653079

P/00/001
Section 29

AUSTRALIA
Patents Act 1990

PATENT REQUEST : STANDARD PATENT

I/We, being the person(s) identified below as the Applicant(s), request the grant of a Standard Patent to the person(s) identified below as the Nominated Person(s), for an invention described in the accompanying complete specification.

Applicant(s) and Nominated Person(s): MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA

Address: LUNGOTEVERE THAON DI REVEL 76
ROME
ITALY

Invention Title: MELAMINIC POLYCONDENSATES

Name(s) of Actual Inventor(s): ROBERTO CIPOLLI; ROBERTO ORIANI
ENRICO MASARATI; GILBERTO NUCIDA

Address for Service: GRIFFITH HACK & CO
509 ST KILDA ROAD
MELBOURNE VIC 3004

Attorney Code: HA

BASIC CONVENTION APPLICATION DETAILS

Application No:	Country:	Application Date:
MI91 A003037	IT	14 November 1991

DATED: 12 November 1992

MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA

GRIFFITH HACK & CO

Patent Attorney for and
on behalf of the Applicant

P/00/008
Section 29(1)
Regulation 3.1(2)

AUSTRALIA
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NOTICE OF ENTITLEMENT

I/We MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA

of LUNGOTEVERE THAON DI REVEL 76
ROME
ITALY

being the applicant(s) in respect of an application for a patent for an invention entitled MELAMINIC POLYCONDENSATES, state the following:

1. The nominated person(s) has/have, for the following reasons, gained entitlement from the actual inventor(s):

   THE NOMINATED PERSON IS THE ASSIGNEE OF THE INVENTORS.

2. The nominated person(s) has/have, for the following reasons, gained entitlement from the basic applicant(s) listed on the patent request:

   THE APPLICANT AND NOMINATED PERSON IS THE BASIC APPLICANT.

3. The basic application(s) listed on the request form is/are the first application(s) made in a Convention country in respect of the invention.

DATE: 12 November 1992

MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA
GRIFFITH HACK & CO

Patent Attorney for and
on behalf of the applicant(s)

AU9228282

(12) PATENT ABRIDGMENT (11) Document No. AU-B-28282/92
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 653079

(54) Title
MELAMINIC POLYCONDENSATES

International Patent Classification(s)
(51)[5] C08G 012/30 C08G 012/10 C08G 012/32

(21) Application No. : 28282/92 (22) Application Date : 12.11.92

(30) Priority Data

(31) Number	(32) Date	(33) Country
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(71) Applicant(s)
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(74) Attorney or Agent
GRIFFITH HACK & CO , GPO Box 1285K, MELBOURNE VIC 3001

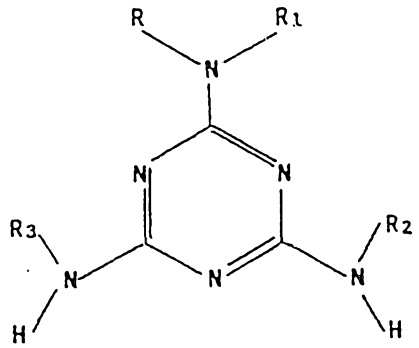
(56) Prior Art Documents
AU 28388/92 C08G 12/32
EP 222330
US 3481903

(57) Claim

1. Aminoplastic resins obtained by means of the polymerisation of a mixture comprising:

(1) from 0 to 50 parts by weight of one or more polyaminic derivatives;

(2) from 50 to 100 parts by weight of one or more derivatives of 2,4,6-triamino-1,3,5-triazine having the general formula (I):



(I)

with formaldehyde or a mixture of formaldehyde and an aldehyde having the general formula (II):

$$R_4-CHO \qquad \text{(II)}$$

.../2

wherein the aldehyde having general formula (II) can be present in an amount of up to 20% by mol, and wherein at least one of radicals from R to R_3 is:

$$-CH_2-(C_mH_{2m})-O-R_5$$

or

$$-CH_2-(C_pH_{2p})-N(R_6)(R_6)$$

wherein:

m = an integer comprised within the range of from 1 to 7;

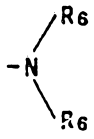
p = an integer comprised within the range of from 1 to 5;

R_5 = H; C_1-C_8 alkyl; C_2-C_6 alkenyl; $-(C_qH_{2q})-O-R_7$ wherein q is an integer comprised within the range of from 1 to 4 and R_7 is H or C_1-C_4 alkyl; C_6-C_{12} cycloalkyl or alkylcycloalkyl;

the radicals R_6, which may be the same or different from each other, are:

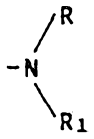
H; C_1-C_8 alkyl; C_2-C_6 alkenyl; C_6-C_{12} cycloalkyl or alkylcycloalkyl; C_1-C_4 hydroxyalkyl;

or the moiety:



is replaced by a heterocyclic radical linked to the alkyl chain through the nitrogen atom, and possibly containing another heteroatom;

or in the general formula (I) the moiety:



is replaced by a heterocyclic radical linked to the triazinic ring through the nitrogen atom, and possibly containing another heteroatom;

the other radicals from R to R_3, which may be the same or different from one another, have the above said meaning, or they are:

H; C_1-C_{18} alkyl; C_2-C_8 alkenyl; C_6-C_{16} cycloalkyl or alkylcycloalkyl, possibly substituted with a hydroxy or C_1-C_4 hydroxyalkyl function.

R_4 is C_1-C_8 alkyl; C_2-C_6 alkenyl; C_6-C_{12} cycloalkyl; C_6-C_{12} aryl, possibly substituded with one or more C_1-C_4 alkyl radicals; aralkyl C_7-C_{16}; aralkenyl C_8-C_{12}.

