

Description

Title of the Invention

Vinyl Chloride Resin Composition and Insulated Electronic Wire Using the Same

Technical Field

[0001]

The present invention concerns a flame retardant resin composition for coating an insulated electronic wire and an insulated electronic wire using the same and it particularly relates to a flame retardant resin composition applicable to electronic wires conforming to UL785 standards and an insulated electronic wire using the same.

Background Art

[0002]

Insulated electronic wires used for internal wirings of electronic equipments are required to be flame retardant so that flames do not propagate along electronic wires upon fire accidents of equipments, etc. and the standards for the flame retardancy of internal wiring materials are specified, for example, in UL785 standards, etc. While a vertical wire flame test (hereinafter referred to as "VW-1 test") is provided as an option in the items required by UL785, since most of insulated electronic wires pass the test and are approved in UL, the VW-1 test is a substantially essential item although this is an optional standard.

Further, other important characteristics of the insulated electronic wires include a tensile elongation retention rate and a voltage withstanding characteristic after aging. They are essential items of the UL785 standards. For the voltage withstanding characteristic, there are a test conducted at a normal temperature and a test conducted in a high temperature circumstance at a rated temperature, in which the test conducted in the high temperature circumstance is

generally severer.

[0003]

Heretofore, as a main material of the coating member for insulated electronic wires, vinyl chloride resins (PVC) have been used. The vinyl chloride resins contain chlorine as a halogen in the chemical structure and the flame retardancy per se is high. However, in a case of using them as the insulating material for electronic wires since the vinyl chloride resins are rigid, they are used with addition of a great amount of a combustible plasticizers for softening. Accordingly, the standards for the flame retardancy described above cannot be satisfied unless a flame retardant is further added.

[0004]

As the flame retardant, antimony trioxide has been used generally. However, since antimony trioxide is an active drug and stringent administration is required upon production and this is a material which is intended to be avoided for the use. Further, antimony trioxide often contains lead or lead compounds as an environmental load substance.

[0005]

Therefore, as a substitute flame retardant for antimony trioxide, metal hydroxides such as aluminum hydroxide and magnesium hydroxide are used. For instance, in the example of a cited document 1, 20 to 40 parts of aluminum hydroxide and magnesium hydroxide are added and used based on 100 parts of vinyl chloride resin.

[0006]

On the other hand, since the vinyl chloride resins are heated to 170°C or higher during molding fabrication and chlorine is detached from the molecular structure, they also involve a problem that the tensile elongation is lowered and the voltage withstanding characteristic in a high temperature circumstance is also degraded remarkably. For preventing this, while lead and lead compound stabilizers having a long lasting heat resistant effect have been used so far,

they are environmental load substances specified as inhibitory substances by the EU RoHS instruction. Accordingly, non-lead stabilizers have been used at present as the substitute therefor in most of insulated electronic wires.

While the non-lead stabilizers provide not so high effect as the lead and lead compound stabilizers, non-lead stabilizers such as of barium zinc type, calcium hydroxide type, calcium zinc type, hydrotalcite type, and metal octylate type are used properly depending on the application use.

Prior Art Document

Patent Document

[0007]

Patent Document 1: JP-A No. 2006-291145

Summary of the Invention

Subject to be Solved by the Invention

[0008]

However, the non-lead stabilizers involve a drawback that the effect thereof is suppressed by metal hydroxides such as aluminum hydroxide or magnesium hydroxide added as the flame retardant. For example, in the method described in the example of the Patent document 1 described above, since the addition amount of the metal hydroxides is excessive, there may be a possibility that the effect of the non-lead stabilizer is decreased and the heat resistance such as the high temperature voltage withstanding characteristic after aging which is an essential item for the characteristics of the insulated electronic wires is deteriorated. In the example of the Patent document 1, only the system of using the vinyl chloride resin and EVA (vinyl acetate resin) together as the resin ingredient is disclosed and it is considered that lowering of the tensile elongation or tensile elongation retention rate after aging is prevented by the addition of the EVA resin at a high vinyl acetate content. However, since an EVA resin at high

VA content is expensive, it is not practical to use the same for inexpensive PVC-coated insulated electronic wires.

[0009]

The present invention has been accomplished taking notice on the subject described above in existent flame retardant resin compositions for coating insulated electronic wires and the object thereof is to provide a non-lead vinyl chloride resin composition which is substantially free of antimony, uses a vinyl chloride resin alone as a base resin, and is excellent in the flame retardancy and the voltage withstanding characteristics (retention rate of insulation breakdown value) and tensile elongation retention rate after aging, as well as an insulated electronic wire using the same.

