degree of flame retardation. Secondly, the elastomer could be treated to incorporate a specific reagent on the chain such as phosphorous (Derouet *et al.*, 1994, Brosse *et al.*, 2000 and Zhu and Shi, 2003). Thirdly, conventional flame retardant additives can be added to rubber compound but the additives generally used suffer from migration and leaching from the bulk of material into the rubbers leading to poor physical and mechanical properties due to the incompatibility of these additives with the macromolecules. This will decrease the durability and affect the performance characteristics of the product. Therefore, it is very important to take into consideration when formulating a flame retardant rubber to compromise between the original physical and mechanical properties

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of the rubber and the modified combustion characteristics (Fabris and Sommer, 1977; Lyon, 1970). Halogen-containing flame retardants and their synergistic systems containing antimony oxide are the most effective and show a good ratio of property to price in flame retardant polymer. However, the uses of these additives have been limited because of the consideration of environmental and life safety. To solve this problem many studies have been done. However, most revealed a need for a combination of halogen and/or synergistic agent as halogen-free flame retardant alone can only reduce the combination rate. No successful instance of using halogen-free flame retardant in natural rubber has been reported. Ramesan reported that the blends of NR and dichlorocarbene modiflied styrene butadiene rubber (DCSBR with 25% chlorine) are considered to be safe for outdoor applications (Ramesan, 2004). Therefore, attempts were made to decrease the tendency of natural rubber to burn in this study, the ability of using halogen and non-halogen flame retardant additives was compared, and the minimum amount requirement for optimization of the formulation for flame retardant was determined.

2. Experimental

2.1 Materials

Natural rubber (RSS-3) and other compounding ingredients such as zinc oxide, stearic acid, sulphur, N-cyclohexyl-2-benzothiazyl sulphenamide (CBS), 2 mercaptobenzimi dazole (vulcanox MB), carbon black (HAF330), aluminium hydroxide (ATH), antimony trioxide, decabromodiphenyl oxide (Great Lake DE-83R), chlorinated paraffins (Plastoil 152) and zinc hydroxystannate (STORFLAM ZHS) were of reagent grade and were purchased from local rubber chemical suppliers.

2.2 Compounding

The preparation of rubber compound was done by mixing rubber (RSS-3) with sequentially added 4 phr ZnO, 1.4 phr vulcanox MB, 2 phr stearic acid, 0.85 phr CBS. Flame retardants were loaded in proportion as described in Table 1, and 2.5 phr sulfur on a laboratory size (160x380 mm) two roll mill model Y-160-M2-8 with friction ratio 1:1.22 in according to the method described by ASTMD3184-80, then stored for 16 hr before testing. The respective cure times at 150°C as measured by t_{90} were then determined using a Monsanto Rheometer, model MDR 20000 following ASTM D5289. The various rubber compounds were compression moulded at 150°C according to their respective t_{90} in the sheet. The dumb-bell shaped and crescent shaped test pieces were prepared for physical testing (300% modulus, tensile strength and elongation at break) and tear resistance tested following ASTM D412-68 and ASTM 624-54. The vulcanizates were also cut in bar shape with dimension of 125x12.5x3 mm and tested with burning tests, both horizontal burning test (HB Test) and vertical burning test (V-Test), according to the UL-94 standard. All thermogravimetry analysis (TGA) tests were carried out using a Mettler Toledo Star System model SDAA 851 at scan heating rate of 20°C min-1 under oxygen atmosphere with a flow rate of 60 ml/min. The weight of the samples was kept within 10-12 mg and run at the range of temperature from ambient from 40 to 850°C

2.3 Flammability test

Horizontal test method for rate of burning and extent and time of burning of self supporting rubbers in a horizontal position was conducted according to ASTM D635-81 (UL-94). Average burning rate is reported as the average of the burning rates of all specimens which have burned to the mark in cm/min. Average time of burning (ATB) and average extent of burning (AEB) were calculated according to Equations (1), (2) and (3), respectively.

