

Description

The present invention relates to a process for the preparation of a cationic aminoplastic resin and its application to water treatment.

5 Aminoplastic resins are well-known and widely used. According to US-A-3,377,274, certain cationic aminoplastic resins such as those described in US-A-2,345,543 and US-A-2,485,079 may be used in the clarification of waters containing small amounts of suspended matter. These re-
10 sins are hydrophilic melamine/formaldehyde or melamine/urea/formaldehyde polymers converted into salt form with an acid. Certain resins with a special composition, such as those described in FR-A-2,257,548 have superior efficiency.

15 In an acidic aqueous medium, these aminoplastic resins in salt form, based on melamine or melamine and urea and formaldehyde, suffer from a mediocre stability which becomes decidedly poor as soon as the storage temperature reaches the ambient temperatures which usually
20 predominate in tropical or equatorial regions. This instability in an acid aqueous medium is well-known and today it forms one of the chief obstacles to their commercial development. Various solutions have been proposed to overcome, more or less partially, this major disadvantage.
25 Thus, US-A-4,182,839 proposes to carry out a partial methylation of the methylol groups in a melamine/formaldehyde resin rendered cationic by condensation with an amino derivative; however, while this modified resin remains highly efficient in the improvement of the strength of paper

in a moist state, it produces no effect, on the other hand, in water treatment, as the comparative examples given hereinafter will demonstrate.

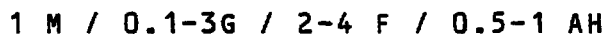
Another solution, taught in US-A-3,645,841, consists in introducing glyoxal or in replacing formaldehyde with glyoxal. These aminotriazine/glyoxal or aminotriazine/glyoxal/formaldehyde resins obtained under pH conditions close to neutrality are incapable of being made water-dispersible; but, when quaternized with dimethyl sulphate, they acquire good solubility in water and become good organic coagulants for waters containing small amounts of suspended or emulsified matter (cf. FR-A-2,424,234). These quaternized aminotriazine/glyoxal or melamine/glyoxal/formaldehyde resins are stable with time at a temperature of 20°C and form efficient coagulants.

It is also known that the condensation of formaldehyde with amino and/or amido groups is catalysed both by acids and by bases. However, to avoid the phenomena of gelling of the condensation medium, the condensation of an aldehyde with a nitrogen derivative is conducted in an alkaline medium and then, when the condensation reaches a certain stage, the condensation is stopped by cooling and dilution with water. When the nitrogen derivative is melamine, and when this dilution is carried out using acidified water, a resin in a cationic form which is dispersible or soluble in this aqueous solution is generally obtained.

The instability in an acidic aqueous medium of the conventional melamine/formaldehyde cationic resins which

are usually employed in water treatment, which in practice very frequently manifests itself as a gradual caking of the resin, is explained by the ability of the methylol groups to form methylene bridges.

5 Now, the Applicant Company has been astonished to find a process for the preparation of water-dispersible cationic aminoplastic resins having excellent properties for application in water treatment, together with remarkable stability with time both at ambient temperature and
10 at higher temperatures in the region of 50°C. These new resins, based on melamine/formaldehyde/glyoxal, are converted into salt form by an inorganic or organic protonic acid or by a mixture of these acids, such as hydrochloric acid, orthophosphoric acid and formic acid. If M denotes
15 melamine, F formaldehyde, G glyoxal, and AH the inorganic or organic acid, the resin according to the invention has the molar composition:



Thus, one mole of melamine corresponds to 0.1 to
20 3 moles of glyoxal, 2 to 4 moles of formaldehyde and 0.5 to 1 mole of inorganic or organic protonic acid or the equivalent quantity of a mixture of these acids. As mentioned earlier, known melamine/formaldehyde/glyoxal resins are not dispersible in an acidic aqueous medium because
25 of an acid hydrolysis which manifests itself as a significant drop in the viscosity of these resins (cf. US-A-3,645,841). Now, the Applicant Company has surprisingly found that, on heating the mixture of the reactants in the molar proportions referred to earlier, it obtains a resin

according to the invention directly and in a single stage, although the reaction is continuously carried out at an acidic pH of between 2 and 5.

