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(54) FLAME-RETARDANT EPOXY RESIN COMPOSITIONS

(71) We, HITACHI LIMITED, a Corporation organised under the laws of Japan of 5-1, 1-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to flame-retardant epoxy resin compositions which can be used in the casting of a fly-back transformer for a television receiver.

A fly-back transformer is produced by the casting of a flame-retardant epoxy resin composition. In the insulation treatment of the fly-back transformer, an epoxy resin flame retarded with a flame retardant such as antimony trioxide or a halogenated organic compound has been used. However, the halogenated organic compound generates harmful hydrogen halides on burning and the antimony trioxide is harmful to human beings. Therefore, epoxy resin compositions flame retarded with these flame retardants give rise to trouble on handling or disposal.

On the other hand, as flame-retardant epoxy resin compositions, there are known (1) from British Patent No. 1,112,139, a composition comprising a polyepoxide containing more than one epoxy group in its molecule and red phosphorus powder, to which a polycarboxylic acid anhydride may be added as curing agent, (2) a composition wherein red phosphorus powder in the above-mentioned composition (1) is replaced by resin-coated red phosphorus powder and (3) a composition comprising a polyepoxide, an amine curing agent, red phosphorus powder and aluminium trihydrate. The said composition (1) comprising 2 to 25 parts by weight of red phosphorus powder per 100 parts by weight of a polyepoxide has a defect in that the red phosphorus ignites on kneading and there is a danger of fire or explosion. Further, a fly-back transformer produced by the casting of said epoxy resin composition flame retarded with red phosphorus shows only inferior flame retardancy in a flame retardancy test on the fly-back transformer (Electric Appliance Control Regulation in Japan). This aspect of may be improved by increasing the amount of the red phosphorus added. However, the increase in the amount of red phosphorus added results in an increase in the viscosity of the flame-retardant epoxy resin composition, deterioration of casting workability and high expense.

In the said composition (2) using resin-coated red phosphorus, there is no danger of the ignition of red phosphorus on kneading. However, the other defects of the composition (1) are not yet obviated.

The said composition (3) improves the flame retardant effect by the use of a combination of red phosphorus powder and aluminium trihydrate powder as

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compared with the use of red phosphorus powder alone or aluminium trihydrate alone. Therefore, the amount of red phosphorus can be decreased, avoiding ignition on kneading. Also, no sedimentation of red phosphorus occurs in contrast with the flame-retardant epoxy resin composition using red phosphorus powder alone. Thus, the defects of the compositions (1) and (2) are obviated in the composition (3).

However, the composition (3) is still unsatisfactory in flame retardancy (Electric Appliance Control Regulations in Japan) and unpractical when applied to the casting of a fly-back transformer.

This aspect may be improved by increasing the amount of red phosphorus and aluminium trihydrate added. However, the increase in the amount added has defects in that the initial viscosity of the resin composition increases, fine gaps in the coil portion of the fly-back transformer are not impregnated, and the pot life of the composition decreases.

As a result of various studies on flame-retardant epoxy resin compositions to obviate the above-mentioned defects it has now been found, in accordance with the present invention, that flame-retardant epoxy resin compositions comprising a polyepoxide, a polycarboxylic acid anhydride curing agent, an imidazole curing accelerator, red phosphorus powder (or preferably red phosphorus powder coated by a thermo-setting resin) and aluminium trihydrate powder, have desirable properties. More particularly, a flame-retardant epoxy resin composition comprising a polyepoxide, a polycarboxylic acid anhydride curing agent, an imidazole curing accelerator, red phosphorus powder and aluminium trihydrate powder is characterized by its lower initial viscosity and its longer pot life (a slower increase in the viscosity of the composition when allowed to stand) as compared with epoxy resin compositions comprising a polyepoxide, an amine curing agent, red phosphorus powder and aluminum trihydrate powder. Further, a flame-retardant epoxy resin composition comprising a polyepoxide, a polycarboxylic acid anhydride curing agent, an imidazole curing accelerator, red phosphorus powder and aluminum trihydrate powder shows a lower initial viscosity and a longer pot life as compared with a flame-retardant epoxy resin composition comprising a polyepoxide, a polycarboxylic acid anhydride curing agent, an imidazole curing accelerator, red phosphorus powder and aluminum trihydrate powder, even if the amount of red phosphorus powder coated by a thermosetting resin and aluminum trihydrate powder in the former composition is identical with the amount of red phosphorus powder and aluminum trihydrate powder in the latter composition. The present invention has been based on these findings.

