



Study on Fire-Retardant Mechanism and Fire-Retardant Recipe of Self-Lock FRP Bolt†

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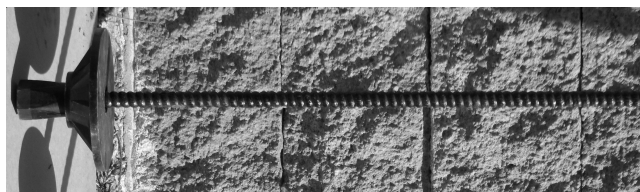
The important significance of the fire-retardant property of fibre reinforced plastics bolt for production safety of coal mine is illustrated. The fire-retardant mechanism of general composite is analyzed. Especially, bromine-antimony compounding fire-retardant characteristics is studied. According to the properties of the raw material of fibre reinforced plastics bolt, appropriate fire retardant agents are choose and tested. The results show the fire-retardant agents have fine performance when ratio of Sb_2O_3 to $C_{12}Br_{10}O$ is 1:4. So the rational experimental recipe of fibre reinforced plastics bolt with fire-retardant characteristics is found.

Keywords: Fibre reinforced plastics, Bolt, Fire-retardant mechanism, Recipe.

INTRODUCTION

Fibre reinforced plastics (FRP) bolt is a kind of bolt product made by composite material. In order to make bolt have cuttability and reduce bolt support cost, self-lock FRP bolt with screw distributing in the whole body shown in Fig. 1 was developed by Anhui University of Science and Technology and Huainan Shunhui Anchor Co., Ltd. The synthetic resin serves as base material and fibre-glass as reinforcing material. The bolt consists of rod with whole screw and self-lock bolt-end. The rod of bolt made of FRP is straight. Rod fibre, which bears tensile force of bolt, is distributed along rod body axis direction. Surface screw distributing with right-hand turn is twisted after fibre goes through the plastic tank. Bolt-end is manufactured by full FRP. Bolt-end screw takes wedge structure with cone. Cone structure can cause friction resistance which connects tray, screw and bolt. The structure advances greatly loading capacity of bolt-end which can resist two times of weighting.

However, FRP bolt is product used in mine. Its main content is unsaturated polyester resin which is important heat convertible resin. The unsaturated polyester resins have perfect comprehensive properties, however it is highly flammable and dense smoke produced when burnt. At the same time, burning affect support strength. Coal mining is special industry. Especially in the coal roadway, for coal is combustible material, it



(a) Bolt photo



(b) Bolt-end photo

Fig. 1. Self-lock FRP bolt with threw distributing in the whole body structure

is easy to cause fire disaster and even gas or coal dust explosion. In addition, high temperature and anoxia, smoke and poison gas produced by burning is very easy to make the staff asphyxiated owing to the limitation of space. Therefore careful consideration should be given to safely use FRP bolt. Every

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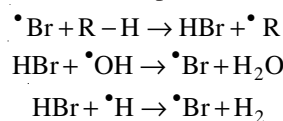
main country in the world draws strict standards and laws. China also draws corresponding national and industrial standards. According to mine industrial standards MT 113-1995, fire-resistant properties is capacity of polymers to go through the following experiments. Firstly, specimen is almost nonflammable or burn out by alcohol blow lamps combustion experiment. Secondly, specimen is similar performance by alcohol lamps combustion experiment. As FRP material is innately flammable, hidden fire trouble from this has been society problem getting a lot of publicity in the world. In order to solve this problem, present method is to reduce flammability and retard burning speed which is function of retardant agents¹. There is considerable progress in retardant agent technology in recent years. Different research institute chooses different retardant method and uses different retardant agents and recipe by lab experiment according to different retardant mechanisms.

Bromine-antimony compounding fire-retardant mechanisms of FRP bolt: Burning is a common phenomenon which is rapid physics and chemical course. When burning, almost of all accompany light and heat. Where there is burning phenomena, there will always be a kind of fuel and atmospheric oxygen. Burning is a chemical reaction with oxygen. The primary condition of the burning reaction is that fuel and oxygen coexist. Fuel and air can form combustion system. Fuel and other oxidants such as nitrates, chlorates, peroxide and nitrogen oxides can also form combustion system. The other condition of burning is temperature of combustion system. Only when the temperature is high enough, will burning take place. If temperature is low, combustion system can slowly oxidize.

Three factors of burning reaction is fuel, oxygen and enough temperature. Above items be short will not cause burning. The mechanism of retardant agents is to restrain one or several burning factors and finally prevent or retard burning. The effect of retardant agents on burning reaction shows as below. Firstly, thermal decomposition of retardant agents in condensed phase take place by heat of burning reaction. However, this is heat absorption course, which slows down the temperature in condensed phase and then defer speed of thermal decomposition. Secondly, after retardant agent is reduced by heat, the radical antagonist of a chain reaction is released to break burning reaction and slow down speed of gas-state reaction. Thirdly, thermal decomposition in catalysis condensed phase forms coking or form layer to block heat transfer. So temperature of condensed phase keeps very low to reduce formation speed of gas-state reaction material, which is similar to take away fuel under boiler. Finally, retardant agents have a change from exothermic to endothermic by heat, which keep from temperature of condensed phase rising. To sum up, function of retardant agent can work in many ways, whose main retardant mechanisms are isolation membrane mechanism free radical acquisition mechanism, cooling mechanism and cooperative formation mechanisms²⁻⁴.

