



(51) International Patent Classification:

C07D 251/30 (2006.01) C09K 21/08 (2006.01)

(21) International Application Number:

PCT/EP2018/077816

(22) International Filing Date:

12 October 2018 (12.10.2018)

Published:

— with international search report (Art. 21(3))

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

17196837.3 17 October 2017 (17.10.2017) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,

(54) Title: PREPARATION OF HALOGEN-BASED FLAME-RETARDANT

(57) Abstract: The present disclosure is directed to halogen-based flame retardants, their preparation and their use in polymers to impart flame retardancy. There is a demand for halogen-based flame retardant that are desirable in view of sustainability, i.e. are biodegradable or non-biocumulative and non-toxic, but still provide the required flame retardancy. To this end the disclosure is directed to process for the preparation of a boron-free halogen-based flame retardant which is prepared by reacting halogeno-alkylcarboxylic acid containing at least two halogen atoms with an unsaturated and/or hydroxyl containing carrier molecule having at least three bonding sites for the halogeno-alkylcarboxylic acid per carrier molecule, the flame retardant per se, its use in polymers and a process for the preparation of flame retardant polymers comprising the flame retardant according to the disclosure.



PREPARATION OF HALOGEN-BASED FLAME-RETARDANT

Technical Field

The present disclosure is directed to halogen-based flame retardants, their preparation
5 and their use in polymers to impart flame retardancy.

Background

Commercial halogen-based flame retardants are mainly based on bromine. However,
such bromine-carbon bond containing compounds are being banned due to a large
10 negative sustainability impact. More specifically, these bromine based flame retardants
are often persistent, bioaccumulative and toxic.

Chlorinated flame retardants are known in the art but are also very persistent and very
bioaccumulative. Therefore, there is a demand for flame retardants that are desirable
in view of sustainability, i.e. are biodegradable, that are not persistent or
15 bioaccumulative and non-toxic, but still provide the required flame retardancy.

In the prior art several attempts were made to develop more sustainable flame
retardants.

In US 3932541 brominated pentaerithritols are prepared by reacting pentaerithritol with
20 HBr or HCl in the liquid phase using an aliphatic carboxylic acid as catalyst. Because
of their relative low halogen-density their flame retardancy will be inadequate. Also,
they will contain carbon-halogen bonds, most likely resulting in non-biodegradable
compounds.

25 In Journ. of Pol. Science, Part A: Polymer Chemistry, Vol 34, 1455-1464 (1996), of
Hongsoo Park, Janghyoun Keun and Kisay Lee, a two component polyurethane flame-
retardant coating was prepared by blending chlorine containing modified polyester and
polyisocyanate. Said chlorine-containing modified polyester was prepared by
polycondensating dichloroacetic acid with butane diol, trimethylolpropane and adipic
30 acid.

This concept was described by Hongsoo Park, Hyun-Sik Hahm and Eun-Kyung Park in Journ. of Appl. Polym. Science, Vol 61, 421-429 (1996) using bromine instead of chlorine containing modified polyester and polyisocyanate.

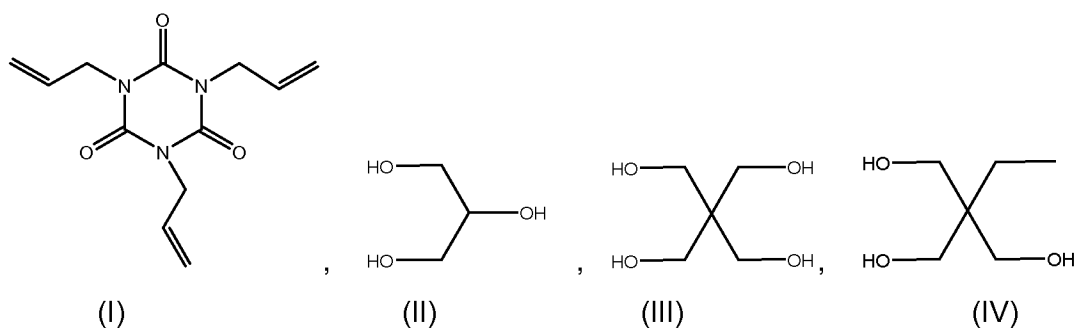
- 5 In Journ. of Islamic Academy of Sciences 4:3, 200-202, 1991 of A.M. Hassan a flame retardant was prepared for paper and paper board. Said flame retardant was a polyurethane of halogenated fatty acid and toluene diisocyanate. This was prepared by mixing coconut oil and castor oil, glycerol, trichloroacetic acid and/or bromoacetic acid. This mixture was then reacted with toluene isocyanate.
- 10 In US2003/009003, B. Köhler, K. Horn and R.-V. Meyer describe the preparation of polyether carbonates produced with the alpha-halocarboxylic (e.g. monochloroacetic acid) esters of polyols as branching agent, whereby the branching agent is incorporated in the polycarbonate by means of ether bridges.
- 15 In general, polymerized flame retardants (such as those described in the Hassan and Park references above) are not desired because they may compromise the compatibility with the polymers to be rendered flame retardant and may detrimentally affect the chemical and physical properties of the polymer.
- 20 In Journ. of Islamic Academy of Sciences 5:3, 149-152, 1992 of A.M. Hassan and E.M. Sadek fire-resistant compounds from diglyceryl borate trichloroacetate were prepared. Boron- containing compounds are less desired as flame retardant for their toxicity and their price.
- 25 There is still a need in the art for biodegradable flame retardants that have adequate flame retardant properties.