Another subject of the present invention is therefore a process for the preparation of these resins.

According to this process, a resin according to the invention is obtained at an acidic pH of between 2 and 5, advantageously between 3 and 3.5 and at a condensation temperature below 100°C, advantageously between 70 and 80°C, by initially mixing all the reactants: melamine, formaldehyde, glyoxal and the inorganic or organic acid or a mixture of these acids, in a quantity of water such that the initial concentration of the reactants is between 20 and 30% by weight, advantageously between 20 and 25% by weight.

The condensation reaction is followed by a viscometric analysis of the reaction medium using a flow viscometer tube with a coefficient K' in the region of $1 \cdot 10^{-3}$. When the viscosity of the reaction medium reaches the value of 35 ± 5 mPa s, as determined at 20°C on a test sample adjusted to a concentration of 20% by weight, the condensation is stopped by cooling and dilution with a quantity of water such that the final resin concentration, expressed in g per 100 g, is between 5 and 20, advantageously between 10 and 15. This final resin concentration is determined by heating 1 g of sample for 1 hour at 140°C.

According to the process of the invention, the reactants are commercial products of technical grade and the

aldehydes: formaldehyde and glyoxal, are used in an aqueous solution, in the form in which they are usually marketed. The inorganic or organic protonic acid is generally chosen from the following acids: hydrochloric acid,
5 orthophosphoric acid, technical formic acid, pure acetic acid, and nitric acid.

The reaction rate depends on the initial concentration of reactants, the pH and the temperature. A reaction rate which is compatible with an economical industrial production is obtained by carrying out the process
10 according to the invention at a pH between 3 and 3.5 with an initial reactant concentration of 20 to 25% by weight and at a temperature of 75-80°C.

The resin according to the invention is in the form of an opalescent aqueous solution with a pH of between 2 and 5, a free glyoxal content, determined by polarography, of less than or equal to 0.1% by weight and a Brookfield viscosity, determined with a model RVT Brookfield viscometer at a speed of 100 revolutions per minute,
15 of 50 $\pm$ 10 mPa s.

The resin according to the invention is stable in storage both at ambient temperature and at 50 $\pm$ 5°C. This stability at 50°C is longer than 3 months. If the change in the Brookfield viscosity of the resin according
25 to the invention is followed as a function of time and at various temperatures, it is seen that this viscosity is stable at ambient temperature and that it rises only very slightly at 50°C. This excellent stability as a function of time and of temperature is probably due to the presence



of glyoxal in the resin. It is found, in fact, that the stability of the resin is proportionately better, the higher the proportion of glyoxal which is employed and combined.

5 It is known to use cationic aminoplastic resins as organic coagulants for waters containing small amounts of suspended, emulsified or dissolved matter. FR-A-2,257,548 teaches that in water treatment with water-soluble melamine/formaldehyde resins the best results are obtained
10 when certain conditions are met in respect of the quantities of formaldehyde and acid which are used. However, the use of these special resins very frequently requires a preliminary determination of the pH of the waters to be treated and, if necessary, its adjustment to a value
15 which is compatible with the type of resin employed, and this presents the disadvantage of adding to the waters to be treated electrolytes which may turn out to be a hindrance when these waters are used. Because of their excellent stability, the resins according to the present invention
20 do not require these laborious operations of determining and adjusting the pH of the waters to be treated; furthermore, when compared to the known aminoplastic resins, they are characterized by better efficiency when used with certain waters such as waters which are rich in
25 dissolved mineral salts, such as, for example, seawater. In addition, when mixed with traditional inorganic coagulants such as aluminium polychloride or ferric chloride, a resin according to the invention develops a complementary effect. A particularly advantageous composition may

consist of a major proportion of the resin according to the invention in water and of 0 to 20% by weight of ferric chloride. It may also be used mixed with traditional organic flocculants such as copolymers derived from

5 acrylamide.

Another subject of the present invention is therefore the application of the resins according to the invention to the treatment of raw waters and waste waters and more especially to raw and waste waters containing small
10 amounts of suspended, emulsified or dissolved matter.

According to this application, the proportion of melamine/formaldehyde/glyoxal resin in salt form may be varied according to the characteristics of the solution, emulsion or suspension to be treated or of the nature or
15 the characteristics of the matter which is present in the latter.