Means for Solving the Subject

[0010]

The present inventors have made earnest studies for attaining the purpose described above and, as a result, have found that the purpose can be attained by using a crosslinked vinyl chloride resin composition containing a vinyl chloride resin, aluminum hydroxide and/or magnesium hydroxide, a plasticizer, and a non-lead stabilizer, in which the content of aluminum hydroxide and/or magnesium hydroxide is 8 to 22 parts by weight based on 100 parts by weight of the content of the vinyl chloride resin, and which is crosslinked after molding, and have accomplished the present invention.

[0011]

That is, a vinyl chloride resin composition according to the invention comprises a vinyl chloride resin, aluminum hydroxide and/or magnesium hydroxide, a plasticizer, and a non-lead stabilizer in which the content of the aluminum hydroxide and/or magnesium hydroxide is 8 to 22 parts by weight based on 100 parts by weight of the content of the vinyl chloride resin, the content of antimony is less than 1000 ppm, and the composition is crosslinked after molding

(Claim 1).

[0012]

Further, in a preferable mode of the vinyl chloride resin composition according to the invention, the aluminum hydroxide and/or magnesium hydroxide is surface treated (Claim 2).

[0013]

Furthermore, an insulated electronic wire according to the invention is formed by coating a conductor with the vinyl chloride resin composition of the invention (Claim 3).

Effect of the Invention

[0014]

According to the present invention, there is provided a non-lead resin composition which is substantially free of antimony, uses a vinyl chloride resin alone as a base resin, and is excellent in the flame retardancy, the voltage withstanding characteristic (retention of insulation breakdown value) and the tensile elongation retention rate after aging, as well as an insulated electronic wire using the same, by using a crosslinked vinyl chloride resin composition containing a vinyl chloride resin, aluminum hydroxide and/or magnesium hydroxide, a plasticizer, and a non-lead stabilizer, in which the content of aluminum hydroxide and/or magnesium hydroxide is from 8 to 22 parts by weight based on 100 parts by weight of the content of the vinyl chloride resin and which is crosslinked after molding.

Mode for Practicing the Invention

[0015]

A vinyl chloride resin composition and an insulated electronic wire using the same according to the invention are to be described specifically.

[0016]

(1) Vinyl chloride resin composition

As has been described above, the vinyl chloride resin composition of the invention

contains a vinyl chloride resin, aluminum hydroxide and/or magnesium hydroxide, a plasticizer, and a non-lead stabilizer. Further, the content of aluminum hydroxide and/or magnesium hydroxide is from 8 to 22 parts by weight based on 100 parts by weight of the content of the vinyl chloride resin. The content of antimony is less than 1000 ppm. Further, crosslinking is conducted after molding. Further, the crosslinked vinyl chloride resin composition of the invention is a non-lead.

[0017]

As the vinyl chloride resin, vinyl chloride resins known so far for insulated electronic wires can be used with no particular restriction and those having an average polymerization degree of 800 to 3200 are preferred with a view point of the balance between the processability and the performance.

[0018]

Aluminum hydroxide and magnesium hydroxide are added as a flame retardant.

Aluminum hydroxide is not particularly restricted so long as it is aluminum hydroxide in the usual meaning which is represented by the chemical formula: $\text{Al}(\text{OH})_3$ and those having a particle diameter from 0.5 μm to 4 μm are preferred with a view point of keeping the outer surface of the electronic wire surface smooth after coating.

Further, magnesium hydroxide is not particularly restricted so long as it is magnesium hydroxide in the usual meaning which is represented by the chemical formula; $\text{Mg}(\text{OH})_2$ and, in the same manner as in aluminum oxide, those having a particle diameter of 0.5 μm to 4 μm are preferred with a view point of keeping the outer surface of the electronic wire surface smooth after coating.

[0019]

Aluminum hydroxide and magnesium hydroxide can be added each alone or in combination and the content thereof is from 8 to 22 parts by weight and, preferably, 8 to 15 parts

by weight in total based on 100 parts by weight of the vinyl chloride resin. No desired flame retardancy can be obtained with the content of less than 8 parts by weight and an undesired effect is given on the tensile strength retention rate and the voltage withstanding characteristic after aging when the content exceeds 22 parts by weight. Further, heat resistance for longer time can be obtained by defining the addition amount to 8 to 15 parts by weight.

[0020]

Further, in an application use that requires the heat resistance for long time, a treatment can be applied, for example, with stearic acid to the surface of aluminum hydroxide and magnesium hydroxide. Since the metal hydroxide can be prevented from direct contact with the stabilizer by the treatment, it is possible to suppress the degradation in the effect of the stabilizer.

