

This Sheet Has Been Replaced



- 1 -

✓
✓
✓1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25

PROCESS FOR PREPARING HALOGENATED IMIDES AND THEIR
APPLICATION AS FLAME-RETARDANT AGENTS

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

Polyhaloimides, in particular tetrabromophthalimides and bis(tetrabromophthalimides), are well known compounds which find application as flame retardants in
10 many inflammable materials, especially 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
15 397-398, as well as patents US 3,873,567 and FR 2,369,261 and applications JP 74-045062 and 75-064377].

However, the preparation processes described in the references cited above give indifferent yields and lead to products which very frequently contain substances
20 that are volatile at the temperatures of use in some polymeric materials, and cause corrosion of moulds. In addition, the use, for their preparation, of organic solvents, in particular, (xylene, toluene, alcohol and acetic acid), most frequently selected on the basis of their capacity
25 to form azeotropic mixtures with water, enabling the water of condensation produced by the imidation reaction to be carried away, or their capacity to dissolve the halogenated



dicarboxylic acid anhydride, necessitates costly operations for separation and recovery of these solvents, as well as means of drying suitable for the removal of organic solvent vapours.

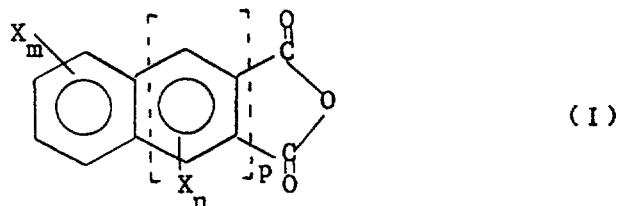
5 The abovementioned disadvantages are to be found, in particular, in the case of polyhaloimides derived from hydrazine and halogenated dicarboxylic acid anhydrides. It has now been found that it is not essential to use an organic solvent in order to dissolve the anhydride and/or
10 remove the water of condensation, and that, by working in aqueous medium under certain conditions, it is possible to obtain, in very high yields and without problems of discharge of effluents and environmental problems, products which, without prior purification, are entirely suitable
15 for the flameproofing of macromolecular substances, including those of which use is made at high temperature, especially above 250°C.

 The process according to the invention, which consists in condensing hydrazine with a halogenated di-
20 carboxylic acid anhydride, is characterized in that the reaction is performed in aqueous medium, at a temperature ranging from 40 to 225°C, with a mole ratio anhydride/hydrazine of less than 2.

 Among halogenated anhydrides which are usable,
25 the following may be mentioned more especially:

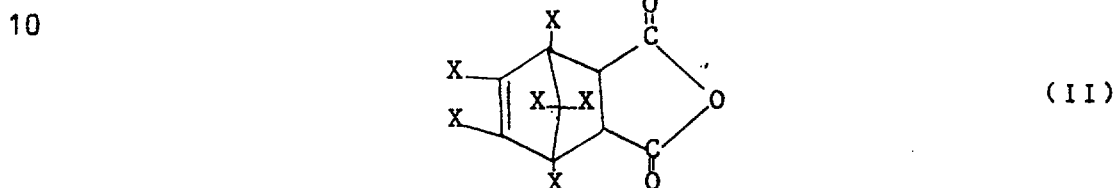
 anhydrides of aromatic (benzene, naphthalene, anthracene) dicarboxylic acids, in particular those of

general formula:



in which X denotes 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; and

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 chlorinated homolog (chlor-endic acid), corresponding to the formula:

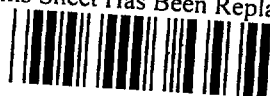


in which X has the same meaning as above. Bromophthalic anhydrides, for example 3,4- (or 3,6- or 4,5-)dibromophthalic anhydride, 3,4,6-tribromophthalic anhydride and more especially tetrabromophthalic anhydride, are preferably used.

