

Description

Because of their remarkable physical properties, polyamides have found many applications.

Despite everything, their development in certain special fields such as, among others, those of the vehicle manufacturing, aeronautics and electrical industry, etc. has been limited because of their excessive flammability.

Many solutions have already been proposed to overcome this, but none have been found wholly satisfactory in practice.

10 Thus, traditional fire-retardant agents based on halogenated organic derivatives such as, for example, decabromodiphenyl ether, by itself or in combination with antimony oxide, generate halogenated acids which are released during the manufacture or the use of polyamides filled in
15 this manner; this results in corrosion hazards in the case of the equipment and in nuisances in the case of the environment.

Phosphorus, which has also been proposed (US Patent no. 3,778,407) is not simple to use, and it also imparts
20 a reddish colour to the polyamides in which it has been incorporated.

Real progress has been obtained through the use of melamine cyanurate (Patents France nos. 79/23,111 and 82/04,446, EP 0,019,768), but this compound is not as
25 efficient, at equal weights, as certain compounds with a high chlorine or bromine content.

Furthermore, it must not be forgotten that, while the additives referred to above reduce the combustibility of the plastics in which they are incorporated, a quality
30 measured by means of the Limiting Oxygen Index (according to NFT standard 51,071 or ASTM standard D 2863), on the other hand, they are without effect on the dripping tendency, a characteristic required in addition to that mentioned above by the ASTM standards D 635 and the UL 94
35 fire test described in Bulletin 94 of the UNDERWRITERS LABORATORIES.

We have found, and this forms the subject matter

of the present invention, that both the combustibility and the dripping tendency of polyamides are reduced if melamine cyanurate and a polyol containing at least four times the alcohol group are incorporated together therein.

5 The combination of melamine cyanurate and polyol is effective in pure polyamides or those to which the usual fillers have been added, such as colourants, heat stabilizers, UV stabilizers, etc., but also, what is more surprising, in plasticized grades containing, among other
10 plasticizers, butylbenzenesulphonamide or octyl parahydroxybenzoate or a mixture thereof.

Improvements are also observed in the case of grades filled, for example, with talc, glass fibres, carbon, and the like.

15 The polyamide compositions with retarded combustibility according to the invention must contain:

- a) at least 35% by weight of polyamides,
 - b) from 0 to 30% of additives, fillers or plasticizers,
 - 20 c) from 1 to 25% by weight of melamine cyanurate,
 - d) from 0.5 to 10% by weight of polyols,
- the sum of all these constituents having to be equal to 100 in each case.

By melamine cyanurate, we understand the compounds
25 resulting from the reaction of melamine with cyanuric acid and, more particularly, the compound resulting from the equimolecular reaction of melamine with cyanuric acid, whether this acid be in its enol or keto form.

Various companies sell such compounds under the
30 name of "melamine cyanurate". It is important to select, by preliminary examinations or tests, those which have the most suitable particle size and the best dispersibility in polyamides, which can easily be verified by inspecting sections under the microscope.

35 By suitable particle size we mean that the results proposed by the invention are achieved when approximately 70% of the particles of the cyanurate employed are smaller than or equal to 30 μ m.

By polyols containing at least four times the alcohol group, we understand:

- tetrols such as erythritol, monopentaerythritol (and its derivatives: di- and tripentaerythritols) and the like
- 5 - pentols such as xylitol, arabitol and the like
- hexols such as mannitol, sorbitol and the like, and the higher homologues.

The said polyols can, of course, be employed by themselves or mixed.

- 10 Monopentaerythritol and sorbitol are particularly suitable for making use of the invention; just as in the case of melamine cyanurate, it is important that they should have a particle size which is suitable for good dispersion in polyamides; products which, having particles
- 15 90% of which are smaller than 10 μ m, are perfectly suitable are to be found without difficulty on the market.

Pentaerythritols had already been mentioned as constituents of intumescent compositions (US Patents 3,810,862, 3,931,081 and 3,936,416), but these, in fact,

20 had to do only with polyolefins; what is very surprising is that these pentaerythritols act in synergy with melamine cyanurate on the polyamides in the manner shown above.

