



(51) International Patent Classification:

C07F 7/08 (2006.01) C07B 63/00 (2006.01)

(21) International Application Number:

PCT/EP2017/081419

(22) International Filing Date:

04 December 2017 (04.12.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

16306620.2 05 December 2016 (05.12.2016) 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, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

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

(54) Title: PROCESS FOR PURIFYING OR DRYING COMPOUNDS COMPRISING 2-HYDROXYPHENYL BENZOTRIAZOLE FUNCTIONS AND SILOXANE FUNCTIONS

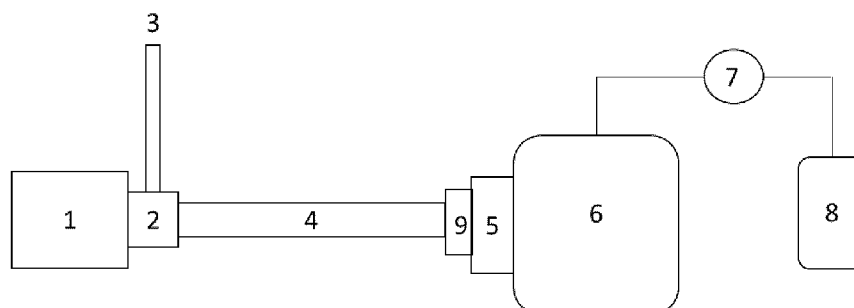


Figure 1.

(57) Abstract: The present invention is directed to a process for purifying or drying a material comprising at least one compound containing at least one 2-hydroxyphenyl benzotriazole function and at least one siloxane function, said process comprising a step wherein the material is submitted to microwave irradiations.



PROCESS FOR PURIFYING OR DRYING COMPOUNDS COMPRISING 2-
HYDROXYPHENYL BENZOTRIAZOLE FUNCTIONS AND SILOXANE
FUNCTIONS

5 This application claims priority to European application No. 16306620.2 filed on December 5, 2016, the whole content of this application being incorporated herein by reference for all purposes.

TECHNICAL FIELD

10 The present invention relates to a process for purifying or drying a material comprising compounds containing 2-hydroxyphenyl benzotriazole and siloxane functions.

BACKGROUND ART

15 Compounds comprising 2-hydroxyphenyl benzotriazole and siloxane functions may be used as a UV filter and they may be prepared by hydrosilylation reaction of a 2-hydroxyphenyl benzotriazole comprising a substituent containing a terminal olefin bond with a siloxane containing compound comprising a SiH function, in the presence of a solvent and a catalyst. Then, the product may be crystallized, washed and filtered in order to obtain the compound in the form of crystals. Said crystals are generally impregnated by liquids resulting from previous steps of preparation.

20 In particular, the final crystallization or recrystallization methods involve the use of a solvent or of a mixture of solvents. Therefore, the product in the form of crystals (solid) may comprise solvents, including water or organic solvents.

25 Document US 2013/0204006 discloses a process for the preparation of a 2-(2H-1,2,3-benzotriazol-2-yl)-4-methyl-6-(2-methyl-3-{1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl}propyl)phenol in a solvent, either ethyl acetate or 2-methyltetrahydrofuran. At the end of the process, the product is precipitated and filtered. Then, the product is washed with a mixture of isopropanol/methanol/water and then dried in order to obtain white crystals. Said document does not disclose the drying method which is used.

30 Conventional drying methods, which allow removing water and/or other organic solvents from a material, generally comprise a step of heating a material, which is therefore a surface heating which necessitates very long times, in particular when the

material has a low melting point, since the heating cannot be performed at a high temperature in order to prevent degradation of the material to be dried and the drying process can therefore be very long. For drying materials having a low melting point and being sensitive to degradation, the traditional industrial methods need to be implemented very cautiously and may be very long, for example they may last 50 hours or more.

It was thus an object of the present invention to develop a process for purifying or drying compounds comprising 2-hydroxyphenyl benzotriazole and siloxane functions which is suitable to dry and purify compounds having a low melting point and which is more efficient and which does not degrade the physical and chemical properties of the compounds.

SUMMARY OF THE INVENTION

A first object of the invention is a process for purifying or drying a material comprising at least one compound containing at least one 2-hydroxyphenyl benzotriazole function and at least one siloxane function, said process comprising a step wherein the material is submitted to microwave irradiations.

According to an embodiment of the invention, the material comprises, before being submitted to microwave irradiations, at least 40% by weight, preferably at least 50% by weight, more preferably at least 60% by weight, even more preferably at least 65% by weight of the at least one compound containing 2-hydroxyphenyl benzotriazole and siloxane functions, based on the total weight of the material.

According to an embodiment of the invention, the material further comprises, before being submitted to microwave irradiations, at least one solvent.

Preferably, the at least one solvent is selected from solvents characterized by a $\tan \delta$ of higher than 0.1, preferably higher than or equal to 0.3, more preferably higher than or equal to 0.4, measured at 2450 MHz at 25°C.

Preferably, the at least one solvent is selected from water, alcohols, organosulfur solvents, organohalogenated solvents, carboxylic acids, and apolar amine solvents.

According to an embodiment, the material comprises, before being submitted to microwave irradiations, from 1 to 60% by weight, preferably from 5 to 55% by weight, more preferably from 10 to 50% by weight, even more preferably from 20 to 45% by weight, of at least one solvent, based on the total weight of the material.

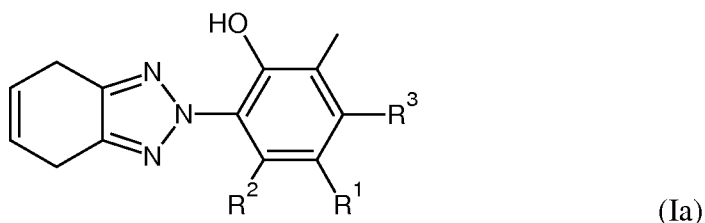
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According to an embodiment, the microwave power density received by the material ranges from 0.001 to 10 kW/kg, preferably from 0.005 to 1 kW/kg, even more preferably from 0.01 to 0.3 kW/kg.

According to an embodiment, the process is performed with a reduced pressure preferably with a pressure ranging from 1 mbar to 500 mbar, preferably from 5 mbar to 200 mbar, more preferably from 10 mbar to 100 mbar.

