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

Polyhaloimides, especially tetrabromophthalimides and bis)tetrabromophthalimides), are well-known compounds which find an application as flame-retardants in many flammable materials, in particular in plastics (see, for example, the paper by S.M. Spatz et al, 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 74-045,062 and 75-064,337).

However, the methods of preparation described in the abovementioned references give mediocre yields and provide products which are in most cases yellow in colour or which discolour when used and which thus impart to the plastics (compounds or moulded articles) a colouring which rules out their use and is unacceptable in a goodly number of applications. Furthermore, these products very frequently contain materials which are volatile at the temperatures of use in certain polymeric materials and which lead to corrosion of the moulds. In addition, the use of organic solvents in their preparation (particularly xylene, toluene, alcohol and acetic acid), which are in most cases chosen for their ability to form azeotropic mixtures with water, making it possible to entrain the water of condensation produced by the imidification reaction or to dissolve the halogenated dicarboxylic acid anhydride, requires costly operations of separation and recovery of these solvents, as well as means of drying which are suitable for the removal of organic solvent vapours.

The abovementioned disadvantages are encountered especially in the case of polyhaloimides derived from hydrazine and from halogenated carboxylic acid anhydrides.

What is more, the availability of this latter raw material requires a prehalogenation of the dicarboxylic acid anhydrides. This factor represents an additional handicap both from the technological and economic standpoint, because the synthesis of these polyhaloimides involves the following sequence of stages:

- halogenation of the carboxylic acid anhydride,
- isolation and purification of the halogenated anhydride obtained.

It has now been found that it is not necessary to isolate and to purify the intermediate halogenated anhydride and that it is not essential to employ an organic solvent to dissolve the anhydride and/or to remove the water of condensation, and that by operating without an organic solvent under certain conditions it is possible to obtain, in very high yields, colourless or very slightly coloured products which, without preliminary purification are perfectly suitable for the fireproofing of macromolecular materials, including those which are used at high temperature, particularly above 250°C.

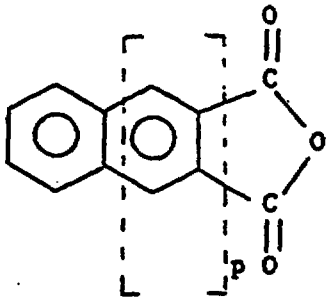
The process according to the invention, which consists in halogenating a dicarboxylic acid anhydride and then reacting hydrazine with the crude halogenation product, is characterised in that:

a) the halogenation of the dicarboxylic acid anhydride is carried out,

b) the preceding phase obtained in a is then reacted with hydrazine.

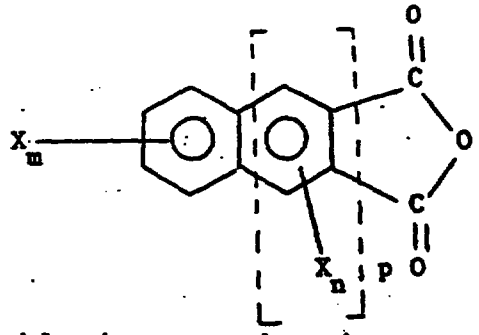
Among the anhydrides which can be employed, those which may be mentioned more particularly are:

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



in which p is an integer ranging from 0 to 2,

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



in which X is a chlorine or a bromine, m varies from 0 to 4, n varies from 0 to 2, m + n is less than 4 + 2p, and p varies from 0 to 2. X may also be a chlorine and a bromine (m + n greater than 1), that is to say that it is possible to have all the combinations of chlorine and bromine in the same molecule.

In accordance with the present invention, a single anhydride or a mixture of several anhydrides may be employed. When a mixture of anhydrides is employed, one or more of them, but not all, may be saturated with halogen. Phthalic anhydride is preferably employed.

The halogenation of the dicarboxylic acid anhydride, stage a, is carried out following methods which are known to the person skilled in the art. The halogenation consists of a chlorination or a bromination, or a chlorination followed by a bromination, or vice versa. Although the halogenation may be partial or total, it is preferably that the halogenation should be continued until products in which m is greater than or equal to 2

are obtained. Advantageously, a single halogen is employed, and preferably bromine.