By polyamides we understand the polymers obtained essentially:

- 25 - by anionic polymerization of one or more lactams such as caprolactam, oenantholactam, lauryllactam, and the like
- or by hydrolytic polycondensation either of the said lactams,
- 30 or of one or more amino acids such as aminocaproic, 7-aminoheptanoic, 11-aminoundecanoic, 12-aminododecanoic acids, and the like
- or of one or more salts or mixtures of diamines such as hexamethylene diamine, dodecamethylene diamine,
- 35 meta-xylylene diamine, bis-p-aminocyclohexylmethane, trimethylhexamethylene diamine, and the like, with diacids such as isophthalic, terephthalic, adipic, azelaic, suberic, sebacic, dodecane dicarboxylic acids, and the like

or of mixtures of all these monomers, which leads to copolyamides.

Under the term "polyamides" we also include polyether amides and polyether ester amides.

5 The effectiveness of the combination of melamine cyanurate and polyol resulting, among other factors, from the monomer(s) from which this polyamide is derived, from the manner in which it has been manufactured and from its molecular weight.

10 Insofar as the first point is concerned, polyamides 6 (derived from caprolactam) and 6.6 (derived from hexamethylene diamine adipate) naturally possess lower combustibility than polyamides 11 and 12 (perhaps because of their higher nitrogen content).

15 Thus, in order to obtain the same result, let us assume an L.O.I. (Limiting Oxygen Index) higher than 33 according to NFT standard 51,071 and a classification V0, as 1.6 and 3.2 mm, according to the UL 94 standard, it would be necessary to incorporate a larger quantity of the
20 mixture of melamine cyanurate and pentaerythritol in polyamides 11 and 12 than in polyamides 6 and 6.6.

 Insofar as the second point is concerned, we mean that we have found that the nature of the adjuvants employed during the manufacture of the polyamide played an
25 essential, unexpected and surprising part in the tendency of this polyamide to be fireproofed by melamine cyanurate and the polyol.

 Let us recall that when a polyamide is manufactured by hydrolytic polycondensation of its monomer, most of the
30 time this polycondensation is carried out in the presence of an adjuvant which may be acidic (such as acetic, adipic, sebacic, dodecanedioic, etc. and phosphoric acid) or basic (such as sodium hydroxide, potassium hydroxide, hexamethylene diamine etc.), the role of this adjuvant being to hydrolyse
35 the monomer when it is a lactam, to accelerate the polycondensation in some cases or, in all cases, to limit the molecular weight.

 For this last reason, we shall call this adjuvant

a chain limiter.

We have found that the compositions consisting of certain polyamides - those resulting from the polycondensation of their monomers in the presence of an acid derived from phosphorus or from an organic acid containing at least 8 carbon atoms, monocarboxylic or dicarboxylic such as, for example, inter alia, pelargonic, azelaic or dodecanedioic (decane dicarboxylic) acid - of melamine cyanurate and of polyol exhibited performances in the flammability tests which were greatly superior to those of the compositions consisting of the same polyamides (same monomer and same molecular weight) but obtained in the presence of another chain limiter, such as, for example, adipic acid, and of the same quantities of melamine cyanurate and of polyol.

By "an acid derived from phosphorus" we mean, among others, ortho- or meta- or pyrophosphoric or phosphorous or hypophosphorous acid, etc., the essential role of this acid being to accelerate the polycondensation reaction while limiting the molecular weight of the final polymer, as explained, inter alia, in patents France nos. 951,924, 1,401,842 and 70.3,855 (pub. 2,110,661).

(It is also known that such acids cause the hydrolytic scission of lactams when such monomers are employed).

At equal dosages of melamine cyanurate and of polyol, a polyamide will be proportionately more non-flammable the more phosphoric acid it contains; thus, a polyamide 11 intended for injection moulding and of a relatively low molecular weight (inherent viscosity ≥ 0.90 , measured in meta-cresol at 25°C at a concentration of 0.5 g per 100 g) obtained by polycondensation of 11-amino-undecanoic acid in the presence of 10 parts per thousand of orthophosphoric acid will show better performance than a polyamide 11 intended for extrusion, of a relatively high molecular weight (inherent viscosity ≥ 1.20) obtained by polycondensation of the same monomer in the presence of only 5 parts per thousand of orthophosphoric acid.

In this case, the inferiority of the extrusion grade can be compensated by increasing the dosages of cyanurate and of polyol.

5 An alternative form of the invention consists in producing compositions with good nonflammability by using polyamides which do not, however, lend themselves to this by their nature, such as polyamides 11 and 12 with adipic acid, for example, or polyamides 11 and 12 containing very little acid derived from phosphorus.

