Research on the formulation of flame retardant coating for fiberglass fabric

Abstract: The further research on coating materials of fiberglass fabric, which is based on the research of flame retardant coating of fiberglass fabric. According to the theoretical analysis and the performance, methyl vinyl silicone rubber as the coating material, and develop the flame retardant coating formulations of fiberglass fabric successfully through the experimental research. Using the double-solvent in the formulation, and research the formulation of flame retardant, dosage, and evaluation of flame retardant performance.
Key words: flame retardant; fiberglass fabric; coating; performance

0 Introduction

With the global economic development, the population is dense, the building is high, and the new building materials is widely used. The increasing fire possibility, and the fire accident has been one of the major disasters in the city. In recent years, the frequent fire accidents have caused heavy casualties and property losses. Now government pays high attention of fire safety, and people's fire awareness is also constantly strengthened. In this paper, the further research on coating materials of fiberglass fabric, which is based on the research of flame retardant coating of fiberglass fabric, and with evaluation of flame retardant performance.

1 The research on the formulation of coating materials.

The flame retardant coating material of fiberglass fabric needs to have the following performance:

(1) Good protection for fiberglass fabric materials.

(2) Good performance of flame retardant, the current flame retardant grade of fabric is up to B1.

(3) High temperature stability, the coating material is able to maintain physical and chemical properties in high temperature (> 200℃) and high humidity environment.; to maximize the retention of the original strength of fiberglass; it will not appear mechanical and thermodynamic defects in the junction between coating materials and fiberglass; no toxic gas; Good air tightness.

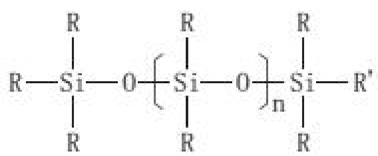
1.1 Selection of coating materials.

We compared the several common organic coating materials, the main chemical properties are shown in Table 1.

Table 1 The main chemical properties of coating materials

Coating Materials	Property	Application	Temp Resistance
PVC	Stable alkali , acid and salt resistance in room temperature, poor in insulation and thermal stability.	Artificial leather , wire netting , insulating paint tube , rain shoes, toys, etc.	About 150℃
polyacrylate	Transparent , good climate resistance , corrosion resistance , good film-formation	Protection of fabric, metal and wood; decoration.	<200℃
Epoxy resin	Transparent , high bond strength , insulation , flammable , alkali resistance.	Adhesives, paints, reinforced plastics.	About 200℃
Silicon rubber	Good performance of high temp resistance, ozone, oxygen, light, climate ageing resistance.	Aerospace, automotive, instrument, medical, daily products, etc.	About 250℃
PTFE	Extensive using temperature, acid alkali antioxidants and organic solvent resistance, insulation, non-combustible property.	Aerospace, automotive, instrument, medical, daily products, etc.	About 300℃

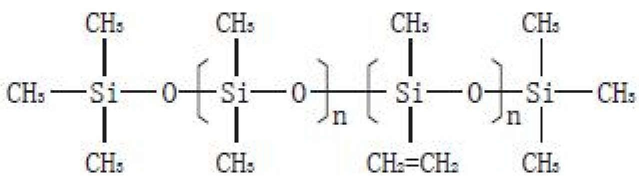
From Table 1, silicone rubber with good temperature resistance, and it' s suitable fire retardant coating material. It is a kind of straight chain macromolecule organic siloxane, molecular weight is in 300,000 above, the general formula as below:



n represents the degree of polymerization, R' reprsents alkyl or hydroxyl, R represents methyl.

From the molecular structure, the main chain is Silicon-oxygen bond, the bond energy is up to 375.55kJ/mol, with the excellent heat resistance, which similar to silicate. The organic groups on the pendant groups, which imparts flexibility to it, and with the characteristics of organic polymer and the inorganic polymer. Thus, there are lots of unique performance, such as high temperature resistance, climate change, electrical insulation, ozone resistance, hydrophobic, physiological inertness, and many other excellent performance. The unique performance of silicon rubber is the stability of high temperature, the long -term working temperature is 200~300℃, it's also up to 375℃ if adding appropriate filler and heat stabilizer. The ignition point of silicon rubber is 450℃, and it's not easy to burn. If it burns, the produced SiO2 is inert, and without toxic and corrosive gases during burning.

There are many kinds of silicon rubber, and the methyl vinyl silicon rubber is dominant in the production, the introduction of the alkenyl can improve the vulcanization activity of silicon rubber, and the hardness of silicone rubber vulcanizing products. The general formula is as below:



The technical index and physical properties are as Table 2.
Thus, we take methyl vinyl silicone rubber (silicon rubber) as the coated material.