Summary

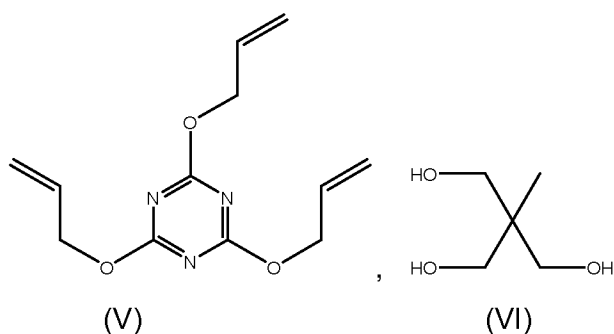
- 30 The disclosure is directed to a process for the preparation of a boron-free halogen-based flame retardant which is prepared by reacting a halogeno-alkylcarboxylic acid containing at least two halogen atoms with an unsaturated and/or hydroxyl containing carrier molecule having at least three bonding sites for the halogeno-alkylcarboxylic

acid per carrier molecule so as to form a biodegradable boron-free halogen-based flame retardant.

The carrier molecule may comprise triallyl isocyanurate (TAIC), glycerol (Glyc),
 5 pentaerythritol (PTT), trimethylol propane (TMP), triallyl cyanurate (TAC), or trimethylol
 ethane (TME) according to the following structures I, II, III, IV, V and VI.



10



The halogeno alkyl carboxylic acid may be di- or tribromoacetic acid or most preferably
 15 di- or trichloroacetic acid.

The boron-free halogen-based flame retardant preferably has a molecular weight of at
 most 7000, more preferably at most 5000.

20 Preferably, the resulting flame retardant comprises 1 to 4 carrier molecules per
 compound.

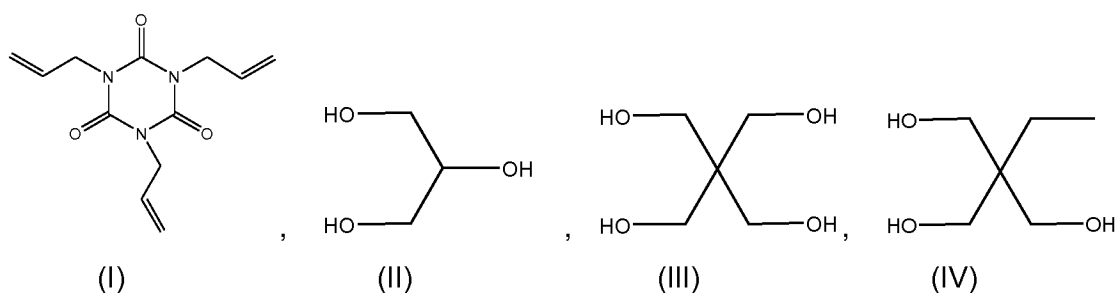
The resulting flame-retardant preferably has at least 4 halogen atoms per molecule,
 preferably between 6-12 halogen atoms per molecule so as to ensure satisfactory

flame retardancy. Preferably, the flame-retardant according to the present invention has a halogen content of at least 25wt%, more preferably at least 30wt%, most preferably at least 40wt%, and preferably lower than 90wt%, based on the total weight of the flame-retardant.

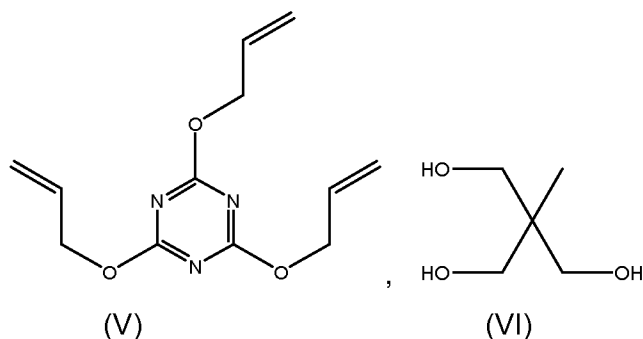
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The disclosure is further directed to a biodegradable halogen-based flame retardant obtainable by the process according to the disclosure comprising an unsaturated and/or hydroxyl containing carrier unit and a halogeno-alkylcarboxylate unit.

- 10 Said unsaturated and/or hydroxyl-containing carrier unit optimally originates from one of the following structures I, II, III, IV, V and VI:



15



- 20 Said halogen-based flame retardant comprises a carrier molecule unit that has been bound to at least two halogeno-alkylcarboxylic acid residues, and preferably at least three halogeno-alkylcarboxylic acid residues.

The disclosure is further directed to the use of the halogen-based flame retardant according to the disclosure to render a polymer flame retardant and to a method for the

preparation of a flame-retardant polymer wherein the flame retardant according to the present invention is blended into a polymer, optionally together with a synergist compound (e.g. antimony(III) oxide, Perkadox® BC (i.e. dicumyl peroxide) or Perkadox® 30 (i.e. 2,3-dimethyl-2,3-diphenyl butane)). Synergist compounds, sometimes denoted as flame-retardant auxiliaries, are compounds which enhance the efficiency of the flame-retardant and these compounds are commonly known in the art (see e.g. US 2016/0340498). Suitable polymer classes include but are not limited to polyolefins (e.g. polypropylene, polyethylene), styrenics (e.g. expanded polystyrene, extruded polystyrene, high impact polystyrene), polyesters, polycarbonates, polyamides, polyacrylates, polyisocyanurate, epoxies/phenolics, natural and synthetic rubbers (eg EPDM), polyethylene terephthalate, polyvinyl chloride, starch and cellulose based polymers, and blends thereof. The most preferred polymers are polyolefins, styrenics and polyesters.

15 Detailed description

The various aspects of the present disclosure will be elucidated further below.

As indicated above, the disclosure is directed to a process for the preparation of a boron-free halogen-based flame retardant which is prepared by reacting halogeno-alkylcarboxylic acid containing at least two halogen atoms with an unsaturated and/or hydroxyl containing carrier molecule containing at least three bonding sites for the halogeno-alkylcarboxylic acid per carrier molecule so as to form a biodegradable boron-free halogen-based flame retardant.

With bonding site is meant here a double carbon-carbon bond or a hydroxyl-group which can react with the halogeno-carboxylic acid under formation of an ester bond.

