

The present invention relates to the synthesis of polyhaloimides and more particularly to that of imides derived from halodicarboxylic acids such as tetrabromophthalic acid.

5 Polyhaloimides, especially tetrabromophthalimides and bis(tetrabromophthalimides), are well-known compounds which find an application as flame-retarding agents in numerous inflammable materials, in particular in plastics (see for example the article of S.M. Spatz et al.
10 entitled "Some N-substituted tetrabromophthalimide fire-retardant additives" in Industrial and Engineering Chemistry Product Research and Development, Vol. 8, No. 4 (1969), pages 397-398, as well as Patents US 3 873 567 and FR 2 369 261 and Applications JP 74-045062 and
15 75-064337).

However, the preparation processes described in the abovementioned references give mediocre yields and provide products which are most often yellow-coloured or which become coloured during their use and thus impart to
20 the plastics (moulded objects or compounds) a colouring which is defective and unacceptable in a good number of uses. Moreover, these products very often contain materials which are, in certain polymeric materials, volatile at the temperatures of use and result in
25 corrosion of the moulds. In addition, the use for their preparation of organic solvents (especially xylene, toluene, alcohol, acetic acid), most often selected on account of their ability to form azeotropic mixtures with water, allowing the water of condensation produced by the
30 imidification reaction to be entrained, or to dissolve the halodicarboxylic acid anhydride, requires expensive operations for the separation and recovery of these solvents, as well as drying means which are suited to the removal of the organic solvent vapours.

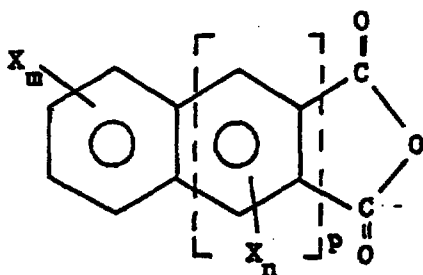
35 The abovementioned disadvantages are especially encountered in the case of polyhaloimides derived from hydrazine and halodicarboxylic acid anhydrides. It has now been found that it is not essential to use an organic solvent in order to dissolve the anhydride and/or to

remove the water of condensation and that, by working in an aqueous medium under specific conditions, it is possible to obtain colourless or very faintly coloured products in very high yields and without effluent waste and environmental problems, which products, without prior purification, are perfectly suitable for giving a flame-retarding treatment to macromolecular materials, including those which are used at high temperature, particularly above 250°C.

The process according to the invention, which consists in condensing hydrazine with a halo dicarboxylic acid anhydride, is characterized in that the reaction is carried out in an aqueous medium, at a temperature ranging from 40 to 225°C, with an anhydride/hydrazine molar ratio substantially equal to 2.

Among the haloanhydrides which may be used, there may more particularly be mentioned:

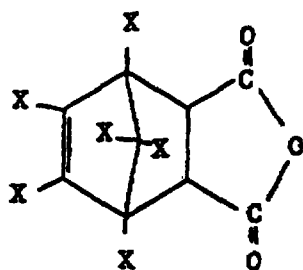
- aromatic dicarboxylic acid anhydrides (benzene, naphthalene, anthracene), especially those of general formula:



(I)

in which X represents a bromine or chlorine atom, m is an integer ranging from 2 to 4 and n and p are integers ranging from 0 to 2;

- anhydrides of cycloaliphatic dicarboxylic acids such as 1,4,5,6,7,7-hexabromobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid and its chloro homologue (chloro-endic acid), corresponding to the formula:



(II)

in which X has the same meaning as above. Bromophthalic anhydrides, for example 3,4-(or 3,6- or 4,5-)dibromophthalic anhydride, 3,4,6-tribromophthalic anhydride and more particularly tetrabromophthalic anhydride, are preferably used.

In accordance with the present invention, a single anhydride or a mixture of two or more anhydrides may be used. Commercial anhydrides often containing a small amount of inorganic acids may be used as they are, without prior purification. It has, in fact, been observed that particularly good results are obtained when the aqueous anhydride solution or dispersion used is strongly acidic (pH lower than 4).

The amount of water forming the reaction medium of the process according to the invention may vary within a wide range, the only condition being that it is sufficient to provide for suitable dispersion of the reactants and to allow good stirring. This condition is generally achieved by using an amount of water such that the content of solid materials in the reaction medium is approximately between 5 and 75% by weight, preferably between 20 and 40%.