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AUSTRALIA

Patents Act 1990

COMPLETE SPECIFICATION

STANDARD PATENT

Applicant(s):

MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA

Invention Title:

MELAMINIC POLYCONDENSATES

The following statement is a full description of this invention, including the best method of performing it known to me/us:

CASE MU 4287

"MELAMINIC POLYCONDENSATES"

The present invention relates to compounds obtained by means of polycondensation of polyaminic compositions, essentially constituted by melaminic derivatives, with aldehydes.

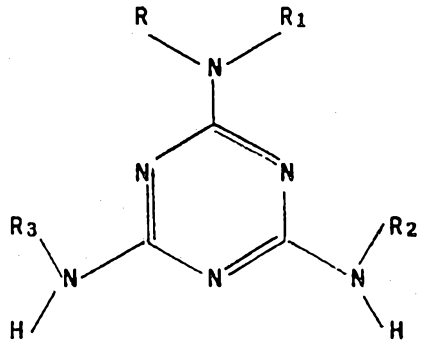
More particularly, the present invention relates to compounds of condensation with aldehydes, preferably formaldehyde, of derivatives of 2,4,6-triamino-1,3,5-triazine.

These compounds are used in the preparation of self-extinguishing polymeric compositions, based on thermoplastic polymers, or polymers endowed with elastomeric properties, in particular olefinic polymers or copolymers, in combination with ammonium or amine phosphates and/or phosphonates.

In particular, the subject matter of the present invention are the aminoplastic resins obtained by means of the polymerisation of a mixture comprising:

(1) from 0 to 50 parts by weight of one or more polyaminic derivatives;

(2) from 50 to 100 parts by weight of one or more derivatives of 2,4,6-triamino-1,3,5-triazine having the general formula (I):



(I)

with formaldehyde or a mixture of formaldehyde and an aldehyde having the general formula (II):

$$R_4-CHO \qquad (II)$$

wherein the aldehyde having the general formula (II) can be present in an amount of up to 20% by mol, and wherein at least one of radicals from R to R_3 is:

$$-CH_2\{C_mH_{2m}\}O-R_5$$

or

$$-CH_2\{C_pH_{2p}\}N\begin{matrix}R_6\\R_6\end{matrix}$$

wherein:

m = an integer comprised within the range of from 1 to 7;

p = an integer comprised within the range of from 1 to 5;

R_5 = H; C_1-C_8 alkyl; C_2-C_6 alkenyl; $-\{C_qH_{2q}\}-O-R_7$ wherein q is an integer comprised within the range of from 1 to 4 and R_7 is H or C_1-C_4 alkyl; C_6-C_{12} cycloalkyl or alkylcycloalkyl;

the radicals R_6, which may be the same or different from each other, are:

H; C_1-C_8 alkyl; C_2-C_6 alkenyl; C_6-C_{12} cycloalkyl or alkylcycloalkyl; C_1-C_4 hydroxyalkyl;

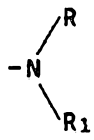
or the moiety:

$$-N\begin{matrix}R_6\\R_6\end{matrix}$$

is replaced by a heterocyclic radical linked to the alkyl chain through the nitrogen atom, and

possibly containing another heteroatom preferably selected from O, S, N;

or in the general formula (I) the moiety:



is replaced by a heterocyclic radical linked to the triazinic ring through the nitrogen atom, and possibly containing another heteroatom preferably selected from O, S, N;

the other radicals from R to R_3, which may be the same or different from one another, have the above said meaning, or they are:

H; C_1-C_{18} alkyl; C_2-C_8 alkenyl; C_6-C_{16} cycloalkyl or alkylcycloalkyl, possibily substituted with a hydroxy or C_1-C_4 hydroxyalkyl function.

R_4 is C_1-C_8 alkyl; C_2-C_6 alkenyl; C_6-C_{12} cycloalkyl; C_6-C_{12} aryl, possibly substituted with one or more C_1-C_4 alkyl radicals; aralkyl C_7-C_{16}; aralkenyl C_8-C_{12}.

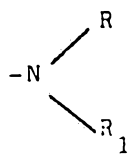
According to a preferred form of practical embodiment of the aminoplastic resins according to the present invention, the polyaminic derivative is selected from compounds containing the 1,3,5-triazine ring, or at least one moiety $\diagdown C{=}O$ and/or $\diagdown C{=}S$.

Examples of radicals from R to R_3 in general formula (I) are:

methyl; ethyl; propyl; isopropyl; n-butyl; isobutyl; tert-butyl; n-pentyl; isopentyl; n-hexyl; tert-hexyl;

