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(54) Method for the manufacture of amino-formaldehyde resins and resins obtained by this method.

(57) A method for the manufacture of an amino-formaldehyde resin. An amino compound is reacted with formaldehyde or paraformaldehyde in the liquid phase, the latter being ensured by the presence of a reactive modifier in the reaction mixture.

The reactive modifier comprises an amino-formaldehyde resin which is capable of reaction with further monomers and capable of rendering the mixture of reactants liquid at least at the temperature at which the reaction is to be carried out.

An amino-formaldehyde resin obtained by this method.

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Croydon Printing Company Ltd.

TITLE MODIFIED
see front page

TECHNICAL FIELD

This invention relates to the manufacture of resins, and in particular the manufacture of aminoformaldehyde resins.

Amino-formaldehyde resins are manufactured on a large scale and used in moulding powders, foams for cavity wall insulation etc, for adhesives and in textile finishing. The most commonly used amino compounds are urea and melamine and their derivatives.

BACKGROUND ART

The usual commercial method for the manufacture of aminoformaldehyde resins such as urea-formaldehyde or melamine-formaldehyde resins is to react the amino compound and formaldehyde in an aqueous system at a temperature of 60 to 90°C.

The product in such cases will inevitably contain a large amount of water which for many uses has to be removed.

Thus the manufacture of moulding powders from such resins requires a lengthy process in which a large volume of water has to be removed.

We have also found that in the production of foam from urea-formaldehyde resin, as used, for example, for insulation purposes, foams of superior resilience may be produced from resins of low water content as described in our UK Patent Application No.51269/77.

It has been disclosed (US Patent No.1,985,937) that polyhydric alcohols can be reacted with methylol ureas, methyl ethers thereof, or dimethyl thiourea to give a clear viscous solution.

It has been disclosed (US Patent No.1,986,067) that urea can be reacted with a glycol and the product condensed with formaldehyde to give a resinous product.

Finally it has been disclosed (UK Patent 1,107,245) that a polyetherurea can be obtained by reacting formaldehyde with glycol to produce a hemiformal, and then reacting the hemiformal with urea or thiourea.

However, in each of these three prior art disclosures the end product is a material containing a high proportion of glycol which has totally unsatisfactory properties when considered as replacement for modern urea-formaldehyde or melamine-formaldehyde resins.

It has been proposed (UK Patent No. 1,390,370) to make amino-formaldehyde resins by reaction, in the absence of solvent, of urea or thiourea, paraformaldehyde, and hexamethylene tetramine in a molar ratio in the range from 1:1.1:0.01 to 1:25:0.2. This proposal, however, suffers from the difficulty that in the solid phase, reaction control is virtually impossible and a consistently satisfactory end product is not obtained.

The present invention is thus concerned with the problem of providing a process for the preparation of amino-formaldehyde resins of lower water content than by the conventional aqueous system, yet avoiding the difficulties of solid phase reaction.

We propose a solution to this problem in the specification of our co-pending UK Patent Application No 21751/77 in which we describe a method for the manufacture of an amino-formaldehyde resin which comprises reacting an amino compound with formaldehyde or paraformaldehyde at a temperature above 60°C in the liquid phase, the liquid phase being ensured by the presence of a minor proportion of a reactive modifier being a compound capable of taking part in said reaction and also capable of modifying the mixture of reactants to be liquid at the temperature at which the reaction is to be carried out. Examples are given in that specification of the production of low-water content resins using various different compounds as reactive modifiers. The products so made are useful resins, but the reactive modifiers described are compounds which not only modify the reaction system to the liquid phase at the reaction temperature, but also modify the properties of the resulting resin from those of a simple urea-or melamine-formaldehyde resin.

The present invention has as its primary objective the preparation of amino-formaldehyde resin of lower water content than those obtained by the conventional aqueous system, whilst avoiding the need to use compounds which will modify the properties of the resin produced.

DESCRIPTION OF THE INVENTION

According to the present invention a method for the manufacture of an aminoformaldehyde resin comprises reacting an amino compound with formaldehyde or paraformaldehyd in the liquid phase characterized in that said compounds are reacted in the presence of a reactive modifier to ensure said liquid phase, said modifier comprising an aminoformaldehyde resin capable of reaction with further monomers, and which is capable of rendering the mixture of reactants liquid at least at the temperature at which the reaction is to be carried out.

The reaction is preferably carried out at a temperature above 60°C and more preferably in the range 70°C to 115°C.

In carrying out the method of this invention water may be omitted, or if added, the amount of water present in the reaction mixture (excluding water formed in the condensation reaction) is preferably less than 6% by weight of the total mixture.