15

According to the present invention, it is possible to use a single anhydride or a mixture of two or more anhydrides. Commercial anhydrides, often containing a small amount of inorganic acids, may be used as such without prior purification. It has been found, in effect, that especially good results are obtained when the aqueous dispersion or solution of anhydride employed is acidic or strongly acidic (pH less than 7).

20



The amount of water forming the reaction medium of the process according to the invention can vary within wide limits, the only condition being that it is sufficient to provide for appropriate dispersion of the reactants and to permit good agitation. This condition is generally fulfilled by using an amount of water such that the content of solid substances in the reaction medium is between approximately 5 and 75% by weight, preferably between 20 and 40%.

10 The reaction may be performed at atmospheric pressure at a temperature ranging from 40 to 100°C or, on condition that it is performed under pressure, at a higher temperature which can range up to 225°C. It is preferable to work at between 100 and 225°C, which corresponds to
15 pressures of between 1 and 25 bars approximately.

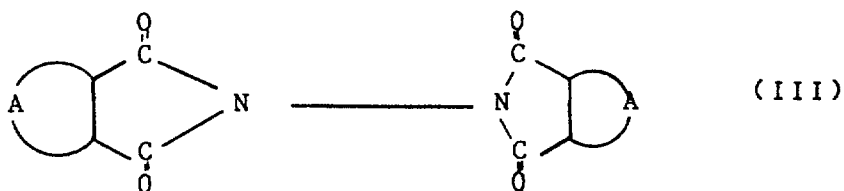
Hydrazine in the form of a hydrate or hydrazinium salt (for example sulphate, hydrohalide, acetate) may be used as such or in the form of a dilute aqueous solution. Preferably, hydrazine hydrate is used in the form of a
20 commercial aqueous solution. The process according to the invention is advantageously carried out by gradually introducing hydrazine into the solution or dispersion of halogenated anhydride, previously heated and maintained with stirring.

25 The reaction time can vary within wide limits, but is generally between 1 and 20 hours. After the reaction medium is cooled, the solid suspension obtained is



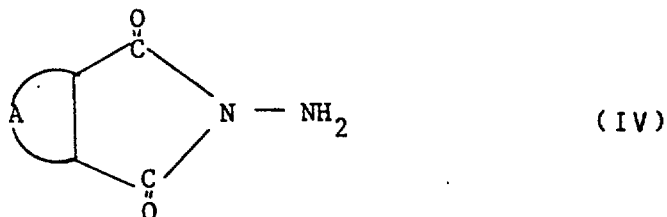
filtered and optionally washed with water to neutrality, and the product is then dried by traditional means of drying.

The mole ratio anhydride/hydrazine can assume various values. If a mole ratio in the vicinity of 2 and a temperature at least equal to 140°C are used, the product obtained generally consists of the bis-(imide) corresponding to the following general structure:



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

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



where A has the same meaning as above, it being possible for this N-aminoimide to be in salt form (sulphate, hydrohalide, acetate). The content of bis(imide) (III) in the product obtained generally increases proportionately as



the reaction temperature approaches 140°C or above.

When a ratio of less than 1 or in the vicinity of 1 is used, the product chiefly obtained is the N-aminoimide of general structure (IV). When the desired product is the N-aminoimide, a quantity of hydrazine of between the stoichiometric amount and a 50% molar excess, and preferably a ratio anhydride/hydrazine substantially equal to 1, is used.

If a mole ratio anhydride/hydrazine of between 1 and 2 is used, a mixture of the above products is obtained, containing an amount of bis(imide) which increases proportionately as the ratio is closer to 2 and as the temperature is raised.

Irrespective of whether the products obtained in accordance with the process according to the invention are pure bis(imides), bis(imide) + N-aminoimide + anhydride mixtures, or N-aminoimide, these products are especially suitable as flame retardants in plastics of any kind. Their incorporation in these plastics may be accomplished by any known method, at doses ranging from 5 to 40% relative to the weight of inflammable substance.