According to an embodiment of the invention, the process is performed at a temperature ranging from -10°C to 45°C, preferably at a temperature ranging from -5°C to 40°C, more preferably from 0 to 35°C.

According to an embodiment of the invention, the compound comprising at least one 2-hydroxyphenyl benzotriazole function and at least one siloxane function comprises at least one 2-hydroxyphenyl benzotriazole function of formula (Ia) and at least one siloxane function of formula (IIa):



wherein the free valence is apparent and wherein:

R^1 , R^2 , R^3 are, independently to each other, selected from hydrogen, linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, and halogens;

R^4 , which may be identical or different, is selected from linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or

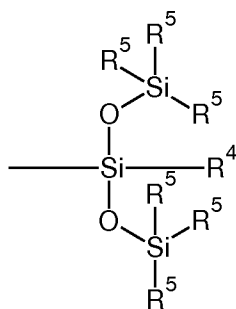
branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom,

R^5 , which may be identical or different, is selected from linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, and from a $-\text{OSiR}^6_3$ radical, R^6 having the same definition as R^5 ;

p represents an integer ranging from 0 to 2.

Preferably, R^2 and R^3 are hydrogen atoms and R^1 is an alkyl radical having from 1 to 8 carbon atoms, more preferably from 1 to 4 carbon atoms.

Preferably, the siloxane function is of formula (IIb):



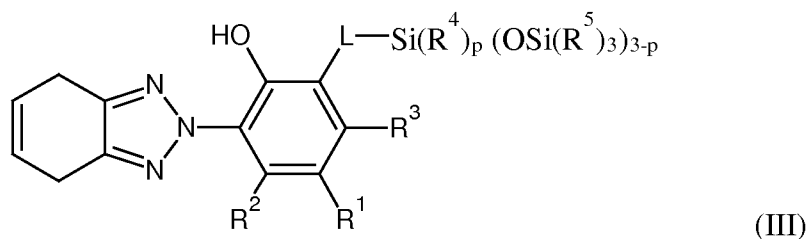
(IIb)

wherein the free valence is apparent, and wherein R^4 and R^5 have the same meaning as the definition given above, preferably R^4 and R^5 , which may be identical or different, are selected from an alkyl radical having from 1 to 8 carbon atoms, more preferably from 1 to 4 carbon atoms.

According to an embodiment of the invention, the material is obtained from a method comprising the following successive steps:

- Reacting a 2-hydroxyphenyl benzotriazole containing compound C' containing at least one carbon-carbon double bond with a siloxane compound D' containing at least one SiH function in a medium comprising at least one catalyst and at least one solvent at a temperature ranging from 40 to 90°C in order to perform a hydrosilylation reaction, thereby a precipitate is obtained,
- Recrystallizing the precipitate with a solvent or a mixture of solvents.

Preferably, the compound containing at least one 2-hydroxyphenyl benzotriazole function and at least one siloxane function responds to the formula (III):



wherein

- 5 R^1 , R^2 and R^3 have the same definition as in formula (Ia) defined above,
 R^4 , R^5 and p have the same definition as in formula (IIa) defined above, and
 L represents a linker which can be a hydrocarbyl radical having from 2 to 40 carbon atoms and optionally comprising at least one carbon-carbon double bond and optionally comprising one or more heteroatoms, such as oxygen atoms.

- 10 The process of the present invention can be performed on materials having a low melting point, for example a melting point lower than 100°C or even lower than 75°C or lower than 60°C. In particular, the process of the invention is not harmful for the treated materials, i.e. the materials and in particular the compounds comprising 2-hydroxyphenyl benzotriazole and siloxane functions keep their properties since they are
 15 not deteriorated by the purifying and drying method of the invention.

The process of the present invention is more efficient than prior art processes since said process may be performed in a shorter time, therefore the productivity of the process is improved.

- 20 The process of the invention allows reducing the energy consumption since it may be performed with a reduced time.

The process of the invention is performed more rapidly than prior art drying method for such compounds and does not modify the physical and chemical properties of said compounds.

BRIEF DESCRIPTION OF THE FIGURES

- 25 Fig. 1 schematically represents an apparatus suitable for implementing the process of the invention.

Fig. 2 represents a graph wherein the humidity of the material in weight percent in function of the treatment time in minutes is illustrated for three different drying processes.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for purifying or drying a material A comprising at least one compound B containing at least one 2-hydroxyphenyl benzotriazole function C and at least one siloxane function D, said process comprising a
5 step wherein the material is submitted to microwave irradiations.

By the expression “purifying or drying a material A”, it is to be understood that during the process, liquids, such as solvents or other impurities are removed by evaporation from the material A, in order to increase the proportion of the compound(s) B in the material A. Within the meaning of the present invention, the term “drying” and
10 “purifying” are indifferently used, although the term “drying” may appear more frequently.

According to an embodiment of the invention, the material A comprises initially (i.e. before treatment by microwave irradiations) at least 40% by weight, preferably at least 50% by weight, more preferably at least 60% by weight, even more preferably at
15 least 65% by weight of at least one compound B containing 2-hydroxyphenyl benzotriazole and siloxane functions, based on the total weight of the material.

The material A may further comprise liquids, which may be impurities or residual solvents originating for example from the process for producing the compound B. Among impurities, mention may be made of the reactants, such as a 2-
20 hydroxybenzotriazole compound and a siloxane compound used to prepare the compound B or of residual solvents, used for example in a final step of recrystallization of the compound B.

Other impurities that can be present in material A are by-products obtained from the synthesis of compound B. They may represent up to around 1% by weight of the
25 weight of the dried material (material at the end of the process of the invention).

According to an embodiment, the liquids represent from 1 to 60% by weight, preferably from 5 to 55% by weight, more preferably from 10 to 50% by weight, even more preferably from 20 to 45% by weight of the total weight of the initial material A (i.e. the material A before treatment by microwave irradiations).

