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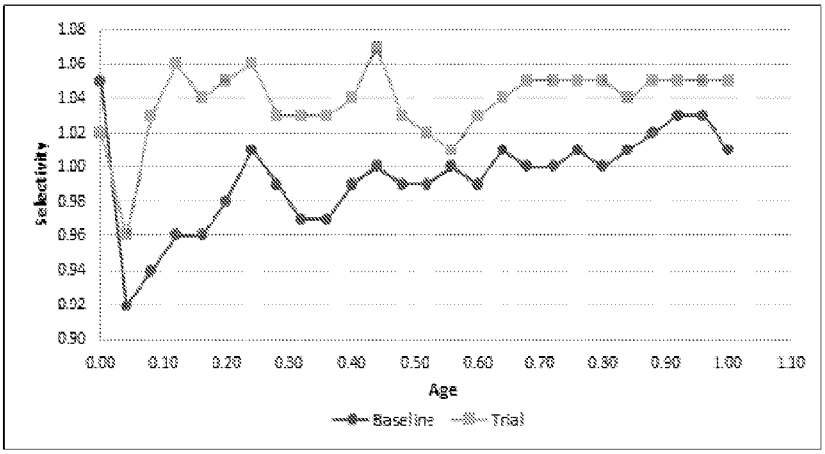
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(54) **Title**: PROCESS FOR PREPARING MONOHYDROGENTRIHALOSILANES

FIGURE 1



(57) **Abstract**: A process for preparing a product including a monohydrogentrihalosilane is disclosed. The process includes the steps of: 1) initially charging a reactor with a contact mass including both fresh silicon and recycled contact mass, where the recycled contact mass is obtained from during or after a production phase of an inorganic Direct Process reaction for production of a monohydrogentrihalosilane; and thereafter 2) feeding to the reactor a hydrogen halide and additional fresh silicon, thereby forming the product.

WO 2016/099833 A1

PROCESS FOR PREPARING MONOHYDROGENTRIHALOSILANES

[0001] This application claims the benefit of U.S. Provisional Patent Application No. 62/094431 filed 19 December 2014 under 35 U.S.C. §119 (e). U.S. Provisional Patent Application No. 62/094431 is hereby incorporated by reference.

Technical Field

[0002] A process for preparing monohydrogentrihalosilanes by the inorganic Direct Process reaction is described herein. The selectivity toward monohydrogentrihalosilanes in the product of the inorganic Direct Process reaction is increased by the process. Monohydrogentrihalosilanes, such as monohydrogentrichlorosilane ($HSiCl_3$), produced by this process are useful as reactants for use in the preparation of valuable silicon products, such as polycrystalline silicon and polysiloxane resin.

Background

[0003] Methods of preparing halosilanes are known in the art. Typically, halosilanes are produced commercially by the Mueller-Rochow Direct Process, which comprises passing a halide compound over zero-valent silicon (Si^0) to obtain a gas-solid direct contact between the Si^0 and the halide compound, resulting in the production of a mixture of halosilane compounds. The typical process for making the Si^0 used in the Direct Process involves carbothermic reduction of silicon dioxide (SiO_2) in an electric arc furnace. In a typical submerged arc furnace process, a mixture of carbon and SiO_2 is added to the top of the furnace. Both alternating current (AC) arc furnaces and direct current (DC) power sources may be used. U.S. Patent 5,009,703 and the references cited therein describe production of Si^0 from SiO_2. The overall reaction can be represented as follows: $SiO_2 + 2C \rightarrow Si^0 + 2CO$. The Si^0 produced by this process is typically at least 98% pure.

[0004] Products, which include mixtures of halogenated silicon containing compounds, are produced by the Direct Process. When an organohalide is used as the halide compound, a copper catalyst and various optional promoters are added to the Si^0, and the product includes a mixture of organohalosilanes (organic Direct Process). When a hydrogen halide is used as the halide compound, the product includes a mixture of inorganic hydrogen-functional halosilanes (inorganic Direct Process). Typically, catalyst and promoters are not added to the Si^0 in the inorganic Direct Process.