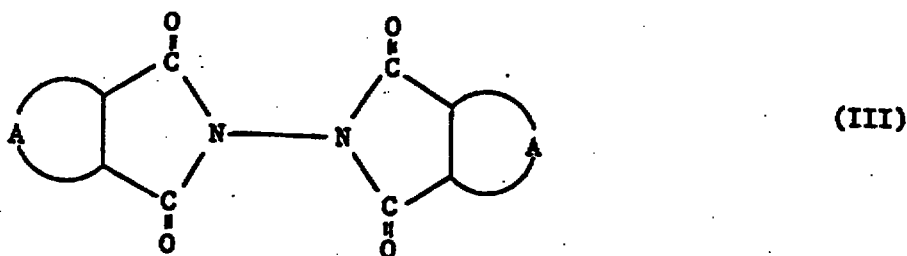
The reaction may be carried out at atmospheric pressure at a temperature ranging from 40 to 100°C or, provided that it is performed under pressure, at a higher temperature which may range up to 225°C. The process is preferably performed between 100 and 225°C, which corresponds to pressures of between 1 and 25 bar approximately.

Hydrazine, in the hydrate or hydrazinium salt form (for example sulfate, hydrohalide or acetate) may be used as it is or in the form of a dilute aqueous

5 solution. Hydrazine hydrate in the form of a commercially available aqueous solution is preferably used. The process according to the invention is advantageously implemented by gradually introducing hydrazine into the haloanhydride solution or dispersion which has been heated beforehand and kept stirring.

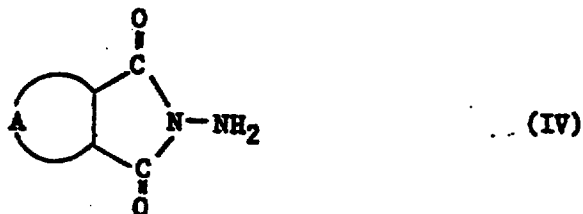
10 The reaction time may vary within a wide range, but is generally between 1 and 20 hours. After cooling the reaction medium, the solid suspension obtained is filtered off and optionally washed with water until neutral, and the product is then dried by standard drying means.

15 When the process according to the invention is carried out at a temperature at least equal to 140°C, the product obtained generally consists of the bisimide corresponding to the following general structure:



in which A represents the haloanhydride residue used.

20 At lower temperatures, the product obtained contains, in addition to the bisimide of formula (III), a variable proportion which may reach 80% by weight of a substantially equimolar mixture of the starting haloanhydride and of the corresponding N-aminoimide of general structure:



25 where A has the same meaning as above, it being possible for this N-aminoimide to be in the salt form (sulfate,

hydrohalide or acetate). The content of bisimide product (III) obtained is generally proportionally greater the closer the reaction temperature is to 140°C.

Whether they are pure bisimides or bisimide + N-aminoimide + anhydride mixtures, the products obtained in accordance with the process according to the invention are particularly suitable as flame-retarding agents in plastics of any nature. Their incorporation into these materials may be carried out by any known method, at doses ranging from 5 to 40% relative to the weight of inflammable material.

The examples which follow, in which the parts and the percentages are expressed by weight, illustrate the invention without limiting it.

15 EXAMPLE 1

1114 parts of commercial tetrabromophthalic anhydride are dispersed in 3000 parts of distilled water in a glass reactor fitted with a stirrer and with a reflux device. The pH of the suspension is 2.2.

20 After bringing this suspension to 60°C, 60 parts of 100% hydrazine hydrate are progressively added over 20 to 30 minutes and the reaction mixture is then brought to 100°C. During the first seven hours of reaction at this temperature, the dispersion is yellow. 1600 parts of
25 distilled water are subsequently added and the mixture is maintained at 100°C for a further 7 hours. A white to ivory-white suspension is then obtained, which is cooled and filtered off on a Büchner funnel. After washing with water to neutral pH and drying under vacuum at 110-120°C,
30 an ivory-white product is obtained with a yield greater than 96%, the analysis of which shows that it contains approximately:

40% of N,N'-bis(tetrabromophthalimide)
30.5% of N-aminotetrabromophthalimide
35 29.5% of tetrabromophthalic anhydride.

These percentages were determined by successive extractions using solvents specific for tetrabromophthalic anhydride and N-aminotetrabromophthalimide (methanol and dimethyl sulphoxide respectively),

N,N'-bis(tetrabromophthalimide) being insoluble in these solvents. Other methods of identification (NMR and IR spectroscopic analyses and DTA and GTA thermal analyses) were also used in order to identify the various compounds.