Although these low water contents in the initial reaction mixture are preferred, low molecular weight liquid resins of low water content are not freely available to use as starting materials at the present time. Thus, we find that a high solids content aqueous solution of a reactant resin (i.e. one capable of reacting with further monomers) can be used successfully as a reactive modifier. The end product when using such a modifier is of lower water content than the products of the usual method of producing such resins. Clearly if desired these products could be used as reactive modifiers in turn, with a correspondingly lower water content in the reaction mixture.

The reactive modifier, i.e. the initial aminoformaldehyde resin; will, when the reaction is completed, form part of the resin produced. The function of the reactive modifier in the method of this invention is to render the reactant mixture a liquid at the temperature of reaction so that the reaction can be carried out in a liquid phase.

The aminoformaldehyde resin used as reactive modifier may be a resin containing the same monomers in the same ratio as the resin being manufactured. However, this need not necessarily be the case and the reactive modifier resin may contain different proportions of monomers, and/or additional or different monomers as desired, provided that it remains capable of carrying out its function as reactive modifier.

Thus the present invention provides a method for manufacturing mixed resins, as well as a means of making aminoformaldehyde resins of low water content.

For example, a urea formaldehyde resin may be produced, using a melamine-formaldehyde resin as the reactive solvent, or vice-versa.

The proportion of the resin used as reactive modifier in the reaction mixture will depend upon the proportion desired, particularly when making a mixed resin, but also will be limited by the extent to which it is capable of liquifying the reaction system. For instance if the reactive modifier is a liquid resin in which the other reactants are highly soluble it need be used in a proportion lower than would be the case if the other reactants were less soluble in it.

In general, however the molar proportion of the resin used as reactive modifier to the total reactants will not be greater than 40% and will preferably be substantially less.

The formaldehyde, e.g. paraformaldehyde and the amino compound are generally added to the reactive modifier separately, whilst warming the mixture, to form the reaction mixture in the desired liquid phase. ThepH of the system during this stage is alkaline. When the three reactants are in the liquid phase the final condensation may be accelerated by acidifying the reaction mixture if this is desirable, but in many cases, particularly when melamine is the amino compound, there is no need to accelerate the reaction in this way.

If the reaction mixture is acidified, the final product is subsequently neutralized or made alkaline before storage.

Other ingredients may be added to the reaction mixture in the normal manner, a particularly useful ingredient when making a urea/formaldehyde resin to be foamed being low molecular weight, partly reacted melamine/formaldehyde resin which improves the film-forming properties of the resin produced.

The invention may be used in conjunction with the method for manufacturing an aminoformaldehyde resin described in our co-pending UK Patent Application No. 21751/77.

EMBODIMENTS OF THE INVENTION

The invention will now be particularly described by means of the following Examples.

Example 1

This example illustrates the preparation of a resin from urea, paraformaldehyde and urea-formaldehyde resin.

The reagent quantities used are detailed in Table 1.

TABLE 1

Reagent	Reagent quantity (g)
UF resin (BU700)	840
Urea (prilled)	1338
91% paraform	923 (includes 83g of H_2O)

This formulation gives a theoretical solids content of 93.0% and an overall urea:formaldehyde molar ratio of 1:1.33.

The preparation of the resin was carried out in a 5 litre split reactor fitted with a stainless steel agitator, a thermometer pocket a reflux condenser and a heating mantle.

The procedure followed in preparing the resin is expressed below in tabular form in Table II.

TABLE II

Time (Mins)	Temperature inside reaction vessel (°C)	Notes
0	R.T.	liquid UF resin charged to reaction vessel. Heating commenced.
40	68	Paraformaldehyde addition begin.
50	88	pH 8 approx. 1/3 of paraform addition completed.

Time (Mins)	Temperature inside reaction vessel (^oC)	Notes
60	86	pH 8 approx 2/3 of paraform addition completed.
70	84	pH 7.5 addition of paraform complete. Reaction mix is low viscosity, almost clear, solution with small particles of solid material suspended in it.
		pH adjusted to 9 with 40% NaOH solution.
100	88	Addition of urea commenced, pH 7.5, heating discontinued.
110	87	1/3 of the urea had been added, the pH was 7 and adjusted to pH8.5 using 40% NaOH.
120	77	2/3 of the urea had been added, the pH was 8, and adjusted to pH 9. Heating was recommenced.
135	70	Urea addition complete, pH was 7.5 and was adjusted to 8.5
145	78	Heating was discontinued and the pH of the mixture was maintained at 8 to 8.5 as exothermic reaction continued.
150	87	-
160	83	-
180	76	-
240	58	-
280	49	The resin was cooled to ambient temperature and a medium viscosity cloudy resin was obtained.

The resin was soluble in water, yielding a cloudy solution.

After standing for 8 days an ambient temperature the resin had set to a firm white paste. This could be dispersed in cold water to yield a milky dispersion of pH 9. It was almost completely soluble in boilding water yielding a faintly opalescent solution containing traces of a gelatinous suspension.