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

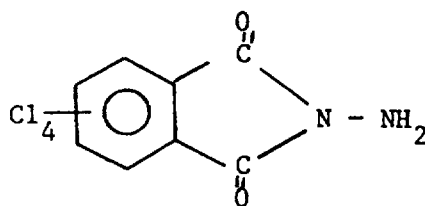
The products were identified by CHN and IR analysis. The yield is expressed relative to the anhydride.



EXAMPLE 1

429 parts of commercial tetrachlorophthalic anhydride are dispersed in 2,000 parts of distilled water in a glass reactor equipped with a stirrer and a refluxing
5 device. The pH of the suspension is 1.5.

After this suspension has been brought to 60°C, 75 parts of 100% pure hydrazine hydrate are added gradually in the course of 20 to 30 minutes, and the reaction mixture is then brought to 100°C. 1,000 parts of distilled
10 water are then added and the mixture is maintained at 100°C for a further 10 hours. A suspension is then obtained, which is cooled and filtered on a Büchner funnel. After the residue is washed with water to neutral pH and dried under vacuum at 110-120°C, a white product is ob-
15 tained in a yield of more than 97%, the elemental and IR analysis of which product confirms the structure:



CHN elemental analysis

		Found	Theory
20	C %	32.3	32.5
	H %	0.7	0.7
	N %	9.0	9.5

EXAMPLE 2

The procedure is as in Example 1, 445 parts of
25 commercial chlorendic anhydride being dispersed in 4,000

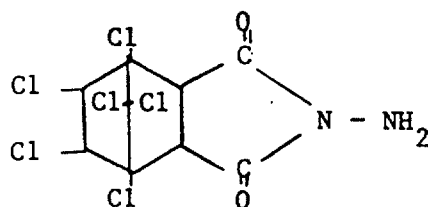
parts of water.

The pH of the suspension is 2.5.

60 g of 100% pure hydrazine hydrate are gradually added to the suspension, brought to 98°C.

5 After 10 hours' reaction at this temperature, the mixture is cooled and the product separated by filtration.

After the residue is washed to neutral pH and dried under vacuum at 110°C-120°C, a grey product is obtained in a yield of more than 90%, the elemental and
10 IR analysis of which product confirms the structure:



CHN elemental analysis

	Measured	Theoretical
C %	27.9	28.1
15 H %	1.7	1.1
N %	7.3	7.3

EXAMPLE 3

1,392 parts of tetrabromophthalic anhydride are dispersed in 4,000 parts of water in a six-litre auto-
20 clave equipped with a stirrer. The pH of the dispersion is 1.5.

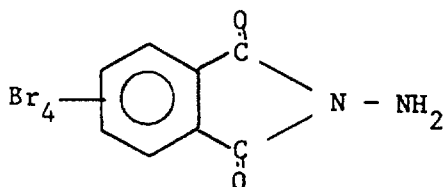
The mixture is brought to 60°C and 225 parts of 100% pure hydrazine hydrate are then added gradually. The suspension is brought to 125°C under pressure and this



temperature is maintained for 10 hours.

After this reaction time, the mixture is cooled and the product separated by filtration.

After the residue is washed to neutral pH and
5 dried under vacuum at 110-120°C, a yellow product is obtained in a yield of more than 90%, the elemental and IR analysis of which product indicates the structure:



CHN analysis

10		Found	Theoretical
	% C	19.58	20.1
	% H	0.32	0.4
	% N	5.68	5.9

EXAMPLE 4

15 The procedure is as in Example 3, but using a 100% molar excess of hydrazine hydrate. The same product is obtained as in Example 3, in a 97.4% yield.

EXAMPLE 5

20 883 p. of commercial tetrabromophthalic anhydride are dispersed in 2,600 p. of distilled water in a four-litre autoclave equipped with a stirrer; this mixture is brought with stirring to a temperature of 170°C, which corresponds to a pressure of between 7.6 and 8 bars.