According to the present invention, there is provided a flame-retardant epoxy resin composition comprising (a) 100 parts by weight of a polyepoxide containing more than one epoxy group in its molecule, (b) 0.8 to 1.2 equivalents of a polycarboxylic acid anhydride curing agent per equivalent of the polyepoxide, (c) 0.5 to 5 parts by weight of an imidazole curing agent per 100 parts by weight of said polyepoxide, (d) aluminum trihydrate powder having an average particle size of 1 to 20 μ and (e) red phosphorus powder and/or red phosphorus powder coated by a thermosetting resin, having an average particle size of 4 to 20 μ , the amount of components (d) and (e) per 100 parts by weight of polyepoxide being within the area obtained graphically by connecting the points A, B, C, D, E, F, G, H and I as described below, wherein the points A, B, C, D, E, F, G, H and I each represent the following compositions:

	Aluminum trihydrate powder (parts by weight)	Red phosphorus powder or red phosphorus powder coated by a thermo-setting resin (parts by weight)
A	72	50
B	83	20
C	103	10
D	160	5
E	220	4
F	198	20
G	178	31
H	154	40
I	112	46

The raw materials used in the present invention will be described in more detail below.

The polyepoxide is preferably in liquid state at 25°C in view of the efficiency of the casting operation of the fly-back transformer. As the polyepoxide, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, polyglycidyl esters of a polycarboxylic acid, such as phthalic acid, terephthalic acid, tetrahydrophthalic acid or hexahydrophthalic acid and polyepoxides obtained by epoxidation of a cyclohexene derivative such as bis(3,4-epoxy-6-methylcyclohexylmethyl) adipate may be used. Here, the above-mentioned polyepoxides may be used alone or in admixture. Also, if necessary, a liquid monoepoxide such as butyl glycidyl ether or phenyl glycidyl ether may be added thereto to reduce their viscosity.

The polycarboxylic acid anhydride curing agent is also preferably in liquid state at room temperature. As the polycarboxylic acid anhydride curing agent, methyltetrahydrophthalic anhydride, methylenedimethylenetetrahydrophthalic anhydride and eutectic mixture of hexahydrophthalic anhydride and phthalic anhydride may be used.

As a curing accelerator usable when an acid anhydride curing agent is used, imidazole compounds, tertiary amine compounds such as tris(dimethylaminomethylphenol) or benzyldimethylamine, ferrocene derivatives, boron trifluoride compounds and piperazine derivatives may be used, but imidazole compounds are most preferable among these compounds and hence are the curing accelerators used in the present invention. The reasons for this are that they give a long pot life (a small change in viscosity with the lapse of time) when mixed with an acid anhydride, that an epoxy resin composition having excellent thermal resistance can be obtained even if a curing temperature is 120°C or less, and that their adhesiveness with magnet wire (a polyurethane layer) used in a fly-back transformer is good and the layer is not changed in quality.

Here, as the imidazole compounds, 2-ethyl-4-methylimidazole, 2-phenylimidazole, 2-methylimidazole, 1-benzyl-2-methylimidazole or 1,2-dimethylimidazole are preferably used.

The average particle size of the aluminum trihydrate powder is essentially 1 to 20 μ , preferably 5 to 15 μ . The average particle size of the red phosphorus powder or red phosphorus powder coated by a thermo-setting resin is essentially 4 to 20 μ , preferably 5 to 15 μ . If the average particle size of aluminum trihydrate powder is less than 1 μ and that of red phosphorus powder or red phosphorus powder coated by thermo-setting resin is less than 4 μ , the viscosity of the resulting resin composition becomes unpractically high. If the average particle size of aluminum trihydrate and that of red phosphorus powder or red phosphorus powder coated by a thermo-setting resin are respectively more than 20 μ , remarkable

sedimentation of aluminum trihydrate powder or red phosphorus powder or red phosphorus powder coated by a thermo-setting resin in the resin composition makes the resin composition impractical.

As for the amount of aluminum trihydrate powder used and the amount of red phosphorus powder and/or red phosphorus powder coated by a thermo-setting resin used, in an epoxy varnish comprising 100 parts by weight of an epoxy resin, an acid anhydride and a curing accelerator, the amounts must be within the area defined by the points A, B, C, D, E, F, G, H, and I in Fig. 1 per 100 parts per weight of a polyepoxide. If a fly-back transformer is produced by the casting of a flame-retardant epoxy resin composition having a composition outside this range, the fly-back transformer thus obtained has unsatisfactory flame retardancy. Also, there is the possibility that the inside of the secondary coil of the fly-back transformer is not satisfactorily impregnated with said epoxy varnish, and voids are easily formed.