10 This alternative form consists in enriching these compositions in acid derived from phosphorus, for example, by adding this acid to the polyamides when they are in the molten state, at the same time as melamine cyanurate and the polyol.

15 We have thus found that to impart to compositions an L.O.I. equal to or higher than 31, a value which they would not otherwise reach, it was necessary to enrich them in acid derived from phosphorus so that the final composition contained from 2 to 20 parts per
20 thousand of this acid, calculated as orthophosphoric acid, relative to the weight of polyamide.

The incorporation of melamine cyanurate and the polyol is carried out by blending these two compounds, finely divided, into the polyamide in the molten state.
25 Any blending equipment which ensures good dispersion can therefore be suitable - twin-screw extruders such as the WERNER and PFLEIDERER, and BUSS type kneaders, are particularly suitable for this purpose.

A simple way of performing the operation consists
30 in dry-blending the polyamide granules, the cyanurate and the polyol and in feeding this blend to a twin-screw extruder.

An extruder can also be continuously fed with, on the one hand, polyamide granules and, on the other hand,
35 a mixture prepared, dry, beforehand, of cyanurate and of polyol.

Masterbatches of polyamide, cyanurate and polyol, which will subsequently be blended with the polyamide, may

also be prepared.

It is also possible, in a first step, to incorporate melamine cyanurate into the polyamide by passing through an extruder and subsequently to refeed the same extruder with the product obtained, to which polyol has been added.

The invention will be made more explicit by the following examples, which do not imply any limitation whatsoever.

We first define the polyamides which will be employed in these examples:

(the inherent viscosity of all these polyamides has been measured at 25°C on their solutions in m-cresol - 0.5 g of polyamide per 100 g of cresol).

A - Adipic polyamide 11 for injection-moulding

11-aminoundecanoic acid, 5 parts per thousand of its weight of adipic acid and water and introduced into a stainless-steel autoclave.

After raising the temperature to 180°C, with all valves closed, the steam pressure has risen to 10 bars.

The pressure is relieved down to atmospheric pressure and, with the temperature being maintained at 250°C, a gentle stream of nitrogen is used to purge out the steam originating from the polycondensation for the time needed to obtain a polymer with an inherent viscosity equal to 1.05, which is extruded out of the autoclave (by increasing the nitrogen pressure) in the form of lace which is solidified by cooling in water - this lace is then cut up into granules, granules which will be dried.

B - Phosphoric polyamide 11 for injection-moulding

A polymer of this kind is prepared by operating as above by charging the autoclave with water and with 11-aminoundecanoic acid, but with 8.5 parts per thousand of orthophosphoric acid by weight of the latter.

Since phosphoric acid has a catalytic action, it will not be necessary to polycondense at 250°C for as long as above in order to obtain a polymer with a viscosity of 1.05.

C - Adipic polyamide 12 for injection-moulding

The same autoclave as that employed above is charged with 30,000 parts by weight of lauryllactam, 3,000 parts of water and 150 parts of adipic acid.

5 The temperature is raised to 280°C and is maintained for 5 hours at a pressure of 25-30 bars.

The pressure is relieved while the temperature is left at 250°C and the polycondensation is continued at 250°C at atmospheric pressure and with a gentle nitrogen
10 purge for the time needed to obtain a polyamide with a viscosity of 1.10.

D - Phosphoric polyamide 12 for injection-moulding

As above, with 30,000 parts of lauryllactam, 3,000 parts of water but 255 parts of orthophosphoric acid (i.e.
15 8.5 parts per thousand).

The pressure hold at 280°C is only for 2 hours. Polycondensation is carried out for the time needed to obtain a polyamide with a viscosity of 1.02.

E - Dodecanedioic polyamide 12 for injection-moulding

20 A polymer of this kind is prepared by operating as in Example C with 30,000 parts of lauryllactam, 3,000 parts of water and 261 parts of dodecanedioic (1,10-decane dicarboxylic) acid.

The polycondensation will be continued until a
25 polymer with an inherent viscosity of 1.00 is obtained.

The granules of these polyamides A, B, C, D and E are used to injection-mould test specimens which are measured for :

30 - the limiting oxygen index according to NFT standard 51-071

- the combustibility according to UL publication 94 (UNDERWRITERS' LABORATORIES) - (examples 1, 6, 12, 18 and 24, see attached table).

35 Furthermore, these polyamides are used to prepare compositions containing

either melamine cyanurate
or monopentaerythritol (or sorbitol)
or both these compounds.