30 According to an embodiment of the invention, the material A comprises at least one solvent.

The solvent may be selected from solvents characterized by a $\tan \delta$ (dielectric dissipation factor) of higher than 0.1, preferably higher than or equal to 0.3, more preferably higher than or equal to 0.4, measured at 2450 MHz at 25°C. D. Bogdal, *Microwave assisted organic synthesis*, Elsevier 2005, gives values for $\tan \delta$. As it is well known for the skilled person:

$$\tan \delta = \varepsilon''/\varepsilon'$$

wherein:

ε'' represents the dielectric loss;

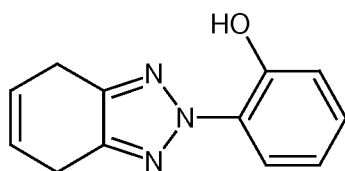
ε' represents the dielectric constant.

Among suitable solvents, mention may be made of alcohols, water, organosulfur solvents, organohalogenated solvents, carboxylic acids, and apolar amine solvents.

Preferably, the solvent is selected from water, alcohols, in particular having from 1 to 12 carbon atoms or from 1 to 6 carbon atoms, and mixture thereof, and more preferably from water, methanol, isopropanol and mixtures thereof.

Preferably, the solvent(s) if present represents from 1 to 60% by weight, preferably from 5 to 55% by weight, more preferably from 10 to 50% by weight, even more preferably from 20 to 45% by weight of the total weight of the initial material A (i.e. the material A before treatment by microwave irradiations).

According to an embodiment, the compound B containing 2-hydroxyphenyl benzotriazole and siloxane functions comprises at least one 2-hydroxyphenyl benzotriazole function of formula (I):



(I)

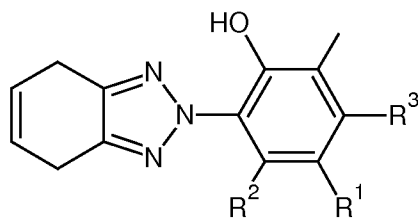
wherein at least one of the cycles can optionally be substituted by one or more substituents selected from linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, and halogens, and

wherein said function of formula (I) can be linked to the rest of the compound B either by the cycle of the benzotriazole or by the cycle of the hydroxyphenyl or by both cycles, preferably said function of formula (I) is linked to the compound B by the cycle of the hydroxyphenyl and more preferably at the ortho position of the hydroxyl group of the hydroxyphenyl;

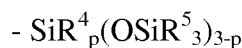
and at least one siloxane function comprising at least one atom succession of type (II) -Si - O - Si-.

According to an embodiment of the invention, the siloxane function is a polysiloxane function, i.e. a function comprising at least: -Si-O-Si-O-Si- linkage.

According to an embodiment, the compound B containing 2-hydroxyphenyl benzotriazole and siloxane functions comprises at least one function 2-hydroxyphenyl benzotriazole of formula (Ia) and at least one siloxane function of formula (IIa):



(Ia)



(IIa)

wherein the free valence is apparent,
and wherein:

R^1 , R^2 , R^3 are, independently to each other, selected from hydrogen, linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, and halogens;

R^4 , which may be identical or different, is selected from linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom,

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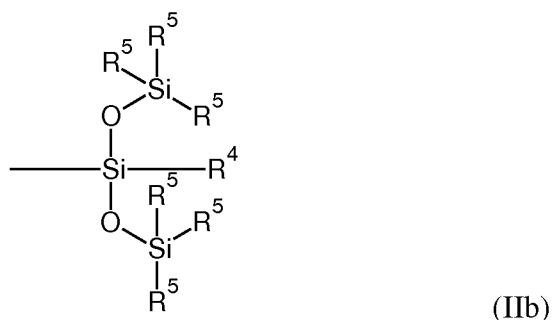
R^5 , which may be identical or different, is selected from linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, and from a $-OSiR^6_3$ radical, R^6 having the same definition as R^5 ;

p represents an integer ranging from 0 to 2.

Preferably, in the formula (Ia), R^2 and R^3 are hydrogen atoms.

Preferably, R^1 is an alkyl radical having from 1 to 8 carbon atoms, more preferably from 1 to 4 carbon atoms.

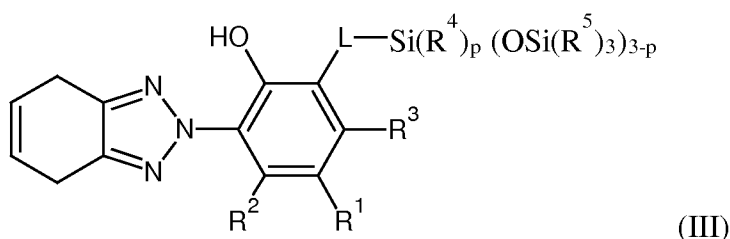
According to an embodiment, the siloxane function is of formula (IIb):



wherein the free valence is apparent,

and wherein R^4 and R^5 have the same meaning as the definition given for formula (IIa), preferably R^4 and R^5 , which may be identical or different, are selected from an alkyl radical having from 1 to 8 carbon atoms, more preferably from 1 to 4 carbon atoms.

According to an embodiment of the invention, the compound B may be represented by the following formula (III):



wherein

R^1 , R^2 and R^3 have the same definition as in formula (Ia),

R^4 , R^5 and p have the same definition as in formula (IIa), and

L represents a linker which can be a hydrocarbyl radical having from 2 to 40 carbon atoms and optionally comprising at least one carbon-carbon double bond and optionally comprising one or more heteroatoms, such as oxygen atoms.

Preferably, in formula (III) above, the linker L represents an alkyl radical or an alkenyl radical, saturated or unsaturated, preferably saturated, comprising from 2 to 30 carbon atoms, preferably from 2 to 20 carbon atoms, more preferably from 2 to 10 carbon atoms. According to an embodiment, the alkyl or alkenyl radical comprises only carbon atoms and hydrogen atoms. The linker corresponds to a terminally unsaturated (carbon-carbon double bond) substituent of the 2-hydroxyphenyl benzotriazole containing compound which has reacted by hydrosilylation with a SiH function of a siloxane compound.

According to an embodiment of the invention, the compound B comprises chemical functions different from 2-hydroxyphenyl benzotriazole and siloxane functions, such as ether, amine, amide, acid, ester, olefin functions. For example, the linker L in formula (III) can comprise one or more chemical functions.