[0021]

Antimony trioxide which has been used so far as the flame retardant cannot be used. This is because it has no effect of providing the flame retardancy to the crosslinked vinyl chloride resin composition which is crosslinked after molding. Accordingly, antimony is not contained substantially in the vinyl chloride resin composition of the invention and the content is less than 1000 ppm. Since antimony which is the active drug is not added or not contained substantially, this is advantageous for manufacture and use.

[0022]

As the plasticizer, plasticizers known so far can be used with no restriction, and trimellitate plasticizers are used preferably and they include, for example, tris-2-ethylhexyl trimellitate, trinormalalkyl trimellitate, and triisodecyl trimellitate, etc.

The content of the plasticizer is preferably from 20 to 80 parts by weight and, more preferably, 30 to 70 parts by weight based on 100 parts by weight of the vinyl chloride resin. A problem may sometimes occur for the bendability of the electronic wire when the content is less

than 20 parts by weight and external scratch resistance may sometimes be degraded when it exceeds 80 parts by weight.

[0023]

As the non-lead stabilizer, those known so far can be used with no particular restriction and they include, for example, non-lead stabilizers such as barium zinc type, calcium hydroxide type, calcium zinc type, hydrotalcite type, and metal octylate type.

The content of the non-lead stabilizer is preferably 2 parts by weight or more and, more preferably, 3 to 15 parts by weight based on 100 parts by weight for the total of the vinyl chloride resin and the flame retardant (aluminum hydroxide and magnesium hydroxide). The life of products may sometimes be shortened at the content of less than 2 parts by weight,

[0024]

Further, UV-ray absorbents, light stabilizers, lubricants, colorants, fillers, processability improvers, and like other modification agents can be used optionally each alone or in combination of two or more of them.

[0025]

The crosslinked vinyl chloride resin composition of the invention can be obtained by crosslinking after molding as described above.

For the crosslinking method, methods known so far can be used with no particular restriction and methods such as chemical crosslinking, silane crosslinking, or radiation induced crosslinking can be used and, particularly, a method of using electron beams is preferred with a view point of the administration and the cost. Further, as crosslinking aid, trimethylol propane trimethacrylate, dipentaerythritol hexaacrylate, etc. may also be used and they can be added, for example, by 2 to 20 parts by weight based on 100 parts by weight of the vinyl chloride resin. Crosslinking sometimes becomes insufficient when it is less than 2 parts by weight and crosslinking sometimes may occur during molding when it exceeds 20 parts by weight.

The degree of crosslinking is preferably 40 to 65% and, preferably, 49 to 60% in terms of the gel fraction.

[0026]

(2) Insulated electronic wire

In the insulated electronic wire of the invention, a conductor is coated with a vinyl chloride resin composition of the invention.

The vinyl chloride resin composition may be coated directly on a conductor, or may be coated as a sheath material over a usual insulated electronic wire. The insulated electronic wire of the invention can be obtained by coating the composition as an insulating layer or a sheath layer by molding means such as extrusion coating, and then crosslinking the vinyl chloride resin by the method of the electron beam irradiation or the like.

The extrusion coating can be conducted, for example, by kneading a vinyl chloride type resin composition before crosslinking by rolls, a bunbury, or an extruder, and subjecting the obtained pellet compound and a conductor to extrusion molding for electronic wire coating by a known extruder for electronic wires provided with a cross head die.

[0027]

As the conductor to be coated, a conductor having an outer diameter of about 0.15 to 7 mm ϕ , etc. can be used. While a conductor formed by twisting tin-plated annealed copper wires together, etc. can be used suitably, the conductor is not restricted to them.

Further, the insulated electronic wire of the invention has an outer diameter, for example, of 0.4 to 11 mm ϕ and the application use thereof includes wirings for a high temperature portion inside equipments such as driers, rice cookers, transformer lead portions, lighting equipments, and air conditioners.

Example

[0028]

The present invention is to be described more specifically by way of examples and comparative example but the invention is not restricted to such examples.

[0029]

(1) Manufacture of vinyl chloride resin composition before crosslinking

Respective materials shown in Table 1 were blended at the ratios described therein and pelleted by kneading and mixing in an open roll mixer heated at 140°C to obtain a vinyl chloride resin composition before crosslinking.

There were used tris-2-ethylhexyl trimellitate as the plasticizer, a hydrotalcite kneading product as the stabilizer, trimethylol propane trimethacrylate as the crosslinking agent, and stearic acid as the lubricant. Aluminum hydroxide surface treated with stearic acid was used depending on the examples.