EXAMPLE 2

The procedure is performed as in Example 1, but adding 2.5 parts of 96% sulphuric acid to the aqueous tetrabromophthalic anhydride suspension. The pH is then 1.1.

An ivory-white product is obtained with a yield greater than 98%, containing approximately:

29% of N,N'-bis(tetrabromophthalimide)

36% of N-aminotetrabromophthalimide (partly in sulphate form)

and 35% of tetrabromophthalic anhydride.

EXAMPLE 3

In a one-litre autoclave fitted with a stirrer, 186 parts of commercial tetrabromophthalic anhydride are dispersed in 600 parts of distilled water brought to 115°C using a heating jacket. The pH of the suspension is 2.2.

10 parts of 100% hydrazine hydrate diluted with 100 parts of distilled water are progressively introduced into the suspension using a pump. At the start of the introduction, the pressure is approximately 3 bar; at the end of the introduction, the pressure is approximately 5 bar and the temperature is 130°C.

These conditions (5 bar, 130°C) are maintained for approximately 8 hours, the reaction mixture is then cooled by circulation of cold water and the suspension obtained is filtered off. After washing with water to neutral pH and drying under vacuum at 100-110°C, a white product is obtained with a yield of 97%, containing approximately:

95% of N,N'-bis(tetrabromophthalimide)

2.6% of N-aminotetrabromophthalimide

and 2.4% of tetrabromophthalic anhydride.

EXAMPLE 4

1335 parts of commercial tetrabromophthalic anhydride are dispersed in 4500 parts of distilled water in a 6-litre autoclave fitted with a stirrer and with a heating means (for example a jacket). The pH of the suspension is 2.2.

This suspension is brought to 150°C, followed by progressive introduction thereto of 72 parts of hydrazine hydrate diluted in 125 parts of distilled water, and the pressure is subsequently maintained between 5 and 6 bar for approximately 5 hours.

The reaction mixture is subsequently cooled by circulation of cold water and the suspension is then filtered off. After washing with water to neutral pH and drying under vacuum at 100-110°C, a white product consisting of virtually pure N,N'-bis(tetrabromophthalimide) is obtained with a yield of 97%.

EXAMPLE 5

890 parts of chlorendic anhydride (1,4,5,6,7,7-hexachlorobicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride) are dispersed in 3000 parts of distilled water in the same apparatus as in Example 1 and the mixture is then brought to 60°C. The pH of the suspension is approximately 2.

60 parts of 100% hydrazine hydrate are subsequently added progressively (over 20 to 30 minutes) and the suspension is then brought to 100°C and maintained at this temperature for approximately 12 hours.

By distillation, part of the water of the reaction mixture is removed until a moist paste is obtained, which is drained and then washed with cold water until neutral and oven-dried under vacuum at 100°C for 8 hours.

An ivory-white product is thus obtained, containing approximately:

90% of N,N'-bis(chlorendimide)
5% of N-aminochlorendimide
and 5% of chlorendic anhydride.

EXAMPLE 6

800 parts of tetrachlorophthalic anhydride are

dispersed in 10000 parts of distilled water in the same apparatus as in Example 1.

The suspension, the pH of which is approximately 2, is subsequently brought to 90°C and 70 parts of 100% hydrazine hydrate are added over approximately 2 hours. After reacting for approximately 12 hours at 98°C, the mixture is cooled and the suspension is filtered off and washed with water until the pH is neutral.

After oven-drying under vacuum, a white product is obtained with a yield greater than 96%, which product is composed of approximately:

68% of N,N'-bis(tetrachlorophthalimide)

16% of N-aminotetrachlorophthalimide

and 16% of tetrachlorophthalic anhydride.

EXAMPLE 7

372 parts of tetrachlorophthalic anhydride and 603 parts of tetrabromophthalic anhydride are dispersed in 4000 parts of distilled water in the same apparatus as in Example 1.

The suspension thus obtained (pH approximately 2) is subsequently brought to 90°C, followed by addition of 65 parts of 100% hydrazine hydrate over 3 to 4 hours and the mixture is left to react for 12 hours at 98°C.

After filtration, washing with water until the pH is neutral and drying under vacuum at 110-120°C for 8 hours, a white product is obtained with a yield greater than 96%, which product is composed of approximately:

- 50% of a mixture of N,N'-bis(tetrachloro- and -bromophthalimides),

- 25% of a mixture of N-aminotetrachlorophthalimide and N-aminotetrabromophthalimide, and

- 25% of a mixture of tetrachloro- and tetrabromophthalic anhydrides.