[0005] Frequently, the inorganic Direct Process has been run in a continuous or semi-batch mode. During a production campaign, the inorganic Direct Process is initiated by charging a reactor with a contact mass comprising fresh silicon that is free of catalyst and

promoters, *e.g.*, Si^0 prepared by carbothermic reduction as described above. A hydrogen halide and additional fresh silicon are added to the reactor to produce the product. When selectivity toward monohydrogentrihalosilane in the product drops to an undesirable level, the production campaign is ended by shutting down the reactor and discarding any silicon remaining therein.

SUMMARY OF THE INVENTION

[0006] A process for preparing a product comprising a monohydrogentrihalosilane of formula $HSiX_3$, where each X is independently a halogen atom with improved selectivity is described herein. The process comprises: 1) charging a reactor with a contact mass of fresh silicon (*e.g.*, Si^0 as described above) and recycled contact mass, where the recycled contact mass is obtained from an inorganic Direct Process reaction for production of a monohydrogentrihalosilane; and, thereafter, 2) feeding to the reactor a hydrogen halide and additional fresh silicon, thereby forming the product. The fresh silicon may be the Si0 described above.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Figure 1 is a graph showing the normalized monomer selectivity (y-axis) vs. normalized age of the contact mass (x-axis) results of Comparative Example 1 (Normalized Average Baseline Selectivity) and Example 1 (Normalized Average Trial Selectivity). Figure 1 is a graph of the data from Table 1 and Table 2, which compares the normalized monomer selectivity over the normalized age from 0 to 1 for the baseline and trial cases. The line labeled Baseline Average Selectivity represents the results of Comparative Example 1, and the line labeled Trial Average Selectivity represents the results of Example 1. This graph shows that the 'drop in monomer selectivity' is significantly reduced using the process described herein.

DETAILED DESCRIPTION OF THE INVENTION

[0008] It is desirable to run the inorganic Direct Process in a continuous or semi-batch mode in campaigns that continue for as long as possible to maximize the yield of product between reactor shutdowns. One of the problems associated with the inorganic Direct Process is controlling the selectivity. Selectivity refers to the amounts of the halogenated silicon containing compounds in the product. There is an industry need to produce monohydrogentrihalosilane, and reduce the number of other halogenated silicon containing compounds produced. The other halogenated silicon containing compounds include monomeric halosilane compounds such as dihydrogendihalosilanes and silicon tetrahalides, and polymeric halogenated silicon containing compounds such as polysilanes and polysiloxanes. For example, when HCl is used as the hydrogen halide, the product of the

inorganic Direct Process may include, in addition to monohydrogentrichlorosilane ($HSiCl_3$); other monomeric halosilane compounds such as dihydrogendichlorosilane (H_2SiCl_2) and silicon tetrachloride ($SiCl_4$). The product may further include polymeric chlorinated silicon containing compounds, such as polychlorosilanes such as hexachlorodisilane (Si_2Cl_6) and/or polychlorosiloxanes such as hexachlorodisiloxane (Si_2OCl_6), and partially hydrogenated polychlorosilanes and polychlorosiloxanes, such as tetrachlorodisiloxane ($H_2Si_2OCl_4$) and pentachlorodisiloxane (HSi_2OCl_5).

[0009] In the inorganic Direct Process, reactivity (*e.g.*, to consume the hydrogen halide and Si^0), and selectivity toward producing monohydrogentrichlorosilane in the product are typically relatively high at the beginning of the process. However, after a relatively short duration, monomer selectivity will drop to an undesirable level, such that the amounts of other halogenated silicon containing compounds (relative to the amount of monohydrogentrihalosilane) in the product increase. In particular, the amount of silicon tetrahalide relative to monohydrogentrihalosilane increases in the product, and this phenomenon, referred to herein as the 'drop in monomer selectivity', will occur for certain duration, after which monomer selectivity will increase to a desired level, thereby increasing the amount of monohydrogentrihalosilane in the product (*i.e.*, the amounts of other halogenated silicon containing compounds decrease relative to the amount of monohydrogentrihalosilane in the product, particularly the amount of silicon tetrahalide decreases). The process will then continue for a longer duration with the desired monomer selectivity in the product. This is referred to herein as the 'production phase'. After the production phase, the amount of polymeric halogenated silicon containing compounds will increase in the product, thus the overall selectivity will drop to an undesirable level (referred to herein as the 'drop in overall selectivity'). Overall selectivity refers to the production of monomeric halosilane compounds as compared to polymeric halogenated silicon containing compounds in the product. When the drop in monomer selectivity occurs, the duration of the drop in monomer selectivity, the duration of the production phase, and when the drop in overall selectivity occurs will each depend on various factors including the type and size of reactor selected, any impurities in the fresh silicon used, the hydrogen halide feed rate selected, the amount of silicon in the reactor, and process temperature selected. However, the inventors found consistently that the drop in monomer selectivity occurs regardless of the factors (described above) and process conditions selected. Therefore, there is an industry need to reduce or eliminate the drop in monomer selectivity when performing the inorganic