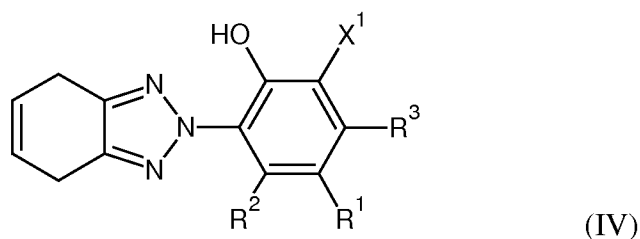
The compound B may for example be the 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-1-disiloxanyl]propyl]phenol.

According to an embodiment of the invention, the material to be dried is obtained from a method comprising the following successive steps:

- Reacting a 2-hydroxyphenyl benzotriazole containing compound C' containing at least one carbon-carbon double bond with a siloxane compound D' containing at least one SiH function in a medium comprising at least one catalyst and at least one solvent at a temperature ranging from 40 to 90°C in order to perform a hydrosilylation reaction, thereby a precipitate is obtained,
- Recrystallizing the precipitate with a solvent or a mixture of solvents.

Methods for preparing the material A are well known for the skilled person and are for example described in document WO2012/055063.

According to an embodiment of the invention, the 2-hydroxyphenyl benzotriazole containing compound C' responds to the formula (IV):



wherein

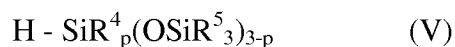
R^1 , R^2 and R^3 have the same definition as in formula (Ia) and

X^1 represents a hydrocarbyl radical having from 2 to 40 carbon atoms and
 5 comprising at least one carbon-carbon double bond and optionally comprising one or more heteroatoms, such as oxygen atoms.

Preferably, X^1 represents a hydrocarbyl radical comprising only carbon atoms and hydrogen atoms.

Preferably, X^1 represents a hydrocarbyl radical having from 2 to 30 carbon atoms,
 10 preferably from 2 to 20 carbon atoms, more preferably from 2 to 10 carbon atoms.

According to an embodiment of the invention, the siloxane compound D' containing at least one SiH function responds to the formula (V):



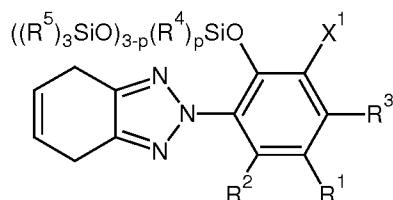
wherein R^4 , R^5 and p have the same definition as in formula (IIa).

15 According to said embodiment wherein the compound B is obtained from the reaction between the compounds C' and D' and with reference to formula (III) defined above, the linker L will be a radical resulting from the reaction between a carbon-carbon double bond of the radical X^1 of the compound C' of formula (IV) and the hydrogen atom of the SiH function of the compound D' of formula (V).

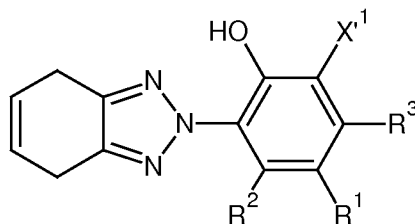
20 The material A may comprise impurities other than solvents, originating from the process for synthesizing the compound B. Among those kinds of impurities, mention may be made of the product of O-silylation of the 2-hydroxyphenyl benzotriazole containing compound C' by a siloxane compound (see as an example formula VI), of the product of terminal olefin function hydrogenation of the 2-hydroxyphenyl benzotriazole containing compound C' (see as an example formula VII), of the
 25 hydrosilylation of olefin-isomer of the 2-hydroxyphenyl benzotriazole containing compound C' (see as an example formula VIII), or of the compound produced by the O-silylation of hydroxyl function of compound B by remaining siloxane (see as an example formula IX), wherein:

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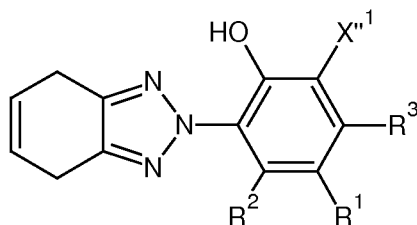
Formula (VI):



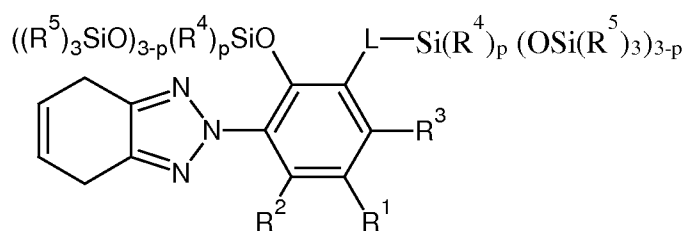
Formula (VII):



Formula (VIII):



Formula (IX):



5 wherein:

X^1 , R^1 , R^2 , R^3 , R^4 , R^5 , L and p have the same meaning as defined above in formula (III) and (IV),

X'^1 corresponds to the radical X^1 that has been hydrogenated, partially or totally, and

10 X''^1 corresponds to an olefin-isomer of the radical X^1 .

As an example, when the compound B is the 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-1-disiloxanyl]propyl]phenol, the compound C' containing at least one carbon-carbon double bond may be the 3-methallyl-2-hydroxy-5-methyl phenyl benzotriazole and the compound D' containing at
15 least one SiH function may be the heptamethyltrisiloxane.

The material A may be in the form of a slurry, a solid, a solution or an emulsion, preferably in the form of a slurry. Such a slurry or a solid can thus be in the form of a powder impregnated by liquids resulting from the process of manufacture thereof.

The material is submitted to microwave irradiations which allow drying or purifying said material. Therefore, during the process of the invention, liquids which may be present in the material A are removed from the material A, generally by evaporation of those liquids.

5 Microwave irradiations are a form of electromagnetic irradiation with wavelengths ranging from one meter to one millimeter, with frequencies ranging from 300 MHz to 300 GHz. Microwave sources or generators suitable for implementing the process of the invention are well known for the skilled person and among them, mention may be made of the magnetron, the gyrotron and the klystron.

10 Microwave apparatus suitable for implementing the process of the invention are commercially available and known for the skilled person. As a matter of example, such an apparatus are available from Sairem, Cober or Püschner Companies.