Bromine-antimony compounding has good flame retardant performance, which is attracting more and more attention. When Sb_2O_3 and $C_{12}Br_{10}O$ are used in compound, they show strong cooperation effect. The burning reaction of polymers is chain reaction between the free radical $\cdot OH$ and $\cdot H$. $C_{12}Br_{10}O$ is dissolved into Br atoms under high temperature due to

material burning. Br atoms have action with polymers to form HBr which reacts with $\cdot OH$, H to produce H_2O and H_2 . Finally chain oxidation will be ended to produce flame retardant effect.



Sb_2O_3 added not only absorbs a part of burning heat, but also has action with HBr to produce $SbBr_3$ gas whose gravity is greater than air. $SbBr_3$ can play a role of separating the oxygen to promote the retardant effect.

Flame retardant recipe research

Flame retardant recipe design: According to flame retardant mechanisms of FRP bolt, the flame retardant recipe is designed on the principle that the retardant agents improve obviously the flame retardant property and at the same time have no side effects on other performances. Results showed that bromine-antimony compounding has a good retardation effect and its main retardant agents are Sb_2O_3 and $C_{12}Br_{10}O$ (Table-1).

TABLE-1 RECIPE OF FLAME RETARDANT FRP BOLT			
Reinforced material	Base material	Retardant agents	Remarks
Twistless roving fibre	Pultrusion resin	Sb_2O_3 , $C_{12}Br_{10}O$	Other function material

Flame retardant recipe experiments: The raw materials including pultrusion resin, Sb_2O_3 , benzoyl peroxide, Zn stearic, phthalate were selected to prepare flame retardant recipe. Pultrusion resin is a kind of yellow liquid whose viscosity is 0.2500-0.4525cpa.s, solid content 60-67 %, water adsorption 0.17 % and gravity 1.23. Sb_2O_3 compounding is a yellowish white crystal powder in which Sb_2O_3 accounts for more than 99 % and there is little other material such as arsenic trioxide, lead oxide, ferric oxide and selenium.

The experimental process is as follows: The specimen is placed at the top of flame of alcohol blast lamps in experiment. The burning time of specimen is related to thickness and stiffness of specimen. The shortest time is not less than 5s and the longest is not longer than 60s. After specimen burns, alcohol blow lamps still firing is moved away and flame burning time and non-flame burning time is recorded by stopwatch.

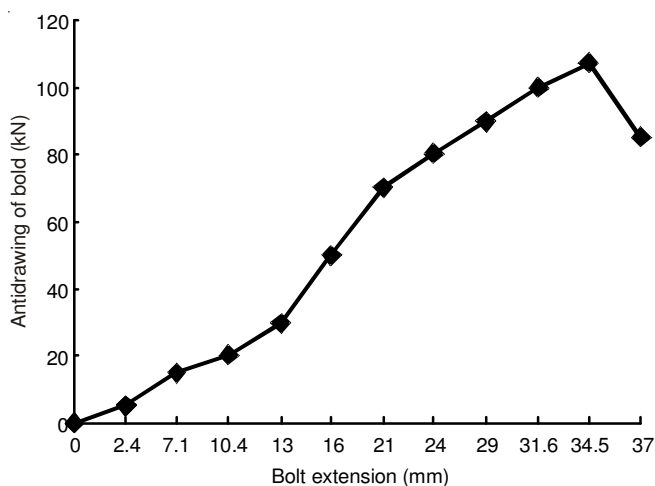
The organic retardant agents serve as main retardant agents in this experiment. The $C_{12}Br_{10}O$ amount is variable while Sb_2O_3 amount does not change. The raw material recipe and retardant effect is shown as Table-2. Test results show flame burning time is obviously shortened with $C_{12}Br_{10}O$ increasing. The flame burning time is shortest when the ration of Sb_2O_3 to $C_{12}Br_{10}O$ is 1:4. If $C_{12}Br_{10}O$ amount is improved furthermore, retardant effect is getting weak, which shows retardant effect is not always increasing with retardant agent increasing, sometimes conversely. The burning experimental results show the retardant agent recipe with the ratio of Sb_2O_3 to $C_{12}Br_{10}O$, 1:4 gets the best retardant effect. In order to testify the recipe, the bolt manufactured by above recipe is test in pull-out test and experiment results show as Fig. 2.

TABLE-2
RAW MATERIAL RECIPE SCHEME OF RETARDANT
AGENT AND RETARDANT EFFECT

Pultrusion resin	Benzoyl peroxide	Sb ₂ O ₃	C ₁₂ Br ₁₀ O	Flame burning time (s)
100	1	1.0	1.0	9.4
100	1	1.0	2.0	8.2
100	1	1.0	3.0	5.8
100	1	1.0	4.0	4.1
100	1	1.0	5.0	5.4



(a) Bolt test photo



(b) Relationship curve between antidrawing force and elongation of bolt

Fig. 2. Self-lock FRP bolt with threw distributing in the whole body structure tensile test

Pull-out test of bolt shows the tensile strength is more than 100 kN and the bolt has certain elongation. The bolt can meet the requirement of coal rib bolt whose tensile strength is not less than 50 kN.

Experimental results show that the retardant agent recipe with the ratio of Sb₂O₃ to C₁₂Br₁₀O, 1:4 gets the best retardant effect to attain retardant goal. At the same time, additive amount is few, so the cost is low.

Conclusion

The flame retardant feature of FRP bolt has the significance on mine safety. The mechanism of retardant agents is to restrain one or several burning factors and finally prevent or retard burning. Bromine-antimony compounding flame retardant is of preferable retardant characteristic. Experiment results show the retardant agent recipe with the ratio of Sb₂O₃ to C₁₂Br₁₀O 1:4 gets the best retardant effect.

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