The wording “unsaturated and/or hydroxyl containing carrier molecule containing at least three bonding sites” therefore denotes a carrier molecule which comprises at least three unsaturated bonds (i.e. carbon-carbon double bonds) or a carrier molecule which comprises at least three hydroxyl groups, or a carrier molecule which comprises unsaturated bonds and hydroxyl groups.

With the term biodegradable is meant that when subjecting the flame retardant to a closed bottle test according the Test guidelines of OECD 1992 (this is Method 301 D:

Closed Bottle of the OECD Guideline for testing of Chemicals, as adopted by the Council on 17th July 1992, "Ready Biodegradability"), the flame retardant can be categorized as being not vPvB (Very Persistent, Very Bioaccumulative) and also not PBT (Persistent, Bioaccumulative, Toxic). The categorization of biodegradability test data, either generated using the above-mentioned test or data taken from literature, is performed by comparing said data with the criteria as set out in REACH Annex XIII to assess the Persistence of substances (ECHA Technical Guidance Document (2017) Guidance on information requirement and chemical safety assessment Chapter R.11; PBT/vPvB assessment version 3.0).

With the term boron-free is meant with less than 5 wt% of boron, preferably less than 2 wt% of boron, more preferably less than 1 wt% of boron, and most preferably less than 0.1 wt% of boron.

The preparation reaction may be conducted under the following conditions: The halogeno-alkylcarboxylic acid, the carrier molecule, and optionally catalyst and optionally solvent are combined and reacted at the given temperature for 1-24 hours, more preferably 3-12 hours. The reaction mixture is then cooled, and the reaction product is subsequently separated from the reaction mixture optionally purified and dried. The solvent used may be an organic solvent such as toluene, xylene, mesitylene or any other suitable solvent. It can be used in combination with a Dean Stark apparatus to remove the formed water from the reaction mixture; in the latter, the reaction is performed under refluxing conditions. The reaction temperature usually ranges from 80-220 °C, more preferably between 100-180 °C.

As is common general knowledge for a skilled person, a suitable catalyst for this reaction may be an acid catalyst such as p-toluene sulfonic acid, triflic acid, any strong organic acid or strongly acidic (co-)polymer or resin (e.g. Nafion® PFSA, Amberlyst® 15 or Dowex® 50WX products). The separation of the product from the reaction mixture may be conducted by extraction such as extraction from a water/alkali mixture. The product may be further purified by washing with e.g. aqueous sodium bicarbonate, and dried.

Preferably, the molecular weight (M_w , mass average molar mass, which is calculated by the formula

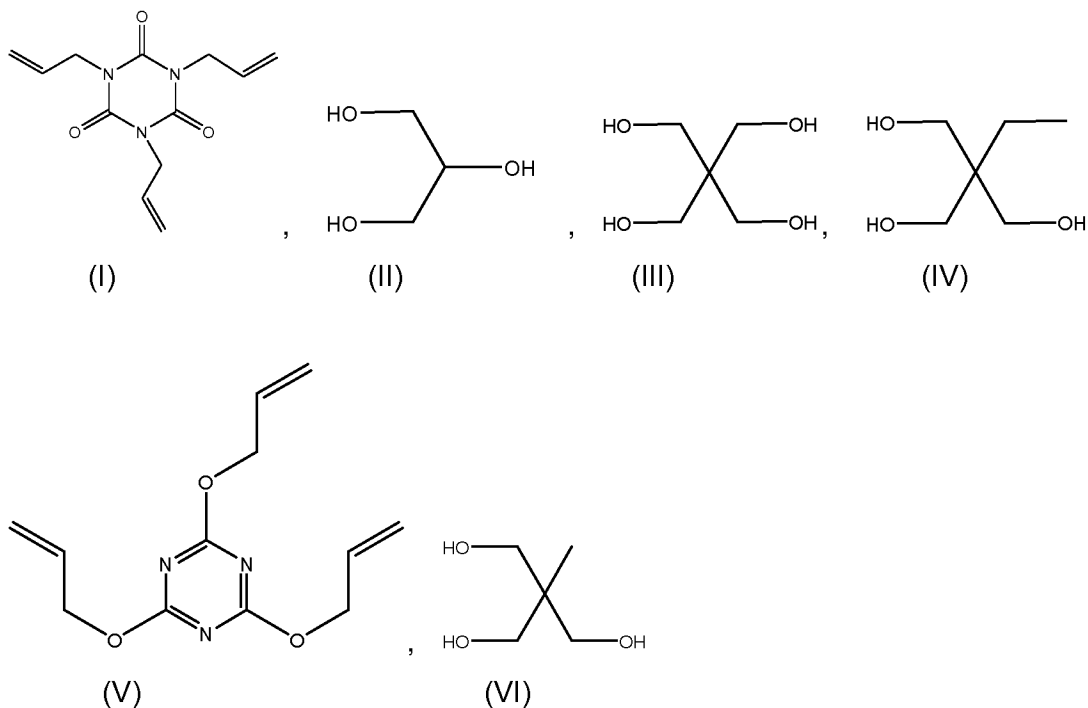
$$\bar{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

- 5 wherein N_i is the number of molecules of molecular mass M_i , as determined with NMR and when relevant with GPC, Gel Permeation Chromatography) of the resulting flame retardant is at most 7000, more preferably at most 5000. More particularly, in case the flame retardant merely contains one carrier molecule, the chemical structure, and thus the M_w , can be confirmed by NMR analysis. In case the flame retardant contains more
10 units, GPC is used to determine the M_w .

If the flame retardant becomes too bulky the compatibility with the polymer to be rendered flame retardant will be compromised too much. Further, the density of the halogen atoms within the compound may become too low and the flame-retardant properties will be detrimentally affected. Preferably, the resulting flame retardant
15 comprises 1 to 4 carrier molecule residues per compound. This is to ensure compatibility with the polymer to be rendered flame retardant and to avoid that the flame retardant detrimentally affects the chemical and physical properties of the polymer to be rendered flame retardant. With the term "residue" is meant the unit in its form after reaction via its bonding sites.