octyl; tert -octyl; decyl; dodecyl; octadecyl; ethenyl; propenyl; butenyl; isobutenyl; hexenyl; octenyl; cyclohexyl; propylcyclohexyl; butylcyclohexyl; decylcyclohexyl; hydroxycyclohexyl; hydroxyethylcyclohexyl; 2-hydroxyethyl; 2-hydroxypropyl; 3-hydroxypropyl; 3-hydroxybutyl; 4-hydroxybutyl; 3-hydroxypentyl; 5-hydroxypentyl; 6-hydroxyhexyl; 3-hydroxy-2,5-dimethylhexyl; 7-hydroxyheptyl; 7-hydroxyoctyl; 2-methoxyethyl; 2-methoxypropyl; 3-methoxypropyl; 4-methoxybutyl; 6-methoxyhexyl; 7-methoxyheptyl; 7-methoxyoctyl; 2-ethoxyethyl; 3-ethoxypropyl; 4-ethoxybutyl; 3-propoxypropyl; 3-butoxypropyl; 4-butoxybutyl; 4-isobutoxybutyl; 5-propoxypentyl; 2-cyclohexyloxyethyl; 2-ethenyloxyethyl; 2-(N,N-dimethylamino) ethyl; 3-(N,N-dimethylamino) propyl; 4-(N,N-dimethylamino) butyl; 5-(N,N-dimethylamino) pentyl; 4-(N,N-diethylamino) butyl; 5-(N,N-diethylamino) pentyl; 5-(N,N-diisopropylamino) pentyl; 3-(N-ethylamino) propyl; 4-(N-methylamino) butyl; 4-(N,N-dipropylamino) butyl; 2-(N,N-diisopropylamino) ethyl; 6-(N-hexenylamino) hexyl; 2-(N-ethenylamino) ethyl; 2-(N-cyclohexylamino) ethyl; 2-(N-2-hydroxyethylamino) ethyl; 2-(2-hydroxyethoxy) ethyl; 2-(2-methoxyethoxy) ethyl; 6-(N-propylamino) hexyl; and so forth.

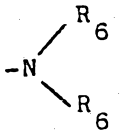
Examples of heterocyclic radicals which may replace the moiety:



in general formula (I) are:

aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4-methylpiperazine; 4-ethylpiperazine; 2-methylpiperazine; 2,5-dimethylpiperazine; 2,3,5,6-tetramethylpiperazine; 2,2,5,5-tetramethylpiperazine; 2-ethylpiperazine; 2,5-diethylpiperazine; and so forth.

Examples of heterocyclic radicals which may replace the moiety:



are:

aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4-methylpiperazine; 4-ethylpiperazine; and so forth.

By "formaldehyde", as this term is used in the instant disclosure and in the appended claims, any forms are meant, in which formaldehyde is usually marketed: aqueous solution, metaformaldehyde, paraformaldehyde.

Examples of R_4 radical in general formula (II) are:

methyl; ethyl; n-propyl; isopropyl; n-butyl; isobutyl; tert -butyl; n-pentyl; isopentyl; n-hexyl; n-eptyl; isoeptyl; n-octyl; ethenyl; propenyl; isobutenyl; sec - butenyl; n-pentenyl; cyclohexyl; phenyl; 2-methylphenyl; 3-methylphenyl; 4-methylphenyl; 4-isopropylphenyl; 2,4,6-trimethylphenyl; 1-phenylethyl; 2-phenylethyl; 2-phenylethenyl; and so forth.

"Polyaminic derivative" means a compound having more than one amine radical, for example: urea; ethyleneurea; thiourea; ethylenethiourea; propyleneurea; melamine; acetoguanamine; propionoguanamine, butyroguanamine; isobutyroguanamine; caprinoguanamine; succinoguanamine; benzoguanamine; metamethylbenzoguanamine; benzylguanamine; hydantoin; piperazine-2,5-dione; barbituric acid; and so forth.

In a preferred embodiment, the aminoplastic resins according to the present invention can be synthetized as follows:

(a) by reacting in a suitable solvent (such as, e.g., water, methyl alcohol, ethyl alcohol, or their mixtures, and so forth), the derivative of 2,4,6-triamino-1,3,5-triazine having the general formula (I), either mixed or not mixed with the polyaminic derivative, with formaldehyde or a mixture of formaldehyde and an aldehyde of general formula (II). The molar ratio of the derivative of general formula (I), or of its mixture with the polyaminic derivative, to formaldehyde, or to the mixture of formaldehyde with the aldehyde of general formula (II), is comprised within the range of from 1:1 to 1:6. The reaction is carried out at a pH value comprised within the range of from 7 to 12, possibly obtained by adding an alkali (such as, for example, potassium carbonate, sodium carbonate, sodium hydroxide, and so forth), at temperatures comprised within the range of from 20°C to solvent boiling point, until a solution is obtained;

(b) causing the resulting reaction product, constituted

by the alkylol derivative, to turn into a resin by feeding it to a mixture of the same solvent, acidified at a pH value comprised within the range of from 1 to 5, by means of the addition of an acid (such as, e.g., sulfuric acid, hydrochloric acid, phosphoric acid, and so forth) and heated at a temperature comprised within the range of from 40°C to the boiling point of the solvent. The resin is formed as a white, finely subdivided solid material. The resulting dispersion is kept further stirred at the selected temperature, during the necessary time to complete the polymerization process, preferably of from 1 to 12 hours. The acidity of the resulting mixture is then neutralized with a base selected from those suggested hereinabove, and the resulting product is filtered off.

The resin is first dried at 100°C, then is submitted to thermal treatment for some hours, preferably of from 1 to 3 hours, in a vacuum oven at 150°C.

In general good quality aminoplastic resins are obtained as white crystalline powders, which are insoluble in water and can be used in self-extinguishing polymeric compositions without further purification.

An alternative synthesis method consists in causing the reactions of the above (a) and (b) steps to take place in one single step, at a pH value comprised within the range of from 1 to 5, and at higher

temperature than 40°C.

Many of derivatives of 2,4,6-triamino-1,3,5-triazine of general formula (I) are known; they can anyway be easily synthetized according to as disclosed in European Patent application publication No. 406,810, to the same Applicant's name.

Condensation compounds obtained by means of the polymerization with aldehydes, preferably formaldehyde, of the melaminic derivatives of general formula (I), either containing or not containing polyaminic derivatives, not cited in the examples, are those reported in table 1.