Phthalic anhydride may be chlorinated in chlorohydrin, for example according to the method described in German Patent DE 1,934,174. According to this method, a solution of phthalic anhydride in chlorohydrin (HSO_3Cl) is prepared, iodine is added and the mixture is heated to 120°C and is then treated with a stream of chlorine containing ICl_3. Phthalic anhydride can also be chlorinated in solution in oleum in the presence of a little iodine, by injecting chlorine into the solution. It is preferably to carry out the chlorination in an oleum medium.

Bromination of phthalic anhydride is carried out, for example, according to the technique described in Patent GB 1,084,375, in which the bromination is carried out in a 65 % oleum medium and is catalysed by iodine and by iron.

Bromination of phthalic anhydride may also be carried out according to the technique described in Patent CH 410,898, in which the bromination is carried out in a sulphuric acid medium (SO_3 content between 20 - 65 %) and in the presence of chlorine.

It is not necessary to isolate the halogenated dicarboxylic acid anhydride from the phase obtained at the end of halogenation.

According to the invention, the stage b is carried out by reacting the preceding phase obtained in a with hydrazine.

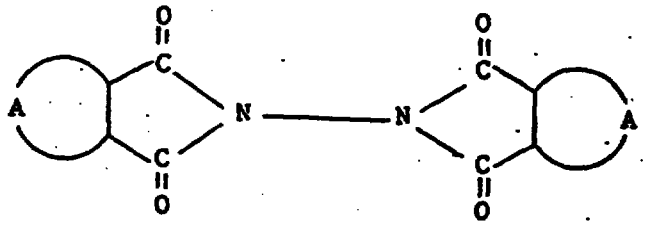
One of the advantages of the invention becomes clearly apparent in this case; it is not necessary to isolate the halogenated intermediate product obtained in stage a before performing the reaction with hydrazine. The hydrazine is used in the form of hydrate or of a hydrazine salt (for example sulphate, a hydrohalide or acetate). Hydrazine or its derivatives may be employed as such or in the form of a sulphuric solution. The quantity of sulphuric acid may vary within wide limits, the only

condition being that it should be sufficient to ensure the appropriate dispersion of the reactants and to permit satisfactory stirring. The molar ratio of halogenated anhydride to hydrazine is below 2, and preferably between 1 and 2. This reaction in stage b may be carried out at atmospheric pressure at temperatures of between 80 and 220°C and preferably 110 and 200°C.

The reaction time may vary within wide limits, but is generally between 1 and 20 hours. After cooling of the reaction mixture, the solid suspension obtained is diluted and is then filtered off and washed with water until neutral and the product is then dried by conventional drying means.

According to a preferred embodiment of the invention, hydrazine in the form of hydrate or of a hydrazinium salt is used in the form of a solution in sulphuric acid, this solution being progressively introduced into the halogenated anhydride phase a obtained previously; the quantity of sulphuric acid and its concentration are calculated so that, at the end of the addition of hydrazine, the reaction mixture advantageously contains 500 to 1,500 ml, and preferably 600 to 1,200 ml, of sulphuric solution per mole of anhydride employed in a, the concentration of this solution being between 80 % H_2SO_4 and 65 % oleum, and preferably between 90 % H_2SO_4 and 40 % oleum.

When stage b of the process according to the invention is carried out at a temperature of at least 130°C, the product obtained generally consists of the bisimide corresponding to the following general structure:



in which A denotes the residue of the halogenated anhydride employed.

The products obtained in accordance with the process according to the invention are particularly suitable as flame-retardants in plastics of all kinds. Their incorporation into these materials may be carried out by any known method in quantities ranging from 5 to 40 % relative to the weight of flammable material.

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

EXAMPLE 1

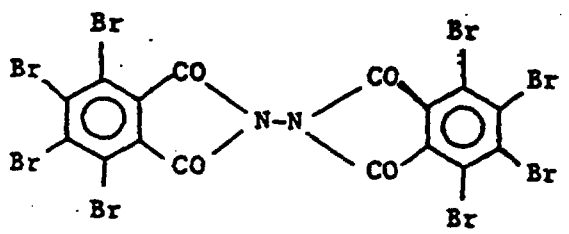
The following are introduced successively into a glass reactor equipped with a stirrer and a reflux device:

- 148 g of phthalic anhydride
- 1.5 g of iodine, and
- 700 g of 65 % oleum

After the mixture has been homogenized, it is heated to 60-70°C and 345 g of bromine are run in over 4 hours; at the end of the addition, the mixture is kept for 4 hours while the temperature is progressively raised to 110°C.