20

It is important that the carrier molecule can bind a large amount of halogens via ester bonds. In principle any compound having multiple (i.e. in total at least three) hydroxy groups and/or unsaturated bonds (i.e. double carbon-carbon bonds) and not being sterically hindered to form ester bonds, may be suitable as carrier molecule as long as
25 it does not have toxic groups. Preferred carrier molecules may comprise triallyl isocyanurate, glycerol, pentaerythritol, trimethylol propane, triallyl cyanurate (TAC), or trimethylol ethane (TME) according to the following structures I, II, III, IV, V and VI.



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These types of carrier molecules provide numerous bonding sites for the halogeno alkyl carboxylic acids via either their unsaturated (carbon-carbon double) bonds or their OH-groups.

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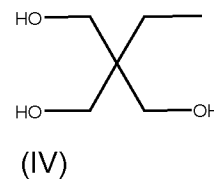
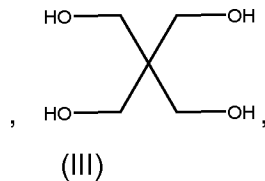
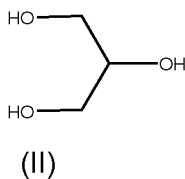
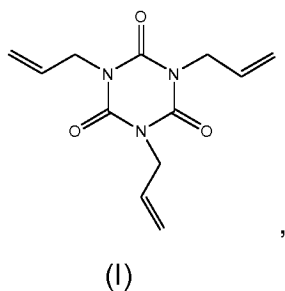
The halogeno alkyl carboxylic acid according to the present invention contains at least two halogen atoms. Suitable halogeno alkyl carboxylic acids comprise di- or tribromoacetic acid, di- or trichloroacetic acid, but also higher halogeno alkyl carboxylic acids such as halogeno propionic acid, halogenobutyric acid and halogeno valeric acid. It goes without saying that these higher alkyl carboxylic acids may be multiple halogenated, such as di-, tri-, tetra-, penta-, septa-, octa-, nona-, and decahalogenated.

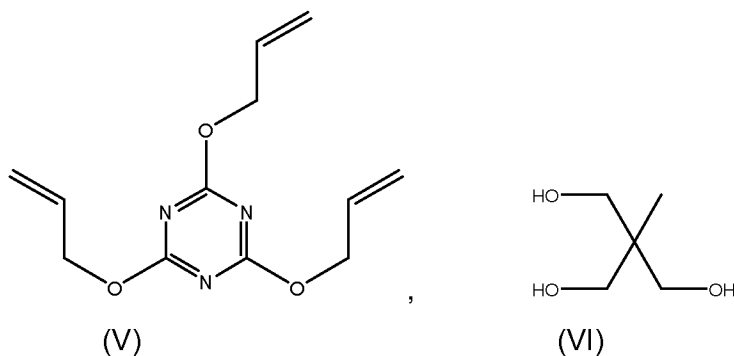
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Preferred are the lower halogeno alkyl carboxylic acids such as di- or tribromoacetic acid or most preferably di- or trichloroacetic acid. It was found that compounds prepared with trichloroacetic acid provided the best flame retardancy, but the other compounds disclosed herein also provide good flame retardancy as well.

20

- The resulting flame-retardant preferably has at least 4 halogen atoms, preferably between 6-12 halogen atoms per molecule so as to ensure satisfactory flame retardancy. More particularly, the flame-retardant preferably has a halogen content of at least 25wt%, meaning that the total weight of the halogens in the flame-retardant is 25% of the total weight of the flame-retardant. More preferably, the flame-retardant has a halogen content of at least 30wt% and most preferably, of at least 40wt%, based on the total weight of the flame-retardant. Preferably, the flame-retardant has a halogen content which is lower than 90wt%, based on the total weight of the flame-retardant.
- 10 The disclosure is further directed to a boron-free halogen-based flame retardant obtainable by the process according to the disclosure comprising an unsaturated and/or hydroxyl residue-containing carrier unit and a halogeno-alkylcarboxylate unit.
- 15 Said halogen-based flame retardant preferably comprises a carrier molecule unit that has been bound to at least three halogeno-alkylcarboxylic acid residues. Preferably the molecular weight, M_w , of the halogen-based flame retardant is at most 7000, more preferably at most 5000. Preferably, the M_w of the halogen-based flame retardant is at least 200, preferably at least 300, most preferably at least 400.
- 20 Said the unsaturated and/or hydroxyl-containing carrier unit optimally originates from one of the following structures I, II, III, IV, V and VI:





5 The disclosure is further directed to the use of the halogen-based flame retardant according to the disclosure to render a polymer flame retardant and to a method for the preparation of a flame retardant polymer wherein the flame retardant according to the disclosure is blended into a polymer, optionally together with a synergist compound, (e.g. antimony(III) oxide Sb_2O_3 , Perkadox® BC or Perkadox® 30), typically in ranges of

10 1-25 wt%. The disclosure is furthermore directed to a method for the preparation of a flame retardant polymer wherein the flame retardant is Suitable polymer classes include but are not limited to polyolefins (e.g. polypropylene, polyethylene), styrenics (e.g. expanded polystyrene, extruded polystyrene, high impact polystyrene), polyesters, polycarbonates, polyamides, polyacrylates, polyisocyanurate, epoxies/phenolics,

15 natural and synthetic rubbers (eg EPDM), polyethylene terephthalate, polyvinyl chloride, starch and cellulose based polymers, and blends thereof. The most preferred polymers are polyolefins, styrenics and polyesters.

The flame retardant can be blended with the polymer in ranges of 1-25 wt%, preferably

20 2-20 wt%, based on the total weight of the polymer. Optionally, also other conventional additives may be blended with the polymer such as other flame retardants, stabilizers, lubricants, UV absorbers, and clarifiers etcetera.