Direct Process in order to provide a consistent amount of monohydrogentrihalosilane in the product produced throughout a campaign.

[0010] Without wishing to be bound by theory, it was thought that the drop in overall selectivity was caused by build up of impurities in the contact mass in the reactor used for the inorganic Direct Process reaction. These impurities may have been introduced with the fresh silicon used as reactant. The Si^0 produced by the carbothermic reduction process described above may be used as fresh silicon in this process, and this Si^0 is typically at least 98% pure. However, the Si^0 contains one or more impurities in addition to the silicon, *e.g.*, the Si^0 further comprises >0% to <2% of one or more of iron (Fe), aluminium (Al), calcium (Ca) and/or titanium (Ti). As a campaign progresses, silicon reacts and is removed from the reactor in the form of the product. However, some or all of the impurities do not react and build up in the contact mass in the reactor as more fresh silicon containing the impurities is added to the reactor. When this amount builds up to a high enough level, the drop in overall selectivity occurs. When the drop in overall selectivity occurs, the silicon is deemed spent (referred to herein "spent silicon") because even if the campaign is continued, overall selectivity will not increase after the drop in overall selectivity occurs. However, the inventors surprisingly found that by combining spent silicon with fresh silicon at the beginning of a subsequent campaign (instead of beginning the subsequent campaign with only fresh silicon), the drop in monomer selectivity was minimized or eliminated in the subsequent campaign without producing additional polymeric halogenated silicon containing compounds or otherwise detrimentally impacting the overall selectivity. This is particularly unexpected because the spent silicon was obtained during the portion of a campaign in which overall selectivity is undesirable (*i.e.*, the spent silicon was obtained after the drop in overall selectivity occurred, therefore increased amounts of polymeric halogenated silicon containing compounds were being formed in the product). Since the spent silicon was obtained from a portion of the campaign in which overall selectivity was poor, it was surprising to find combining this spent silicon with fresh silicon improved monomer selectivity (by minimizing or eliminating the drop in monomer selectivity) without detrimentally impacting overall selectivity in a subsequent campaign. This is also particularly surprising because the inorganic Direct Process is typically uncatalyzed, unlike the organic Direct Process described above. In contrast to the organic Direct Process, the process described herein does not require the addition of a copper catalyst or a promoter to the fresh silicon to achieve high yields or improve selectivity. Therefore, the spent silicon of the inorganic Direct Process does not contain catalyst and/or promoter that can be recycled in a subsequent campaign.

[0011] Furthermore, the inventors surprisingly found that adding spent silicon later in the process (*e.g.*, during or after the drop in monomer selectivity, and/or during the production phase) could be detrimental to overall selectivity. Adding spent silicon to the reactor at any time in a campaign other than at the initial charge of contact mass resulted in more polymeric halogenated silicon containing compounds being formed in the product than would have occurred if the spent silicon had not been added later in the process.

[0012] The inventors further found that taking contact mass from the reactor during or after the production phase of a campaign (*i.e.*, after the drop in monomer selectivity ended) would also improve monomer selectivity when combined with fresh silicon in the initial charge in the reactor at the beginning of a subsequent campaign. Without wishing to be bound by theory, it is thought that the impurities introduced into the reactor with the fresh silicon build up in the contact mass as a campaign progresses, and that after the first drop in monomer selectivity ends and the production phase of a campaign begins, the contact mass in the reactor contains sufficient impurities to improve monomer selectivity without detrimentally affecting overall selectivity, when used as a portion of an initial charge of contact mass for a subsequent campaign. Therefore, the process described herein may be performed using recycled contact mass, which is contact mass taken from inside the reactor during or after the production phase of a campaign when sufficient impurities have concentrated in the contact mass to provide the benefit of reducing or eliminating the drop in monomer selectivity.