 According to an embodiment of the process, the microwave power density received by the material A during the process ranges from 0.001 to 10 kW/kg, preferably from 0.005 to 1 kW/kg, even more preferably from 0.01 to 0.3 kW/kg. The power density refers to the power in W received per kg of material A to be dried (initial).

 According to an embodiment of the process, the microwave frequencies sent by a microwave source range from 800 MHz to 6000 MHz. Preferably, the frequency used is selected from the frequencies approved for industrial applications (such as medical, domestic or scientific applications), for example the frequency may be ranged from 875 MHz to 950 MHz or from 2400 MHz to 2500 MHz or also from 5725 MHz to 5875 MHz. For an industrial scale, a frequency ranging from 875 MHz to 950 MHz, such as 915 MHz, will be preferred for a greater energetic efficiency.

25 The “power received by the material” within the meaning of the present invention, is the power effectively received and which reaches the material A. Indeed, the power received by the material may be different from the power emitted by the microwave source because of absorption phenomenon through the installation (walls of drum for example) and/or losses (reflected power), between the source and the material to be dried.

30 Preferably, the microwave irradiations work in multimode, which allows irradiating all the volume of the cavity containing the material A, which allows

increasing the homogeneity of the irradiation of the material A. According to this embodiment in multimode, the size of the cavity containing the material A is greater than the wavelength of the irradiation.

The process may be a continuous process or a batch process, preferably a batch process. In a batch process, at the end of the drying/purifying, the microwave irradiations are stopped. The end of the drying/purifying may be evaluated by measuring the amount of the compound B containing at least one 2-hydroxyphenyl benzotriazole function C and at least one siloxane function D and/or by measuring the amount of the liquid(s), generally of the solvent(s), in the product obtained. Those measurements can be made with methods well known for the skilled person, such as gas chromatography.

Fig. 1 schematically illustrates an example of an apparatus suitable for implementing the process of the invention. The apparatus illustrated in Fig. 1 comprises a microwave generator 1. A circulator 2 controls the direction of the incident wave and transfers the reflected energy to a measuring antenna 3, which allows quantifying the energy absorbed by the medium and thus the energetic efficiency. A waveguide 4 transports the microwave from the generator 1 to the cavity 6. A structure 5 which does not absorb the microwaves and which is resistant to the vacuum can also be present between the waveguide 4 and the cavity 6. The structure 5 is designed in order that all the system is adapted in impedance. The cavity 6 comprises the material A to be dried and may be put under vacuum during the process for drying/purifying. The cavity 6 may be provided with stirring means, such as tangled arms, not represented in Fig. 1. An element 9 can adjust the impedance of the apparatus during the drying process (for example a 3stub). A vacuum pump may also be present (not represented in Fig. 1).

The apparatus may also comprise a condenser 7 used to condense the evaporated liquids that are removed from the material A during the process. A container 8 may recover the liquids, such as the solvents, that are condensed in the condenser 7.

According to an embodiment, the process is performed with a reduced pressure generally in a closed system, preferably a cavity, preferably with a pressure ranging from 1 mbar (100 Pa) to 500 mbar (50000 Pa), preferably from 5 mbar (500 Pa) to 200 mbar (20000 Pa), more preferably from 10 mbar (1000 Pa) to 100 mbar (10000 Pa).

The microwave irradiations may be sent by a source placed outside the closed system under vacuum comprising the material. In such a case, the wall of the closed system can absorb a part of the power transmitted by the microwave source. After the drying, in order to increase the pressure in the system, an inert gas, such as nitrogen,
5 may be introduced.

According to an embodiment, the process is performed at a temperature ranging from -10°C to 45°C, preferably at a temperature ranging from -5°C to 40°C, more preferably from 0 to 35°C. The temperature is most preferably less than the melting point of the material A to be dried. It is possible to cool the microwave cavity for
10 example by a double jacket device around the microwave cavity, if the temperature of the microwave cavity increases in a too significant manner due to the microwave irradiation and/or to an optional stirring, for example if the temperature is higher than 50°C or higher than 45°C.

The drying (or purifying) time may notably depend on the amount of material. For
15 example the drying time may be of about 20 minutes to 2 hours for 1 kg of material.

The choice of the temperature, of the pressure and of the power will also allow modulating the drying time.

According to an embodiment of the invention, in order to improve the homogeneity of the treatment, the material is in motion during the process, for example
20 the movement can be a rotation or an oscillation.

When the material is in rotation, the rotation speed can range from 1 to 100 rpm, preferably from 1 to 40 rpm, more preferably from 1 rpm to 10 rpm. According to said embodiment, the material may be placed in a turntable within a microwave cavity.

When the material is in oscillation, the oscillation may be characterized by 10 to
25 30 oscillations per minute. According to said embodiment, the material may be placed in a closed system (such as a cylinder) and said closed system is put in oscillation, and the microwave irradiations are received through said closed system.

According to an embodiment, the material A is in motion in the cavity. The cavity comprising the material A may be provided by stirring means in order to stir the
30 material A and increase the homogeneity of the irradiation through the material A.

During the process of the invention, solvents are removed. The proportion of solvent(s) in the material A at the end of the process of the invention is lower than the

proportion of solvent(s) in the material A before beginning of the process of the invention.

According to an embodiment, after the drying or purifying process, the total amount of solvent(s) is less than 1000 ppm by weight, preferably less than 500 ppm by weight, more preferably less than 100 ppm by weight, based on the total weight of the material at the end of the process.

During the process of the invention, impurities other than solvents, such as the reactants, by-products, or catalysts used to prepare the compound B, may also be removed.

The proportion of compound(s) B in the material A at the end of the process of the invention is higher than the proportion of compound(s) B in the material A before beginning of the process of the invention.

According to an embodiment, after the drying or purifying process, the total amount of compound(s) B is higher than or equal to 90% by weight, preferably higher than or equal to 95% by weight, more preferably higher than or equal to 98% by weight, based on the total weight of the material at the end of the process.

The inventors surprisingly found that such materials can be efficiently dried or purified with microwave irradiations since for example the average drying time for removing solvents from the material with the claimed process is reduced by a factor of 50 as compared to a conventional heating method. In particular, it has been observed that a compound B comprising 2-hydroxyphenyl benzotriazole and siloxane functions, and in particular a compound B of formula (III) defined above, does not absorb or absorb little microwave irradiations whereas the solvent(s) (or other impurities), in particular the solvents used to prepare the compound B, absorb a lot microwave irradiations.