TABLE 1

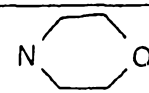
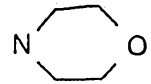
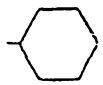
COMPOUND N°	Derivative of General Formula (I)			Polyaminic derivative		R_4-CHO		molar ratio polyamines / aldehydes
	R — N — R_1	R_2	R_3	Designation	% by weight	R_4	Mol %	
1		H	H	—		—		1:6
2	$CH_2CH_2OCH_3$ H	H	H	Benzoguanamine	30	—		1:3
3	$(CH_2)_5OH$ H	H	H	—		—		1:5
4		H	H	—		n-C_3H_7	10	1:1.5
5		H	H	Acetoguanamine	25	—		1:2.5
6	$(CH_2)_2OH$ 	H	H	—		—		1:2
7	$(CH_2)_3N(C_2H_5)_2$ H	H	H	—		—		1:4
8	CH_2CH_2OH H	H	H	Ethyleneurea	15	—		1:2
9	$CH_2CH_2OCH_3$ H	$CH_2CH_2OCH_3$	H	Succino-guanamine	15	—		1:2.8

TABLE 1 (continuation)

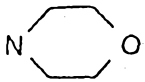
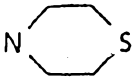
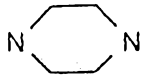
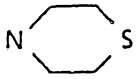
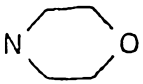
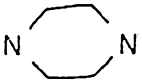
COMPOUND N°	Derivative of General Formula (I)			Polyaminic derivative		R_4-CHO		Molar ratio polyamines / aldehydes
	R — N — R_1	R_2	R_3	Designation	% by weight	R_4	Mol %	
10	CH_2CH_2OH H	H	H	urea	20	—		1:2,5
11		H	H	—		i-C_4H_9	5	1:2
12		t-C_4H_9	H	—		—		1:3
13		H	H	—		—		1.
14	$(CH_2)_2OCH_3$ $(CH_2)_2OCH_3$	H	H	Benzyl-guanamine	15	—		1:3
15	$(CH_2)_2O(CH_2)_2OH$ H	H	H	—		—		1:4
16		H	H	Ethyleneurea	25	—		1:1,5
17	CH_2CH_2OH H	H	H	Melamine	30	—		1:5
18	$(CH_2)_3OCH_3$ H	$(CH_2)_3OCH_3$	$(CH_2)_3OCH_3$	—		—		1:2,8

TABLE 1 (continuation)

COMPOUND N°	Derivative of General Formula (I)			Polyaminic derivative		R_4-CHO		Molar ratio polyamines / aldehydes
	$R-N(R_1)-$	R_2	R_3	Designation	% by weight	R_4	Mol %	
19		H	H	Melamine	50	——		1:4.5
20	CH_2CH_2OH H	CH_2CH_2OH	H	——		——		1:3
21		H	H	——		——		1:2
22	$(CH_2)_3OC_2H_5$ H	H	H	——		——		1:2,5
23		$(CH_2)_2OCH_3$	H	——		——		1:1
24		H	H	Piperazine-2,5-dione	10	——		1:3
25		H	H	——		C_2H_5	15	1:2,5
26		H	H	Melamine	25	i-C_3H_7	8	1:3,5
27	$CH_2CH_2OCH_3$ H	C_2H_5	C_2H_5	——		——		1:2,5

The examples reported in the following illustrate the characteristics of the invention without limiting it.

Example 1

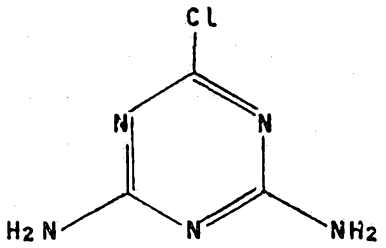
184.5 g of cyanuric chloride and 800 cm^3 of acetone are charged to a reactor of 3 litres of capacity, equipped with stirrer, thermometer, dripping funnel, reflux condenser and heating bath.

With stirring, the reaction mixture is heated up to 40°C in order to obtain a solution, then 284 g of an aqueous solution of ammonia at 30% by weight are added during a 1 hour and 30 minutes time.

The reaction mixture is subsequently heated up to 45°C and is kept 4 hours at this temperature.

After cooling, the resulting product is filtered off and is washed on the filter with water.

After oven drying at 50-60°C under vacuum, 113 g of intermediate (III):



(III)

are obtained as a white, infusible, crystalline powder containing 24.12% of chlorine (theoretical chlorine content = 24.36%).

72.8 g of intermediate (III), 350 cm^3 of water and then, with stirring, 44 g of piperidine are charged to a reaction vessel of 1 litre of capacity equipped with stirrer, thermometer, addition funnel, reflux condenser

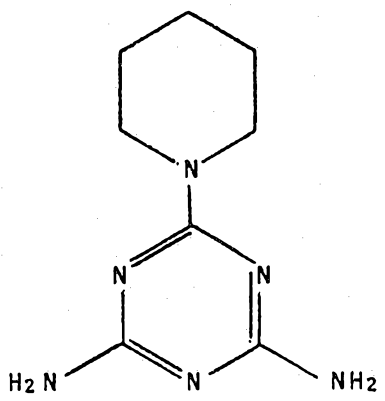
and heating bath.

The reaction mixture is heated up to boiling temperature and then is kept under refluxing conditions for 4 hours.

The reaction mixture is then caused to reflux for a further 8 hours, with 20 g of sodium hydroxide in 50 cm^3 of water being added portionwise, so as to keep the reaction mixture pH value comprised within the range of from 7 to 8.

The reaction mixture is cooled down to room temperature, the resulting product is filtered off, and the filter cake is washed on the same filter with cold water.