In general, the resin according to the invention is used in dosages, expressed as 100% resin, of between 1 and 500 ppm, preferably 1 to 20 ppm for raw waters and 20
20 to 300 ppm for waste waters. When other products are used together with the resin according to the invention, the proportion of resin may be reduced or increased, depending on the nature and the quantity of these other products.

According to the present invention, it is possible
25 to precipitate or to flocculate quickly not only materials which are dispersed in suspension or emulsion form, but also certain materials dissolved in the waters to be treated. Because of its excellent stability, the resin according to the invention may be used in combination with 0 to

20% by weight of an inorganic or organic acid chosen from hydrochloric, nitric, orthophosphoric, acetic and formic acids, or their mixtures. An advantageous composition for the treatment of certain waters may consist of a combination of a major proportion of a resin according to the invention and a proportion of between 0 and 20% by weight of orthophosphoric acid.

The examples and comparative examples given below describe the present invention in greater detail. They are given by way of illustration and without limiting the invention in any way.

Example 1

A mixture of:

201 g of glyoxal as 40% w/w aqueous solution,
318 g of formaldehyde as 52.4% w/w aqueous solution,
175 g of crystallized melamine,
75 g of 37% w/w hydrochloric acid, and
1,187 g of demineralized water
is heated to 75-80°C.

The condensation is followed by means of flow viscometry analysis. When the viscosity reaches a value of 35 ± 5 mPa s, determined at 20°C and at a dilution of 20% w/w using an Oswald-type (sic) viscometer with a coefficient K' of approximately 0.001,

1,044 g of demineralized water are added and then the reaction mixture is cooled rapidly to 20°C.

In this manner 3 kg of a resin of molar composition M1 / G1 / F4 / HCl 0.55 are obtained, with a viscosity of 50 ± 10 mPa s, determined at 20°C using a model RVT Brookfield viscometer rotating at a speed of 100 revolutions per minute. This resin has a pH = 3, a free glyoxal content of 0.1% w/w as determined by polarography, a solids content of $12.5 \pm 0.5\%$ w/w, as obtained by heating a 1 g sample for 1 h at 140°C and a cationicity of 1.6 meq/g.

Examples 2 to 4

10 By proceeding as in Example 1, but replacing hydrochloric acid by various other acids, the following resins, defined by their molar compositions, are obtained.

M1 / G1 / F4 / HNO₃ 0.6

characteristics of the resin: pH = 3.15

15 Brookfield viscosity, V 100, 20°C = 34 mPa s
cationicity: 1.73 meq/g

solids content (1g/1h/140°C): 12.3% w/w

M1 / G1 / F4 / HCOOH 0.7

characteristics of the resin: pH = 3.5

20 Brookfield viscosity, V 100, 20°C = 29 mPa s
cationicity: 1.44 meq/g

solids content (1g/1h/140°C): 7.3% w/w

M1 / G1 / F4 / H₃PO₄ 0.8

characteristics of the resin: pH = 2.35

25 Brookfield viscosity, V 100, 20°C = 39 mPa s
cationicity: 1.81 meq/g

solids content (1g/1h/140°C): 12.1% w/w

Example 5

Comparative example

A resin A as described in the example of US-A-4,182,839 is prepared. This resin, with a molar composition M1 / F15 / TEA 0.75 / HCl 0.8, where the abbreviation TEA denotes triethanolamine, has a pH of 7.0, a cationicity of 0.83 meq/g and a Brookfield viscosity, V_{100} , determined at 20°C, of 57 mPa s.

Example 6

10 Comparative example

The following mixture is heated at 70-75°C:

45.82 g (0.363 mole) of melamine,

81.82 g (1.36 mole) of formaldehyde as 50% w/w aqueous solution,

15 35.86 g (0.363 mole) of 37% w/w concentrated hydrochloric acid,

503.17 g of distilled water.

When the viscosity of the reaction medium is close to 5 mPa s, as determined with a flow viscometer at 20°C, the reaction mixture is rapidly cooled and is then diluted with 333.33 g of distilled water. In this way 1 kg of resin is obtained, with a solids content of 7.72% w/w (after drying for 1 h at 140°C), a pH of 1.4, a Brookfield viscosity of 20 mPa s, as determined at 20°C at a speed of 20 100 revolutions per minute, and a measured cationicity of 2.30 meq/g. This resin has the following molar composition: M1 / F 3.75 / PCl 1 (sic).