Biodegradability tests (carried out in according to the guidelines mentioned above)

25 show that the flame retardants according to the present invention are classified as not being Very Persistent, Very Biocumulative (vPvB) and also not Persistent, bioaccumulative, Toxic (PBT).

It is noted that various elements of the present disclosure, including but not limited to preferred ranges for the various parameters, can be combined unless they are mutually exclusive.

- 5 The disclosure will be elucidated by the following examples without being limited thereto or thereby.

Examples

10

Example 1 (Preparation of flame retardant with pentaerythritol as carrier molecule: PTT-TCA)

A 250 mL three-neck round-bottom flask equipped with a thermometer, a magnetic stirrer and a Dean Stark apparatus (filled with toluene) connected to a water condenser,
15 was loaded with 5.0 g (0.036 mol, 1.0 equivalent) of pentaerythritol (PTT), 30.0 g (0.182 mol, 5.0 equivalents) of trichloroacetic acid, 200 mL of toluene and 3.0 g (0.016 mol, 0.4 equivalent) of para-toluenesulfonic acid then purged with nitrogen gas. The mixture was heated to reflux and stirred at this temperature for 6h then cooled down and allowed to stand overnight at room temperature. The mixture was poured into a
20 mixture of 200 g of ice and 200 mL of aqueous sodium hydroxide 10% solution. The layers were separated; the organic layer was washed with three times 100 mL of aqueous sodium bicarbonate 5% solution then 200 mL of water, dried over anhydrous sodium sulphate. After filtration, toluene was removed on the rotating evaporator (15 mbar, 120°C, 20 min) to afford 16.8 g of white crystalline material (Yield 63%,
25 assay >97%).

^1H NMR (400 MHz, CDCl_3 , 25°C) δ (ppm): 4.53 (singlet, 8H); ^{13}C NMR (100 MHz, CDCl_3 , 25°C) δ (ppm): 43.7, 65.3, 88.9, 161.0.

30 Example 2 (Preparation of flame retardant with pentaerythritol as carrier molecule: PTT-MCA)

A 500 mL three necks round-bottom flask equipped with a Dean Stark apparatus (filled with extra xylene) with a water condenser, a thermometer and a magnetic stirrer was

loaded with 24.0 g (0.176 mol, 1.0 equiv.) of PTT, 100.0 g (1.058 mol, 6.0 equiv.) of MCA, 276.0 g of xylene and 3.4 g (0.018 mol, 0.1 equiv.) of PTSA then purged with nitrogen gas. The mixture was heated to reflux and stirred at this temperature for 14h then cooled down to RT. The xylene was removed under reduced pressure by means of a rotating evaporator (30 mbar, 60°C, 30 min) to afford a highly viscous yellow-brown oil. This oil was dissolved in 120 mL of dichloromethane; the obtained solution was washed with seven times 90 mL of aqueous sodium bicarbonate 5% solution then 200 mL of water, dried over anhydrous sodium sulphate. After filtration, the mixture was concentrated under reduced pressure by means of a rotating evaporator (30 mbar, 60°C, 30 min) to afford 38 g of pale yellow powder (Yield 49%, assay >98%).
¹H NMR (400 MHz, CDCl₃, 25°C) δ (ppm): 4.09 (singlet, 8H), 4.28 (singlet, 8H); ¹³C NMR (100 MHz, CDCl₃, 25°C) δ (ppm): 40.5, 42.6, 63.3, 166.7.

Example 3 (Preparation of flame retardant with triallyl isocyanurate as carrier molecule: TAIC-TCA)

A 100 mL three-neck round-bottom flask equipped with a water condenser, a thermometer and a magnetic stirrer was loaded with 7.5 g of TAIC (0.029 mol, 1.0 equivalent), 73.0 g (0.442 mol, 15.0 equivalents) of trichloroacetic acid and 1.0 g (0.005 mol, 0.18 equivalent) of para-toluenesulfonic acid then purged with nitrogen gas. The mixture was heated to 140 °C and stirred at this temperature for 6h then cooled down and allowed to stand overnight at room temperature. Some of the TCA was removed from the mixture by means of a rotating evaporator (10 mbar, 120 °C, 20 min) then the obtained material was dissolved in 100 mL of diethyl ether. The obtained solution was washed with five times 25 mL of aqueous sodium bicarbonate 5% solution, 10 mL of water, dried on anhydrous sodium sulphate then filtrated. The diethyl ether was removed on the rotating evaporator (15 mbar, 120°C, 20 min) to afford 13.7 g of solid brown material (Yield 64%, assay >97%).
¹H NMR (600 MHz, CDCl₃, 25°C) δ (ppm): 1.45 (9H, multiplet), 3.95 (3H, multiplet), 4.38 (3H, multiplet), 5.34 (3H, multiplet); ¹³C NMR (150 MHz, CDCl₃, 25°C) δ (ppm): 17.16, 17.20, 17.24, 46.32, 46.41, 73.98, 74.10, 74.22, 89.7, 148.54, 148.60, 148.64, 161.72, 161.74, 161.75.

Example 5 (Preparation of flame retardant with triallyl isocyanurate as carrier molecule: TAIC-MCA)

The TAIC-MCA flame retardant was prepared from triallyl isocyanurate and MCA (monochloroacetic acid) using the procedure given as Example 3 with extended
5 reaction time (12h).

¹H NMR (400 MHz, CDCl₃, 25°C) δ (ppm): 1.33 & 1.34 (9H, 2 doublets), 3.91 (3H, multiplet), 3.99 (6H, multiplet), 4.23 (3H, multiplet), 5.36 (3H, multiplet).

