

Description

The invention relates to a copper laminated hard paper formed from a flame-resistant moulded laminated plastics material based on a cellulose containing support material and an impregnating lacquer formed from a phenolic resol with additions of plasticisers.

Such moulded laminated plastics materials based on phenolic resol resins, to some extent with epoxide additions or based on cresol-resol resins, which are modified with wood oils, are, in the case of the phenolic resol resin system, produced with phosphoric acid ester as plasticiser in large quantities.

While the mechanical and electrical quality and the flame-resistance of the copper hard papers produced in this way are completely satisfactory, not all requirements with respect to improved ability to be stamped in the cold, reduced tear formation, especially when producing groups of holes for integrated circuits, as well as negligible hole blocking, can yet be met by these systems.

It has been established, upon further investigation of these properties, that the best values with respect to ability to be cold stamped when cold stamping holes with 0.8 mm diameter without hole blocking, whilst simultaneously meeting the standard IEC 249-2-7 FVO, are achieved best of all by resols plasticised when producing resin through addition of wood oil, linseed oil or fatty acids. The production of such resins is, however, comparatively expensive and such resins are not suitable for simple impregnation.

The underlying object of the invention is to

propose a copper laminated hard paper with improved ability to be stamped in the cold and with low necessary stamping force, without hole blocking, whilst realizing physical properties according to IEC 249-2-7 FVO.

This object is achieved in accordance with the invention according to the features set out in the characterising part of claim 1.

According to claim 2, a copper laminated hard paper is preferred, in which case the impregnating lacquer lies within the following ranges of composition:

ammoniacal condensed phenolic resol resin	from 40 to 42,
low molecular phenolic resin	from 8 to 12,
diphenylcresyl phosphate	from 28 to 32,
hexamethylenetetramine	from 1 to 4,
tetrabromobisphenol A	from 3 to 5
and	

from 10 to 20 % by weight of the polyurethane component as a reaction product of polyethylene glycol, polypropylene glycol and p-nonylphenol with toluene-2,4-diisocyanate.

The use of the polyurethane component proposed according to the invention gives the thus modified copper laminated hard papers based on the indicated phenolic resol resin system a superior capacity for being cold stamped. Furthermore, the force, to be applied by the stamping apparatus, relative to a needle, for the withdrawal of the stamping needle from the laminate is likewise considerably reduced. With the copper laminated hard papers built up according to the invention from polyurethane-modified phenolic resol resin systems, the stamping force and the stripping force and the noise development when stamping may be reduced considerably and the life of the stamping

needles may be substantially increased.

The polyurethane component used according to the invention reacts with the described phenolic resol and thus gives rise to an elasticity hitherto unknown for pure phenolic resins which are used in the preparation of laminates. This elasticity was hitherto only known in respect of cresol phenolic resins modified by wood oil, linseed oil or fatty acids. When using such resin types, measures in terms of process technology and environmental measures have to be taken, which measures are not necessary to this extent with use of the proposal according to the invention. It has been shown, however, that the ratios of quantities to be used for the polyurethane component and the construction of the overall system are quite critical with respect to the other technical requirements in respect of a moulded laminated plastics material. In particular, the following demands must be met:

good homogenization of the impregnating lacquer system with the support material for sufficient transparency of the finished laminates, low water absorption lying within the specification, sufficient thermal stability, good layer bonding and stability during storage for the preregs, classification in the fire class according to UL 94 V0, low level of bulging, little shrinkage and sufficient resistance to bending.

In order to achieve these requirements, a series of measures discussed in the following was taken into account. A start was made with an impregnating lacquer based on a phenolic resol resin system according to German Auslegeschrift 2 426 862. In particular, the content of hexamethylenetetramine had to be optimised in order to avoid incompatibility with the polyurethane component used according to the invention as well as with regard to the stability of

the preregs during storage. The proportion of low molecular phenolic resol is determinative for the impregnating effect and accordingly also for the specification of the water absorption and di-electric properties.

Furthermore, the incorporation of epoxy resins for improvement of the thermal stability was taken into account. The addition of epoxy resins does indeed lead again to an increase in the stamping force and stripping force and, furthermore, the preregs with impregnating lacquers, which contained epoxy resins, did not show, in part, already after a storage time for the impregnated papers of 24 hours, sufficient bonding of the individual preregs when pressing was carried out.