Example 7

A waste water having a chemical oxygen demand, C.O.D., of 510 mg/l, determined in accordance with the AFNOR standard NF T 90-101, is treated with various quantities either of a resin prepared according to Example 1, or of ferric chloride. After the coagulant has been added all at once to the water to be treated, the suspension is stirred at 140 revolutions per minute for 3 min, and then the turbidity of the supernatant is determined after a rest period of 20 min, using a commercial turbidimeter. The measured turbidity is expressed in N.T.U. units, sometimes also referred to as Jackson units.

The following results are obtained as a function of the dosage of coagulant, expressed in ppm of dry product.

Dosage in ppm	Turbidity of the supernatant, expressed in N.T.U. units	
	Resin according to Example 1	Ferric chloride
0	80	80
20	35	
30	17	
60	3	
80	1	
160	0.8	
25	200	30
	260	20
	340	14
	400	10

It is also noted that the size of the aggregates formed with the resin according to Example 1 is much greater than that obtained with ferric chloride.

Example 8

5 Successive tests are carried out to determine the minimum dosage of coagulant to produce a turbidity of 10 NTU when treating a suspension of silica of low particle size (mean diameter $0.2 \mu\text{m}$, Syton W30, registered trademark, marketed by the Monsanto Company) containing 1.08 g/L
10 (turbidity) (sic) of this suspension after 5 min of stirring: 160 NTU) under the following conditions):

preparation of an aqueous solution of coagulant by introducing 10 cm^3 of resin as such into a 100-cm^3 graduated flask and making up to 100 cm^3
15 cm^3 with drinking water,
introducing the dosage of coagulant all at once into 500 cm^3 of test suspension,
Stirring at 50 revolutions per minute for 3 min, then standing at rest for 30 min,
20 careful withdrawal of 25 cm^3 of supernatant and determination of its turbidity using a commercial turbidimeter, and
construction of the turbidity curve as a function of the dosage of coagulant.

25 The following results are obtained by using the resin prepared according to Example 1, which has a solids content of 12.5% w/w:

Dosage of coagulant		Measured turbidity expressed in NTU
Expressed in cm ³ of the dilute solution	Expressed in ppm of dry resin	
2	50	30
2.25	56.2	17
2.5	62.5	9
2.75	68.7	9

- 10 0.245 cm³ of resin prepared according to Example 1, that is 61.2 ppm, is needed to reduce the turbidity of a silica suspension from 160 NTU to 10 NTU.

Example 9

- 15 Treatment of a refinery effluent containing 230 ppm of hydrocarbons.

The residual hydrocarbon content, expressed in ppm, is determined in accordance with the AFNOR standard T 90-203, as a function of time, expressed in minutes, for
20 an aqueous solution containing 230 ppm of hydrocarbons after the addition of 2.5 ppm, expressed on dry basis, of resin according to Example 1.

The following results are obtained at a temperature of 20°C.

Time in		Residual hydrocarbon content,
minutes		expressed in ppm
	0	230
	2.5	200
5	5	170
	7.5	140
	10	110
	12.5	80
	15	50
10	20	30

Example 10

Test of clarification of a synthetic seawater.

A suspension of the "seawater" type is prepared by dispersing in a town water containing 30 g/l of sodium chloride, 4 g/l of anhydrous sodium sulphate and 0.2 g/l of sodium bicarbonate, 2.5 ppm of solica (sic) of small particle size, mean particle diameter: 0.2 μm (Syton W30, registered trademark).

In addition, an acidified resin solution is prepared by adding 80 g of 98% crystallized orthophosphoric acid to 1 litre of resin prepared according to Example 1.

A sample of this suspension is treated with 11.2 ppm of the above solution, and then this sample and an untreated control sample are filtered through a sand filter at a rate of 5 m/h. The corresponding eluates are collected as 200-cm³ fractions and the turbidity of each fraction is then measured with a commercial turbidimeter.