In all these tests we have employed:

- melamine cyanurate from the Austrian company CHEMIE LINZ A.G., in which 70% of the particles are close to 25 microns in diameter, and having the formula



- monopentaerythritol from the CELANESE Company
- sorbitol from the LAMBERT-RIVIERE Company sold under the trademark Sorbitol E 420 Neosorb powder.

10 All these compositions were prepared by following the same procedure which we shall describe only for example 4:

A BUSS cokneader is fed continuously with :

- on the one hand, (by means of a SODER type S 200 metering pump with a spiral screw) with granules of adipic polyamide 11 obtained in A,

- on the other hand (by means of a SODER type T 20 metering pump with twin screws) with a mixture produced beforehand (in a HENSCHALL type high speed mixer) of 10 kg of melamine cyanurate and of 2 kg of monopentaerythritol.

20 The settings are such that there are 88 kg of polyamide per 12 kg of the above mixture.

The temperature of the cokneader is set at about 235°C. The lace leaving this machine, which is fitted with a multihole die, is cooled with water and chopped into granules.

25 Test specimens, injection-moulded by means of the said granules, suitably dried, are used to perform the combustibility tests indicated below.

30 Example no. 17 - Introduction of phosphoric acid during extrusion

A BUSS cokneader is fed with:

- on the one hand, a premix of 8,120 parts of polyamide 12 granules containing 5 parts per thousand of adipic acid and obtained in C and of 85 parts of ortho-phosphoric acid,

- and, on the other hand, a mixture of 1,500 parts of melamine cyanurate and 295 parts of monopentaerythritol.

The temperature of the cokneader is in the

neighbourhood of 205°C.

The extruded lace is cooled and chopped into granules which permit the test specimens required for the combustibility tests to be injection-moulded.

5 All the results collated in the attached table clearly show that:

1./ The addition of melamine cyanurate alone (examples 2, 3, 7, 8, 13, 14, 19, 20, 25) affords only limited gains in nonflammability.

10 Only a few points are gained in L.O.I. and the UL classification still remains V2.

2./ The addition of monopentaerythritol alone (examples 9, 10, 21, 22) gives no gain.

15 3./ On the other hand, the joint addition of cyanurate and of monopentaerythritol improves the performances (examples 5, 16) more markedly in a general manner.

The gains are considerable (L.O.I. higher than 31, V0 classification 3.2 mm) when the compositions contain phosphoric acid

20 either because the polyamides employed already contained it (examples 11 and 23)

or because it has been added (example 17)

or when the compositions contain dodecanedioic acid (examples 26 and 27).

25 4./ Sorbitol jointly with cyanurate increases the L.O.I. considerably (example 28).

Example no. 29 - Preparation of plasticized and fireproofed polyamide 11

A WERNER ZDSK 53 extruder is fed with :

30 - on the one hand, 7,000 parts of polyamide granules obtained as in example 8 but with 5 parts per thousand of orthophosphoric acid (instead of 8.5) and with an inherent viscosity of 1.55

35 - on the other hand, a premix of 1,500 parts of melamine cyanurate, 300 parts of monopentaerythritol, 100 parts of IRGANOX 1010 and 50 parts of TINUVIN P (these last two compounds, intended to protect the composition against ageing, are manufactured by the CIBA-GEIGY Company).

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MIXTURE COMPOSITION, PARTS BY WEIGHT						RESULTS OF THE FLAMMABILITY TESTS		
Example No.	POLYAMIDE		ADDITIVES ADDED DURING EXTRUSION			Limiting oxygen index	Classification in the UL 94 test	
	Nature	Parts	Melamine cyanurate	POLYOL				Orthophosphoric acid
				Nature	Parts			
1	Adipic polyamide 11 (A)	100	0	Monopentaerythritol	0	0	V2 V2	
2	"	90	10	"	0	0	V2 V2	
3	"	80	20	"	0	0	V2 V2	
4	"	88	10	"	2	0	V2 V2	
5	"	76	20	"	4	0	V2 V2	
6	Phosphoric polyamide 11 (B)	100	0	"	0	0	V2 V2	
7	"	90	10	"	0	0	V2 V2	
8	"	80	20	"	0	0	V2 V2	
9	"	98	0	"	2	0	V2 V2	
10	"	96	0	"	4	0	V2 V2	
11	"	88	10	"	2	0	V0 V0 V0	

(TABLE CONT.)