[0013] The recycled contact mass may or may not be spent silicon. Recycled contact mass may be contact mass that is removed from the reactor during or after the production phase of a campaign. Alternatively, recycled contact mass may be left in the reactor if the reactor is shut down after the drop in monomer selectivity ends, but before the drop in overall selectivity occurs. The recycled contact mass may be up to 85% silicon with the balance being impurities that have concentrated during the campaign as silicon was reacted and removed from the reactor as product. Alternatively, recycled contact mass may be >0% to 85% silicon; alternatively 30% to 82% silicon, alternatively 30% to 80% silicon, alternatively 30% to 70% silicon; with the balance being impurities. Alternatively, recycled contact mass may be 40% to 85%. Alternatively, spent silicon may be used in the process described herein.

[0014] When the fresh silicon and recycled contact mass are combined to form an initial charge of contact mass in the reactor, the amounts of fresh silicon and recycled contact mass are selected to provide the initial charge of contact mass with a silicon content of 50%

to 95%, alternatively 70% to 90%, alternatively 80% to 90%, alternatively 85% to 90%, alternatively 82% to 90%, and alternatively 80% to 85%; with the balances being impurities.

[0015] Therefore, the process described herein is a process for preparing a product comprising a monohydrogentrihalosilane of formula $HSiX_3$, where each X is independently a halogen atom. The process has improved monomer selectivity over the inorganic Direct Process practiced previously in which no recycled contact mass is charged in the reactor at the beginning of a campaign. In a first embodiment, the process comprises:

1) charging a reactor with a contact mass of fresh silicon and recycled contact mass, where the recycled contact mass is obtained during or after a production phase of an inorganic Direct Process reaction for production of a monohydrogentrihalosilane; and, thereafter,

2) feeding to the reactor a hydrogen halide and additional fresh silicon, thereby forming the product.

More specifically, in a second embodiment, the process may comprise:

1) charging a reactor with a contact mass of fresh silicon and spent silicon, where the spent silicon is obtained after a drop in overall selectivity occurs in an inorganic Direct Process reaction for production of a monohydrogentrihalosilane; and, thereafter,

2) feeding to the reactor a hydrogen halide and additional fresh silicon, thereby forming the product.

[0016] The fresh silicon may be Si^0 obtained from the carbothermic reduction process described above. Particle size of the fresh silicon may be any particle size suitable for use in the reactor selected for the process. However, for example, when a fluidized bed reactor is used, the fresh silicon may have a particle size up to 150 micrometers (μm). Standard methods for producing fresh silicon in particulate form can be used, for example, the use of a roller or ball mill to grind silicon lumps. The fresh silicon may be further classified as to particle size distribution by means of, for example, screening or use of mechanical aerodynamic classifiers such as a rotating classifier.

[0017] Recycled contact mass is obtained from an inorganic Direct Process reaction for production of a monohydrogentrihalosilane. The recycled contact mass is obtained during or after the production phase of a campaign (*e.g.*, not during or before the drop in monomer selectivity that occurs when a fresh silicon contact mass is used in the inorganic Direct Process). In one embodiment, all or a portion of the recycled contact mass is left in the reactor after a campaign ends (*i.e.*, after the production phase, and after the hydrogen halide and fresh silicon are no longer fed to the reactor). The campaign may be ended during the production phase before the drop in overall selectivity occurs. Alternatively, the campaign

may be ended after the drop in overall selectivity occurs (in which case the recycled contact mass left in the reactor will be spent silicon). Fresh silicon may then be added to the same reactor with the recycled contact mass, thereby forming the initial charge of contact mass including fresh silicon and recycled contact mass at the beginning of a subsequent campaign. In an alternative embodiment, the recycled contact mass is removed from the reactor, and all or a portion of the recycled contact mass is charged into a different reactor with fresh silicon to form a contact mass at the beginning of a different campaign. In the process described herein, recycled contact mass is only added in the initial charge in the reactor at the beginning of a campaign. Recycled contact mass is not added to a campaign after beginning to feed the hydrogen halide.