After drying in an oven at 60°C under vacuum, 90 g of 2,4-diamino-6-piperidino-1,3,5-triazine (IV):



(IV)

are obtained as a white crystal powder having m.p. = 215-217°C (m.p. = melting point).

The structure of intermediates (III) and (IV) was confirmed by IR spectroscopic analysis.

300 cm^3 of water, 0.7 g of sodium carbonate, 114.3 g of an aqueous solution at 37% by weight of formaldehyde and, with stirring, 78 g of intermediate

(IV) are charged to the same reactor of 1 litre of capacity.

The reaction mass is heated up to 65°C, until a solution is obtained (about 1 hour).

The resulting solution, kept at 65°C, is added, during a 2 hour time, to a reactor of 2 litres of capacity, equipped in the same way as the preceding reactors, containing 380 cm^3 of water and 3.0 g of sulfuric acid at 96%, heated at 90-95°C. A white precipitate is formed.

When addition is complete, the resulting dispersion is heated up to boiling temperature and is kept refluxing for 3 hours.

Then 450 cm^3 of water are added, with the temperature being allowed to decrease down to 60°C, and the reaction mass is subsequently neutralized by adding 2.4 g of sodium carbonate.

The reaction mass is kept at the temperature of 60°C for 1 hour, and the resulting product is subsequently filtered, with the filter cake being washed on the same filter with hot water.

By drying the filter cake in an oven at 100°C, and subsequently submitting it to a thermal treatment at 150°C for 2 hours under vacuum, 84.8 g of resin are obtained as a white crystalline powder having a melting point higher than 300°C.

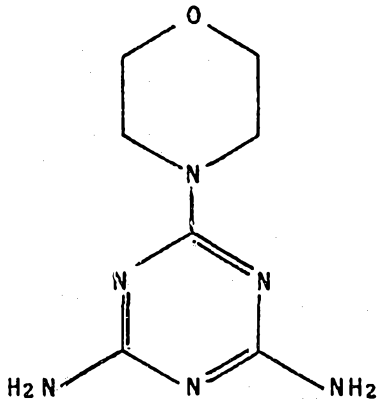
Example 2

91 g of intermediate (III), 240 cm^3 of toluene and 100 g of morpholine are charged to the same reaction equipment of 1 litre of capacity as disclosed in

Example 1.

The reaction mixture is heated up to 65-70°C and is kept at that temperature for 2 hours; the reaction mixture is then heated up to boiling temperature and is kept refluxing for 1 hour.

The reaction mixture is allowed to cool down to room temperature, and then the resulting product is isolated by filtration. The filter cake is washed with plentiful water, and, after drying, 92 g of 2,4-diamino-6-morpholino-1,3,5-triazine (V):



(V)

are obtained as a white crystalline powder with m.p. = 248°C-250°C.

The structure of intermediate (V) was confirmed by NMR analysis.

300 cm^3 of water, 0.7 g of sodium carbonate, 91.2 g of a solution at 37% by weight of formaldehyde, and, with stirring, 73.5 g of intermediate (V) are charged to the same reactor of 1 litre of capacity.

The reaction mass is heated at 65°C for 15 minutes, until a solution is obtained.

Such a solution, kept at 65°C, is fed, during a 2 hour time, to the same reactor of 2 litres of capacity

as disclosed in Example 1, containing 350 cm^3 of water and 3.0 g of sulfuric acid at 96%, heated at 90°C.

A white solid is formed. The reaction mixture is heated up to boiling temperature and is kept under refluxing conditions for 3 hours.

450 cm^3 of water areadded, with the temperature being allowed to decrease down to 60°C, and the reaction mass is neutralized by means of the addition of 2.4 g of sodium carbonate.

Then, proceeding as disclosed in Example 1, 77.3 g of resin are obtained as a white crystalline powder having a melting point higher than 300°C.

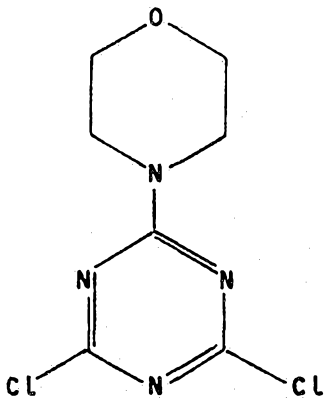
Example 3

184.5 g of cyanuric chloride and 1300 cm^3 of methylene chloride are charged to the same equipment of 3 litres of capacity as disclosed in Example 1, but initially equipped with a cooling bath.

With cooling from the outside, 87.2 g of morpholine and 40 g of sodium hydroxide dissolved in 150 cm^3 are simultaneously added during a 3 hour time, with the reaction pH being kept comprised within the range of from 5 to 7, and the temperature being kept comprised within the range of from 0 to 3 °C.

The temperature of 0-3°C is maintained for a further 3 hours, then the aqueous phase is separated.

By distilling methylene chloride off, 230 g of intermediate (VI):



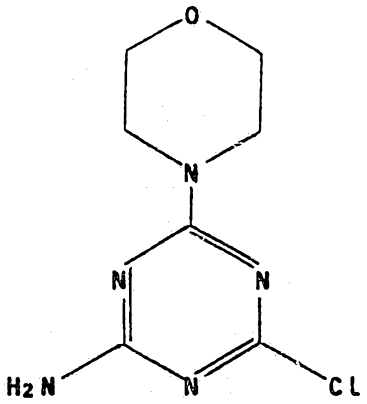
(VI)

is obtained as a white crystalline powder with m.p. = 155-157°C; purity higher than 98% (as determined by gas-chromatography) and a chlorine content of 29.87% (theoretical value: 30.21%).