MIXTURE COMPOSITION, PARTS BY WEIGHT					RESULTS OF THE FLAMMABILITY TESTS				
Example No.	POLYAMIDE		ADDITIVES ADDED DURING EXTRUSION			Limiting oxygen index	Classification in the UL 94 test		
	Nature	Parts	Melamine cyanurate	POLYOL			Orthophosphoric acid	Test specimen thickness	
				Nature	Parts				
12	Adipic polyamide 12 (G)	100	0	"	0	0	21	V2	V2
13	"	90	10	"	0	0	25	V2	V2
14	"	80	20	"	0	0	28	V2	V2
15	"	88	10	"	2	0	28	V2	V2
16	"	76	20	"	4	0	29	V2	V2
17	"	81.2	15	"	2.95	0.85	31.9	V2	V0
18	Phosphoric polyamide 12 (D)	100	0	"	0	0	22	V2	V2
19	"	90	10	"	0	0	25	V2	V2
20	"	75	25	"	0	0	26	V2	V2
21	"	98	0	"	2	0	22	V2	V2
22	"	96	0	"	4	0	22	V2	V2
23	"	82	15	"	3	0	35	V2	V0
24	Dodecanedioic polyamide 12 (E)	100	0	"	0	0	22	V2	V2
25	"	80	20	"	0	0	29	V2	V2
26	"	80	17	"	3	0	33	V0	V0
27	"	82	15	"	3	0	31	V0	V0
28	Phosphoric polyamide 11 (B)	81	"	SORBITOL	2	0	30.6	V2	V2

A metering pump is also used to introduce 1,200 parts of butylbenzenesulphonamide into the molten mixture at 240°C, in the region of the third barrel.

The extruded lace, cooled, is chopped in granules 5 which allow the test specimens required for the flammability tests to be injection-moulded.

The limiting oxygen index is 25 (without cyanurate or pentaerythritol it would be 21) and the product is classified V0 in the UL 94 test at 3.2 mm thickness 10 (otherwise, the test specimen would burn completely).

CLAIMS

1. Compositions with retarded combustibility, consisting of polyamide obtained particularly by anionic polymerization of lactams or by hydrolytic polycondensation of their monomers in the presence of a chain limiter and of melamine cyanurate, which are characterized in that they additionally include a polyol containing at least four times the alcohol group, the said cyanurate and polyol being uniformly dispersed in the said polyamides in the following proportions by weight:

- a) at least 35% of polyamides,
- b) from 0 to 30% of additives, fillers or plasticizers,
- c) from 1 to 25% of melamine cyanurate in the form of particles, 70% of which are below 30 μ m in size, and
- d) from 0.5 to 10% of polyol,

the sum of the constituents shown under a) to d) having to be equal to 100 in each case.

2. Compositions according to Claim 1, characterized in that the polyol is chosen from the group including monopentaerythritol and sorbitol.

3. Compositions according to either of Claims 1 and 2, characterized in that they include an acid derived from phosphorus in a proportion of 2 to 20 parts per thousand of the weight of the polyamides, this acid being calculated as orthophosphoric acid.

4. Compositions according to Claim 3, characterized in that the acid derived from phosphorus is chosen from the group including the orthophosphoric, metaphosphoric, pyrophosphoric, phosphorous and hypophosphorous acids or mixtures thereof.

5. Process for the manufacture of the compositions according to either of Claims 3 and 4, characterized in that the acid derived from phosphorus is introduced in the form of a chain limiter during the hydrolytic polycondensation of the monomers giving rise to the polyamides.

6. Process for the manufacture of the compositions according to either of Claims 3 and 4, characterized in

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b2
b2

that they are enriched in acid derived from phosphorus by addition of this acid to the polyamides of which they consist.

7. Compositions according to any one of Claims 1 to 4, characterized in that they consist of polyamides 11 or 12 obtained by hydrolytic polycondensation of their corresponding monomers in the presence of dodecanedioic acid.

Patentansprüche

1. Gemische mit verzögerter Brennbarkeit aus Polyamiden, die insbesondere durch anionische Polymerisation von Laktamen oder durch hydrolytische Polykondensation ihrer Monomere in Anwesenheit eines Kettenlängenbegrenzers und von Melamincyanurat hergestellt wurden, dadurch gekennzeichnet, daß sie zusätzlich ein Polyol mit mindestens 4 Alkoholgruppen enthalten und daß das genannte Cyanurat und Polyol in den genannten Polyamiden in folgenden Gewichtsverhältnissen gleichmäßig verteilt sind:

- a) mindestens 35 % Polyamide
- b) 0 bis 30 % Zusätze, Füllstoffe oder Weichmacher
- c) 1 bis 25 % Melamincyanurat in Form von Körnern, von denen 70 % eine Größe unter 30 µm aufweisen.
- d) 0,5 bis 10 % Polyol,

wobei die Summe der unter a) bis d) angegebenen Bestandteile in jedem Fall gleich 100 sein muß.