Also, the viscosity of a flame-retardant epoxy resin composition having a composition within the above-mentioned range is 2 to 70 poise at 25°C. If the viscosity is lower than 2 poise, the flame retardancy of the resulting fly-back transformer is unsatisfactory. Also, if the viscosity is higher than 70 poise, an unsatisfactorily impregnated fly-back transformer is produced.

The red phosphorus powder used in the present invention may be untreated, but is preferably coated by a thermo-setting resin.

As the resin composition for surface coating, a water-dispersible one is preferable in view of the efficiency of surface coating of red phosphorus powder, and a heat-resistant one is preferable and one having excellent wettability for the epoxy resin composition is preferable in view of the physical properties of the resulting flame-retardant epoxy resin composition. Thus, phenol resin is most suitable.

When a fly-back transformer is produced by casting the above-mentioned flame-retardant epoxy resin composition, the following effects can be obtained:

(a) Since fine gaps in the coil portion of the fly-back transformer can be impregnated with the resin, partial discharge occurs only with difficulty and the life of the transformer becomes long.

(b) The flame-retardancy of the fly-back transformer does not cause trouble in its practical use (Electric Appliance Control Regulation in Japan).

(c) A magnet wire and electrode are not corroded.

(d) Harmful gases or smoke is produced only with difficulty even if the fly-back transformer is damaged.

(e) The fly-back transformer shows a stable output voltage. Thus, even if the fly-back transformer is allowed to stand at a high temperature and a high humidity, a change in high voltage regulation characteristics (a change in output voltage with a change in beam current) is small. This is caused by the change rate of dielectric properties of the flame-retardant epoxy resin compositions according to the present invention.

(f) Even if the fly-back transformer is discarded, there are few problems of environmental pollution.

According to the present invention, a fly-back transformer having these advantages can be produced efficiently.

The flame-retardant epoxy resin compositions according to the present invention have advantages in that (1) they have a lower viscosity and therefore show a longer pot life and better workability on casting as compared with prior art flame-retardant epoxy resin compositions and (2) they are superior in operational safety to the prior art compositions.

Also, if necessary, a coloring agent such as titanium white or red iron oxide, a silane coupling agent, a titanate coupling agent or a silicone defoaming agent, may be added to the flame-retardant epoxy resin compositions according to the present invention. Even if these auxiliary materials are added, the properties of the fly-back transformer are not deteriorated. As the silane coupling agent, for example, γ -glycidioxypropyltrimethoxydilane may be used. It is preferably used in an amount of 0.3 to 2.5 parts by weight, and desirably 0.5 to 1.0 part by weight, per 100 parts by weight of the polyepoxide. If the amount added is less than 0.3 part by weight, the adhesiveness improving effect of the silane coupling agent can not be displayed. Also, if the amount added is more than 2.5 parts by weight, the thermo-setting property and the glass transmission temperature after curing of the resin composition are remarkably reduced.

In the accompanying drawings:—

Fig. 1 shows the amount of red phosphorus powder and/or thermo-setting

resin-coated red phosphorus powder and the amount of aluminum trihydrate powder respectively which can be added to the polyepoxide; Fig. 2 is a sectional view of a fly-back transformer; Fig. 3 is a schematic representation showing a test method for the flame-retardancy of a fly-back transformer; and Fig. 4 shows the change in the viscosity of a flame-retardant epoxy resin composition.

The following Examples serve to illustrate the present invention.

Example 1.

Flame-retardant epoxy resin compositions having the compositions as shown in the "Composition" row of Table 1 were respectively poured into the coil portion of a fly-back transformer as shown in Fig. 2 from above at a temperature of 20 to 30°C and a pressure of 2 to 4 mmHg and then heated to 60°C for 4 hours and at 105°C for 7 hours to obtain a flame-retardant epoxy resin composition cast fly-back transformer.