The following results are obtained:

Eluates collected	Turbidity of the eluates expressed in NTU	
	Test	Control test
5 0- 200	0.71	0.95
200- 400	0.74	0.83
400- 600	0.34	0.81
600- 800	0.25	0.81
800-1000	0.20	0.81
10 1000-1200	0.17	0.81
1200-1400	0.16	0.81
1400-1600	0.13	0.81
1600-1800	0.12	0.81

Example 11

15 An aqueous emulsion containing 250 ppm of residual refinery oil is prepared. After a treatment for 1 min using an Ultraturax (registered trademark) apparatus, followed by stirring at 200 revolutions per minute for 1 min and at 45 revolutions per minute for 14 minutes, various

20 samples of this emulsion are treated with various dosages of resins to be tested. The turbidity of the samples is then measured after 5 min of flotation with pressurized water.

The following results are obtained:

Dosage of resin used, expressed in ppm	Measured turbidity, expressed in NTU				
	Resin accord- ing to Example 1	Resin accord- ing to Example 2	Resin accord- ing to Example 3	Resin accord- ing to Example 4	Resin accord- ing to Example 5
5	0.5	65	65	65	65
	1	40	40	36	42
	2.5	14	14	10	14
10	5	7	7	4	8
					92

Example 12

Filtration test

A suspension is prepared, containing 20 g/l of sodium chloride, 5 ppm of silica of small particle size, mean particle diameter: 0.2 μm (Syton W30, registered trademark) and 1 ppm of chlorine.

This suspension has a pH of 7.5 to 8.

This test consists in assessing the efficiency of a coagulant by measuring the percentage removal of particles with a diameter of less than 2 μm after filtration at a rate of 50 m/h through a sand filter 38.5 cm^3 (sic) in cross-section, which has a 1-m filter layer filled with sand of 0.75 mm mean particle size. The particle count is obtained with a Coultronic (registered trademark) apparatus. The number of particles with a diameter of less than 2 μm per cm^3 before treatment and before filtration is $\bar{M} = 8,600$, $\delta = 6,150$ and after filtration

$$\bar{M} = 4,050, \delta = 3,500.$$

The following results are obtained:

Dosage of resin used in ppm	Percentage removal of particles with a diameter of less than 2 μm	
	Resin according to Example 1	Resin, according to Example 2
0.5		
0.75	67%	< 40%
1	93-95%	< 40%
10 1.5	94-97%	< 40%
2		< 40%
3		< 40%

Example 13

Blocking capacity

15 A suspension is prepared, containing 20 g/l of sodium chloride, 2 ppm of silica of small particle size, mean particle diameter: 0.2 μm (Syton W30, registered trademark) and 1 ppm of chlorine. This suspension has a pH of 7.5-8.0 and a turbidity of 1 NTU.

20 This test consists in calculating the blocking capacity of a 0.45 μm , 47 mm diameter Millipore (registered trademark) filter through which the above suspension, treated with various dosages of the coagulant to be tested, is filtered. This is done by measuring with a stopwatch
25 the flow time of 500 cm^3 of this treated suspension at a pressure of 2.1 bars, T_i being the initial measured time expressed in minutes, and then after an operating period

of 15 min during which the treated suspension is filtered through this filter, again measuring with a stopwatch the flow time of 500 cm³ at the same pressure, T_g being the measured time expressed in minutes. The blocking power
5 at a pressure of 2.1 bars is given by the equation.

$$P_{2.1} = 100 (1 - T_i/T_g)$$

and the Fouling Index, FI, is calculated from the relationship

$$FI = P_{2.1}/T \quad (\text{sic})$$

10 where T denotes the time, expressed in minutes, separating the measurement of the times T_i and T_g, that is T = 15.