53 parts of 100% pure hydrazine hydrate, diluted



with 200 parts of distilled water (mole ratio TBPA/HH = 1.8), are introduced gradually into the stirred suspension by means of a pump.

5 The reaction medium is maintained, still at 170°C, for 6 hours, and is then cooled and filtered and the product washed. After being dried at 100-110°C under vacuum, a white product is obtained in a 95% yield, containing:

83% of N,N'-bis(tetrabromophthalimide)

14% of N-aminotetrabromophthalimide

10 3 % of tetrabromophthalic anhydride

EXAMPLE 6

The efficacy of the products according to the invention as flame-retardant agents for plastics was tested according to the following general procedure:

15 Using a planetary or "barrel" type mixer, the resin in powder or granule form is mixed with the test flame-retardant and the optional additives (antimony trioxide, paraffin) in the proportions indicated in the following tables. After homogenization, the mixture is
20 extruded by means of a suitable extruder (twin-screw, single-screw or "Buss type") equipped or otherwise with a means of outgassing, working at the extrusion temperature stated by the supplier of the resin and linked with the melting point of the polymer. The compound obtained,
25 optionally granulated, is then converted to test specimens for measurement by means of an injection moulding press working at the appropriate temperatures. These test



specimens are then subjected to standardized tests of fire resistance UL94 at 3.2 mm and 1.6 mm (Standard NF T51072) and oxygen value OV % (Standard NF T51071).

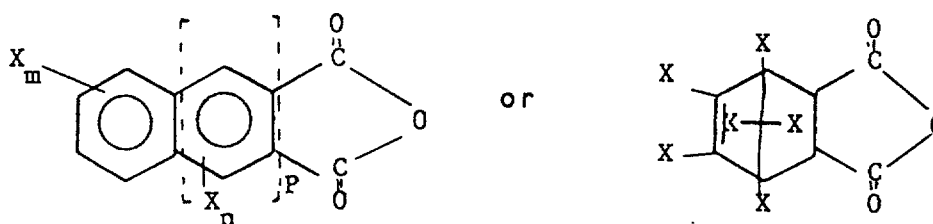
The Table A summarizes the results obtained in the case of polybutylene terephthalate (TMNO-ORGATER, granules marketed by the Applicant).

	TEST NO.	I control	II	III	IV
10	Flame retardant of Example no.	None	1	3	5
15	Composition (parts by weight) TMNO-ORGATER resin Flame retardant Antimony trioxide Paraffin	1000 0 0 0	1000 142 74 18	1000 160 76 18	1000 186 78 18
20	Results of the tests: UL94 OV % Colour of the test specimen:	NC 22 white	VO 27.6 ivory white	VO 32.2 yellow	VO 31.3 ivory white



CLAIMS

1. Process for preparing halogenated imides by the condensation of hydrazine and a halogenated dicarboxylic acid anhydride, characterized in that the reaction is performed in aqueous medium, at a temperature ranging from 40 to 225°C, with a mole ratio anhydride/hydrazine of less than 2.
2. The process according to Claim 1, in which the reaction is performed under pressure at a temperature of at least 140°C.
3. Process according to Claim 1 or 2, in which the reaction is performed starting with an aqueous dispersion or solution of anhydride having a pH of less than 7.
4. Process according to one of Claims 1 to 3, in which an anhydride of formula:



where X denotes 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, is used.

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

6. Process according to one of Claims 1 to 5, in





which hydrazine is used in the form of a hydrate or hydrazinium salt.

7. Process according to one of Claims 1 to 6, in which a mole ratio anhydride/hydrazine of between 1 and 2 is used.

8. Process according to one of Claims 1 to 6, in which a mole ratio anhydride/hydrazine substantially equal to 1 is used.

9. Application of the products obtained according to the process of one of Claims 1 to 8 to the fireproofing of plastics.

10. Plastics fireproofed by means of a product obtained according to the process of one of Claims 1 to 8.