TABLE 1

Sample No.		1	2	3	4	5	6	7	8	9	10	11	12	13	
Materials, property, etc.	Polyepoxide	Diglycidyl ether of bisphenol A	100	100	—	—	100	100	100	100	100	100	100	100	
		Diglycidyl ester of tetrahydrophthalic acid	—	—	100	100	—	—	—	—	—	—	—	—	—
	Anhydride curing agent	Methyltetrahydrophthalic anhydride	80	—	90	—	—	—	—	—	—	—	—	80	—
		Methylenedimethylenetetrahydrophthalic anhydride	—	80	—	90	80	80	80	80	80	80	80	—	80
	Composition (parts by weight)	Accelerator	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Flame retardant, filler	Aluminum trihydrate powder (average particle size 8μ)	120	120	160	140	72	83	103	220	198	178	154	120	154	
		20	20	15	15	50	20	10	4	20	31	40	20	40	
	Red phosphorus powder (average particle size 6μ)	20	20	15	15	50	20	10	4	20	31	40	20	40	
Silane coupling agent	γ-Glycidoxypropyltrimethoxysilane	—	—	—	—	—	—	—	—	—	—	—	1.0	1.0	
		44	33	34	30	22	24	25	67	72	67	43	44	43	
Viscosity of resin composition at 25°C (poise)															
Conditions for pro- ducing fly- back trans- former	Conditions for pouring resin composition	Temperature: 20 — 30°C Pressure: 2 — 4 mmHg													
	Curing conditions	60°C/4 hour + 105°C/7 hour													

Fig. 2 is a cross sectional view of the fly-back transformer thus obtained. The fly-back transformer can be produced by installing a primary bobbin (5), a secondary bobbin (3), a primary coil (6) and a secondary coil (4) in a case (2), drawing a high voltage lead wire (7) out of the secondary coil (4), and then pouring a resin solution (1) for impregnation and coating.

As shown in Fig. 3, the bottom of the case (2) of the respective flame-retardant epoxy resin composition cast fly-back transformers thus obtained was exposed to the oxidizing flame (9) of a gas burner (8) to carry out a flame retardancy test (Electric Appliance Control Regulation in Japan). As a result, all of the fly-back transformers passed the test and the amount of smoke on burning was all small as shown in the "Properties of fly-back transformer" row of Table 2.

Thereafter, the flame-retardant epoxy resin composition cast fly-back transformers were respectively cut as shown in Fig. 2 and the impregnation of the secondary coil with the flame-retardant epoxy resin compositions and the presence or absence of voids in the coils were observed. As a result, the impregnation was good and no void existed as shown in the "Properties of fly-back transformer" row of Table. 2.

TABLE 2

Properties, etc.		Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Properties of fly-back transformer	Dispersibility of flame retardant and filler (microscopic observation of dispersibility when stirred by a labo stirrer for 30 minutes)		Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
	Amount of phosphine gas generated (10 ⁻⁶ ml per transformer) (the amount generated on curing of the resin, measured by gas chromatography)		25	22	21	21	30	26	22	14	22	30	33	25	33
	Flame retardancy UL94 (thickness 1/16 inch)		V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0	V-0
Properties of resin compo- sition-	Tracking resistance * [C.T.I.] (volts)		600	600	600	600	600	600	600	600	600	600	600	600	600
	Arc resistance ** (seconds)		160	140	180	140	120	120	140	180	180	160	160	160	160
	Flame retardancy (Electric Appliance Control Regulation in Japan)		Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed	Passed
	Amount of smoke generated on burning		Small	Small	Small	Small	Small	Small	Small	Small	Small	Small	Small	Small	Small
	Impregnation ***		0	0	0	0	0	0	0	0	0	0	0	0	0
	Presence of voids in coils ****		0	0	0	0	0	0	0	0	0	0	0	0	0
	High voltage ***** regulation (kV) 60°C, after standing at 95% RH for 1000 hours		1.8	1.8	1.8	1.9	2.0	1.7	1.9	1.8	2.0	1.9	1.7	1.4	1.4

Notes for Table 2.

*: IEC publication 112

**: JIS K-6911

***: The coils were cut and observed microscopically.

O : Good X : Poor

****: The coils were cut and observed microscopically.

O : No void existed X : Voids existed

*****: A change in output voltage when a beam current was changed.

5 Further, the fly-back transformers were allowed to stand at a high temperature (60°C) and a high humidity (95% RH) for 1000 hours and then operated. High voltage regulation was measured by varying a beam current. As a result, it was found that the high voltage regulation was good and showed almost no change as compared with the initial values in all cases as shown in the "Properties of fly-back transformer" row of Table 2. (The initial values for the cast fly-back transformers were all 1.5 kV.) 5

10 Also, the dispersibility of flame retardant and filler which is important in the preparation of flame-retardant epoxy resin compositions was very good in all cases as is clear from the "Dispersibility of flame retardant and filler" row of Table 2. Therefor, special mixing means such as roller kneading were not required. Further, the amount of the phosphine gas generated on curing of the fly-back transformers was measured by gas chromatography. As a result, it was found that the amount of the said harmful gas generated was very small and caused no trouble with regard to safety as shown in the "Amount of phosphine gas generated per transformer" row of Table 2. Further, the flame-retardant epoxy resin compositions having the compositions as shown in the "Composition" row of Table 2 were cured at 60°C for 4 hours and at 105°C for 7 hours and the flame retardancy, tracking resistance and arc resistance of the resin compositions were examined. As a result, it was found that the flame retardancy was V—O, tracking resistance was 600 volts and arc resistance was 120 to 180 seconds. 10