1.2 The research of basic coating formulation.
Due to the coating material is refined silicon rubber, and the silicon rubber is not flame retardant, so we must take the vulcanizer, solvent, colorant, fire retardant, and other auxiliaries into consideration of the formulation.

1.2.1 Vulcanizer
The organic peroxides are also be chosen as the vulcanizer for silicon rubber. The Mechanism of vulcanization, which organic peroxides promotes crosslinking of organic group of the rubber. Because of our vulcanization processing is under hot air and room pressure, so it is better to choose high active DCBP. DCBP, which with low vulcanized temperature, short vulcanized time, and decompounded easily, the dosage of DCBP is 0.5%～5% of silicon rubber.

Table 2 Technical data of methyl vinyl silicone rubber

Item	Index
Molecular weight	350 000～650 000
Volatile matter (150℃,3h)/%	<3
Solubleness	Soluble in benzene
Acid-base	neutral
Ethylene content	0.08~0.25
Tensile strength/Mpa	1.90~6.86
Elongation/%	200~300
Hardness (Shore)	40~60
Brittleness temperature/℃	- 60
Volume resistance/Ω·	1015-1016
Surface resistance/Ω	1013-1015
Permittivity/F·m-1	3.5
Dielectric dissipation factor/red	4×10-3
Breakdown strength/KV·-1	15~18

1.2.2 Colorant

Choosing the environmental dedicated masterbatch for silicon rubber, the dosage is as per customer' s requirements, and it depend on the depth of the color.

1.2.3 Solvent

If only use one solvent in the formulation, the solvent will volatilize and cause the defects on the surface, bubble will appear in serous situation, or stomata will appear. In order to improve the quality of surface, we take the the two kinds of solvent, solvent A with high boiling point, solvent B with low boiling point, the difference of boiling temperature is about 50℃. In the experiment, with the same processing, using 2 kinds of solvent and different ratio of the formulation, after the heat treatment of the oven, the result is as Table 3.

According to the surface of fabric, and processing, the ratio of solvent A and solvent B is 1:1.

1.3 Research of flame retardant system

The silicon rubber is not flame retardant, it is necessary to modify its flame retardation. The normal physical method is adding fire retardant and flame-retardant filler in the silicon rubber material to be fireproof.

Table 3 The effects of drying temperature and surface quality under different ratio of solvent

Solvent A/solvent B (ratio)	Surface quality	Drying temperature /℃
0:1	Large quantity of bubbles and stomatas on the fabric, the coating is easy to be dried.	160
0.25:0.75	Small quantity of bubbles and stomatas on the fabric, the coating is easy to be dried.	170
0.5:0.5	Almost none bubble and stomata on the fabric, the coating is not easy to be dried.	180
0.75:0.25	Almost none bubble and stomata on the fabric, the coating is easy to be dried.	195
1:0	Small quantity of bubbles and stomatas, the coating is not easy to be dried.	200

1.3.1 Selection of the flame retardant system

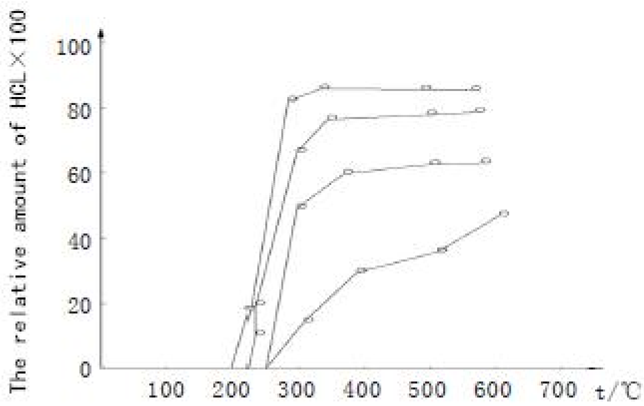
The requirements of choosing the flame retardant: (1) high-efficiency (small dosage of fire retardant for unit property); (2) Non-toxic /low toxicity; (3) good thermostability (decomposition temperature: 250∽400℃); (4) do not influence the flamed retardant material too much; (5) As little of toxic gas and dense smoke as possible when burning. Thus, it is necessary to take the smoke suppression and fire retardant into consideration while choosing the flame retardant.

Flame retardant divides to organic and inorganic flame retardant. The organic flame retardant: Organic halide series (organic bromine, organochlorine), organic phosphorus, nitrogen flame retardants series. Inorganic flame retardants including aluminum-magnesium series, antimony series, boron series and so on.