$$\text{ATB} = \Sigma\,(\text{t-30s})/\text{number of specimens} \qquad (1)$$

$$\text{AEB (mm)} = \Sigma\,(\text{100 mm-unburned length}) / \text{number of specimens} \qquad (2)$$

$$\text{Burning rate} = 450 / (t - t_1) \quad \text{(cm/min)} \qquad (3)$$

Vertical burning rates of all samples were measured. UL-94 test results are classified by burning ratings V-0, V-1 or V-2. V-0 rating presents the best flame retardant of polymeric materials. In this research the amount and types of flame retardants on flammability property were studied as follows

1) Effect of brominated flame retardant loading

2) Minimum amount requirement of brominated: antimony oxide at 3:1

3) Effect of chlorinated flame retardant loading

4) Effect of zinc hydroxystannate (Storflam ZHS) loading

5) Comparison of halogen and halogen free flame retardant efficiency

3. Results and Discussion

According to Table 1 and Figure 1, antimony was fixed at 15 phr and decabrodiphenyl oxide was varied to form weight ratios of brominated to antimony oxide of 1:1, 2:1 and 3:1. The effect of aluminium hydroxide (ATH) on burning test was also studied. The experimental results in Table 1 demonstrate that values of average time of burning (ATB) and average extent of burning (AEB) decreased with increasing weight ratio of brominated to antimony oxide. ATH also reduced the ATB and AEB values. HB-test value of brominated flame retardant system reached the best value at a weight ratio of 3:1 with ATH added. This system showed no ignition of fire. The minimum requirement weight ratio of brominated to antimony oxide for 3:1 on burning test are

Table 1. Halogen flame retardant formulation with HB-test

Ingredients	1	2	3	4	5
RSS-3	100	100	100	100	100
ZnO	4	4	4	4	4
Vulcanox MB	1.4	1.4	1.4	1.4	1.4
carbon black	45	45	45	45	45
stearic acid	2	2	2	2	2
Aluminium hydroxide	-	-	22	-	22
antimony trioxide	15	15	15	15	15
Decabromo diphenyl oxide	15	30	30	45	45
CBS	0.85	0.85	0.85	0.85	0.85
sulfur	1.5	1.5	1.5	1.5	1.5
Flammability test					
average time of burning, (ATB, sec.)	397±87	312±72	208±49	265±91	124±36
average extent of burning, (AEB, mm.)	24±6	17±4	16±3	15±4	15±3
burning rate, cm/min	-	-	-	-	-
ignition of the fire	-	-	-	-	-

- inflamed

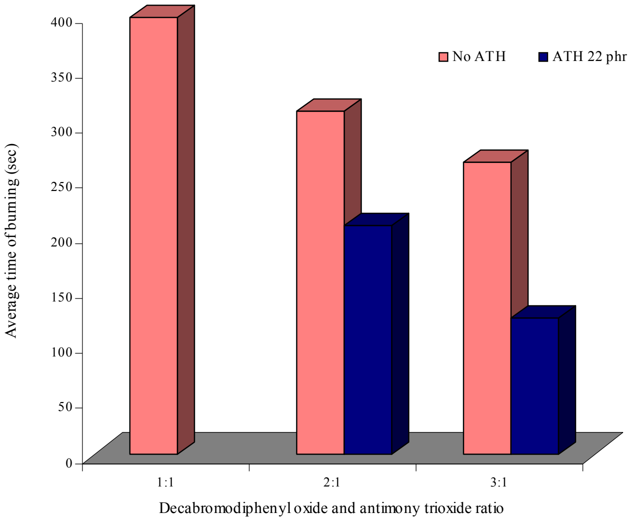

Figure 1. Average time of burning of brominated flame retardant

shown in Table 2. When the weight ratio of brominated to antimony oxide was 3:1 with ATH 22 phr in the system, it needed at least 21 phr of brominated and 7 phr of antimony oxide to show effective flame retardancy in NR. The ATB value at each weight ratio of brominated to antimony oxide did not differ significantly among them. In addition, the AEB value increased with decreasing the amount of brominated to antimony oxide weight ratio. Moreover, all weight ratio of 3:1 system showed no ignition of fire except at 15 phr of brominated and 5 phr of antimony oxide.