Up to now, microwave drying methods do not lead to materials having a residual solvent content of tens of ppm. Therefore, contrary to what is generally admitted in the field of microwave drying methods, the inventors surprisingly found that the material A containing the compound B defined in the present invention can be dried by microwave in order to obtain a very low amount of residual solvents, for example an amount as low as 10 ppm by weight or less, without degradation (chemical and/or physical) of the compound B comprising 2-hydroxyphenyl benzotriazole and siloxane functions. Indeed,

the drying process does not alter the properties of the active compound B which can be used as an active ingredient in formulations, for example as an UV filter in cosmetic applications.

Should the disclosure of any patents, patent applications and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

The following examples show the effectiveness of the process and further explain the process of the present invention.

10 EXAMPLES

Example 1: Description of the material

The material A comprises the following compound B: 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]-1-disiloxanyl]propyl]phenol.

15 The material A also comprises residual amounts of water, isopropanol and methanol.

The material A may be prepared according to the process described in document WO 2012/055063.

A benzotriazole containing compound (commercially available 3-methallyl-2-hydroxy-5-methyl phenyl benzotriazole; 3900 g; 13.96 mol) is charged into a reactor with a catalyst (2.24g Karstedt Pt catalyst; 10.05% Pt) in the presence of a solvent (Ethyl acetate; 3170g). Then, the siloxane containing compound (commercially available heptamethyltrisiloxane; 3200 g; 14.38 mol) is added into the reactor during one and a half hour. The reactor is maintained at a temperature of 60°C during about 5 hours.

Then, the solvent of the reaction of hydrosilylation is eliminated for example by heating under vacuum at temperatures higher than compound B melting point (~60°C, 20mbar). Then, the crystallization solvent (containing 1430g of water, 3140 g of isopropanol and 9380 g of methanol) is added at 60°C and the medium is cooled to about 0-10°C. The precipitate obtained may be additionally filtered and the cake is washed with the recrystallization solvent (containing 156g of water and 2950g of

methanol) 2 times to eliminate impurities formed during the synthesis such as remaining benzotriazole.

The material A in the form of a slurry of 10 kg comprising about 30% by weight of solvent is therefore obtained and used as a starting material in Example 2.

5

Example 2: drying or purifying process of the material of Example 1.

The system used in the examples in order to compare a drying process of the prior art and a drying process of the invention is a planetary mixer which has been provided with a microwave device capable of emitting and controlling the wave from the source
10 until the cavity containing the material A to be dried. The frequency of the microwave source used in the examples is 2450 MHz. For each test, the material is stirred with a rate of 8-9 rpm.

A comparative drying process (Comp.1) has been performed without microwave irradiations using a double jacket heating of the cavity containing the material A and
15 two drying processes according to the invention (Inv.1, Inv.2 and Inv.3) have been performed with microwave irradiations. Inv.1 and Inv.3 has been performed with microwave irradiations and without a double jacket heating of the cavity containing the material A; Inv.2 has been performed with microwave irradiations and with a double jacket heating of the cavity containing the material A.

20 The features of the processes are described in table 1 below.

Table 1: features of the drying processes

	Comp.1	Inv.1	Inv.2	Inv.3
material A weight (kg)	10.00	11.02	8.84	11.54
Initial humidity (%)	35.3	35.0	35.6	35.3
microwave power transmitted (W)	0	750	750	750
double jacket temperature (°C)	35	-	35	-
double jacket flowrate (l/h)	2200	-	2200	-
power density received (kW/kg)	0	0.062	0.077	0.065
maximal temperature (°C)	31	32	40	34
pressure (mbar)	42/38	42/38	40/42	40/30
mean reflected power (W)	0	69	69	61

In the table 1:

- The Initial humidity has been evaluated by measuring the final humidity and the amount of recovered condensates. The final humidity has been measured in the dried material by gas chromatography by quantifying residual solvents, mainly isopropanol and methanol.
- The pressures correspond to the pressures set during the drying process. The pressure has been slightly modified during the process in a non-significant manner.
- The maximal temperature corresponds to the highest temperature measured during the process, for example using a pyrometer.
- The mean reflected power corresponds to the microwave power reflected by the system and which will not reach the material A.
- The power density received is the power density received by the material A and has been calculated thanks to the microwave power transmitted, the mean reflected power and the weight of the material A.

The results of the processes are described in table 2 below.

Table 2: Results of the drying processes

	Comp.1	Inv.1	Inv.2	Inv.3
treatment time (min)	246	140	89	148
isopropanol/methanol final (ppm)	556/174	65/31	30/8	53/21

The amounts of isopropanol and methanol in the final material are measured by gas chromatography in the dried material obtained at the end of the process and is expressed in ppm by weight.

In table 2, it can be observed that the Comparative test 1 using a drying method of the prior art (heating under vacuum) leads to a dried material having a higher amount of isopropanol and methanol, even with a higher treatment time.

In table 2, it can be observed that Inv.1 and Inv.3 tests lead to a dried material having an amount of isopropanol of less than 100 ppm and an amount of methanol of less than 100 ppm, values which are currently accepted. It can also be observed that Inv.2 test leads to a dried material having the lowest amounts of isopropanol and methanol.

In Fig. 2, the humidity of the material in weight percent in function of the treatment time (min) is represented.

In Fig. 2, it can be observed that the final humidity of the material decreases more rapidly with a drying method using microwave irradiations (Inv.1 represented by □ and Inv. 2 represented by ○) than with a drying method without microwave irradiations (Comp.1 represented by ●). We can also observe that the drying method of the invention with an additional heating (Inv.2) is more rapid than the drying method of the invention without the double jacket heating (Inv.1).

- Flowability of the dried materials

The flowability of the dried materials has been evaluated by measuring the flowability index.

The flowability index based on strength measurements is determined on a ring shear tester (Brookfield Powder Flow Tester) according to the instructions of the standard ASTM D6128 (Jenike method).

The results of the measurements of flowability index are described in table 3 below.