[0018] The process described herein may optionally further comprise a preheating step before step 2). In the process described herein, the contact mass in step 1) may optionally be heated for a certain time in an inert atmosphere at a temperature of 200 °C to 350 °C, alternatively 200 °C to 280 °C, before beginning to add the hydrogen halide to the reactor. Without wishing to be bound by theory, it is thought that preheating may improve reactivity and/or fluidization of the contents of the reactor.

[0019] Hydrogen halides are known in the art and are commercially available. The hydrogen halide may optionally be preheated and/or vaporized before it is fed into the reactor. The hydrogen halide may be hydrogen bromide (HBr), hydrogen chloride (HCl), or hydrogen iodide (HI). Alternatively, the hydrogen halide may be HCl.

[0020] The reaction of a hydrogen halide with a particulate contact mass is a surface reaction. More available silicon surface gives more potential for reaction in a given volume, so reaction rate is related to the specific surface area of the particles of silicon available. Smaller particles have high specific surface areas and react away quickly while larger particles have a lower specific surface area and a corresponding lower reaction rate. Furthermore, when the process is run a continuous or semi-batch mode, the particles of silicon spend a finite residence time in the reactor, therefore, faster reacting small particles are more likely to be consumed to give high silicon conversion (high yield) and consequently fewer unreacted particles of spent silicon.

[0021] In the process described herein, the product typically comprises more than one monomeric halosilane compound described by general formula $H_xSiX_{(4-x)}$, where subscript x has an average value of 0 to 3, and X is a halogen atom. Alternatively, each X may be a chlorine atom. When X is Cl, the monomeric halosilane compounds in the product include H_2SiCl_2, $HSiCl_3$, and $SiCl_4$. The product may further comprise polymeric halogenated

silicon containing compounds, as described above, however, the product may predominantly comprise $HSiCl_3$ and $SiCl_4$.

[0022] The process may optionally further comprise one or more additional steps (in addition to the steps described above). The process may optionally further comprise: 3) feeding to the reactor additional hydrogen halide without fresh silicon after step 2). When this step is present, the amount of silicon in the contact mass is depleted. The process may optionally further comprise repeating steps 1) and 2) (and when present step 3)) one or more times in additional subsequent production campaigns.

[0023] The relative amounts of recycled contact mass and fresh silicon in the contact mass initially charged in the reactor at the beginning of a campaign may vary depending on factors including length of the campaign, rate at which the fresh silicon and hydrogen halide are fed to the reactor in step 2), whether step 3) is performed, reactor size, and whether the optional step of feeding additional hydrogen halide without fresh silicon is performed in the immediately preceding campaign (*i.e.*, the campaign from which the spent silicon was obtained). However, the spent silicon may be present in an amount of 5% to 90% and the fresh silicon may be present in an amount of 5% to 95%. Alternatively, the spent silicon may be present in an amount of 10% to 60%, and the fresh silicon may be present in an amount of 40% to 90%, in the contact mass charged in the reactor at the beginning of a campaign. Alternatively, the recycled contact mass may be present in an amount of 5% to 95% and the fresh silicon may be present in an amount of 5% to 95% charged in the reactor at the beginning of a campaign. Alternatively, the recycled contact mass may be present in an amount of 10% to 90% and the fresh silicon may be present in an amount of 10% to 90% of the contact mass charged in the reactor. Alternatively, the recycled contact mass may be present in an amount of 15% to 85% and the fresh silicon may be present in an amount of 15% to 85% of the contact mass charged in the reactor. Alternatively, the recycled contact mass may be present in an amount of 20% to 80% and the fresh silicon may be present in an amount of 20% to 80% of the contact mass charged in the reactor.

[0024] The process may be performed under conventional pressure and temperature conditions for the inorganic Direct Process, for example temperature in step 2) and/or optional step 3) of feeding additional hydrogen halide without fresh silicon) may be 250 °C to 350 °C, alternatively 280 °C to 340 °C. Pressure is not critical, however, the pressure may range from 0 to 10 atmospheres gauge, alternatively 1 to 5 atmospheres gauge.