EXAMPLE 8

153 parts of 1,4,5,6,7,7-hexabromobicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic anhydride, hereinafter referred to as "bromendic anhydride" and prepared from hexabromocyclopentadiene and maleic anhydride, are

dispersed in 500 parts of distilled water in the same apparatus as in Example 1. The pH of the suspension is approximately 2.3.

5 The mixture is brought to 97°C, followed by progressive addition (over 20 to 30 minutes) of 6 parts of 100% hydrazine hydrate, and the mixture is subsequently maintained at 100°C for approximately 12 hours.

10 Part of the water is removed by distillation until a moist paste is obtained, which is drained and then washed with cold water until the pH is neutral and oven-dried under vacuum at 100-110°C for 8 hours. A faintly-coloured product is thus obtained, which is composed of approximately:

15 65% of N,N'-bis(bromendimide)
17.5% of N-aminobromendimide
and 17.5% of bromendic anhydride.

EXAMPLE 9 (comparative)

20 619 parts of tetrabromophthalic anhydride are dissolved, at 66°C, in 1500 parts of methanol in the same apparatus as in Example 1. After complete dissolution, 34 parts of 100% hydrazine hydrate are added and the mixture is then maintained at 67°C for approximately 8 hours.

25 After cooling, filtration and washing with methanol, and then with water, a yellow product containing no tetrabromophthalic anhydride and consisting mainly of N-aminotetrabromophthalimide with a small amount of N,N'-bis(tetrabromophthalimide) and other unidentified
30 products is obtained with a yield of approximately 75%.

EXAMPLE 10 (comparative)

35 619 parts of tetrabromophthalic anhydride are introduced into 750 parts of dimethylformamide and 1250 parts of xylene in the same apparatus as in Example 1 and the mixture is then brought to 100°C. A yellow solution is thus obtained, to which are added 34 parts of 100% hydrazine hydrate. The mixture is subsequently brought to 138°C and maintained at this temperature for approximately 8 hours, while removing the

water of formation by azeotropic distillation with xylene.

After cooling, filtration, washing with hexane and drying under vacuum, a yellow product containing no
5 tetrabromophthalic anhydride and consisting mainly of N,N'-bis(tetrabromophthalimide) with a small amount of N-aminotetrabromophthalimide and other unidentified products is obtained with a yield of approximately 78%.

EXAMPLE 11

10 The effectiveness of the products according to the invention as flame-retarding agents for plastics was tested according to the following general experimental procedure:

With the aid of a mixer of the planetary or
15 "barrel" type, the resin, in powder or granule form, is mixed, in the proportions indicated in the following tables, with the flame-retarding agent to be tested and the optional additives (antimony trioxide and paraffin). After homogenization, the mixture is extruded using a
20 suitable extruder (twin-screw, single-screw or "Buss" type) which may or may not be equipped with a means for degassing, the extrusion being carried out at the extrusion temperature indicated by the resin supplier and which is related to the melting point of the polymer. The
25 compound obtained, optionally granulated, is subsequently converted into measurement test samples using an injector press working at suitable temperatures. These test samples are subsequently subjected to the standardized
30 fire resistance test UL94 at 3.2 mm and 1.6 mm (NF Standard T51072) and the standardized oxygen number test ON% (NF Standard T51071).

Table A summarizes the results obtained in the case of polybutylene terephthalate (TMNO-ORGATER, granules marketed by the Applicant).

35 Table B collates the results obtained with the product of Example 1 and other resins, namely:

- Polypropylene (PK-1060 P marketed by the company HOECHST in powder form),
- Polyamide 12 (AMNO-RILSAN marketed by the

Applicant in granule form),

- ABS resin (UGIKRAL SF marketed by the company
CdF-Chimie in powder form).

TABLE A

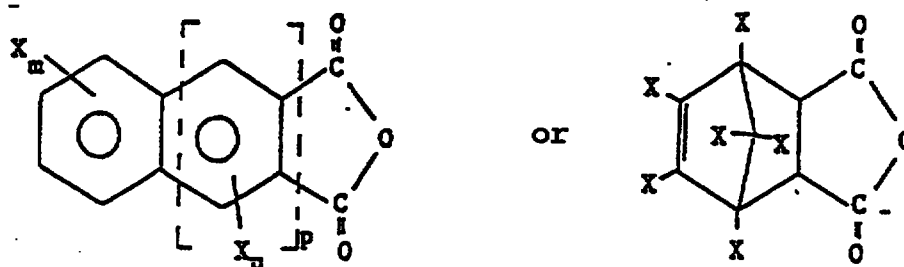
TEST No.	I control	II	III	IV	V	VI	VII (comparative)	VIII
Flame-retarding agent of Example No.	None	1	4	5	6	7	9	10
Composition (parts by weight):								
- TMNO-ORGATER resin	1000	790	3160	3449	3402	3290	1559	1559
- Flame-retarding agent	0	126	588	308	355	467	290	290
- Antimony trioxide	0	60	246	243	243	243	121	121
- Paraffin	0	15	60	60	60	60	30	30
Results of the tests:								
- UL94	NC	VO	VO	V2	V2	VO	VO	VO
- ON%	22	32.6	31.3	25.1	23.7	27.6	30.1	31.7
Colour of the test sample:	white	ivory- white	white	slight- ly grey	ivory- white	ivory- white	yellow	yellow