Dosage of resin used, expressed 15 <u>in ppm</u>	<u>Fouling Index</u>	
	Resin according to Example 1	Resin according to Example 6
0.5		not measurable
1	5.6	not measurable
1 then 0.5		5.6

Claims

20 1. Process for the preparation of water-dispersible cationic aminoplastic resins based on melamine, formaldehyde and glyoxal, characterized in that all the components of the resin are reacted hot, at a temperature below or equal to 100°C, at an acidic pH of between 2 and 5, in
25 molar proportions corresponding to 2 to 4 moles of formaldehyde, 0.1 to 3 moles of glyoxal and 0.5 to 1 mole of inorganic or organic acid or the equivalent quantity of a

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of 15 min during which the treated suspension is filtered through this filter, again measuring with a stopwatch the flow time of 500 cm³ at the same pressure, T_g being the measured time expressed in minutes. The blocking power
5 at a pressure of 2.1 bars is given by the equation.

$$P_{2.1} = 100 (1 - T_i/T_g)$$

and the Fouling Index, FI, is calculated from the relationship

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Dosage of resin used, expressed 15 <u>in ppm</u>	<u>Fouling Index</u>	
	Resin according to Example 1	Resin according to Example 6
0.5		not measurable
1	5.6	not measurable
1 then 0.5		5.6

Claims

- 20 1. Process for the preparation of water-dispersible cationic aminoplastic resins based on melamine, formaldehyde and glyoxal, characterized in that all the components of the resin are reacted hot, at a temperature below or equal to 100°C, at an acidic pH of between 2 and 5, in
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10 where T denotes the time, expressed in minutes, separating the measurement of the times T_i and T_g , that is $T = 15$.

Dosage of resin used, expressed 15 <u>in ppm</u>	<u>Fouling Index</u>	
	Resin according to Example 1	Resin according to Example 6
0.5		not measurable
1	5.6	not measurable
<u>1 then 0.5</u>		<u>5.6</u>

Claims

20 1. Process for the preparation of water-dispersible cationic aminoplastic resins based on melamine, formaldehyde and glyoxal, characterized in that all the components of the resin are reacted hot, at a temperature below or equal to 100°C , at an acidic pH of between 2 and 5, in
25 molar proportions corresponding to 2 to 4 moles of formaldehyde, 0.1 to 3 moles of glyoxal and 0.5 to 1 mole of inorganic or organic acid or the equivalent quantity of a



(40)

mixture of these acids per 1 mole of melamine in a mass of water such that the initial concentration of reactants is between 20 and 30 g per 100 g and that when the condensation has reached a certain stage determined by a value of the viscosity of the reaction mixture of 35 ± 5 mPa s, as determined on a sample which is cooled and diluted to 20 g per 100 g, the reaction is stopped by cooling and dilution with water.

2. Process according to Claim 1, characterized in that 1 mole of melamine, 4 moles of formaldehyde, 1 mole of glyoxal and 0.55 mole of hydrochloric acid are reacted together.

3. Process according to Claim 1, characterized in that 1 mole of melamine, 4 moles of formaldehyde, 1 mole of glyoxal and 0.8 mole of orthophosphoric acid are reacted together.

4. Process according to any one of Claims 1 to 3, characterized in that the inorganic or organic acid is chosen from hydrochloric, nitric, orthophosphoric, acetic and formic acids.

5. Process according to any one of Claims 1 to 4, characterized in that the condensation reaction is advantageously carried out at a pH of between 3 and 3.5.

6. Process according to any one of Claims 1 to 5, characterized in that the condensation is advantageously conducted at a temperature between 75 and 80°C.

7. Application of the resins obtained by the process according to Claim 1 to the treatment of raw waters and waste waters.



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8. Application according to Claim 7, characterized in that the cationic aminoplastic resins are advantageously used for the treatment of raw waters and waste waters containing a small quantity of suspended, emulsified and/or dissolved matter.
9. Application according to Claim 7, characterized in that the cationic aminoplastic resins are used for the treatment of waste waters containing mineral salts, such as seawater.
10. Application according to any one of Claims 7 to 9, characterized in that the cationic aminoplastic resins are used together with an inorganic coagulant or an organic coagulant.
11. Application according to Claim 10, characterized in that the inorganic coagulant is a coagulant based on ferric chloride.
12. Application according to any one of Claims 7 to 11, characterized in that the cationic aminoplastic resins are used for raw waters in dosages of between 1 and 20 ppm.
13. Application according to any one of Claims 7 to 11, characterized in that the cationic aminoplastic resins are used for waste waters in dosages of between 20 and 500 ppm.
14. Application according to any one of Claims 7 to 13, characterized in that an aqueous coagulant composition is used, containing a major proportion of a resin obtained by the process according to Claim 1 and a proportion of between 0 and 20% by weight of an inorganic or organic acid chosen from hydrochloric, nitric, orthosporic (sic),



acetic and formic acids or a mixture of these acids.