15 The fly-back transformers produced by the casting of these flame-retardant epoxy resin compositions not only operated properly but also maintained their good properties for a long period of time even if they were operated at a severe temperature. 15

20 The flame-retardant epoxy resin compositions (samples Nos. 12 and 13) containing a silane coupling agent show good hygroscopicity and, for example, are superior in high voltage regulation to the resin compositions (samples Nos. 1 to 11) containing no silane coupling agent. 20

25 Although not described in the example, it is possible to blend various additives such as a defoaming agent, a voltage stabilizer, a coloring agent, a surfactant, etc. into the resin compositions. Also, the flame-retardant epoxy resin compositions according to the present invention are also applicable to systems for a fly-back transformer other than the system as shown in Fig. 2 such as fly-back transformers of a plastic film-layer insulation system, small multi-purpose fly-back transformers wherein diodes, resistors, capacitors, etc. are installed, fly-back transformers wherein a case is replaced by a metal mould, insulated fly-back transformers of a dip coat system, etc. 25

40 Example 2. 40

45 Cast fly-back transformers as shown in Fig. 2 were produced with flame-retardant epoxy resin compositions having the compositions as shown in the "Composition" row of Table 3 in the same manner as in Example 1. With regard to the fly-back transformers thus obtained, various tests were carried out in the same manner as in Example 1. The results obtained are shown in Table 4. Also, the flame-retardant epoxy resin compositions having the compositions Nos. 1—11 in Table 3 show an initial viscosity and a change in viscosity during standing as shown 45

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by curve (10) in Fig. 4. Also, the flame-retardant epoxy resin compositions having the compositions Nos. 1—11 in Table 1 show an initial viscosity and a change in viscosity during standing as shown by curve (11) in Fig. 4. Thus, the flame-retardant epoxy compositions in Table 3 are all superior in initial viscosity and a change in viscosity with the lapse of time to the corresponding flame-retardant epoxy resin compositions in Table 1. Therefore, the resin compositions in Table 3 have a longer pot life and better workability on casting as compared with the resin compositions in Table 1.

The flame-retardant epoxy resin compositions (samples Nos. 12 and 13 in Table 3) containing a silane coupling agent show good hygroscopicity and, for example, are superior in high voltage regulations to the resin compositions (samples Nos. 1 to 11 in Table 3) containing no coupling agent.

TABLE 3

Sample No.															
1	2	3	4	5	6	7	8	9	10	11	12	13			
Materials, property, etc.	Diglycidyl ether of bisphenol A	100	100	—	—	100	100	100	100	100	100	100			
	Diglycidyl ester of tetrahydrophthalic acid	—	—	100	100	—	—	—	—	—	—	—			
	Methyltetrahydro- phthalic anhydride	80	—	90	—	—	—	—	—	—	80	—			
	Methylendomethylene- tetrahydrophthalic anhydride	—	80	—	90	80	80	80	80	80	—	80			
	2-Ethyl-4-methyl- imidazole	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0			
Composition (parts by weight)	Flame retardant, filler	120	120	160	140	72	83	103	220	198	178	154	120	154	
	Silane coupling agent	20	20	15	15	50	20	10	4	20	31	40	20	40	
	γ-Glycidloxy- propyltrimethoxy-silane	—	—	—	—	—	—	—	—	—	—	1.0	1.0	1.0	
Viscosity of resin composition at 25°C. (poise)		36	27	28	25	18	20	21	55	60	55	36	35		
Conditions for pro- ducing fly- back trans- former	Conditions for pouring resin composition	Temperature: 20 — 30°C Pressure: 2 — 4 mmHg													
	Curing conditions	60 °C/4 hours + 105°C/7 hours													

(12)