Example 6 (Preparation of flame retardant with glycerol as carrier molecule: Glyc-TCA)

A 250 mL three-neck round-bottom flask equipped with a thermometer, a magnetic stirrer and a Dean Stark apparatus (filled with toluene) connected to a water condenser, was loaded with 6.0 g (0.064 mol, 1.0 equivalent) of glycerol (Glyc), 54.0 g (0.327 mol, 5.1 equivalents) of trichloroacetic acid, 180 mL of toluene and 2.4 g (0.012 mol, 0.2
15 equivalent) of para-toluenesulfonic acid then purged with nitrogen gas. The mixture was heated to reflux and stirred at this temperature for 12h then cooled down and allowed to stand overnight at room temperature. The mixture was poured into a mixture of 180 g of ice and 200 g of aqueous sodium hydroxide 10% solution. The layers were separated; the organic layer was washed with twice 100 mL of aqueous sodium
20 bicarbonate 5% solution then 200 mL of water, dried over anhydrous sodium sulphate. After filtration, toluene was removed on the rotating evaporator (15 mbar, 120°C, 20 min) to afford 30.1 g of slightly yellow oily liquid material (Yield 85%, assay >95%).

¹H NMR (400 MHz, CDCl₃, 25°C) δ (ppm): 4.62 (doublet of doublet, 2H), 4.77 (doublet of doublet, 2H), 5.60 (multiplet, 1H); ¹³C NMR (100 MHz, CDCl₃, 25°C) δ (ppm): 65.0,
25 72.7, 88.9, 161.0, 161.3.

Example 7 (Preparation of flame retardant with trimethylol propane as carrier molecule: TMP-TCA)

The molecule TMP-TCA was prepared from trimethylol propane and TCA, applying the
30 procedure given in Example 1.

¹H NMR (400 MHz, CDCl₃, 25°C) δ (ppm): 1.02 (triplet, 3H), 1.60 (quadruplet, 2H), 4.39 (singlet, 6H); ¹³C NMR (100 MHz, CDCl₃, 25°C) δ (ppm): 7.3, 23.0, 42.2, 67.5, 89.3, 161.3.

Example 8: Evaluation of flame retardancy in PolyPropylene (PP) formulations

The well-known UL 94 test was used for evaluating the flame retardancy. In this test a 12.7x1.27 cm specimen (polypropylene comprising the flame retardant to be tested, along with a synergist compound; the thickness of the specimens can be varied
5 between 0.7 and 3 mm; in this Example, the thickness of the specimen was 2 mm) was held with a clamp above a burner that was placed above a piece of cotton of specific height and diameter, at specific distance from the flame. If the specimen caught fire and glowing or flaming combustion reached the holding clamp, it was categorized as non-retardant (NR). If it was not the case and if the cotton underneath the burner got
10 ignited by drips from the specimen, the material was categorized as V2. If the specimen did not burn up to reaching the holding clamp, nor did it cause the cotton to ignite, then the flaming combustion time was measured. If it took up to 10 seconds for the specimen to stop burning, it was considered to fall in the V0 category, while a flaming combustion time up to 30 seconds the material was said to fall in the V1
15 category.

Burning tests were conducted of polypropylene comprising various amounts of flame retardants and synergist according to the disclosure prepared with methods similar to the method described in Example 3 and compared to commercial standard Armoquell® FR 930. To this end specimens of polypropylene (MFI 4) were made comprising either
20 4 wt% flame retardant and 2 wt% Timonox® White Star (i.e. antimony(III) oxide, Sb_2O_3), and 0.5 wt% of the thermal stabilizer Irganox® B225, 8 wt% flame retardant, 4 wt% Timonox® White Star and 0.5 wt% Irganox® B225, or 12 wt% flame retardant, 6 wt% Timonox® White Star and 0.5 wt% Irganox® B225. All results of the burning test are compiled in TABLE I:

25

TABLE I

Formulation / FR	None	FR 930	TAIC-MCA	TAIC-TCA	PTT-MCA	PTT-TCA	Glyc-TCA
4 wt% FR & 2 wt% Sb ₂ O ₃	NR	V2	n.d.	NR	n.d.	n.d.	n.d.
8 wt% FR & 4 wt% Sb ₂ O ₃		V0	NR	V2	n.d.	n.d.	n.d.
12 wt% FR & 6 wt% Sb ₂ O ₃		n.d.	n.d.	V2	NR	V0	V0

(n.d.: not determined)

- 5 It can be concluded that the flame retardants prepared by reaction of TCA (trichloroacetic acid) with TAIC (triallyl isocyanurate), PTT (pentaerythritol) and Glyc (glycerol) provided significant flame retardant properties to the corresponding formulated PP samples. On the contrary, the use of the compounds prepared by reaction of MCA with TAIC and PTT did not result in significantly improved flame
- 10 retardancy properties of the formulated polypropylene. These experiments further show that flame retardants need to contain at least four halogen atoms per molecule to provide significant flame retardancy effect.

15 **Example 9: Evaluation of flame retardancy in PolyStyrene (PS) formulations**

- 20 g of suspension consisting of PS (Crystal clear, BASF), flame retardant and Timonox® White Star (i.e. antimony (III) oxide, Sb₂O₃) in dichloromethane were poured into a metallic Petri box (diameter 10 cm). The solvent was allowed to evaporate at room temperature in a fume cupboard for at least 2 days, affording (ca. 4 g) films. Then
- 20 specimens (7.0 x 1.5 cm) were cut from the films and subjected to a modified UL94 test: the specimens were exposed to flame twice during 1s (instead of twice 10 s in the original standard method). The flame retardancy of the specimen was rated by applying the same methodology described in Example 4 above, demonstrating a clear retardancy effect of the prepared esters. The results are shown in TABLE II.

TABLE II

Formulation	None; no synergist	FR 930	TAIC-TCA	PTT-TCA	Glyc-TCA	TMP-TCA
12 wt% FR & 6 wt% Sb ₂ O ₃	NR	V0	V2	NR	V2	V2
16 wt% FR & 8 wt% Sb ₂ O ₃	NR	n.d.	V0	V0	V0/V1	V1
16 wt% FR & 4 wt% Sb ₂ O ₃	NR	n.d.	V0	V0	n.d.	n.d.
16 wt% FR & 0 wt% Sb ₂ O ₃	NR	n.d.	V2	NR	n.d.	n.d.