According to Table 3 and Figure 2, the weight ratio of chlorinated to antimony was varied from 6:1 with and without ATH and at a weight ratio of 3:1 with same amount as weight ratio of brominated formulations (21:7 and 30:10 phr) and were studied using the burning test. It was found that the 6:1 weight ratio of chlorinated to antimony showed lower efficiency than the 3:1 ratio. In addition, there was a limited amount of antimony oxide used in the system 3:1 weight ratio. It needed antimony oxide at least 10 phr for best efficiency. Even though using higher weight ratio of chlorinated to antimony and higher amount of chlorinated flame retardant, this system showed no ignition of fire as the amount of antimony oxide may not have been sufficient to play a role as a flame retardant. When compared to brominated system, chlorinated system seems to have lower efficiency than brominated at the same weight ratio. In this case it needs at least 30 phr of chlorinated and 10 phr of antimony oxide to show the most effective flame retardancy in NR.

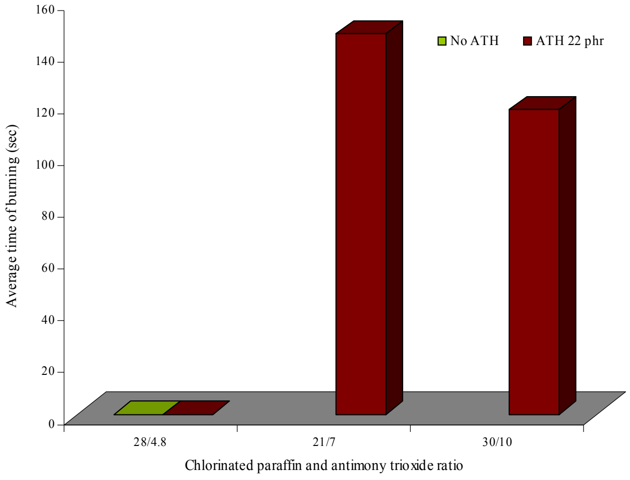

Figure 2. Average time of burning of chlorinated flame retardant

Table 2. Brominated : antimony oxide at various weight ratios of 3:1 formulation with HB-test

Ingredients	6	7	8	9	10
RSS-3	100	100	100	100	100
ZnO	4	4	4	4	4
Vulcanox MB	1.4	1.4	1.4	1.4	1.4
carbon black	45	45	45	45	45
stearic acid	2	2	2	2	2
aluminium hydroxide	22	22	22	22	22
antimony trioxide	15	12	10	7	5
Decabromodiphenyl oxide	45	36	30	21	15
CBS	0.85	0.85	0.85	0.85	0.85
sulfur	1.5	1.5	1.5	1.5	1.5
Flammability test					
average time of burning, (ATB, sec.)	124±36	124±23	121±24	135±6	128±19
average extent of burning, (AEB, mm.)	15±3	15±4	19±2	24±2	28±3
burning rate, cm/min	-	-	-	-	slightly
ignition of the fire	-	-	-	-	+

++ flamed and burned all sample
+ flamed after glowing combustion for a few seconds
- inflamed