[0030]

[Table 1]

	Vinyl chloride resin composition before crosslinking (unit; parts by weight)								
	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comp. Example 1	Comp. Example 2	Comp. Example 3
Vinyl chloride resin	100	100	100	100	100	100	100	100	100
Plasticizer	55	55	55	55	55	55	55	55	55
Antimony trioxide	-	-	-	-	-	-	1	-	-
Aluminum hydroxide	8	15	22	-	-	-	-	5	30
Surface treated aluminum hydroxide	-	-	-	8	15	22	-	-	-
Clay (insulation reinforcement)	10	10	10	10	10	10	10	10	10
Stabilizer	11	11	11	11	11	11	10	10	12
Crosslinker	5	5	5	5	5	5	5	5	5
Lubricant	1	1	1	1	1	1	-	1	1
Ratio of stabilizer	5.8%	5.6%	5.4%	5.8%	5.6%	5.4%	5.5%	5.4%	5.6%

[0031]

(2) Manufacture of insulated electronic wire

A conductor (outer diameter: 0.62 mmφ) comprising twisted tin-plated annealed

copper wires by the number of 12 each of 0.16 mm ϕ outer diameter was used as the conductor. The vinyl chloride resin composition described above was formed by a melt extrusion method over the conductor to obtain specimens (insulated electronic wire) in which the conductor was coated with each of the vinyl chloride resin compositions. The thickness of the insulation layer comprising the vinyl chloride resin composition was 0.49 mm.

Then, the insulation layer was crosslinked by irradiation of electron beams to each of the insulated electronic wires (Examples 1 to 6, Comparative Examples 1 to 3).

[0032]

Evaluation for the following various characteristics on the insulated electronic wires in each of the examples described above is shown in Table 2.

[Flame Retardancy Test]

A vertical flame test was conducted at $n = 5$ specified in the VW-1 test according to UL785 and it was judged as pass where all of five wires were passed and judged as failed where even one of them was failed.

[0033]

[Insulation breakdown value retention rate after aging]

The initial insulation breakdown value was measured and the value was defined as V . Specimens of electronic wires were set at 120°C, 140°C, and 160°C, the time till the insulation breakdown value was lowered to $V/2$ was measured and, based on thereon, an Arrhenius plot was drawn and it was judged as pass where the time till the insulation breakdown value was lowered to $V/2$ at 105°C was 40,000 hr or more and judged as failed for those where the time was less than 40,000 hr.

[0034]

[Tensile elongation retention after aging]

The initial tensile elongation at break was measured and the value was defined as

E. Samples for electronic wires were set at 120°C, 140°C, and 160°C, the time till the tensile elongation at break was lowered to E/2 was measured and, based thereon, an Arrhenius plot was drawn and it was judged as pass where the time till the tensile elongation at break was lowered to E/2 at 105°C was 40,000 hr or more and judged as failed for those where the time was less than 40,000 hr.

[0035]

[Table 2]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comp. Example 1	Comp. Example 2	Comp. Example 3
VW-1 flame retardancy test	pass	pass	pass	pass	pass	pass	failure	failure	pass
Insulation breakdown value retention rate after aging(105°C)	pass	pass	pass	pass	pass	pass	pass	pass	failed
Tensile elongation retention rate after aging	pass	pass	pass	pass	pass	pass	pass	pass	failed

[0036]

It can be seen from Table 2 that insulated electronic wires of the invention (Examples 1 to 6) have well-balanced characteristics in view of the flame retardancy, the insulation breakdown value retention rate, and the tensile elongation retention rate after aging, unlike the comparative examples.

[0037]

While the present invention has been described specifically with reference to specific embodiments, it will be apparent to a person skilled in the art that they can be modified and improved variously without departing the spirit and the scope of the invention.

The present application is based on Japanese Patent application filed on July 24, 2009 (Japanese Patent Application No. 2009-172828), the entire of which is cited herein. Further, all

of references cited herein are incorporated as a whole.

Claims

1. A vinyl chloride resin composition comprising a vinyl chloride resin, aluminum hydroxide and/or magnesium hydroxide, a plasticizer, and a non-lead stabilizer in which

the content of the aluminum hydroxide and/or magnesium hydroxide is 8 to 22 parts by weight based on 100 parts by weight of the content of the vinyl chloride resin,

the content of antimony is less than 1000 ppm, and

the composition is crosslinked after molding.

2. A vinyl chloride resin composition according to claim 1, wherein the aluminum hydroxide and/or magnesium hydroxide is surface treated.

3. An insulated electronic wire in which a conductor is coated with the vinyl chloride resin composition according to claim 1 or 2.