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(54) HARDENERS FOR AMINOPLAST ADHESIVES AND BINDERS

(71) We, PRODUITS CHIMIQUES UGINE KUHLMANN, a French Body Corporate, of 25 boulevard de l'Amiral Bruix 75116 PARIS, France, 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 a hardener for aminoplast adhesives and binders.

It is known according to French Addition Certificate No. 2 200 341 that one can use phthalic acid or anhydride as a hardener for aminoplast adhesives and binders. However, because of the low solubility of these products in water it is necessary to use them dissolved in a solvent.

In French Patent No. 2 268 047 there are described as hardeners for aminoplast resins the monoamides of maleic or fumaric acids. These products have the drawback of needing to be used in a complex and expensive manner.

The hardeners most widely used at the present time with these types of resin are more often than not water-soluble acids or their ammonium salts such as the chloride, bromide, sulphate, phosphate and oxalate. As a result of their reaction with the unstable formaldehyde available in these adhesives or binders they provide the acidity necessary for a cold or hot hardening.

According to the present invention one obtains in a very simple and not expensive manner a hardener for aminoplast resins which offers all the qualities required.

Accordingly, the present invention provides a hardener for an aminoplast resin, the hardener being obtained by neutralising to a pH of from 4.50 to 5.40 an aqueous effluent generated during the manufacture of phthalic anhydride

by the catalytic oxidation of ortho xylene or naphthalene, the density of the effluents being adjusted to a value of from 1.130 to 1.030 at 30°C.

Preferably, the density of the effluents is adjusted to a value of from 1.050 to 1.110 at 30°C.

In the manufacture of phthalic anhydride according to the above-mentioned processes, aqueous effluents are generated at the stripping tower or the tower in which the gases leaving the synthesis reactor are washed with water. The quantity of acids or anhydrides in these aqueous effluents varies and depends on the conditions of operation of the manufacturing plant in question.

Generally speaking the composition (in parts by weight) of these aqueous effluents, per 100 parts by weight of dry organic matter, is as follows:

- Maleic anhydride . . . . .	43 to 90	60
- Fumaric acid . . . . .	0 to 3	
- Citronic acid . . . . .	3 to 7.5	
- Benzoic acid . . . . .	1 to 4.5	
- Phthalic anhydride . . . . .	5.5 to 38	65
- Phthalide . . . . .	0.5 to 4	

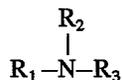
The weight of dry organic matter is determined by heating 3 g of aqueous effluent for 2 hours at 95°C.

In order to obtain the hardeners of the invention, it may be necessary to adjust the density of these aqueous effluents by the addition of water prior to their neutralisation.

For the purpose of their conversion into hardeners for aminoplast adhesives and binders these aqueous effluents are neutralised to a pH of from 4.50 to 5.40, preferably:

- by means of ammonia;
- by one or more amines of the general formula:

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5 in which  $R_1$ ,  $R_2$ ,  $R_3$  represent a hydrogen atom or an optionally substituted alkyl radical containing 1 to 6 carbon atoms and possibly carrying a phenoxy group or an alkoxy group with 1 to 2 carbon atoms,  $R_1$ ,  $R_2$  and/or  $R_3$  being the same or different and at least one of  $R_1$ ,  $R_2$  and  $R_3$  being other than hydrogen; — or by means of a cyclic amine containing 4 or 5 carbon atoms and capable of containing in its molecule an atom of oxygen, sulphur and/or a second nitrogen atom.

15 Examples of suitable amine neutralising agents are monomethylamine, n-butylamine, dimethylamine, methylhexylamine, trimethylamine, piperidine, pyrrolidine and morpholine.

20 However, for economic reasons ammonia remains the most interesting neutralising agent.

The resultant neutralised effluents may be used directly as hardeners for aminoplast binders and adhesives, although it is preferable to filter them so as to eliminate any solid impurities which may be present in the effluent.