TABLE B

RESIN	Composition (parts by weight)			Results of the tests		Colour of the test sample
	Resin	Flame-retarding agent of Example 1	Antimony trioxide	UL94	ON%	
PK 1060 P	1000 (control)	0	0	NC	18	white
"	522	359	119	VO	25	ivory-white
AMNO-RILSAN	1000 (control)	0	0	V2 (at 3.2mm)	22	slightly yellow
"	877	96	26	VO	29.4	pale yellow
UGIKRAL SF	1000 (control)	0	0	NC	18	beige
"	766	150	50	VO (at 3.2mm)	25.6	light beige

Claims for the States: AT, BE, CH, LI, DE, ES, FR, GB, GR, IT, LU, NL, SE

1. Process for the preparation of haloimides by condensation of hydrazine and a halodicarboxylic acid anhydride of formula



where X represents a bromine or chlorine atom, m is an integer ranging from 2 to 4 and n and p are integers ranging from 0 to 2, or a mixture of such anhydrides, characterized in that the reaction is carried out in an aqueous medium, at a temperature ranging from 40 to 225°C, with an anhydride/hydrazine molar ratio substantially equal to 2.

2. Process according to Claim 1, in which the process is performed under pressure at a temperature of at least 140°C.

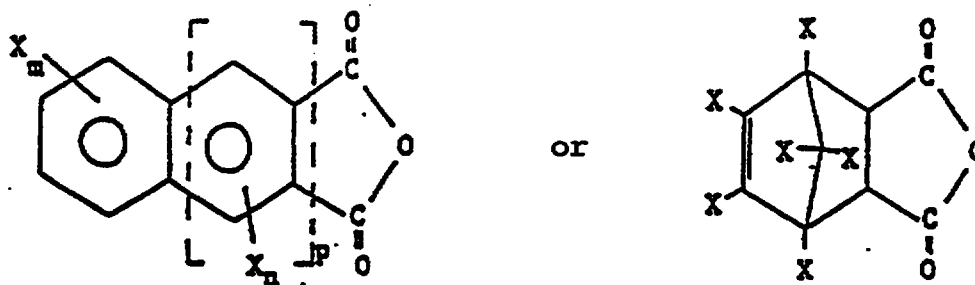
3. Process according to Claim 1 or 2, in which an aqueous anhydride solution or dispersion having a pH lower than 4 is used as starting material.

4. Process according to Claim 1, in which tetrabromophthalic anhydride, tetrachlorophthalic anhydride, chlorendic anhydride, bromendic anhydride or in a mixture of these anhydrides is used.

5. Process according to Claim 1 to 4, in which hydrazine is used in the hydrate or hydrazinium salt form.

6. Flame-retardant compositions based on substantially colourless halodicarboxylic acid bisimide, which may be obtained according to one of Claims 1 to 5, resulting from the condensation of hydrazine and halodicarboxylic acid anhydride of formula





where X represents a bromine or chlorine atom, m is an integer ranging from 2 to 4 and n and p are integers ranging from 0 to 2, or a mixture of such anhydrides, characterized in that they also contain, in addition to the abovementioned bisimide, up to 80% by weight of a substantially equimolar mixture of the N-aminoimide and the anhydride of the said halodicarboxylic acid.

7. Compositions according to Claim 6, consisting of N,N'-bis(tetrabromophthalimide), N-amino-tetrabromophthalimide and tetrabromophthalic anhydride.

8. Application of the products obtained according to the process of one of Claims 1 to 5 or of the compositions according to Claim 6 or 7, to the flame-retarding treatment of plastics.

9. Plastics which are given a flame-retarding treatment using a product obtained according to the process of one of Claims 1 to 5 or using a composition according to Claim 6 or 7.