[0025] The process may further comprise enabling the product to leave the reactor whereby the monohydrogentrihalosilane, hydrogen, and unreacted hydrogen halide elutriate a proportion of the contact mass. For example, when the process is run in a continuous or

semi-batch mode, the process further comprises removing product from the reactor during step 2). Fresh silicon is added to the reactor during step 2) to replace silicon consumed by the inorganic Direct Process reaction and silicon elutriated with the product. Fresh silicon may be added continuously or intermittently during step 2). However, in this process contact mass need not be removed from the reactor other than by elutriation during step 2).

[0026] Alternatively, the process may further comprise recovering the monohydrogentrihalosilane from the product. Recovering the monohydrogentrihalosilane may be performed after step 2), and/or after step 3), when step 3) is present. Recovering may be performed by conventional means, such as distillation of the product. The monohydrogentrihalosilane is useful as a reactant for the production of valuable silicon materials such as polycrystalline silicon and/or polysiloxane resin. The process may optionally further comprise recovering other halogenated silicon containing compounds (in addition to the monohydrogentrihalosilane) from the product. For example, silicon tetrahalides, such as silicon tetrachloride, may be isolated and used as reactants for fumed silica production. Alternatively, the product (*e.g.*, including a mixture of $HSiCl_3$ and $SiCl_4$) may be used as a reactant for fumed silica production without isolation of the monomeric halosilane species in the product.

[0027] The process may optionally further comprise removing a portion of the contact mass from the reactor during the production phase of a campaign. The contact mass removed may be replaced with fresh silicon (*e.g.*, by increasing the feed rate of the fresh silicon fed to the process in step 2)). The process may optionally further comprise a purging step and/or a treating step. "Purging" means to introduce a gas stream into a container to remove unwanted materials. Unwanted materials that may be present in the reactor are, for example, O_2 and H_2O. Purging the reactor may be done before step 1), after step 1) and before step 2) and/or after step 2); alternatively, before step 1). Purging may be accomplished with an inert gas, such as argon, nitrogen, or helium or with a reactive gas, such as an inorganic halosilane, *e.g.*, silicon tetrachloride, which reacts with moisture thereby removing it. "Treating" means to introduce a gas stream into a container to pre-treat a component before contacting the component with another component. Treating before step 1) may be done to at least partially remove any oxide layer that may be present on the surfaces of the particles of fresh silicon. In the first embodiment, treating may be performed after step 1) and before step 2). In the second embodiment, treating may be performed after step 1) and before step 2).

[0028] The process described herein may be performed in any reactor suitable for contacting gases and solids. For example, the reactor can be a packed bed reactor, a

stirred bed reactor, a vibrating bed reactor, a moving bed reactor, a re-circulating bed reactor, or a fluidized bed reactor. Alternatively, the reactor may be a fluidized bed reactor. The contact mass and the hydrogen halide may be contacted by, *e.g.*, fluidizing the contact mass in a fluidized bed reactor. The hydrogen halide, or a mixture of hydrogen halide and an inert gas may be used to fluidize the contact mass. For example, suitable inert gases include nitrogen, helium, argon, and mixtures thereof. Different campaigns may be performed in the same reactor. Alternatively an initial campaign and a subsequent campaign may be performed in different reactors.

EXAMPLES

[0029] These examples are intended to illustrate some embodiments of the invention and should not be interpreted as limiting the scope of the invention set forth in the claims.

Comparative Example 1 – Production of $HSiCl_3$ using the Direct Process with no Recycled Contact Mass

[0030] A fluidized bed reactor was charged with a contact mass of fresh silicon powder. The fresh silicon was fluidized with an inert gas and heated to 240 °C. The reaction was initiated with the addition of hydrogen chloride gas and maintained in a temperature range of 280 °C to 320 °C during the campaign. The inventory of contact mass in the reactor was maintained by continually adding more fresh silicon to replace silicon that was reacted in the chlorosilane synthesis reaction and that left the reactor with the product due to elutriation. This process was repeated three more times using the same conditions, for a total of four campaigns as controls. The results of these four campaigns were averaged, and the average results are presented in Table 1 below. The normalized age from 0 to 1 covers the 'drop in monomer selectivity' and the subsequent 'increase in monomer selectivity' to the desired level for each campaign. The monomer selectivity was also normalized with 1 being the average monomer selectivity over the normalized age from 0 to 1 for the four control campaigns.