25 These hardeners may be prepared continuously or discontinuously. In order to prepare them continuously, it is sufficient to add diluting water and the neutralising agent, preferably in aqueous solution, to the effluents leaving the water scrubbing tower at rates of flow regulated so as to obtain a final solution having the density at 30°C and the pH which are necessary for the purpose of the invention.

35 According to the discontinuous process it is possible, for example, to add successively or simultaneously to the effluents agitated in a reactor equipped with a cooling system the water and neutralising agents in quantities which are sufficient to obtain the specified pH and density at 30°C. Generally speaking, the reaction temperature is maintained below 60°C.

40 The solutions of hardener thus obtained will keep when stored. They remain clear down to a temperature in the vicinity of 0°C. At lower temperatures than this a crystallisation is produced which is easily reversed by simple heating.

45 For convenience of storage it may be advantageous to recover the hardener in the form of a powder. In this case it is sufficient to recover the hardener from the treated effluents by crystallisation, by evaporation to dryness or by any other known means. The powder obtained may easily be made into an aqueous solution at ambient temperatures and possesses the same hardening properties as the aqueous solution of treated effluents.

50 The hardeners of the present invention are obtained in a condition in which they are ready for use. They are generally used at the rate of 1.5 to 15 per cent by weight, reckoned on the

weight of dry matter of the aminoplast resin to be hardened, the dry matter of the aminoplast resin being determined by heating 1 g of commercial aminoplast resin for 2 hours at 120°C.

The hardener of the present invention is particularly suitable for urea/formaldehyde, melamine/formaldehyde, melamine/urea/formaldehyde resins, whether or not modified by the addition of phenol in their preparation.

75 Apart from their excellent qualities as hardeners for aminoplast binders and adhesives, the treated effluents present have the additional advantage that they make use of the residual liquors from the manufacture of phthalic anhydride by the catalytic oxidation of ortho xylene or naphthalene. The disposal of these residual liquors usually poses a problem, since they cannot be discharged into sewers owing to the danger of pollution. They are generally destroyed by evaporation and calcination or else treated chemically or biologically prior to disposal, which results in a loss of products and a comparatively troublesome manipulation.

80 The following Examples illustrate the present invention.

#### EXAMPLE 1

To 36 kg of aqueous effluent coming from the manufacture of phthalic anhydride by the catalytic oxidation of ortho xylene and having the following composition per 100 parts by weight of dry organic matter:

— Maleic anhydride . . . . .	77	
— Citraconic acid . . . . .	5	
— Benzoic acid . . . . .	3	100
— Phthalic anhydride . . . . .	14	
— Phthalide . . . . .	1	

one adds 10 litres of water at 50°C so as to obtain a density at 30°C of 1.087.

The dry extract of this solution is 29.4% and the pH is 1.15.

One then adds at 20°C 8.2 kg of 26% by weight ammonia. The pH of the solution obtained is 5.

The resultant solution after filtration constitutes the hardener I A.

#### EXAMPLE 2

2kg of hardener I A of Example 1 are evaporated to dryness under the following conditions: pressure, 20 mm of mercury—temperature, 70°C. One then obtains 480 g of residue which, after crushing, takes the form of a grey powder; this powder is then dissolved in water at 25°C at the rate of 120 g per 380 g of water. The solution thus obtained has a pH of 4.6 and constitutes the hardener I B.

#### EXAMPLE 3

To 45 kg of aqueous effluent having a density at 30°C of 1.086 and having the following composition per 100 parts by weight of dry organic matter:

— Maleic anhydride . . . . .	62.7	
— Citraconic acid . . . . .	4.1	
— Benzoic acid . . . . .	2.4	
— Phthalic anhydride . . . . .	30	130

— Phthalide . . . . . 0.8  
 one adds 7.9 kg of 26% by weight ammonia.  
 The solution obtained, having a pH of 5.1 and  
 a density at 20°C of 1.085, constitutes the  
 5 hardener II.