A solution of 107 g of hydrazine sulphate dissolved in 1,000 g of 96 % H_2SO_4 is then introduced over 2 hours, while the temperature is progressively raised from 110 to 180°C, and the reaction mixture is kept at this temperature for approximately 11 hours.

After cooling, dilution with water, filtering and washing the solid obtained until neutral, followed by drying, 430 g of a white solid are obtained (yield = 93 %), its infrared spectrum corresponding to the formula:



EXAMPLE 2

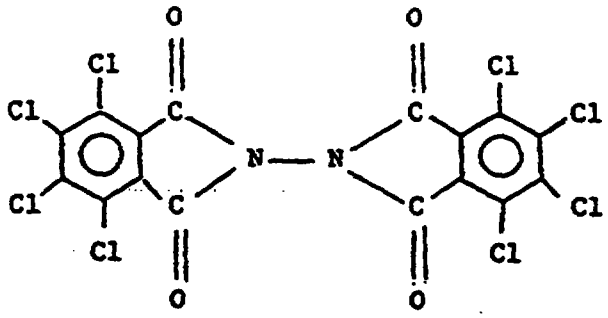
The following are introduced successively into the same apparatus as in the preceding example:

- 148 g of phthalic anhydride
- 1.5 g of iodine, and
- 700 g of 65 % oleum.

After the phthalic anhydride has dissolved, the reaction mixture is heated to 40°C, that is to say to its boiling temperature, and chlorine is injected at a rate of 90 g/h; this introduction of chlorine is kept up for 5 hours, while the temperature is progressively raised to 130°C.

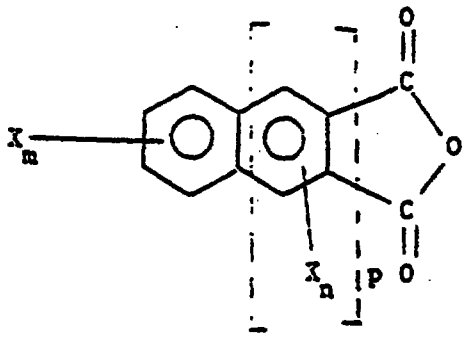
After cooling, a solution of 90 g of hydrazine sulphate in 900 g of 96 % sulphuric acid is run in over two hours, while being heated progressively to 100-110°C; after the introduction of hydrazine the temperature is raised to 170°C and kept thereat for 11 hours.

The reaction mixture is then cooled, diluted with water, and the solid obtained is filtered off and washed until neutral; after drying, a white solid is obtained in a weight yield of 92 %, its infrared spectrum corresponding to the formula:



CLAIMS

1. Process for the preparation of halogenated bisimides from halogen, dicarboxylic acid anhydride of formula



in which:

- X denotes a chlorine or bromine atom,
- n, m and p are integers,
- m varies from 0 to 4,
- n and p vary from 0 to 2,
- m + n is smaller than 4 + 2p, and
- X may be a chlorine and a bromine if m + n > 1

or a mixture of such anhydrides,
and hydrazine, characterised in that without using an organic solvent:

a) halogenation of the dicarboxylic acid anhydride is carried out,

b) the preceding phase obtained in a is then reacted with hydrazine used in a molar ratio of halogenated anhydride to hydrazine of less than 2, at a temperature between 80°C and 220°C.

2. Process according to Claim 1, characterised in that the anhydride is preferably phthalic anhydride.

3. Process according to Claim 1, characterised in that the halogen is preferably bromine.

4. Process according to one of Claims 1 to 3, characterised in that in stage a a halogenation is carried out such that m is greater than or equal to 2.

5. Process according to one of Claims 1 to 4, characterised in that hydrazine is preferably employed in the form of hydrazine sulphate dissolved in sulphuric acid.

* C L M S *

6. Process according to one of Claims 1 to 5, characterised in that stage b is carried out between 110°C and 220°C.

* C L M S *