The Organic halide flame retardant, with low price, good efficient of fireproofing, wide adaptation range, easy to mix with polymer evenly. The most common series is organic bromine , which with the most efficient of fire retardant, however, the shortage is lots of smoke when burning and cracking. Inorganic aluminum-magnesium series, with good performance of decreasing the smoke, especially inhibit the hydrogen halide, thus we consider to combine the aluminum-magnesium with organic halide into the fire retardant.

From picture 1, It shows that magnesium hydrate is perfect to the inhibition of HCl. Meanwhile, the decomposition temperature of magnesium hydrate is the highest (340℃), thus, magnesium hydrate is very suitable for fire retardant in high temperature environment.

The flame retardants mechanism of antimony and boron in inorganic flame retardants are almost same. Antimony oxide is the most commonly used flame retardant, It reacts with halide to form antimony halide at high temperature, which is a volatile substance with higher boiling point, so it can stay in the burning area to isolate oxygen for a long time. Antimony halide can also promote dehydrohalogenation and surface carbonization of polymer- flame retardant in the liquid-solid phase. Thus, it will be good flame retardant effect to combine antimony oxide with halogen flame retardant.



Pic 1, Different kinds of flame retardant inhibits HCl

Because of the own limitations of carious types of lame retardant, and in order to achieve the good flame retardant effect, using the magnesium hydroxide as the main flame retardant, which with high temperature resistance and smoke suppression, meanwhile, combining the organic brominated and antimony series flame retardants, and to get the most efficient flame retardant.

1.3.2 The confirmation of silicon rubber flame retardant formulation and evaluation.

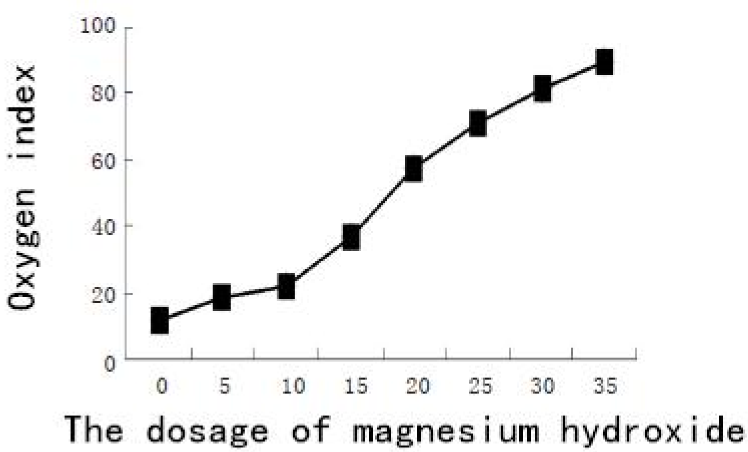
After confirming the the flame retardant system through many times of experiments, we get the final silicon rubber flame retardant formulation. The purpose is to get the best effect of flame retardant, one the other side, the mechanics performance of silicon rubber coated fabric will not be effected largely. What’s more, introducing the dispersing agent — metallic soap, which can improve the dispersion uniformity of flame retardant in the silicone rubber.

1.3.2.1 The dosage of main flame retardant magnesium hydroxide and performance evaluation

(1) The dosage of Magnesium hydroxide to the oxygen index of silicon rubber

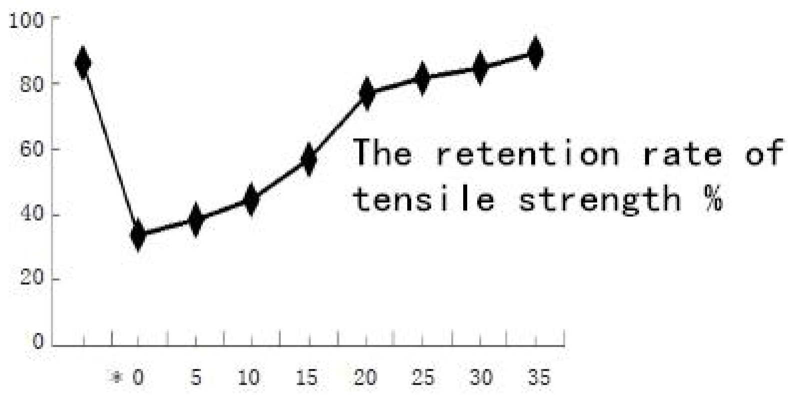
The evaluation of flame retardant can be taken from Oxygen index. According to formulary requirement, the oxygen should be greater than 26, the materials will be with fire retardant property. After changing the dosage of Magnesium hydroxide, and observing the Oxygen index, we get the curve of picture 2.
After increasing the dosage of the Magnesium hydroxide in the silicone rubber system, the Oxygen Index is increased in the whole system. Thus, for the flame retardant effect, the more dosage of Magnesium hydroxide, the better effect will be.