**EXAMPLE 4**

To 36 kg of effluent possessing a composition  
 of organic matter identical to that of Example 1,  
 10 one adds 1 litre of water at 50°C. The density of  
 the solution obtained is 1.107 at 30°C.

The dry extract of the solution is 36%. One  
 then carries out a neutralisation with 7.8 kg of  
 26% by weight ammonia and the resultant sol-  
 15 ution is filtered through filter paper.

The final solution, having a pH of 5, consti-  
 tutes the hardener III.

**EXAMPLE 5**

20 One proceeds as in Example 1 with, at the  
 beginning 36 kg of effluents of the same compo-  
 sition as regards organic matter, but replacing  
 the 8.3 kg of 26% by weight ammonia by 9.5  
 kg of 40% by weight monomethylamine in  
 25 water.

The solution obtained, having a pH of 4.6,  
 constitutes the hardener IV.

**EXAMPLE 6**

30 One proceeds as in Example 5, but replacing  
 9.5 kg of monomethylamine by 10.5 kg of  
 morpholine.

The solution obtained, having a pH of 4.6,  
 constitutes the hardener V.

**EXAMPLE 7**

35 One proceeds as in Example 6, but replacing  
 10.5 kg of morpholine by 12.5 kg of diisopropy-  
 lamine. The final solution, having a pH of 4.7,  
 40 constitutes the hardener VI.

**EXAMPLE 8**

45 To 100 parts by weight of a commercial  
 melamine/urea/formaldehyde resin having a dry  
 extract of 65%, one adds successively 18 parts  
 by weight of an aqueous emulsion of paraffin

containing 45% by weight, 7 parts by weight of  
 hardener I A or VI and 1.8 parts by weight of  
 water. The aqueous emulsion of paraffin used is a  
 commercial product prepared from paraffin  
 wax with a melting point of from 55°C to 80°C. 70

One then measures the gelling time at 100°C;  
 this being defined as the time measured from  
 the introduction of 6 g of the above mixture  
 contained in a test tube until the commence-  
 ment of gelling. 75

In the same way one prepares a control  
 adhesive mixture by adding to 100 parts by  
 weight of resin 18 parts by weight of a 45% by  
 weight paraffin wax emulsion, 5.3 parts by  
 weight of a 15% by weight solution of ammo-  
 80 nium chloride, 1 part by weight of concentrated  
 ammonia of 22° Be and 2.5 parts by weight  
 of water.

The gelling times found with the different  
 hardeners are shown in the table below: 85

Gelling time in seconds at 100°C	
Mixture containing the hardener I A . . . . .	68
Mixture containing the hardener VI . . . . .	69
Mixture containing the ammonium chloride . .	70

One projects by spraying 22 parts by weight  
 of one of the adhesive mixtures on to 100 parts  
 by weight of wood chips, a mixture of poplar  
 and birch, containing 6% of water. The chips  
 are then shaped into a mat which is then heated  
 at 162°C under a pressure of 25 daN/cm<sup>2</sup>. The  
 duration of compression is 4 minutes for a  
 thickness of board of 20 mm, that is to say 12  
 105 seconds per mm.

The boards thus manufactured are then sub-  
 jected to the tests of French standard CTB—H.

The results obtained, which are the mean  
 value of 10 tests, are set out in the table below: 110

Mechanical properties of the boards	Mixture containing hardener I A	Mixture containing hardener VI	Mixture containing ammonium chloride
Gross thickness (mm)	19.6	19.5	19.6
Density	0.688	0.687	0.688
55 Transverse tensile strength when dry (kg/cm <sup>2</sup> )	11.5	11.3	10.8
60 Transverse tensile strength after cycle V313 (kg/cm <sup>2</sup> )	6.3	6.2	5.2
Swelling in water at 20°C after 24 hours (%)	2.5	2.7	3
65 Swelling after cycle V313 (%)	3.6	3.8	4.3

It is observed that the results obtained with the hardeners of the present invention are distinctly superior to those obtained from ammonium chloride, particularly after cycle V313.