TABLE 4

Properties, etc.	Sample No.	1	2	3	4	5	6	7
Dispersibility of flame retardant and filler (microscopic observation of dispersibility when stirred by a labo stirrer for 30 minutes)		Good	Good	Good	Good	Good	Good	Good
Amount of phosphine gas generated (10^{-6} ml per transformer) (the amount generated on curing of the resin, measured by gas chromatography)		23	20	18	19	28	24	20
Properties of resin composition	Flame retardancy UL94 (thickness 1/16 inch)	V-0	V-0	V-0	V-0	V-0	V-0	V-0
	Tracking resistance * [C.T.I.] (volts)	600	600	600	600	600	600	600
	Arc resistance ** (seconds)	160	140	180	140	120	120	140
Properties of fly-back transformer	Flame retardancy (Electric Appliance Control Regulation in Japan)	Passed	Passed	Passed	Passed	Passed	Passed	Passed
	Amount of smoke generated on burning	Small	Small	Small	Small	Small	Small	Small
	Impregnation ***	0	0	0	0	0	0	0
	Presence of voids in coils ****	0	0	0	0	0	0	0
	High voltage ***** regulation (kV) 60°C, after standing at 95% RH for 1000 hours	1.8	1.8	1.8	1.9	1.9	1.9	1.8

TABLE 4 (Cont'd)

8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good
12	21	29	32	23	32	16	0	30	35	8	28	18	33	18	0	26
V-0	V-0	V-0	V-0	V-0	V-0	V-1	V-0	V-0	V-0	V-2	V-2	V-1	V-0	V-0	V-0	V-0
600	600	600	600	600	600	300	600	600	600	250	250	600	600	600	600	600
180	180	160	160	160	160	100	180	190	160	80	90	100	150	200	130	130
Passed	Passed	Passed	Passed	Passed	Passed	Re-jected	Passed	Passed	Passed	Re-jected	Re-jected	Re-jected	Passed	Passed	Passed	Passed
Small	Small	Small	Small	Small	Small	Medium	Small	Small	Small	Medium	Medium	Small	Small	Small	Large	Small
0	0	0	0	0	0	0	X	X	X	0	0	0	X	X	0	X
0	0	0	0	0	0	0	X	X	X	0	0	0	X	X	0	X
1.9	1.9	2.0	1.9	1.5	1.4	1.9	1.9	2.1	1.7	1.9	2.0	1.7	2.1	2.3	2.0	6.1

Footnotes for Table 4.

*: IEC publication 112

**: JIS K-6911

***: The coils were cut and observed microscopically.

O: Good

X: Poor

****: The coils were cut and observed microscopically.

O: No voids existed

X: Voids existed

*****: A change in output voltage when a beam current was changed.

Comparative Example.

The composition, etc., of epoxy resin compositions as comparative example are shown in Table 5 and their properties are shown in samples Nos. 14—24 of Table 4. The fly-back transformers produced by the casting of the epoxy resin composition Nos. 14, 18 and 19 in Table 5 were unsatisfactory in flame retardancy since the amounts of phenol resin coated red phosphorus powder and aluminum trihydrate powder were small. Also, the fly-back transformers produced by the casting of the epoxy resin compositions Nos. 15, 16 and 17 were satisfactory in flame retardancy since phenol resin-coated red phosphorus powder and aluminum trihydrate powder were blended in a large amount. (See Table 4, the "Properties of fly-back transformer" row, Nos. 14—19). However, the resin compositions Nos. 15, 16 and 17 showed poor fluidity and caused entrainment of air on pouring. Since the entrained air was difficult to detrain, voids remained in the coils as shown in the "Properties of fly-back transformer" row of Table 4. Thus, no fly-back transformer having a long life was able to be obtained.

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TABLE 5

Materials, property, etc			Sample No.											
Composition (parts by weight)	Polyepoxide	Diglycidyl ether of bisphenol A	14	15	16	17	18	19	20	21	22	23	24	
	Anhydride curing agent	Methyltetrahydro- phthalic anhydride	80	80	80	80	80	80	80	80	80	80	—	
	Amine curing agent	Bis(3-methyl-4- aminocyclohexyl)- methane	—	—	—	—	—	—	—	—	—	—	30	
	Accelerator	2-Ethyl-4-methyl- imidazole	1	1	1	1	1	1	1	1	1	1	—	
	Flame retardant, filler	Aluminum trihydrate powder (average particle size 8μ)	80	250	200	150	60	60	90	130	230	120	120	
		Phenol resin-coated red phosphorus powder (average particle size 6μ)	10	—	30	50	6	40	—	—	—	—	20	
		Red phosphorus powder (average particle size 6μ)	—	—	—	—	—	—	10	50	10	—	—	
		Hexabromobenzene	—	—	—	—	—	—	—	—	—	30	—	
	Viscosity of resin composition at 25°C (poise)	Antimony trioxide	—	—	—	—	—	—	—	—	—	—	15	—
			17	80	80	55	22	20	25	45	75	38	60	
		Temperature: 20 — 30°C Pressure: 2 — 4 mmHg												
Conditions for producing fly- back trans- former	Conditions for pouring resin composition	60°C/4 hours + 105°C/7 hours												
	Curing conditions													

The epoxy resin composition having the composition No. 20 in Table 5 was rejected in the flame retardancy test since the contents of red phosphorus powder and aluminum trihydrate powder were low. Also, epoxy resin compositions having the compositions Nos. 21 and 22 in Table 5 showed poor impregnation and the formation of voids in coils since the total amount of red phosphorus and aluminum trihydrate powder was large. (Table 4, Nos. 20, 21 and 22).