The following tables give a summary of these interrelationships and contain an example (No. 1) as well as four comparative examples (Nos. 11, 12, 13, 14).

In Table 1, a composition according to the invention is given as Example 1 in which there is reference, in particular, to the low stamping force of 380 N and the low stripping force of 90 N. Examples 11, 12, 13 and 14 do not come under the compositions claimed according to the invention and are no longer acceptable with regard to the different specifications.

Thus, compared with comparative Example 11, a clear improvement in the stamping force and stripping force is to be noted. Compared with comparative examples 12, 13 and 14 there is, it is true, a comparable stamping force and stripping force, but these compositions do not meet the requirements of the flame class V 0 and with regard to the storage time of the preregs. Moreover, comparative Example 12 is clearly worse with regard to the water absorption and the internal resistance.

The polyurethane of the component E consists of a reaction product of polyethylene glycol,

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polypropylene glycol and p-nonylphenol with toluene-
2,4-diisocyanate.

(17)

Table 1

	Starting materials (proportion of solids)	Unit	Example 1
A)	ammoniacal condensed phenolic resol resin	% by wt.	40
B)	low molecular phenolic resin	"	10
C)	diphenylcresyl phosphate	"	30
D)	epoxy resin, liquid	"	--
E)	polyurethane	"	14
F)	hexamethylenetetramine	"	3
G)	tetrabromobisphenol A	"	3
H)	pentabromodiphenyl ether	"	--
I)	other	"	--
	Proportion of solvent	Unit	
a)	Methanol	%	--
b)	Ethanol	%	--
c)	Acetone	%	25
	Properties	Unit	
1)	general appearance	--	very transparent
2)	transparency (coloured wedge method)	grade	1
3)	layer bonding	"	1
4)	soldering bath 260°C	sec.	30
5)	H ₂ O-absorption	mg	50
6)	internal resistance .10 ¹⁰ according to D96/23	Ω (Ohm)	3
7)	flame class	UL 94	V 0
8)	storage time for prepreg.	days	>180
9)	stamping force	N	380
10)	stripping force	N	90
11)	bending resistance longitudinal	N	145
12)	bending resistance transverse	N	120

Table 2

Comparative Examples				
	11	12	13	14
A)	61	50	39	40.7
B)	--	--	10	10
C)	33	30	30	30
D)	--	5	--	--
E)	--	15	10	10
F)	6	--	--	1
G)	--	--	3	4
H)	--	--	3	--
I)	--	--	5	4.3
a)	20	20	--	--
b)	--	--	--	--
c)	--	--	25	25
1)	clear, homogeneous	very transparent	slightly cloudy	very transparent
2)	2	1	1	1
3)	1	1	1	1
4)	15	30	12	50
5)	45	90	50	40
6)	0.5	0.001	0.9	10
7)	V 0	HB	V 1	V1
8)	>365	1	6	12
9)	500	360	400	360
10)	160	60	100	80
11)	145	100	145	120
12)	125	80	120	100



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Claims:

1. Copper laminated hard paper formed from a flame-resistant moulded laminated plastics material based on a cellulose containing support and an impregnating lacquer formed from a phenolic resol with additions of plasticisers, characterised in that the impregnating lacquer possesses the following composition:

ammoniacal condensed phenolic

resol resin from 35 to 50

low molecular phenolic resin from 0 to 12

diphenylcresyl phosphate from 20 to 35

hexamethylenetetramine from 1 to 6

tetrabromobisphenol A from 0 to 5

pentabromodiphenyl ether from 0 to 3 % by weight
and

from 5 to 20% by weight of a polyurethane component formed from a reaction product of polyethylene glycol-polypropylene glycol and p-nonylphenol with toluene-2,4-diisocyanate with the following composition:

$(-O-CH_2-CH_2-)_m$ from 15 to 20,

$(-O-CH_2-CH(CH_3)-)_n$ from 50 to 60,

toluene-2,4-diisocyanate from 8 to 12,

nonylphenol from 10 to 15 % by weight

2. Copper laminated hard paper according to claim 1, characterised in that the impregnating lacquer contains

ammoniacal condensed phenolic

resol resin from 40 to 42,

low molecular phenolic resin from 8 to 12,

diphenylcresyl phosphate from 28 to 32,

hexamethylenetetramine from 1 to 4,

tetrabromobisphenol A from 3 to 5 % by weight

and

from 10 to 15% by weight of the polyurethane component.