**EXAMPLE 9**

For each hardener one prepares 2 adhesive mixtures: mixture E is intended for glueing the outer layers of a laminated chip board; mixture I is intended for the inner layer. These adhesive

mixtures are obtained by adding to 100 parts by weight of a commercial melamine/urea/formaldehyde resin having a dry extract of 65% varying quantities, expressed in parts by weight, of paraffin wax emulsion, water, ammonia, hardener IV or V or a 15% by weight aqueous solution of ammonium chloride.

The gelling times are measured.

The compositions of the adhesive mixtures and the gelling times found are set out in the table below:

Adhesive mixture	Hardener IV		Hardener V		Ammonium chloride	
	I	E	I	E	I	E
Melamine/urea/formaldehyde resin	100	100	100	100	100	100
45% by weight paraffin wax emulsion in water	5	5	5	5	5	5
20% by weight ammonia	0	0	0	0	0.3	0.8
Hardener	8	5	8	5	8	5
Water	7	12	7	12	7	12
Gelling time at 100°C, in seconds	90	112	84	105	60	83

3-ply chip boards are manufactured, the external layers being obtained using fine birch chips having a moisture content of 4%, and the inner layer using coarse chips of a mixture of poplar and birch having a moisture content of 4.8%.

The glueing of the chips is carried out by spraying with the selected adhesive mixture, so that the chips used for the outer layers contain 14% by weight of dry binder reckoned on the weight of the dry wood, and the chips for the outer layers contain 12%.

An assembly is formed by superimposing a layer of fine chips, a layer of coarse chips and a layer of glued fine chips so that there is 30%

in 2 x 15% by weight of fine chips to 70% by weight of coarse chips and one obtains after pressing a board having a density of from 0.670 to 0.720.

The assembly is then subjected to a compression of 25 daN/cm<sup>2</sup> at 170°C for 5 minutes and 30 seconds.

The boards thus manufactured are then subjected to the tests of French standards CTB-H and NF B 51 262 of September 1972, the latter relating to the tensile strength after the cycle V100.

The principle results obtained, based on an average of 10 tests, are set out in the table below:

Mechanical properties of the boards	Hardener IV	Hardener V	Ammonium chloride
Gross thickness (mm)	19.59	18.45	18.40
Density	0.692	0.693	0.673
Transverse tensile strength when dry (kg/cm <sup>2</sup> )	10.8	11.1	9.7
Transverse tensile strength after cycle V100 (kg/cm <sup>2</sup> )	2.1	2.1	1.9

	Swelling after cycle V100 (%)	20.5	21	21	
5	Swelling after 24 hrs in water at 20°C (%)	6.0	5.9	6.0	70
	Flexure when dry (kg/cm <sup>2</sup> )	161	161	134	

10 It will be seen that the boards made with the hardeners IV and V satisfy the above-mentioned standards and possesses better mechanical properties than those made with ammonium chloride as hardener. 75

15 **EXAMPLE 10**

On samples of plywood of 10 mm thickness one applies 180 g/m<sup>2</sup> of a mixture of 100 parts by weight of phenol-modified melamine/urea/formaldehyde resin as described in Example 3 of French Patent No. 2 172 841, and 3 parts by weight of a solution of the hardener of Example 1.

20 The samples are subjected to a pressure of 7 kg/cm<sup>2</sup> at 120°C for 12 minutes. The plywoods obtained have a smooth and hard surface without any cracks.

25 By way of comparison, one repeats the above operation by replacing the hardener by 2.1 parts by weight of 2 N formic acid. The surface of the plywood obtained is seen to be covered with countless small cracks.

30 **EXAMPLE 11**

The use of the hardener as described in Example 1 improves the kinetics of hardening of glues.