100 g of a solution at 30% by weight of ammonia, 100 cm^3 of water and 70.5 g of intermediate (VI) are charged to a reactor of 0.5 litre of capacity, equipped as in Example 1.

The reaction mixture is firstly heated up to 50°C and is kept 7 hours at this temperature; then is allowed to cool down to room temperature and the obtained product is filtered off and the filter cake is washed with water.

By drying the filter cake, 58 g of intermediate (VII):



(VII)

are obtained as a white crystalline powder with m.p. = 189-191°C and a chlorine content of 16.28% (theoretical value: 16.47%).

The structure of intermediates (VI) and (VII) was also confirmed by IR spectroscopic analysis.

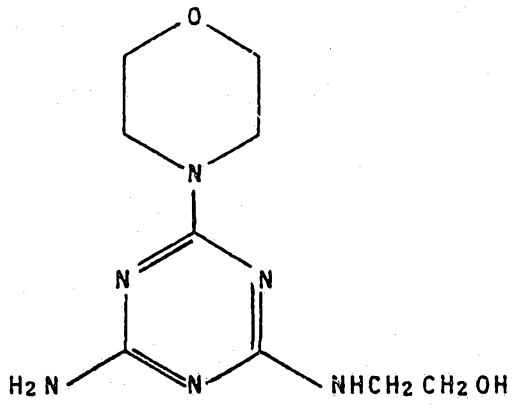
58 g of intermediate (VII) and 300 cm^3 of water and then, with stirring, 18 g of 2-aminoethanol are charged to the same reaction equipment as disclosed above.

The reaction mixture is heated up to boiling temperature and is allowed to reflux for 3 hours.

The reaction mixture is then allowed to reflux for a further 3 hours, while 11.8 g of sodium hydroxide in 50 cm^3 of water are added portionwise, so as to keep the reaction pH value comprised within the range of from 7 to 8.

The reaction mass is cooled, the resulting product is filtered off, and the filter cake is washed with water.

After drying, 58 g of 2-amino-4-(2-hydroxyethyl)amino-6-morpholino-1,3,5-triazine (VIII):



(VIII)

are obtained as a white crystalline powder with a melting point of 159-161°C.

The structure of intermediate (VIII) was confirmed by IR spectroscopic analysis.

200 cm^3 of water, 51.1 g of a solution at 37% by weight of formaldehyde, and, with stirring, 50.0 g of intermediate (VIII) are charged to the same reaction apparatus of 0.5 litre of capacity.

The reaction mixture is kept heated at 60°C during 45 minutes, until a solution is obtained.

The resulting solution, kept at 60°C, is added during a 2 hour time to a reactor of 1 litre of capacity, fitted as the preceding ones, containing 250 cm^3 of water and 3.7 g of an aqueous solution at 37% by weight of hydrochloric acid, heated at 90-95°C. A white solid material is formed.

The reaction mass is heated up to boiling temperature and is kept refluxing for 3 hours.

250 cm^3 of water are added, with the reaction temperature being allowed to decrease down to 60°C, and the reaction mass is neutralized by means of the addition of 1.5 g of sodium hydroxide.

Then, proceeding as disclosed in Example 1, 52.1 g of resin are obtained as a white crystalline powder having m.p. higher than 300°C.

Example 4

100 cm^3 of methanol, 101.5 g of a solution at 37% by weight of formaldehyde and, with stirring, 49.0 g of intermediate (V) of Example 2 and 31.5 g of 2,4,6-triamino-1,3,5-triazine (melamine) are added to the same reaction equipment of 0.5 litre of capacity as disclosed in Example 3.

The reaction mass is heated up to 70°C for 45 minutes, until a solution is obtained.

The resulting solution, kept at 70°C, is fed during a 30 minute time to a reactor of 2 litres of capacity fitted as the preceding reactors, containing 400 cm^3 of water, 200 cm^3 of methanol and 2.9 g of phosphoric acid at 85% by weight, heated up to 75°C.

A precipitate is not immediately formed.

Therefore, the solution is heated up to its boiling temperature and is kept refluxing for approximately 8 hours, during which a white solid precipitates.

350 cm^3 of water are added, with the dispersion temperature being allowed to decrease down to 60°C, and the dispersion is neutralized by means of the addition of 3.1 g of sodium hydroxide.

Then, by proceeding according to the operating modalities as disclosed in Example 1, 90 g of resin are obtained as a white crystalline powder having a melting point higher than 300°C.

Example 5

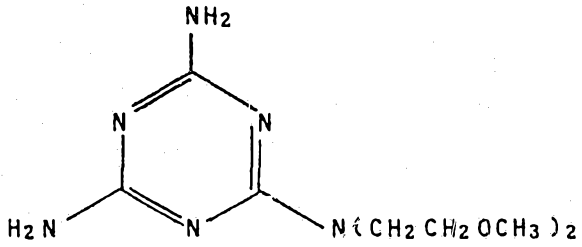
350 cm^3 of water, 72.8 g of intermediate (III) of Example 1, and then, with stirring, 68 g of N,N-bis (2-methoxyethyl) amine are charged to the same reactor of 1 litre of capacity as disclosed in Example 1.

The reaction mixture is heated up to boiling and is kept under refluxing conditions for 4 hours.

The reaction mixture is then allowed to reflux for a further 8 hours, while 20 g of sodium hydroxide in 50 cm^3 of water are added portionwise, in order to keep the reaction pH value comprised within the range of from 7 to 8.

The reaction mixture is cooled down to room temperature, the resulting product is filtered off and the filter cake is washed on the same filter with water.

After drying in an oven at 60°C under vacuum, 90 g of 2,4-diamino-6-bis (2-methoxyethyl) amino-1,3,5-triazine (IX):



(IX)

are obtained as a white crystalline powder having m.p. = 124-128°C.