Table 3: results of flowability index

	Comp.1	Inv.2	Inv.3
Flowability index	1.56	3.17	2.04
isopropanol/methanol final (ppm)	556/174	30/8	53/21

In table 3, it can be observed that the Comparative test 1 having a higher amount of isopropanol and methanol after drying by using drying method of the prior art (heating under vacuum) has a low flowability index of much less than 2, leading to a very cohesive dried material.

We can observe that the use of a drying method of the present invention with microwave irradiations makes it possible to obtain a dried material having a good flowability greater than 2, while having a low amount of isopropanol and methanol.

We can also observe that the flowability of the dried material is further enhanced when the drying method of the invention is combined with an additional heating (Inv.2). In this case, the flowability index is greater than 3, which can be considered as significant, while having an amount of residual solvents less than 50 ppm.

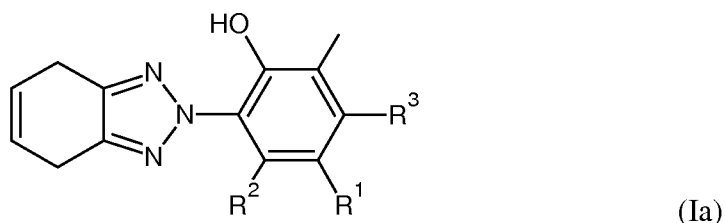
The examination of the tables 1 to 3 shows that the drying method in accordance to the invention (Inv.3) makes it possible to obtain a good treatment time/residual solvents/flowability compromise, especially with an additional heating to microwave irradiations (Inv.3), with respect to the comparative method without microwave irradiations (Comp.1).

CLAIMS

1. A process for purifying or drying a material comprising at least one compound containing at least one 2-hydroxyphenyl benzotriazole function and at least one siloxane function, said process comprising a step wherein the material is submitted to microwave
5 irradiations.
2. The process according to claim 1, wherein the material comprises, before being submitted to microwave irradiations, at least 40% by weight, preferably at least 50% by weight, more preferably at least 60% by weight, even more preferably at least 65% by weight of the at least one compound containing 2-hydroxyphenyl benzotriazole and
10 siloxane functions, based on the total weight of the material.
3. The process according to claim 1 or 2, wherein the material further comprises, before being submitted to microwave irradiations, at least one solvent.
4. The process according to claim 3, wherein the at least one solvent is selected from solvents characterized by a $\tan \delta$ of higher than 0.1, preferably higher than or equal to 0.3, more preferably higher than or equal to 0.4, measured at 2450 MHz at
15 25°C.
5. The process according to claim 3 or 4, wherein the at least one solvent is selected from water, alcohols, organosulfur solvents, organohalogenated solvents, carboxylic acids, and apolar amine solvents.
- 20 6. The process according to any one of claims 3 to 5, wherein the material comprises, before being submitted to microwave irradiations, from 1 to 60% by weight, preferably from 5 to 55% by weight, more preferably from 10 to 50% by weight, even more preferably from 20 to 45% by weight, of at least one solvent, based on the total weight of the material.
- 25 7. The process according to any one of claims 1 to 6, wherein the microwave power density received by the material ranges from 0.001 to 10 kW/kg, preferably from 0.005 to 1 kW/kg, even more preferably from 0.01 to 0.3 kW/kg.
- 30 8. The process according to any one of claims 1 to 7, wherein the process is performed with a reduced pressure preferably with a pressure ranging from 1 mbar to 500 mbar, preferably from 5 mbar to 200 mbar, more preferably from 10 mbar to 100 mbar.

9. The process according to any one of claims 1 to 8, wherein the process is performed at a temperature ranging from -10°C to 45°C, preferably at a temperature ranging from -5°C to 40°C, more preferably from 0 to 35°C.

10. The process according to any one of claims 1 to 9, wherein the compound
5 comprising at least one 2-hydroxyphenyl benzotriazole function and at least one siloxane function comprises at least one 2-hydroxyphenyl benzotriazole function of formula (Ia) and at least one siloxane function of formula (IIa):



10



wherein the free valence is apparent and wherein:

R^1 , R^2 , R^3 are, independently to each other, selected from hydrogen, linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally
15 comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, and halogens;

R^4 , which may be identical or different, is selected from linear or branched alkyl
20 radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom,

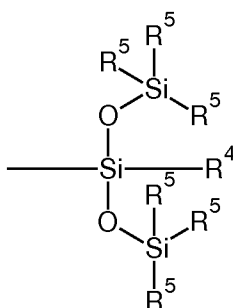
25 R^5 , which may be identical or different, is selected from linear or branched alkyl radicals preferably comprising from 1 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkenyl radicals preferably comprising from 2 to 12 carbon atoms and optionally comprising at least one halogen atom, linear or branched alkoxy radicals preferably comprising from 1 to 12 carbon atoms and

optionally comprising at least one halogen atom, and from a $-\text{OSiR}^6_3$ radical, R^6 having the same definition as R^5 ;

p represents an integer ranging from 0 to 2.

11. The process according to claim 10, wherein R^2 and R^3 are hydrogen atoms and R^1 is an alkyl radical having from 1 to 8 carbon atoms, more preferably from 1 to 4 carbon atoms.

12. The process according to claim 10 or 11, wherein the siloxane function is of formula (IIb):



(IIb)

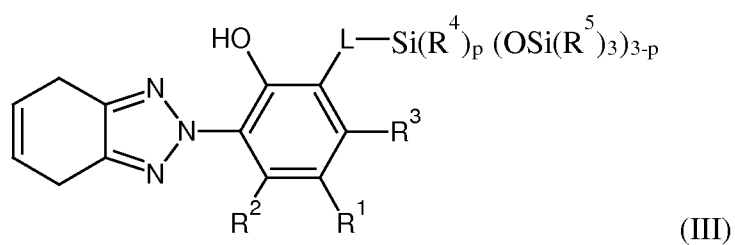
10 wherein the free valence is apparent, and wherein R^4 and R^5 have the same meaning as the definition given in claim 10, preferably R^4 and R^5 , which may be identical or different, are selected from an alkyl radical having from 1 to 8 carbon atoms, more preferably from 1 to 4 carbon atoms.