Example 2

This example illustrates the preparation of a resin from urea, paraformaldehyde, urea-formaldehyde resin and melamine formaldehyde resin.

In this case the melamine-formaldehyde resin, paraformaldehyde and urea are dissolved in turn in the U.F. resin under alkaline conditions and then allowed to react under acid conditions.

The reagent quantities used are detailed below in Table III.

Table III

Reagent Quantity	Reagent	Notes
1200 g	U.F. resin in water (76% reactive solids)	The ratio of Urea to formaldehyde in the resin is 1:1.6.
402 g	Melamine-formaldehyde resin BL 35	10% w/w based on other reagents.
1320 g	Paraform (91%)	40 moles F) U/F ratio
1500 g	Urea	25 moles U) = 1:1.6

The U.F. resin was charged to a reaction vessel provided with a heating/cooling jacket and fitted with a stirrer, thermometer and reflux condenser. The pH of the resin was adjusted to 10 with 40% NaOH and heating and stirring commenced.

When the temperature in the vessel had reached 35°C gradual addition of the BL35 M.F. resin was commenced, the total addition taking 15 minutes and the temperature rising to 56°C during that period. The temperature was then increased gradually to 78°C when gradual addition of the paraformaldehyde was commenced. During addition of the paraform, which took 55 minutes, the pH was maintained above 8 by addition of 40% NaOH as necessary (2ml NaOH added together) and the temperature was held at 85 to 90°C.

Gradual addition of urea was then commenced with the heating off, the temperature and pH being held as for the paraform addition, heating and adding 40% NaOH as necessary.

When the urea addition was complete the pH of the mixture was allowed to fall to 6 and 2 ml of Ammonium Sulphamate added, the reaction being continued over the following 45 minutes. During the reaction the temperature was held in the range 85° to 90°C and the pH in the range 5½ to 7 by periodic additions of Ammonium Sulphamate. After the 45 minutes the pH was raised to 8½ by adding 3 ml of NaOH and forced cooling of the reaction vessel was begun.

A hazy resin solution was obtained having a viscosity of 13,360 poise at 24½°C and a low water content.

Example 3

This example illustrates the use of an aqueous solution of a melamine-formaldehyde resin as reactive modifier in the preparation of a melamine formaldehyde resin.

The reagents used are tabulated below in Table IV.

TABLE IV

Reagent	Quantity (g)	Moles
Distilled Water	300	
M.F. Resin (BL 34)*	300	
Paraform (91%)	660	20
Melamine	840	6 2/3rds

* BL 34 resin is a spray-dried Melamine-Formaldehyde resin of M:F ratio 1:2.0, containing 2% free moisture and an SRY solids content of 93%.

(Its usual use is in impregnation of print and overlay papers in laminating)

This formulation gives a total water content of 17% by weight in the reaction mixture.

The procedure followed in preparing the resin is expressed in tabular form below in Table V.

TABLE V

Time (Mins)	Temperature inside reaction vessel (°C)	pH	Notes
0	24		Water charged and heated
15	40		BL 34 resin addition begun
20	42	9	BL 34 addition complete, some undissolved lumps
30	52	9	Paraform addition begun
40	42	8½	Paraform addition complete, Stirrable slurry, temperature increasing
50	85	6	5 ml 70 TW NaOH added raising pH to 9. Clear solution obtained. Melamine addition begun, dissolving readily with exotherm.
100	80	9	Melamine addition complete later additions not yet dissolved, solution opaque, further 6 ml 70 TW NaOH has been required to keep pH above 8
110	84	10	Opaque solution clearing, temperature increased
120	90	9½	Clear resin, some undissolved lumps (insoluble)
125	89	9	Resin run off into bottles and cooled

The resin produced had a viscosity of 22,560 poise at 24°C and an SRY solids content of 77.7%.

Example 4

This example illustrates the preparation of a mixed resin using a Uron resin as reactive modifier and urea and paraform as the other reactants. The reagents used are detailed in Table VI.

TABLE VI

Reagent	Quantity	Moles
Bis(methoxymethyl) uron resin	600 g	
91% Paraform	330 g	= 20 moles formaldehyde
Urea	300 g	10

The bis (methoxymethyl) uron resin is a liquid with a solids content of 95% to 100%.

The procedure followed was as follows. The uron resin was charged to a reaction vessel, stirred and heated. The pH of the resin was 8.5. When the temperature reached 62°C paraform addition was commenced, the temperature being kept in the range 60 to 65°C and the pH at 8.5. The paraform addition was complete after 30 mins, and the mix was maintai at 62 to 64°C for a further 75 mins. The paraform was not completely dissolved. Urea addition was then begun, maintaining the same temperature and pH, and was completed in 60 mins during which time the solids were dissolving giving a white opaque resin. After a further 28 mins the solids were totally dissolved, the pH was 7½ and the resin was opaque. Heating was stopped and the liquid resin gradual cleared.