Table 3. Chlorinated flame retardant formulation with HB-test

Ingredients	11*	12	13	14
RSS-3	100	100	100	100
ZnO	4	4	4	4
Vulcanox MB	1.4	1.4	1.4	1.4
carbon black	45	45	45	45
stearic acid	2	2	2	2
aluminium hydroxide	22	-	22	22
antimony trioxide	4.8	4.8	7	10
chlorinated paraffin	28	28	21	30
CBS	0.85	0.85	0.85	0.85
sulfur	1.5		1.5	1.5
Flammability test				
average time of burning, (ATB, sec.)	-		147±18	118±14
average extent of burning (AEB, mm.)	-	-	18±2	19±2
burning rate, cm/min	10±3	11±2	slightly	-
ignition of the fire	++	++	+	-

++ flamed and burned all sample
+ flamed after glowing combustion for a few seconds
- inflamed

Zinc hydroxystannate (ZHS) was studied as a halogen-free flame retardant. The efficiency results of this flame retardant are shown in Table 4. It was found that using ZHS by itself could not extinguish the flame on HB-test. Aluminium hydroxide (ATH) could reduce ATB and absolutely stop the flame on HB-test. It still had a little light at the end of the specimen but did not further extend in the specimen. Moreover, every weight ratio of ZHS to ATH still showed ignition of fire on the specimens as shown in Figure 3 (bottom row). However, when ATH was increased to 150 phr with ZHS 7.5 phr, this system could reach V-0 rating as observed in Table 5. Therefore, at the weight ratio of ZHS to ATH was increased

Table 4. Halogen free flame retardant formulation with HB-test

Ingredients	15	16	17	18	19
RSS-3	100	100	100	100	100
ZnO	4	4	4	4	4
Vulcanox MB	1.4	1.4	1.4	1.4	1.4
carbon black	45	45	45	45	45
stearic acid	2	2	2	2	2
aluminium hydroxide	-	150	125	125	150
Zinc hydroxy stannate	5	5	7.5	10	10
CBS	0.85	0.85	0.85	0.85	0.85
sulfur	1.5	1.5	1.5	1.5	1.5
Flammability test					
average time of burning, (ATB, sec.)	-	78±10	75±7	75±13	41±6
average extent of burning, (AEB, mm.)	-	16±1	14±2	16±1	14±2
burning rate, cm/min	18±1	-	-	-	-
ignition of the fire	++	+	+	+	+

++ flamed and burned all sample
+ flamed after glowing combustion for a few seconds
- inflamed

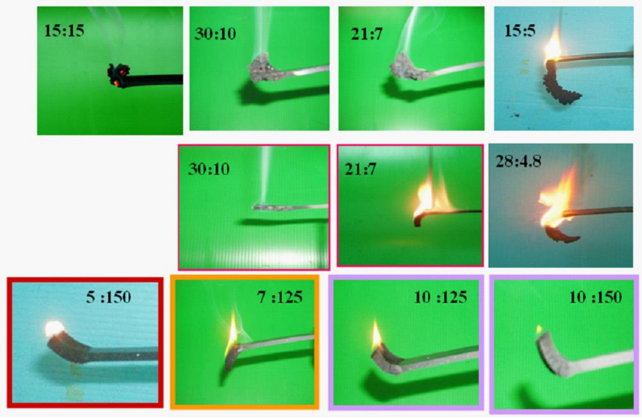

Figure 3. HB-test of various flame retardant formulations
Upper row present various brominated
Middle row present various chlorinated
Bottom row present various ZHS

to 10:150 phr, HB-test value of ZHS system reached the best value. HB-test results of various flame retardant formulations as shown in Figure 3. This figure shows that the halogen system is better than the halogen-free system. Brominated system is the most effective flame retardant in NR, followed by chlorinated and ZHS, respectively. To show the most effective flame retardancy in NR for each system, it needs at least 21 phr of brominated with 7 phr of ATH or 30 phr of chlorinated with 10 phr of ATH or ZHS to ATH is 10:150 phr.