2. Gemische nach Patentanspruch 1, dadurch gekennzeichnet, daß das Polyol aus der Monopentaerythritol und Sorbitol enthaltenden Gruppe ausgewählt ist.

3. Gemische nach einem der Patentansprüche 1 und 2, dadurch gekennzeichnet, daß sie eine vom Phosphor abgeleitete Säure im Verhältnis von 2 bis 20 Teilen auf Tausend Gewichtsteile der Polyamide enthalten, wobei diese Säure als Orthophosphorsäure berechnet wird.

4. Gemische nach Patentanspruch 3, dadurch gekennzeichnet, daß die vom Phosphor abgeleitete Säure aus der Gruppe gewählt wird, die Ortho-, Meta-, Pyrophosphorsäure, phosphorige und hypophosphorige Säure oder deren Gemische umfaßt.

5. Verfahren zur Herstellung der Gemische nach einem der Patentansprüche 3 und 4, dadurch gekennzeichnet, daß die vom Phosphor abgeleitete Säure als Kettenlängenbegrenzer bei der hydrolytischen Polykondensation der die Polyamide bildenden Monomere zugesetzt wird.

6. Verfahren zur Herstellung der Gemische nach einem der Patentansprüche 3 und 4, dadurch gekennzeichnet, daß man sie mit von Phosphor abgeleiteter Säure durch Zusatz dieser Säure zu den sie bildenden Polyamiden anreichert.

7. Gemische nach irgendeinem der Patentansprüche 1 bis 4, dadurch gekennzeichnet, daß sie aus den durch hydrolytische Polykondensation ihrer jeweiligen Monomere in Anwesenheit von Dodecan-di-säure hergestellten Polyamiden 11 oder 12 bestehen.

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7. Gemische nach irgendeinem der Patentansprüche 1 bis 4, dadurch gekennzeichnet, daß sie aus den durch hydrolytische Polykondensation ihrer jeweiligen Monomere in Anwesenheit von Dodecan-di-säure hergestellten Polyamiden 11 oder 12 bestehen.

Claims

1. Compositions with retarded combustibility, consisting of polyamide obtained particularly by anionic polymerization of lactams or by hydrolytic polycondensation of their monomers in the presence of a chain limiter and of melamine cyanurate, which are characterized in that they additionally include a polyol containing at least four times the alcohol group, the said cyanurate and polyol being uniformly dispersed in the said polyamides in the following proportions by weight:

- a) at least 35 % of polyamides,
 - b) from 0 to 30 % of additives, fillers or plasticizers,
 - c) from 1 to 25 % of melamine cyanurate in the form of particles, 70 % of which are below 30 µm in size, and
 - d) from 0,5 to 10 % of polyol,
- the sum of the constituents shown under a) to d) having to be equal to 100 in each case.

2. Compositions according to Claim 1, characterized in that the polyol is chosen from the group including monopentaerythritol and sorbitol.

3. Compositions according to either of Claims 1 and 2, characterized in that they include an acid derived from phosphorus in a proportion of 2 to 20 parts per thousand of the weight of the polyamides, this acid being calculated as orthophosphoric acid.

4. Compositions according to Claim 3, characterized in that the acid derived from phosphorus is chosen from the group including the orthophosphoric, metaphosphoric, pyrophosphoric, phosphorous and hypophosphorous acids or mixtures thereof.

5. Process for the manufacture of the compositions according to either of Claims 3 and 4, characterized in that the acid derived from phosphorus is introduced in the form of a chain 1 limiter during the hydrolytic polycondensation of the monomers giving rise to the polyamides.

6. Process for the manufacture of the compositions according to either of Claims 3 and 4, characterized in that they are enriched in acid derived from phosphorus by addition of this acid to the polyamides of which they consist.

7. Compositions according to any one of Claims 1 to 4, characterized in that they consist of polyamides 11 or 12 obtained by hydrolytic polycondensation of their corresponding monomers in the presence of dodecanedioic acid.