(2) The dosage of Magnesium hydroxide to the retention rate of silicone rubber coated fabric strength.



Pic 2 The dosage of Magnesium hydroxide to the oxygen index of silicon rubber

Using the Magnesium hydroxide as the main flame retardant, and combining with a kind of halogen flame retardant. Changing the dosage of Magnesium hydroxide, the retention rate of tensile strength of fireproof silicon rubber coated fabric will be turned out as picture 3.



The mass fraction of Magnesium hydroxide

* The blank sample: silicone rubber coated fiberglass fabric without flame retardant

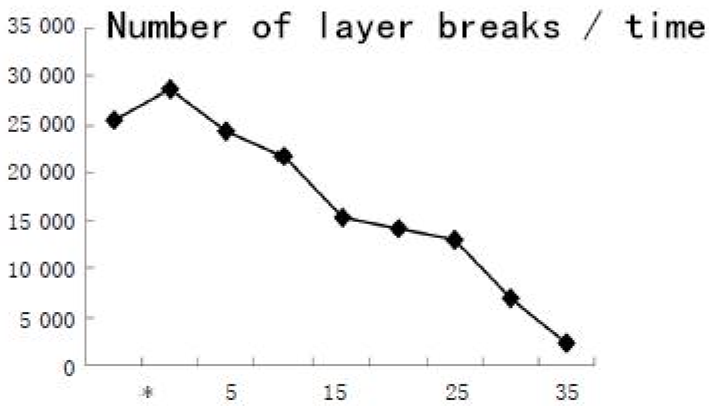
Pic 3 Tensile strength retention of flame retardant silicone coated fiberglass fabric

From the above picture, the tensile strength of silicon rubber coated fiberglass fabric is decreasing under the high temperature and high humidity environment, and the strength is decreasing much obviously when there is halogen; Using the Magnesium hydroxide, the dosage of Magnesium hydroxide is increasing, the retention rate of strength of silicon rubber coated fiberglass fabric is also increased. When the dosage of Magnesium hydroxide is over 20, the quantity of Magnesium hydroxide is enough to absorb halogen hydride, the excessive Magnesium hydroxide can only decrease the air permeability of silicon rubber, however, the effect is not obvious as the halogen hydride during the absorbing, thus, the strength retention rate increased with slow speed.

(3) The effect of Magnesium hydroxide to the strength of the silicon coating

In order to evaluate the magnesium hydroxide to the strength of the silicon rubber coating, fabric folding tester is used to test the flame retardant silicon rubber coated fabric.

According to the experimental results, which is concluded that the dosage of magnesium hydroxide and coating toughness curve, and shown in picture 4. As to the picture, when the dosage of Magnesium hydroxide is less than 15, and before breaking of the base material, the coating is still not fractured, and this is similar to property of silicon rubber which not adding any flame retardant , so excluding the variability of the data to affect the number of fracture, the toughness of silicon rubber does not change. When dosage of magnesium hydroxide is more than 15, as a measure of coating toughness index, the number of fracture with unilateral decline, so the toughness of the magnesium hydroxide of silicone rubber, which with a negative effect, and it has a little influence under the certain range, in the toughness of the silicone rubber coating has no obvious change. However, dosage of Magnesium hydroxide beyond a certain range, however, the toughness of coating declined directly, so the toughness of silicone rubber is associated negatively with the dosage of the magnesium hydroxide.



The mass fraction of Magnesium hydroxide

* The Blank sample: silicone rubber coated fiberglass fabric without flame retardant

Pic 4, the curve of Magnesium hydroxide dosage and coating toughness

According to the comprehensive evaluation of magnesium hydroxide dosage to oxygen index, strength retention under high temperature and high humidity environment, and the influence of the coating toughness, eventually, the dosage of magnesium hydroxide is 10%～25%.

1.3.2.2 The confirmation of flame retardant formulation and evaluation.

According the above information, we list the four different kinds of flame retardant silicon rubber formulation (as table 4), then evaluate the property of silicone rubber flame retardant, strength retention rate under high temperature, strength retention under high temperature and high humidity (boiling water resistance), the silicone rubber flame retardant system formulation was finally determined.

(1)The evaluation of oxygen index to flame retardant.

The detailed data is as table 5

Table 5, The oxygen index of different flame retardant silicon rubber formulation

Formulation	1#	2#	3#	4#
Oxygen Index	53	58	38	51

According to the standards, it turned out that the above formulations can provide flame retardant to fabrics effectively.