The structure of intermediate (IX) was confirmed by NMR analysis.

320 cm^3 of water, 1.0 g of potassium carbonate, 30 g of paraformaldehyde and, with stirring, 80.0 g of

intermediate (IX) are charged to the same reactor of 1 litre of capacity.

The reaction mass is heated up to 60°C for 20 minutes, until a solution is obtained.

The resulting solution, kept at 60°C, is added during a 1 hour time to a reactor of 2 litres of capacity, equipped as the preceding ones, containing 400 cm^3 of water and 3.2 g of sulfuric acid at 96%, heated at 90°C.

A white precipitate is formed.

The reaction dispersion is kept at 90°C for a further 4 hours, then 500 cm^3 of water are added, with the reaction temperature being allowed to decrease down to 50°C, and the reaction mass is neutralized by means of the addition of 3.2 g of potassium carbonate.

By subsequently proceeding as disclosed in Example 1, 88.7 g of resin are obtained as a crystalline white powder having a melting point higher than 300°C.

Examples 6-16

By operating under analogous conditions to as disclosed in Examples from 1 to 5, the polycondensation products are prepared which are obtained by reacting with formaldehyde the melaminic derivatives of general formula (I), either containing or not containing polyaminic derivatives, which are reported in following Table 2, and having a melting point higher than 300°C.

TABLE 2

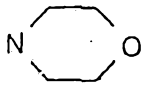
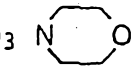
EXAMPLE N°	Derivative of General Formula (I)			Polyaminic derivative		R_4 - CHO		Molar ratio polyamines / aldehydes
	R — N — R_1	R_2	R_3	Designation	% by weight	R_4	Mol %	
6	CH_2CH_2OH H	H	H	—		—		1:2.5
7		$CH_2 - CH = CH_2$	H	—		—		1:2,5
8		H	H	—		—		1:3
9	CH_2CH_2OH H	CH_2CH_2OH	CH_2CH_2OH	—		—		1:2.2
10	$(CH_2)_3$  H	H	H	—		—		1:2,5
11		H	H	Ethyleneurea	40	—		1:1,4
12	$(CH_2)_2OCH = CH_2$ H	H	H	—		—		1:3
13	$(CH_2)_2OH$ $(CH_2)_2OH$	H	H	—		—		1:2,5

TABLE 2 (continuation)

EXAMPLE N°	Derivative of General Formula (I)			Polyaminic derivative		R_4-CHO		Molar ratio polyamines / aldehydes
	R — N — R_1	R_2	R_3	Designation	% by weight	R_4	Mol %	
14		H	H	—		—		1:5
15	$CH_2CH_2OCH_3$ H	$(CH_2)_2OCH_3$	$(CH_2)_2OCH_3$	—		—		1:3
16	CH_2CH_2OH H	CH_2CH_2OH	H	—		—		1:2,4

Example 17

70 g of isotactic polypropylene flakes, having a Melt Flow Index equal to 12 and containing 96% by weight of a fraction insoluble in n-heptane; 8.3 g of the product of Example 3; 20.7 g of ammonium polyphosphate (Exolit 422 ex Hoechst); 0.67 g of dilauryl-thiopropionate and 0.33 g of pentaerythritol tetra[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] are blended and moulded on a MOORE platen press, by operating for 7 minutes at a pressure of 40 kg/cm^2.

Specimens are obtained as small slabs of approximately 3 mm of thickness, and on them the level of self-extinguishment is determined by measuring the oxygen index (L.O.I. according to ASTM D-2863/77) on a STANTON REDCROFT instrument, and applying the "Vertical Burning Test", which makes it possible the material to be classified at the three levels 94 V-0, 94 V-1 and 94 V-2 according to UL 94 standards (published by "Underwriters Laboratories" - USA).

The following results were obtained:

L.O.I. = 37.5

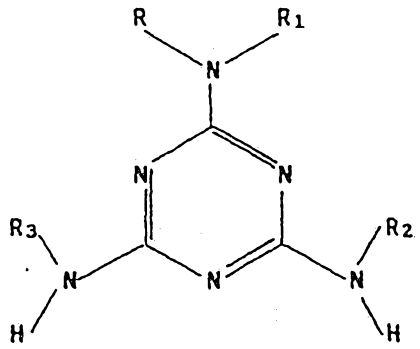
UL 94 = Class V-0.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Aminoplastic resins obtained by means of the polymerisation of a mixture comprising:

(1) from 0 to 50 parts by weight of one or more polyaminic derivatives;

(2) from 50 to 100 parts by weight of one or more derivatives of 2,4,6-triamino-1,3,5-triazine having the general formula (I):



(I)

with formaldehyde or a mixture of formaldehyde and an aldehyde having the general formula (II):

$$R_4\text{-}CHO \qquad \text{(II)}$$

wherein the aldehyde having general formula (II) can be present in an amount of up to 20% by mol, and wherein at least one of radicals from R to R_3 is:

$$-CH_2\text{-}(C_mH_{2m})\text{-}O\text{-}R_5$$

or

$$-CH_2\text{-}(C_pH_{2p})\text{-}N(R_6)(R_6)$$

wherein:

m = an integer comprised within the range of from 1 to 7;

p = an integer comprised within the range of from

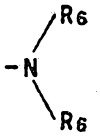
1 5
Z_1 to Z_5;

R_5 = H; C_1-C_8 alkyl; C_2-C_6 alkenyl; $-[-C_qH_{2q}-]-O-R_7$ wherein q is an integer comprised within the range of from 1 to 4 and R_7 is H or C_1-C_4 alkyl; C_6-C_{12} cycloalkyl or alkylcycloalkyl;

the radicals R_6, which may be the same or different from each other, are:

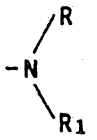
H; C_1-C_8 alkyl; C_2-C_6 alkenyl; C_6-C_{12} cycloalkyl or alkylcycloalkyl; C_1-C_4 hydroxyalkyl;

or the moiety:



is replaced by a heterocyclic radical linked to the alkyl chain through the nitrogen atom, and possibly containing another heteroatom;

or in the general formula (I) the moiety:



is replaced by a heterocyclic radical linked to the triazinic ring through the nitrogen atom, and possibly containing another heteroatom;

the other radicals from R to R_3, which may be the same or different from one another, have the above said meaning, or they are:

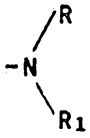
H; C_1-C_{18} alkyl; C_2-C_8 alkenyl; C_6-C_{16} cycloalkyl or alkylcycloalkyl, possibly substituted with a hydroxy or C_1-C_4 hydroxyalkyl function.

R_4 is C_1-C_8 alkyl; C_2-C_6 alkenyl; C_6-C_{12}

cycloalkyl; C_6-C_{12} aryl, possibly substituted with one or more C_1-C_4 alkyl radicals; aralkyl C_7-C_{16}; aralkenyl C_8-C_{12}.

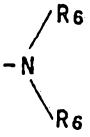
2. Aminoplastic resins according to claim 1, in which the polyaminic derivative is selected from compounds containing the 1,3,5-triazine ring, or at least one moiety $>C=O$ and/or $>C=S$.

3. Aminoplastic resins according to claims 1 or 2, in which the moiety:



in general formula (I) is replaced by heterocyclic radicals selected from:
aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4-methylpiperazine; 4-ethylpiperazine; 2-methylpiperazine; 2,5-dimethylpiperazine; 2,3,5,6-tetramethylpiperazine; 2,2,5,5-tetramethylpiperazine; 2-ethylpiperazine; 2,5-diethylpiperazine.

4. Aminoplastic resins according to any of the preceding claims, in which the moiety:



is replaced by a heterocyclic radical selected from:
aziridine; pyrrolidine; piperidine; morpholine; thiomorpholine; piperazine; 4-methylpiperazine; 4-ethylpiperazine.

5. Aminoplastic resins according to any of the

preceding claims, in which the polyaminic derivative is selected from:

urea; ethyleneurea; propyleneurea; thiourea; ethylenethiourea; melamine; acetoguanamine; propionoguanamine; butyroguanamine; isobutyroguanamine; caprinoguanamine; succinoguanamine; benzoguanamine; metamethylbenzoguanamine; benzylguanamine; hydantoin; piperazine-2,5-dione; barbituric acid.

6. Aminoplastic resins according to any of the preceding claims, in which R_4 radical is selected from: methyl; ethyl; n-propyl; isopropyl; n-butyl; isobutyl; tert-butyl; n-pentyl; isopentyl; n-hexyl; n-eptyl; isoeptyl; n-octyl; ethenyl; propenyl; isobutenyl; sec-butenyl; n-pentenyl; cyclohexyl; phenyl; 2-methylphenyl; 3-methylphenyl; 4-methylphenyl; 4-isopropylphenyl; 2,4,6-trimethylphenyl; 1-phenylethyl; 2-phenylethyl; 2-phenylethenyl.

7. Process for preparing the aminoplastic resins according to any of the preceding claims, comprising:

(a) reacting the derivative of general formula (I), either mixed with the polyaminic derivative or not mixed with it, with formaldehyde or a mixture of formaldehyde containing up to 20% by mol of an aldehyde of general formula (II);

(b) acidifying the resulting reaction product down to a pH comprised within the range of from 1 to 5.

8. Process according to claim 7, in which the reaction (a) is carried out with a molar ratio of the derivative of general formula (I), or its mixture with the polyaminic derivative, to formaldehyde, or its

mixture with the aldehyde of general formula (II), comprised within the range of from 1:1 to 1:6.

9. Process according to claim 7 or 8, in which the reaction (a) is carried out at a temperature comprised within the range of from 20°C to the boiling point of the solvent used, and the reaction (b) is carried out at a temperature comprised within the range of from 40°C up to the solvent boiling point.

10. Process according to claim 7, 8 or 9, in which the reactions of (a) and (b) stages are carried out in one single step at a temperature higher than 40°C.

DATED THIS 12TH DAY OF NOVEMBER 1992

MINISTERO DELL'UNIVERSITA' E DELLA RICERCA SCIENTIFICA E TECNOLOGICA

By its Patent Attorneys:
GRIFFITH HACK & CO.

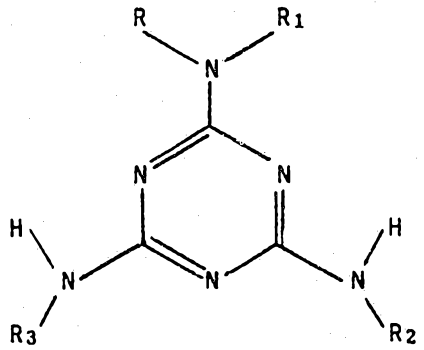
Fellows Institute of Patent Attorneys of Australia

CASE MU 4287

"MELAMINIC POLYCONDENSATES"

Abstract

Condensation compounds obtained by means of the polymerization of polyaminic compositions essentially constituted by derivatives of 2,4,6-triamino-1,3,5-triazine having the general formula (I):



(I)

with aldehydes, preferably formaldehyde.