When cold the resin slowly became a white paste.

Example 5

This example illustrates the preparation of a mixed resin usi a methylated melamine-formaldehyde resin as reactive modifier and urea and paraform as the other reactants.

The reagents used are detailed below in Table VII

TABLE VII

Reagent	Quantity (g)	Moles
Methylated Melamine formaldehyde resin BC309*(90% solids)	800	
Paraform (91%)	440	= 131/3rd moles formaldehyde
Urea	400	6 2/3rd moles

*BC 309 is a liquid resin commercially available from British Industrial Plastics Limited and has a solids content of 90% (SRY solids content 80%).

The procedure followed is given below in tabular form in Table VIII.

TABLE VIII

Time (Mins)	Temperature inside reaction vessel (°C)	pH	Notes
0	22		BC 309 Resin charged, heating and stirring begun
20	62	9	Paraform addition begun Temperature kept at 60 to 65°C
80	63	9	Paraform addition complete not dissolved but mix easily stirrable
130	60	8.5	Paraform still undissolved urea addition begun, keeping the temperature at 60 to 65°C.
170	62	8.5	urea addition complete, solids dissolving, white opaque liquid. Increase temperature

Time (Mins)	Temperature inside reaction vessel (°C)	pH	Notes
195	81	8.5	Solids dissolved, temperature held at 80 to 85°C
205	82		heating stopped, cooling resin
216	77	8.5	Clear resin with dispersed air bubbles. Sample taken for solids determination.
305	38		Resin bottled.

The resin produced was a pasty solid when cold, and had an SRY solids content of 79.8%

It should be noted that the SRY solids content quoted in the above Examples were measured by heating weighed samples of the resins for 3 hours, at 120°C to drive off water of reaction, the residue being regarded as the solids content of the resin. These values should therefore not be confused with the frequently quoted value of resin solids in aqueous solution, in which the non-aqueous content is all taken to be solids, and therefore is generally a very much higher percentage figure.

WHAT WE CLAIM IS

1. A method for the manufacture of an amino-formaldehyde resin which comprises reacting an amino compound with formaldehyde or paraformaldehyde in the liquid phase characterised in that said compounds are reacted in the presence of a reactive modifier to ensure said liquid phase, said modifier comprising an amino-formaldehyde resin capable of reaction with further monomers and capable of rendering the mixture of reactants liquid at least at the temperature at which the reaction is to be carried out.

2. A method according to Claim 1 in which the reaction is carried out at a temperature above 60°C.

3. A method according to Claim 2 in which the reaction is carried out between 70°C and 115°C.

4. A method according to Claim 1, or 2 or 3 in which the reactive modifier is a low molecular weight liquid amino-formaldehyde resin having a water content of less than 10% by weight.

5. A method according to Claim 1, 2 or 3 in which the reactive modifier is an aminoformaldehyde resin capable of reacting with further monomers and in solution in water, the solution having a solids content of at least 50% by weight.

6. A method according to any one of the preceding claims in which the reactive modifier is a resin containing the same monomers in the same ratio as the resin being manufactured.

7. A method according to any one of the preceding claims in which the amino compound to be reacted with formaldehyde or paraformaldehyde is melamine or urea.

8. A method according to any one of the preceding claims in which the reactive modifier is selected from urea formaldehyde resins, melamine formaldehyde resins and methylated melamine formaldehyde resins.

9. A method according to any one of the preceding claims in which the amount of water present in the reaction mixture is less than 6% by weight of the total mixture.

10. A method for the manufacture of an amino-formaldehyde resin substantially as described herein in example 1 or 2.

11. A method for the manufacture of an amino-formaldehyde resin substantially as described herein in example 3, 4 or 5.

12. An amino-formaldehyde resin manufactured by a method as claimed in any one of the preceding claims.

European Patent Office

EUROPEAN SEARCH REPORT

0000096

Application number EP 78 30 0026

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	US - A - 3 308 098 (J.J.NEMES) * Claims; column 3, lines 57-69; examples *	1-12
X	FR - A - 1 484 507 (MONTECATINI) * Abstract *	1-12
X	GB - A - 1 317 774 (B.I.P.) * Claims; page 2, lines 10-56 *	1-12
X	US - A - 2 329 172 (L.SMIDTH) * Claims; page 3, left-hand column, lines 21-60 *	1-12
A	FR - A - 2 062 186 (STAMICARBON) * Claims *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.²)

C 08 G 12/02

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

C 08 G 12/00
C 08 G 12/02
C 08 G 12/04
C 08 G 12/12
C 08 G 12/32

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
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E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	14-09-1978	DERAEDT