15. Application according to Claim 14, characterized in that the acid is orthophosphoric acid.

16. Application according to any one of Claims 7 to 5 13, characterized in that it contains a major proportion of resin according to one of Claims 1 to 3 and a proportion of between 0 and 20% of ferric chloride.

Patentansprüche (as printed)

1. Verfahren zur Herstellung von in Wasser dispergierbaren, kationischen Aminoplastharzen auf Basis von Melamin, Formaldehyd und Glyoxal, dadurch gekennzeichnet, dass man in der Wärme bei einer Temperatur unterhalb von oder gleich 100° C im sauren pH-Bereich zwischen 2 und 5 die Gesamtheit der Bestandteile des Harzes in Molverhältnissen, welche 2 bis 4 Mol Formaldehyd, 0,1 bis 3 Mol Glyoxal und 0,5 bis 1 Mol anorganischer oder organischer Säure oder der äquivalenten Menge einer Mischung dieser Säuren auf 1 Mol Melamin entspricht, in einer solchen Wassermenge reagieren lässt, dass die Anfangskonzentration an Reaktionsteilnehmern zwischen 20 und 30 g auf 100 g liegt, und dass die Reaktion, wenn die Kondensation in einem bestimmten Stadium angelangt ist, das durch einen Viskositätswert des Reaktionsmediums von 35 ± 5 mPa.s, gemessen an einer abgekühlten und auf 20 g pro 100 g verdünnten Probe, bestimmt ist, durch Abkühlung und Verdünnung mit Wasser angehalten wird.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass man die Gesamtheit von 1 Mol Melamin, 4 Mol Formaldehyd, 1 Mol Glyoxal und 0,55 Mol Chlorwasserstoffsäure miteinander reagieren lässt.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass man die Gesamtheit von 1 Mol Melamin, 4 Mol Formaldehyd, 1 Mol Glyoxal und 0,8 Mol Orthophosphorsäure miteinander reagieren lässt.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, dass die anorganische oder organische Säure unter Chlorwasserstoffsäure, Salpetersäure, Orthophosphorsäure, Essigsäure und Ameisensäure ausgewählt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die Kondensationsreaktion vorteilhafterweise bei einem pH-Wert zwischen 3 und 3,5 durchgeführt wird.

6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, dass die Kondensation vorteilhafterweise bei einer Temperatur zwischen 75 und 80° C durchgeführt wird.

7. Anwendung der nach dem Verfahren nach Anspruch 1 erhaltenen Harze zur Behandlung von Rohwässern und Schmutzwässern.

8. Anwendung nach Anspruch 7, dadurch gekennzeichnet, dass die kationischen Aminoplastharze vorteilhafterweise zur Behandlung von Rohwässern und von Schmutzwässern, welche wenig mit suspendierten Materialien beladen sind, in Emulsion und/oder in Lösung verwendet werden.

9. Anwendung nach Anspruch 7, dadurch gekennzeichnet, dass die kationischen Aminoplastharze zur Behandlung von Schmutzwässern, welche mit Mineralsalzen beladen sind, wie Meerwasser, verwendet werden.

10. Anwendung nach einem der Ansprüche 7 bis 9, dadurch gekennzeichnet, dass die kationischen Aminoplastharze zusammen mit einem anorganischen (mineralischen) Koagulieremittel oder einem organischen Koagulieremittel verwendet werden.

11. Anwendung nach Anspruch 10, dadurch gekennzeichnet, dass das anorganische (mineralische) Koagulieremittel ein Koagulieremittel auf Basis von Eisen(III)-chlorid ist.

12. Anwendung nach einem der Ansprüche 7 bis 11, dadurch gekennzeichnet, dass die kationischen Aminoplastharze für Rohwässer in Dosierungsmengen zwischen 1 und 20 ppm verwendet werden.

13. Anwendung nach einem der Ansprüche 7 bis 11, dadurch gekennzeichnet, dass die kationischen Aminoplastharze für Schmutzwässer in Dosierungsmengen zwischen 20 und 500 ppm verwendet werden.