The experimental results of vertical burning rate are shown in Table 5. It was observed that all chlorinated systems were out of the standard value, which contrasts with HB-test at a weight ratio of chlorinated to antimony oxide is 30:10 with ATH 22 phr. When ATH is loaded lower than 150 phr, even if ZHS is increased to 10 phr, the vertical burning rates were out of standard. However, it reached V-1 rating when the weight ratio of ZHS to ATH was 10:25 phr. In addition, it reached V-0 rating when ATH was increased to 150 phr at any amount of ZHS between 7.5 to 15 phr and with the weight ratio of brominated to antimony oxide is 21:7 phr.

Table 5. Burning test results from V-test

Flame retardants system	Classification
NR without FR	burned
Br:Sb2O3=21:7+ATH 22 phr	V-0
Br: Sb2O3=15:5+ATH 22 phr	below standard
Br:Sb2O3=36:12+ATH 22 phr	below standard
Br:Sb2O3=30:10+ATH 22 phr	below standard
Cl:Sb2O3=21:7+ ATH 22 phr	burned
ZHS:ATH=5:150	V-0
ZHS:ATH=7.5:100	burned
ZHS:ATH=7.5:125	burned
ZHS:ATH=7.5:150	V-0
ZHS:ATH=10:100	burned
ZHS:ATH=10:125	V-1
ZHS:ATH=10:150	V-0
ZHS:ATH=12.5:150	V-0
ZHS:ATH=15:150	V-0

The thermal degradation behavior of NR with various flame retardant blends at heating rate of 20°C min^{-1} is shown