Table 4, different flame retardant silicon rubber formulation

Formulation	1#	3#	4#
Silicon rubber	50	50	50
DCBP	2.5	2.5	2.5
Decabromodiphenyl ether	10	/	/
Chloride paraffin--70	/	13	13
Antimonous oxide	3	9	9
Ferric hydroxide	20	20	20
Metallic soap	/	3	8

(2)The strength retention rate of Strength - high temperature, and Strength - high temperature & high humidity (boiling water resistance).

The strength retention rate testing of different flame retardant silicon rubber formulation under high temperature and boiling environment, testing result as table 6.

Table 6, different flame retardant silicon rubber formulation to the strength retention rate.

Formulation	1#	2#	3#	4#
Warp strength retention rate of high-temp fabric /%	70.1	84.7	87.8	92.9
Warp strength retention rate of corrosion protection fabric/%	53.8	82.4	87.3	92.1

From table 6, for 4 # formula under 2 conditions, the fabric strength retention rate is the highest. Our analysis: 1 # and 2 # , antimonous oxide content is less as a synergistic flame retardants , resulting in the halide does not react well with it to form isolated oxygenated antimony halides, more free hydrogen halide corrode the fabric at high temperature and high temperature-high humidity, reducing the strength of the fabric; 1 # formula does not contain dispersant, it can not guarantee a small amount of synergistic flame retardant has good dispersion and play a role, resulting in the lowest strength retention. The synergistic flame retardant content of 3 # and 4 # formulations increased, and the halide was converted into antimony halide under high temperature and high temperature-high humidity condition, the fabric was protected and the strength retention rate of fabric was improved; The content of dispersant get to 8, it can play a better role of synergetic flame retardants. Through the four formulations, we also analyzed that using specific halide flame retardant has little effect on the fabric strength retention rate. Based on the comprehensive analysis, we confirmed that the flame retardant formulation system of flame retardant coated fiberglass fabric is 4 #.

1.4 Evaluation of fiberglass flame retardant coating

1.4.1 Evaluation of mechanical property

We focused on the evaluation of tensile strength and tear strength of coated fabrics. GB/T769.5-2001 (Determination of tensile strength and elongation at break of fiberglass) as the test standard, test three types of the product according to the standard, the specific data in Table 7.

Table 7 Technical data of tensile strength and tear strength

Item		KTC0101	KTC0105	KTC0111
Weight/g・M^{-2}		620	940	1200
Thickness/mm		0.60	0.93	1.20
Tensile strength/N・$50mm^{-1}$	Warp	6 266	5244	5469
	Weft	4 519	4787	6236
Tear strength /N・$50mm^{-1}$	Warp	306	404	634
	Weft	277	518	912

The data in the table shows that all the mechanical properties have reached the standard

1.4.2 Evaluation of flame retardancy

About the coated fabric flame-retardant properties, we sent samples for testing. The authoritative testing department adopts GB 8624-1997 (classification method of combustion performance of building materials) and decomposition standard GB / T8626, GB / 18625, testing of flame retardant fabric highest level B1 . Specific indicators and test results showed in Table 8.

Item		Standard	Testing result		
			KTC0101	KTC0105	KTC0111
GB/T8626, The flame tip does not reach the graduation line And does not allow the drops to burn the filter paper /s		<20	<0	<20	<20
			No drops	No drops	No drops
GB/T8625	The average length of each pic/cm	15	35.67	4.33	36.25
	Remaining length of any pic/cm	>0	30	21	31
	The average temperature peak of smoke for each test/℃	200	82.33	89.67	83.75
GB/ T 8627, Smoke density level/SDR		75	20	81	24
GB 8624, Flame retardant level		1	B1	B1	B1

From the data of the table, the 3 types fire retardant coated fiberglass fabric reach the highest flame retardant level B1.

1.4.3 Determination of bursting performance of coated fabrics

We refer to GB/T 8878-2002 in the marbles bursting strength test method to test the coating fabric bursting strength (Ball diameter is 2cm, circle diameter is 2.5cm, descending speed is 10～11cm /min). Take 5 pieces of specimen, insert the specimen into the ring and then contact the ball. The specific measurement results in Table 9.

Bursting strength

Item	KTC0101	KTC0105	KTC0111
Bursting strength/N	1 453	1 846	1 958

2 Conclusion

Through the theoretical analysis and performance study, methyl vinyl silicone rubber was chosen as the main coating, and the flame retardant coating formula of glass fiber fabric was successfully developed through experiment. Using two solvents in the formula, the dosage and flame retardancy of the flame retardant were also studied emphatically, and the fabric flame retardant level reached the highest B1 level finally.