14. Anwendung nach einem der Ansprüche 7 bis 13, dadurch gekennzeichnet, dass eine wässrige Koagulierzusammensetzung eingesetzt wird, welche einen Hauptanteil eines nach dem Verfahren nach Anspruch 1 erhaltenen Harzes und einen Anteil zwischen 0 und 20 Gew.-% einer anorganischen oder organischen Säure, ausgewählt unter Chlorwasserstoffsäure, Salpetersäure, Orthophosphorsäure, Essigsäure und Ameisensäure, oder einer Mischung dieser Säuren, einschliesst.

15. Anwendung nach Anspruch 14, dadurch gekennzeichnet, dass die Säure Orthophosphorsäure ist.

16. Anwendung nach einem der Ansprüche 7 bis 13, dadurch gekennzeichnet, dass sie einen Hauptanteil des Harzes nach einem der Ansprüche 1 bis 3 und einen zwischen 0 und 20% liegenden Anteil von Eisen(III)-chlorid einschliesst.



* C L M S *

Claims (as printed)

1. A process for preparation of aminoplast cationic resins dispersible in water and based on melamine, formaldehyde and glyoxal, characterized by hot reacting at a temperature lower than or equal to 100° C at an acid pH comprised between 2 and 5, all the constituents of the resin in molar proportions corresponding to 2 to 4 moles of formaldehyde, 0.1 to 3 moles of glyoxal and 0.5 to 1 mole of mineral or organic acid, or the equivalent quantity of a mixture of such acids for one mole of melamine in a quantity of water such that the initial concentration of reactives is comprised between 20 and 30 g for 100 g, and when the condensation reached a certain level giving a viscosity value of the reaction medium of 35 ± 5 mPa.s determined on a cooled sample diluted to 20 g for 100 g, the reaction is stopped by cooling down and water dilution.

2. A process according to claim 1, characterized by reacting together one mole of melamine, 4 moles of formaldehyde, one mole of glyoxal and 0.55 mole of hydrochloric acid.

3. A process according to claim 1, characterized by reacting together one mole of melamine, 4 moles of formaldehyde, one mole of glyoxal and 0.8 mole of orthophosphoric acid.

4. A process according to any one of claims 1 to 3, characterized by selecting the mineral or organic acid from hydrochloric, nitric, orthophosphoric, acetic and formic acids.

5. A process according to any one of claims 1 to 4, characterized by realizing the condensation reaction advantageously at a pH comprised between 3 and 3.5.

6. A process according to any one of claims 1 to 5, characterized by carrying out the condensation advantageously at a temperature comprised between 75 and 80° C.

7. The application of the resins obtained by the process according to claim 1 to the treatment of raw waters and residual waters.

8. An application according to claim 7, characterized by using the cationic aminoplast resins

advantageously for treating raw waters and residual waters little loaded with materials in suspension, emulsion and/or solution.

9. An application according to claim 7, characterized by using the cationic aminoplast resins for treating residual waters loaded with mineral salts such as sea water.

10. An application according to any one of claims 7 to 9, characterized by using the cationic aminoplast resins together with a mineral coagulant or an organic coagulant.

11. An application according to claim 10, characterized in that the mineral coagulant is a coagulant based on ferric chloride.

12. An application according to any of claims 7 to 11, characterized by using the cationic aminoplast resins for raw waters at doses comprised between 1 and 20 ppm.

13. An application according to any one of claims 7 to 11, characterized by using the cationic aminoplast resins for residual waters at doses comprised between 20 and 500 ppm.

14. An application according to any one of claims 7 to 13, characterized by utilizing an aqueous coagulant composition comprising a major proportion of a resin obtained by the process according to claim 1, and a proportion comprised between 0 and 20% by weight of a mineral or organic acid selected from hydrochloric, nitric, orthophosphoric, acetic and formic acids, or a mixture of such acids.

15. An application according to claim 14, characterized in that the acid is orthophosphoric acid.

16. An application according to any one of claims 7 to 13, characterized in that it includes a major proportion of resin according to one of claims 1 to 3 and a proportion comprised between 0 and 20% of ferric chloride.