35 The aim of this Example is to predict

	Hardener	15% by weight solution of ammonium chloride		Hardener of Example 1	
40	% by weight	10	5	10	5
45	Gelling time at 80°C (seconds)	18	13	9	8
	Weight in kg— T° 80°C				
50	1 mm after setting	0.6	0.5	0.8	0.8
	2 mm after setting	0.8	0.7	1.4	1.2
	3 mm after setting	1.0	0.8	1.8	1.3
55	4 mm after setting	1.2	1.1	2.1	1.5
	5 mm after setting	1.5	1.3	2.4	1.7

**EXAMPLE 12**

60 To 100 parts by weight of a commercial urea/formaldehyde glue having a dry matter content of 65% one adds 40 parts by weight of rye flour, 30 parts by weight of water and 10 parts by weight of hardener I A, III, IB or a comparative product, the latter consisting of 30 parts by weight of hexamethylene

whether the glue will or will not lead to pieces coming unstuck on leaving the press, when sticking together structures subjected to very high stresses at the level of the assembly of pieces of wood.

To measure the kinetics of hardening one proceeds in the following manner:

80 — Into a metal container one places 100 g of commercial urea/formaldehyde resin containing 65% of dry matter which is then heated to 80°C. The container is then placed in a thermostatically controlled bath at 80°C and one adds the hardener whilst agitating the glue. As soon as the addition of the hardener is completed, one sets off a stopwatch and measures the gelling time of the adhesive mixture.

85 As soon as this mixture has gelled, one proceeds immediately to measuring the "increase in hardness" the latter being defined as the variation over time of the load placed on the plate of a penetrometer and necessary to cause a rod having a cross-section of 1 mm<sup>2</sup> to penetrate into the hardened resin.

A comparative test was performed using ammonium chloride as hardener.

100 The results are set out in the table below:

tetramine, 50 parts by weight of urea, 20 parts by weight of ammonium chloride and 100 parts by weight of water. The mixture is homogenised and used for the glueing of plywood.

5-ply boards are made using sheets of okume wood with 5% moisture and each of the adhesive mixtures defined above.

65 120

The glueing is carried out by spreading by means of a roller 200 g of one of the adhesive mixtures per square metre of wood sheet. The four outer sheets are coated with adhesive on their respective inner surfaces and the central sheet is not coated with adhesive.

The board is shaped by superimposing the 5 sheets and crossing them in such a way that the grain of two adjacent sheets is at right angles; the whole is subjected to a compression of 25 daN/cm<sup>2</sup> at 110°C for 5 minutes.

One assesses the quality of glueing of the panels thus made by attributing a grade of 0 to 10 according to the appearance of coming unstuck with a knife after the immersion of the test pieces for 72 hours in water at 20°C or after immersion for 3 hours in water at 70°C, followed by an immersion for 24 hours in water at 20°C (test A 70). The grade 0 corresponds to total unsticking in the level of glueing and grade 10 is attributed when the break is produced in the wood ply, the level of glue remaining completely covered by wood fibres.

The results, which are average values for 10 samples, are set out below:

	Adhesive mixture containing the			
	Comparative product	Hardener I A	Hardener I B	Hardener III
Mark after test A70	3.3	4.3	4.1	4.6
Mark after 72 hours of immersion in water at 20°C	4.8	5.2	5.1	5.1

The results show once again the superiority of the hardener of the present invention as compared with the ammonium chloride hardener.

**EXAMPLE 13**

The process of Example 9 for the manufacture of the adhesive mixtures E and I is repeated. One adds to 100 parts of a commercial urea/formaldehyde resin having a dry extract of 67.5%, varying quantities of paraffin wax emulsion, water, ammonia, hardener II, I B, or a 15% by weight solution of ammonium chloride in water.