In the epoxy resin composition as shown in the "Compositions" row of Table 5, No. 23, flame retardancy is afforded by blending a halogenated organic compound flame retardant and antimony trioxide. The resin composition was not practically preferable in that a large amount of black smoke and harmful gases are generated on burning as shown in the "Amount of smoke generated on burning" row of Table 4. Also, the epoxy resin composition No. 24 in Table 5, which is an example wherein an amine curing agent is used, had defects in that the impregnating property of the fly-back transformer as produced with the resin composition was poor and voids were formed in coils as shown in the "Properties of fly-back transformer" row of Table 4. Also, the epoxy resin composition No. 24 in Table 5 shows an initial viscosity and a change in viscosity during standing as shown by curve 12 in Fig. 4. Further, when the fly-back transformer produced with the epoxy composition was allowed to stand at a high temperature and a high humidity, it showed a variation in high voltage regulation.

As described above, the insulation treatment of fly-back transformer coils with the flame-retardant epoxy resin compositions according to the present invention has the following advantages:

(a) Fine gaps in the coil portion of the fly-back transformer can satisfactorily be impregnated with the resin, and thereby partial discharge occurs with difficulty as compared with prior art resin compositions.

(b) The pot life of the resin is prolonged and thereby workability on the insulation treatment of the fly-back transformer is improved.

(c) The fly-back transformer insulated with the said flame retardant epoxy resin compositions can pass a flame retardancy test (Electric Appliance Control Regulation in Japan).

Additionally, the fly-back transformer insulated with the flame-retardant epoxy resin compositions according to the present invention has an excellent characteristic that its output voltage is stable.

WHAT WE CLAIM IS:—

1. A flame-retardant epoxy resin composition comprising (a) 100 parts by weight of a polyepoxide containing more than one epoxy group in its molecule, (b) 0.8 to 1.2 equivalents of a polycarboxylic acid anhydride curing agent per equivalent of the polyepoxide, (c) 0.5 to 5 parts by weight of an imidazole curing accelerator per 100 parts by weight of said polyepoxide, (d) aluminum trihydrate powder having an average particle size of 1 to 20 μ and (e) red phosphorus powder and/or red phosphorus powder coated by a thermo-setting resin, having an average particle size of 4 to 20 μ , the amounts of components (d) and (e) per 100 parts by weight of polyepoxide being within the area obtained graphically by connecting the points A, B, C, D, E, F, G, H and I as described below, wherein the points A, B, C, D, E, F, G, H and I each represent the following compositions:

The epoxy resin composition having the composition No. 20 in Table 5 was rejected in the flame retardancy test since the contents of red phosphorus powder and aluminum trihydrate powder were low. Also, epoxy resin compositions having the compositions Nos. 21 and 22 in Table 5 showed poor impregnation and the formation of voids in coils since the total amount of red phosphorus and aluminum trihydrate powder was large. (Table 4, Nos. 20, 21 and 22).

In the epoxy resin composition as shown in the "Compositions" row of Table 5, No. 23, flame retardancy is afforded by blending a halogenated organic compound flame retardant and antimony trioxide. The resin composition was not practically preferable in that a large amount of black smoke and harmful gases are generated on burning as shown in the "Amount of smoke generated on burning" row of Table 4. Also, the epoxy resin composition No. 24 in Table 5, which is an example wherein an amine curing agent is used, had defects in that the impregnating property of the fly-back transformer as produced with the resin composition was poor and voids were formed in coils as shown in the "Properties of fly-back transformer" row of Table 4. Also, the epoxy resin composition No. 24 in Table 5 shows an initial viscosity and a change in viscosity during standing as shown by curve 12 in Fig. 4. Further, when the fly-back transformer produced with the epoxy composition was allowed to stand at a high temperature and a high humidity, it showed a variation in high voltage regulation.

As described above, the insulation treatment of fly-back transformer coils with the flame-retardant epoxy resin compositions according to the present invention has the following advantages:

(a) Fine gaps in the coil portion of the fly-back transformer can satisfactorily be impregnated with the resin, and thereby partial discharge occurs with difficulty as compared with prior art resin compositions.