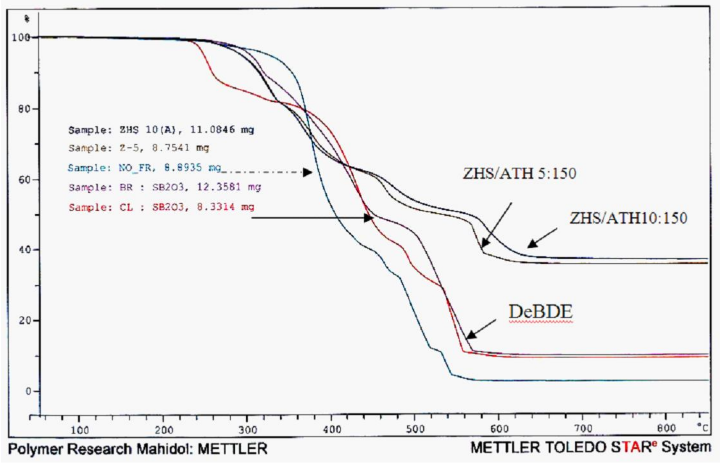

Figure 4. TGA curves of various flame retardant formulations

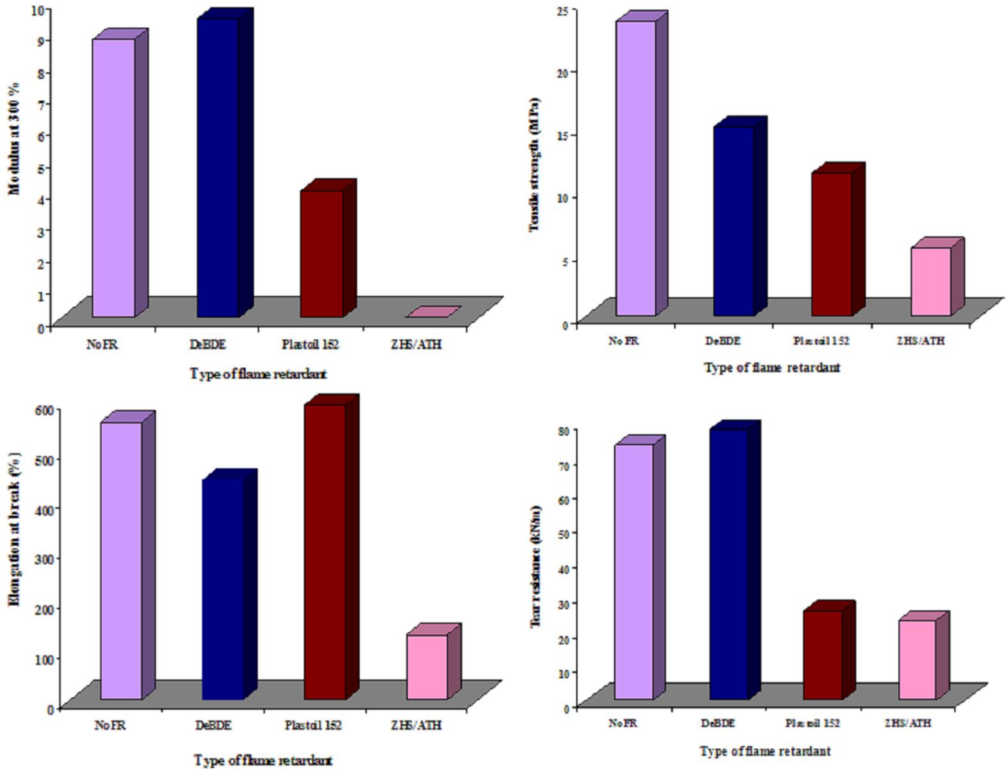

Figure 5. Mechanical properties of various free retardants used

in Figure 4. As TGA plots, the initial degradation steps correspond to the compounding ingredients, such as zinc oxide, stearic acid, antioxidant and accelerator, etc. The degradation of NR starts at an earlier temperature of 296°C (Ramesan, 2004) but with flame retardant, NR starts to degrade at temperature of 570 and 580°C for ZHS flame retardant blends at 5:150 and 10:150 ratio of ZHS to ATH, 540°C for chlorinated flame retardant blends, and 510°C for brominated flame retardant blends. However, chlorinated flame retardant seem to show higher degradation temperature at the final step but it starts to degrade at a lower temperature than brominated flame retardant at a temperature of 254°C, which corresponds to hydrogen chloride gas from the reaction of the system (Katz and Milewski, 1978). In addition, it was found that natural rubber with halogen-free flame retardant provides a rate of degradation less than that of halogen-flame retardant and without flame retardant respectively, as seen from the slope in Figure 4 which depends on the relative amount of residue. The highest residue from halogen-free flame retardant is 35.38 and 36.63%

resulting in slow burning rate due to the char barrier layer. Moreover, the residue amount of natural rubber without flame retardant is very low from additives added in the compound then resulting in burning all the sample which approved by both V-test and HB test. Finally, the ZHS to ATH system showed a lower average time of burning and average extent of burning than both halogen flame retardant systems since the halogen-free system spent a higher amount of ATH. This chemical has water in its structure and releases water with alumina at a temperature of about 300°C (Murphy, 2001). That's why the average time of burning is prolonged.

The effects of flame retardant systems on mechanical properties are shown in Figure 5. Brominated system with a weight ratio of brominated to antimony oxide of 1:7 phr showed the best value in 300% modulus, tensile strength, elongation at break and tear resistance while ZHS system expressed the lowest values in all mechanical properties, especially with 300% modulus, and the medium mechanical properties are obtained from the chlorinated system.

4. Conclusions

Brominated system with a weight ratio of brominated flame retardant decabromodiphenyl) to antimony oxide of 21:7 phr shows the most effective flame retardancy in NR and the best mechanical properties. Chlorinated system with a weight ratio of chlorinated flame retardant (Plastoil 152) to antimony oxide of 30:10 phr is the minimum requirement for being effective flame retardancy in NR.

With ZHS system, it needed ATH at least 150 phr with any amount of ZHS from 5 phr. However, at the weight ratio of ZHS to ATH is increased to 10:150 phr, HB-test value of ZHS system reaches the best value. It could reach V-0 rating when ATH is increased to 150 phr at any amount of ZHS between 5 to 15 phr and with the weight ratio of brominated flame retardant to antimony oxide of 1:7 phr.

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