One measures the gelling time at 100°C. The compositions of the adhesive mixtures and the gelling times found are set out in the table below:

	Adhesive mixture	Hardener II		Hardener I B		Ammonium chloride hardener	
		I	E	I	E	I	E
		67.5% urea/formaldehyde resin	100	100	100	100	100
45%	45% paraffin wax emulsion	5	5	5	5	5	5
50%	20% ammonia	0	0	0	0	0.5	1
	Water	5	10	5	10	5	10
	Hardener	7	3	7	3	7	3
55%	Gelling time at 100°C (seconds)	70	99	68	95	70	110

The process described in Example 9 for the manufacture of 3-ply chip boards is repeated, but using a glueing rate of 11% instead of 14% for the outer layers and 8% instead of 12% for the inner layer. The assembly of layers, is subjected to a compression of 25 daN/cm<sup>2</sup> at 165°C for 4 minutes and 30 seconds instead of 25 daN/cm<sup>2</sup> at 170°C for 5 minutes and 30 seconds.

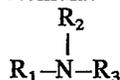
The main mechanical properties of the boards thus obtained, being averages of 10 tests, are set out in the table below:

It is found that the mechanical properties of the boards made with the hardeners of the pre-

	Mechanical properties of the boards	Hardener II	Hardener I B	Ammonium chloride hardener	
5	Gross thickness (mm)	18.73	18.72	18.76	70
	Density	0.657	0.658	0.656	
10	Transverse tensile strength when dry (kg/cm <sup>2</sup> )	7.9	8.0	7.1	75
	Flexure when dry (kg/cm <sup>2</sup> )	135	140	121	
15	Transverse tensile strength after immersion in water at 40°C for 2 hrs 30 mins. (kg/cm <sup>2</sup> )	2.4	2.4	2.2	80
20	Swelling after 24 hrs in water at 20°C (%)	12.8	12.5	12.6	85
	Swelling after 2 hrs 30 mins in water at 40°C (%)	14.7	14.6	14.7	
25	sent invention are superior to those of boards manufactured with ammonium chloride. <b>EXAMPLE 14</b> To 100 parts of a commercial melamine/		then applied on to a chip board and the whole is subjected to a pressure of 15 kg/cm <sup>2</sup> at 150°C for periods of from 70 to 180 seconds.		90
30	formaldehyde resin having a dry matter content of 55%, one adds 1 part of hardener of Example 1 and the mixture is homogenised. Wallpaper weighing 110 g/m <sup>2</sup> is impregnated with the above mixture until one obtains a rate of absorption of the resin of 60% by weight, and it is then dried so as to obtain a residual moisture content of 5 to 7%, determined by heating at 160°C for 5 minutes. This paper after treatment in this way is		By way of comparison, one carries out the same operations as those described above but replacing the catalyst of Example 1 by an equivalent quantity of 15% by weight aqueous solution of formic acid. In both cases one obtains on leaving the press glued materials having a perfectly smooth surface: one then determines the resistance to cracking of these materials after heating at 85°C for 14 hours. The principal results are set out below:		95
35					100
40					105
	<b>Heating test at 85°C</b>	<b>Appearance of surface with hardener of Example 1</b>	<b>Appearance of surface with hardener formic acid</b>		
45	<b>Pressing time</b>	70 secs.	no cracks	no cracks	110
		90 secs.	no cracks	no cracks	
		120 secs.	no cracks	slight cracks	
50		150 secs.	no cracks	numerous cracks	115
		180 secs.	no cracks	numerous cracks	
55	These results show once again the superiority of the hardener of Example 1 over the formic acid hardener. <b>WHAT WE CLAIM IS:</b> 1. A hardener for an aminoplast resin, the hardener being obtained by neutralising to a pH of from 4.50 to 5.40 an aqueous effluent generated during the manufacture of phthalic anhydride by the catalytic oxidation of ortho xylene or naphthalene, the density of the effluent being adjusted to a value of from 1.130 to 1.030 at 30°C.		2. A hardener according to Claim 1, wherein the aqueous effluents from which the hardener is prepared contain per 100 parts by weight of dry organic matter: — 43 to 90 parts of maleic anhydride — 0 to 3 parts of fumaric acid — 3 to 7.5 parts of fumaric acid — 1 to 4.5 parts of benzoic acid — 5.5 to 38 parts of phthalic anhydride — 0.5 to 4 parts of phthalide. 3. A hardener according to Claim 1 or Claim 2, wherein the aqueous effluents from which the		120
60					125
65					130

hardener is prepared are neutralised with ammonia.