(n.d.: not determined)

5

Example 10: Biodegradability tests

Biodegradation of an organic chemical refers to the reduction in complexity of the chemical through metabolic activity of microorganisms. Under aerobic conditions, microorganisms convert organic substances in carbon dioxide, water and biomass.

- 10 The theoretical oxygen demand (ThOD) of the tested compounds was calculated from their molecular formulae and molecular weights as follows:

$$ThOD_{NH_3} (mgO_2 / mg) = \frac{16(2C + 0.5(H - Cl - 3N) + 3S + 2.5P + 0.5Na - O)}{MW}$$

Provided that the oxygen concentrations in all bottles at the start of the test were equal, the amounts of oxygen consumed in the bottles were calculated as follows:

- 15 **Oxygen consumption (mg/L) = $M_c - M_t$** , with

M_c = the mean oxygen level in the control bottle only containing inoculum, n-days after the start of the test.

M_t = the mean oxygen concentration in the bottles containing the test substance and inoculum, n-days after the start of the test.

- 20 The BOD (mg/mg) of the test substance was calculated by dividing the oxygen consumption by the concentration of the test substance in the closed bottle. The biodegradation was calculated as the ratio of the BOD to ThOD.

The biodegradability of trimethylol propane (TMP), of a mixture prepared according to the procedure described by Hongsoo Park, Hyun-Sik Hahm and Eun-Kyung Park in Journ. of Appl. Polym. Science, Vol 61, pp.421-429 (1996), and of two flame retardants according to the present invention was evaluated using Closed Bottle tests. These tests were performed according to Test Guidelines (OECD 1992), as mentioned in the description. The bottles were incubated in the dark at temperatures ranging from 22 to 24 °C; the biodegradation was measured by following the course of the oxygen decrease in the bottles. The pH of the media was 7.3 (activated sludge) and 8.0 (river water) at the start of the test. The pH was 7.2±0.1 (activated sludge) and 7.9±0.1 (river water) at day 28.

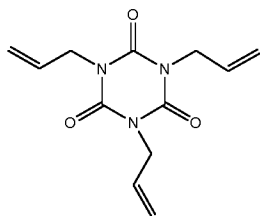
TMP was found to be not persistent, with a biodegradation level of 66% after 21 days in both activated sludge and river water. A reaction mixture of stoichiometric amounts of TMP and 2,3-dibromopropionic acid, prepared according to the procedure described by Hongsoo Park, Hyun-Sik Hahm and Eun-Kyung Park in Journ. of Appl. Polym. Science, Vol 61, 421-429 (1996) on page 423 (section "Syntheses of 2,3-Dibromo Modified Polyesters – 2,3-DBP/TMP Intermediate"), was found to be persistent, as less than 40% biodegradation was measured in both activated sludge and river water after 84 days.

The closed bottle test of the substance PTT-TCA, a flame-retardant according to the present invention, resulted in biodegradation of 65% within 6 weeks and 66% within 8 weeks with activated sludge and river water, respectively. The test substance should therefore be classified as not persistent. Pentaerythritol is inherently biodegradable and TCA was found to reach a biodegradation above 60% within 8 weeks in both activated sludge and river water. Biodegradation of the ester and both hydrolysis products within 60 days allows classification as not persistent. These results clearly demonstrate that the substance PTT-TCA is not a vPvB (Very Persistent, Very Bioaccumulative) nor a PBT (Persistent, Bioaccumulative, Toxic) compound.

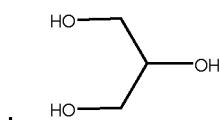
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Claims

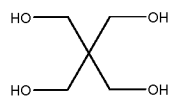
1. Process for the preparation of a boron-free halogen-based flame retardant which is prepared by reacting halogeno-alkylcarboxylic acid containing at least two halogen atoms with an unsaturated and/or hydroxyl containing carrier molecule that has at least three bonding sites for the halogeno-alkylcarboxylic acid per carrier molecule to form a biodegradable boron-free halogen-based flame retardant.
2. Process according to claim 1 wherein in the resulting biodegradable boron-free halogen-based flame retardant at least two of the at least three bonding sites of the carrier molecule are occupied.
3. Process according to claim 1 wherein the boron-free halogen-based flame retardant has a molecular weight of at most 7000, preferably at most 5000.
4. Process according to any one of the preceding claims wherein the carrier molecule comprises triallyl isocyanurate, glycerol, pentaerythritol, trimethylol propane, triallyl cyanurate (TAC), or trimethylol ethane (TME) according to the following structures I, II, III, IV, V and VI.



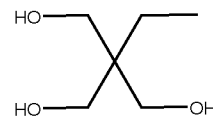
(I)



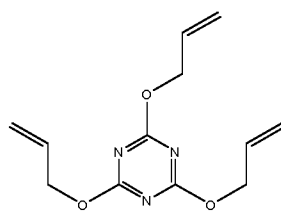
(II)



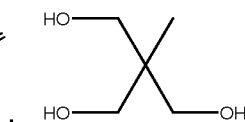
(III)



(IV)