(b) The pot life of the resin is prolonged and thereby workability on the insulation treatment of the fly-back transformer is improved.

(c) The fly-back transformer insulated with the said flame retardant epoxy resin compositions can pass a flame retardancy test (Electric Appliance Control Regulation in Japan).

Additionally, the fly-back transformer insulated with the flame-retardant epoxy resin compositions according to the present invention has an excellent characteristic that its output voltage is stable.

WHAT WE CLAIM IS:—

1. A flame-retardant epoxy resin composition comprising (a) 100 parts by weight of a polyepoxide containing more than one epoxy group in its molecule, (b) 0.8 to 1.2 equivalents of a polycarboxylic acid anhydride curing agent per equivalent of the polyepoxide, (c) 0.5 to 5 parts by weight of an imidazole curing accelerator per 100 parts by weight of said polyepoxide, (d) aluminum trihydrate powder having an average particle size of 1 to 20 μ and (e) red phosphorus powder and/or red phosphorus powder coated by a thermo-setting resin, having an average particle size of 4 to 20 μ , the amounts of components (d) and (e) per 100 parts by weight of polyepoxide being within the area obtained graphically by connecting the points A, B, C, D, E, F, G, H and I as described below, wherein the points A, B, C, D, E, F, G, H and I each represent the following compositions:



* C L M S *

	Aluminum trihydrate powder (parts by weight)	Red phosphorus powder or red phosphorus powder coated by a thermo-setting resin (parts by weight)
A	72	50
B	83	20
C	103	10
D	160	5
E	220	4
F	198	20
G	178	31
H	154	40
I	112	46

2. A composition according to claim 1 wherein component (e) is red phosphorus powder coated by a thermo-setting resin.

3. A composition according to claim 1 or 2 wherein the polyepoxide is a diglycidyl ether of bisphenol A, a diglycidyl ether of bisphenol F, a polyglycidyl ester of a polycarboxylic acid or an epoxidized cyclohexene derivative; the curing agent is methyltetrahydrophthalic anhydride, methylenedimethylenetetrahydrophthalic anhydride or a eutectic mixture of hexahydrophthalic anhydride and phthalic anhydride; the curing accelerator is 2-ethyl-4-methylimidazole, 2-phenylimidazole, 2-methylimidazole, 1-benzyl-2-methylimidazole or 1,2-dimethylimidazole, the aluminum trihydrate powder has an average particle size of 5 to 15 μ , and the red phosphorus powder or red phosphorus powder coated by a thermo-setting resin has an average particle size of 5 to 15 μ .

4. A composition according to claim 3, wherein the polyepoxide is a diglycidyl ether of bisphenol A or diglycidyl tetrahydrophthalate, the curing agent is methyltetrahydrophthalic anhydride or methylenedimethylenetetrahydrophthalic anhydride, the curing accelerator is 2-ethyl-4-methylimidazole, the aluminum trihydrate powder has an average particle size of 8 μ , and the red phosphorus powder or red phosphorus powder coated by a thermosetting resin has an average particle size of 6 μ .

5. A composition according to any one of the preceding claims, wherein 0.3 to 2.5 parts by weight of a silane coupling agent is added to 100 parts by weight of polyepoxide.

6. A composition according to claim 5, wherein the silane coupling agent is γ -glycidioxypropyltrimethoxysilane.

7. A composition according to claim 2 wherein the polyepoxide and curing accelerator are as defined in claim 3 and the curing agent is methyltetrahydrophthalic anhydride or methylenedimethylenetetrahydrophthalic anhydride.

8. A composition according to claim 7 wherein the polyepoxide, curing agent and curing accelerator are as defined in claim 4.

9. A composition according to any one claims 2, 7 and 8 which contains 1.0 parts by weight per 100 parts by weight of polyepoxide of γ -glycidioxypropyltrimethoxysilane.

10. A composition according to claim 1, substantially as herein before described with reference to any one of the Examples.

11. A composition according to claim 2, substantially as hereinbefore described with reference to Samples 12 and 13 of Example 2.

12. A method of insulating a fly-back transformer which comprises embedding the coils of the transformer with a composition as claimed in any one of claims 1, 3 to 6 and 10.



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13. A method of insulating a fly-back transformer which comprises embedding the coils of the transformer with a composition as claimed in any one of claims 2, 7 to 9 and 11.

5 14. A fly-back transformer in which the coils are insulated with a composition as claimed in any one of claims 1, 3 to 6 and 10.

15. A fly-back transformer in which the coils are insulated with a composition as claimed in any one of claims 2, 7 to 9 and 11.

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