4. A hardener according to Claim 1 or Claim 2, wherein the aqueous effluents from which the hardener is prepared are neutralised with an amine of the formula:



- 10 in which  $R_1, R_2, R_3$  represent a hydrogen atom or an optionally substituted alkyl radical containing 1 to 6 carbon atoms,  $R_1, R_2$  and/or  $R_3$  being the same or different and at least one of  $R_1, R_2$  and  $R_3$  being other than hydrogen.

- 15 5. A hardener according to Claim 4, wherein the alkyl radical is substituted by phenoxy groups or alkoxy groups having 1 or 2 carbon atoms.

- 20 6. A hardener according to Claim 1 or Claim 2, wherein the aqueous effluents from which the hardener is prepared are neutralised with a cyclic amine containing 4 or 5 carbon atoms.

- 25 7. A hardener according to Claim 6, wherein the cyclic amine contains in its molecule an atom of oxygen, sulphur and/or a second nitrogen atom.

- 30 8. A hardener for an aminoplast resin according to Claim 1, substantially as described in any one of the foregoing Examples 1 to 7.

- 35 9. A method of preparing a hardener for an aminoplast resin, wherein an aqueous effluent generated during the manufacture of phthalic anhydride by the catalytic oxidation of ortho xylene or naphthalene is neutralised to a pH of from 4.50 to 5.40 and the density of the effluents is adjusted to a value of from 1.130 to 1.030 at 30°C.

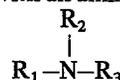
- 40 10. A method according to Claim 9, wherein the aqueous effluents contain per 100 parts by weight of dry organic matter:

- 43 to 90 parts of maleic anhydride
- 0 to 3 parts of fumaric acid
- 3 to 7.5 parts of citraconic acid
- 1 to 4.5 parts of benzoic acid
- 45 — 5.5 to 38 parts of phthalic anhydride
- 0.5 to 4 parts of phthalide

- 50 11. A method according to Claim 9 or Claim 10, wherein the aqueous effluents are neutralised with ammonia.

12. A method according to Claim 9, or Claim 10, wherein the aqueous effluents are

neutralised with an amine of the formula:



in which  $R_1, R_2, R_3$  represent a hydrogen atom or an optionally substituted alkyl radical containing 1 to 6 carbon atoms,  $R_1, R_2$  and/or  $R_3$  being the same or different and at least one of  $R_1, R_2$  and  $R_3$  being other than a hydrogen atom.

13. A method according to Claim 12, wherein the alkyl radical is substituted by phenoxy groups or alkoxy groups having 1 to 2 carbon atoms.

14. A method according to Claim 9 or Claim 10, wherein the aqueous effluents are neutralised with a cyclic amine containing 4 or 5 carbon atoms.

15. A method according to Claim 14, wherein the cyclic amine contains in its molecule an atom of oxygen, sulphur and/or a second nitrogen atom.

16. A method of preparing a hardener for an aminoplast resin, substantially as described in any one of the foregoing Examples 1 to 7.

17. A hardener for an aminoplast resin when prepared by a method as Claimed in any one of Claim 9 to 16.

18. A thermosettable composition including an aminoplast resin and a hardener as claimed in any one of Claims 1 to 8 and 17.

19. A thermosettable composition according to Claim 18, including 1.5 to 15% by weight of hardener solution, based on the weight of dry matter of the aminoplast resin.

20. A thermosettable composition according to Claim 18, substantially as described in any one of the foregoing Examples 8 to 14.

21. A process for the elimination of residual liquors coming from the manufacture of phthalic anhydride by the catalytic oxidation of ortho xylene or naphthalene, characterised by the fact that the liquors are converted into hardeners for aminoplast resin in accordance with any one of Claims 1 to 7.

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