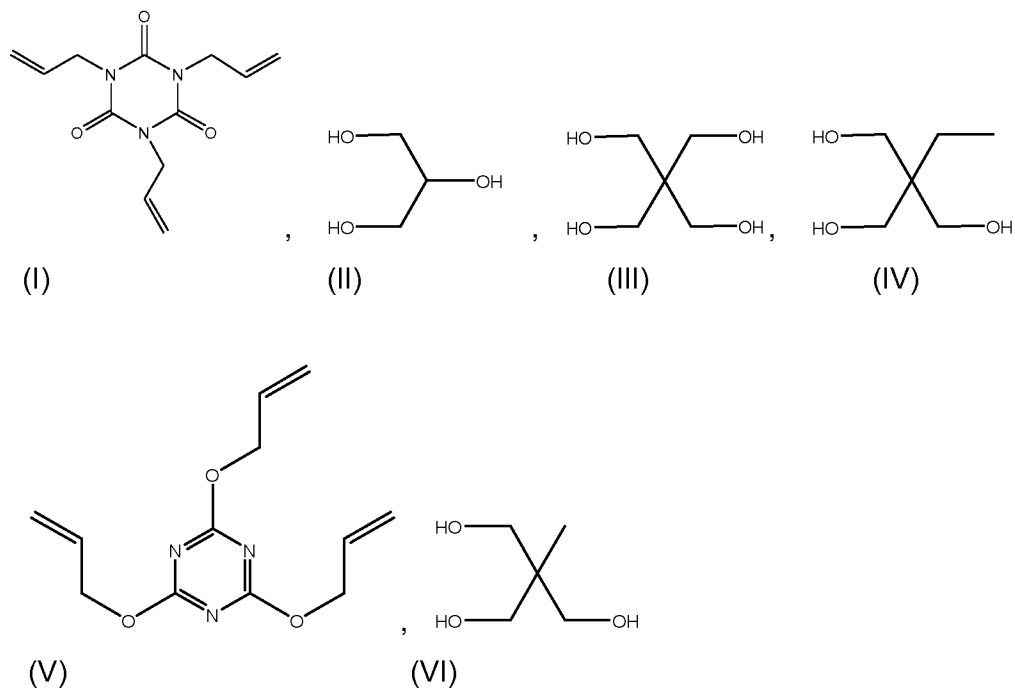


(V)



(VI)

5. Process according to any one of the preceding claims, wherein the halogeno alkyl carboxylic acid is di- or tribromoacetic acid or most preferably di- or trichloroacetic acid.
- 5 6. Process according to any one of the preceding claims wherein the resulting flame retardant comprises 1 to 4 carrier molecules per compound.
7. Process according to any one of the preceding claims wherein the resulting flame-retardant has at least 4 halogen atoms per molecule, preferably between
10 6-12 halogen atoms per molecule.
8. Process according to any one of the preceding claims wherein the resulting flame-retardant has a halogen content of at least 25wt%, more preferably at least 30wt%, most preferably at least 40wt%, and preferably lower than 90wt%.
- 15 9. Biodegradable boron-free halogen-based flame retardant obtainable by the process according to claims 1-8 comprising an unsaturated and/or hydroxyl residue - containing carrier unit and a halogeno-alkylcarboxylate unit.
- 20 10. Biodegradable boron-free halogen-based flame retardant according to claim 9 comprising a carrier molecule unit that has been bound to at least three halogeno-alkylcarboxylic acid residues.
- 25 11. Biodegradable boron-free halogen-based flame retardant according to claim 9 or 10 which has a molecular weight of at most 7000, preferably at most 5000.
12. Biodegradable boron-free halogen based flame retardant according to any one of claims 9 to 11 comprising an unsaturated and/or hydroxyl residue-containing carrier unit originating from one of the following structures I, II, III, IV, V or VI:
- 30



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13. Biodegradable boron-free halogen based flame retardant according to claim 12 which is the reaction product of halogeno-alkylcarboxylic acid with triallyl isocyanurate (TAIC, (I)) or triallyl cyanurate (TAC, (V)).
14. Biodegradable boron-free halogen based flame retardant according to any one of claims 9-13 wherein the halogeno alkyl carboxylic acid is di- or tribromoacetic acid or most preferably di- or trichloroacetic acid.
15. Use of the biodegradable halogen-based flame retardant according to any one of claims 9-14 to render a polymer flame retardant.
16. Method for the preparation of a flame-retardant polymer wherein a halogen-based flame retardant according to any one of claims 9-14 is blended into a polymer.

20

17. Method according to claim 16 wherein the polymer is selected from the group consisting of polyolefins, styrenics, polyesters, polycarbonates, polyamides, polyacrylates, polyisocyanurate, epoxies/phenolics, natural and synthetic rubbers (e.g. EPDM), polyethylene terephthalate, polyvinyl chloride, starch and cellulose based polymers, and blends thereof.
- 5

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/077816

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D251/30 C09K21/08
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HONG-SOO PARK ET AL: "PREPARATION AND CHARACTERISTICS OF TWO-COMPONENT POLYURETHANE FLAME RETARDANT COATINGS USING 2,3-DIBROMO MODIFIED POLYESTERS", JOURNAL OF APPLIED POLYMER SCIENCE, WILEY, vol. 61, no. 3, 18 July 1996 (1996-07-18), pages 421-429, XP000634712, ISSN: 0021-8995, DOI: 10.1002/(SICI)1097-4628(19960718)61:3<421: AID-APP4>3.0.CO;2-K the whole document	1-17
A	US 2003/009003 A1 (KOEHLER BURKHARD [US] ET AL) 9 January 2003 (2003-01-09) claims; examples ----- -/-	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

13 November 2018

Date of mailing of the international search report

22/11/2018

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2018/077816

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 468 480 A (BARDA HENRY J [US]) 28 August 1984 (1984-08-28) claims; examples -----	1-17
Y	US 2 947 736 A (LUNDBERG LENNART A) 2 August 1960 (1960-08-02) the whole document -----	1-17

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2018/077816

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2003009003	A1	09-01-2003	AT 248876 T 15-09-2003
		AU 2004601 A 25-06-2001	
		CN 1411481 A 16-04-2003	
		DE 19960776 A1 21-06-2001	
		EP 1242501 A1 25-09-2002	
		ES 2206336 T3 16-05-2004	
		JP 2003517069 A 20-05-2003	
		US 2003009003 A1 09-01-2003	
		WO 0144346 A1 21-06-2001	

US 4468480	A	28-08-1984	NONE

US 2947736	A	02-08-1960	FR 1192474 A 27-10-1959
		US 2947736 A 02-08-1960	