13. The process according to any one of claims 1 to 12, wherein the material is obtained from a method comprising the following successive steps:

- Reacting a 2-hydroxyphenyl benzotriazole containing compound C' containing at least one carbon-carbon double bond with a siloxane compound D' containing at least one SiH function in a medium comprising at least one catalyst and at least one solvent at a temperature ranging from 40 to 90°C in order to perform a hydrosilylation reaction, thereby a precipitate is obtained,
- Recrystallizing the precipitate with a solvent or a mixture of solvents.

14. The process according to any one of claims 1 to 13, wherein the compound containing at least one 2-hydroxyphenyl benzotriazole function and at least one siloxane function responds to the formula (III):

- 25 -



wherein

R^1 , R^2 and R^3 have the same definition as in formula (Ia) defined in claim 10,

R^4 , R^5 and p have the same definition as in formula (IIa) defined in claim 10, and

- 5 L represents a linker which can be a hydrocarbyl radical having from 2 to 40 carbon atoms and optionally comprising at least one carbon-carbon double bond and optionally comprising one or more heteroatoms, such as oxygen atoms.

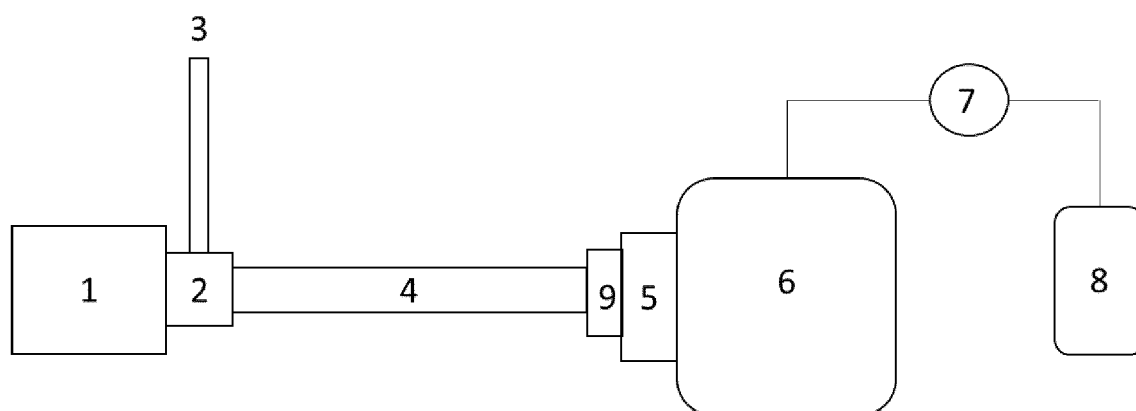


Figure 1.

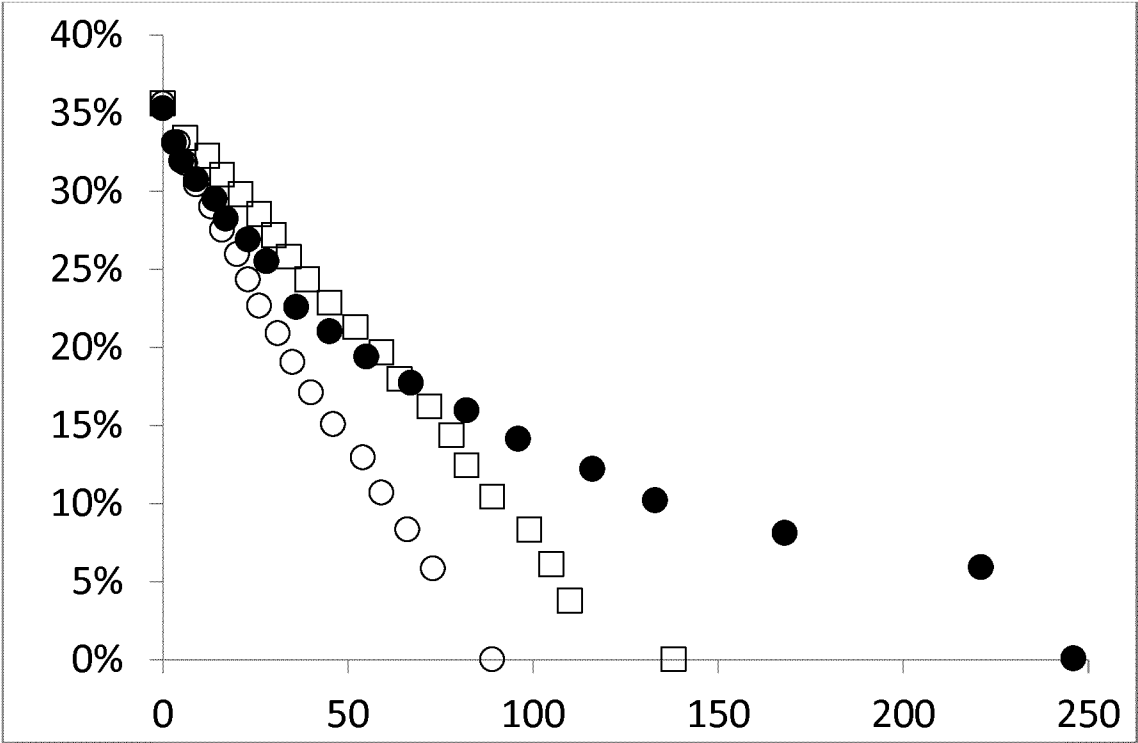


Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/081419A. CLASSIFICATION OF SUBJECT MATTER
INV. C07F7/08 C07B63/00
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)
C07F C07B

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/055064 A1 (OREAL [FR]; RICHARD HERVE [FR]; GUERREIRO PATRICIO [CN]; GUO JIANPING) 3 May 2012 (2012-05-03) cited in the application the whole document -----	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"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

23 January 2018

Date of mailing of the international search report

01/02/2018

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Diederer, Jeroen

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2017/081419

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2012055064 A1	03-05-2012	BR 112013003083 A2	05-07-2016
		CN 103153966 A	12-06-2013
		EP 2632905 A1	04-09-2013
		ES 2545254 T3	09-09-2015
		US 2013204006 A1	08-08-2013
		WO 2012055064 A1	03-05-2012