Table 1

Normalized Age	Normalized Average Baseline Monomer Selectivity
0.00	1.05
0.04	0.92
0.08	0.94
0.12	0.96
0.16	0.96
0.20	0.98
0.24	1.01
0.28	0.99

0.32	0.97
0.36	0.97
0.40	0.99
0.44	1.00
0.48	0.99
0.52	0.99
0.56	1.00
0.60	0.99
0.64	1.01
0.68	1.00
0.72	1.00
0.76	1.01
0.80	1.00
0.84	1.01
0.88	1.02
0.92	1.03
0.96	1.03
1.00	1.01

Example 1

[0031] After the production phase of a campaign performed as described above in Comparative Example 1, the reactor was shut down, and recycled contact mass remained in the reactor. A portion of this recycled contact mass was removed from the reactor. However, 35% of the recycled contact mass remaining after the campaign as described in Comparative Example 1 was left in the reactor. The reactor was then charged with an additional amount of the same fresh silicon powder as described above in Comparative Example 1. As a result, the reactor contained an amount of fresh silicon : recycled contact mass of 2:1. A campaign was then performed in the reactor using the same conditions as the campaign described above in Comparative Example 1. This campaign was able to reach target selectivity and able to start the production phase in less than 10% of the time required for the control campaigns described in Comparative Example 1. The trial was repeated again, but this time 13% of the recycled contact mass from the previous campaign was left in the reactor. The reactor was then charged with an amount of fresh silicon sufficient to provide a ratio of fresh silicon : recycled contact mass of 8:1. This campaign showed similar results, also reaching selectivity sufficient to start the production phase at a Normalized Age less than 100% of the Normalized Age of the control sample in Comparative Example 1. The averaged results of these two trials are shown below in Table 2.

Table 2

Normalized Age	Normalized Average Trial Monomer Selectivity

0.00	1.02
0.04	0.96
0.08	1.03
0.12	1.06
0.16	1.04
0.20	1.05
0.24	1.06
0.28	1.03
0.32	1.03
0.36	1.03
0.40	1.04
0.44	1.07
0.48	1.03
0.52	1.02
0.56	1.01
0.60	1.03
0.64	1.04
0.68	1.05
0.72	1.05
0.76	1.05
0.80	1.05
0.84	1.04
0.88	1.05
0.92	1.05
0.96	1.05
1.00	1.05

Industrial Applicability

[0032] It can be readily seen in Comparative Example 1 that the average campaign is unable to achieve selectivity above baseline until 64% through this period. However, in Example 1, the process described herein shows an average selectivity greater than 1 during this period, representing an improvement to the process of Comparative Example 1.

[0033] The Brief Summary of the Invention and the Abstract are hereby incorporated by reference. All ratios, percentages, and other amounts are by weight, unless otherwise indicated. The articles 'a', 'an', and 'the' each refer to one or more, unless otherwise indicated by the context of the specification.

[0034] The disclosure of ranges includes the range itself and also anything subsumed therein, as well as endpoints. For example, disclosure of a range of 2.0 to 4.0 includes not only the range of 2.0 to 4.0, but also 2.1, 2.3, 3.4, 3.5, and 4.0 individually, as well as any other number subsumed in the range. Furthermore, disclosure of a range of, for example,

2.0 to 4.0 includes the subsets of, for example, 2.1 to 3.5, 2.3 to 3.4, 2.6 to 3.7, and 3.8 to 4.0, as well as any other subset subsumed in the range.

[0035] With respect to any Markush groups relied upon herein for describing particular features or aspects of various embodiments, it is to be appreciated that different, special, and/or unexpected results may be obtained from each member of the respective Markush group independent from all other Markush members. Each member of a Markush group may be relied upon individually and or in combination with any other member or members of the group, and each member provides adequate support for specific embodiments within the scope of the appended claims. For example, disclosure of the Markush group: alkyl, aryl, and carbocyclic includes the member alkyl individually; the subgroup alkyl and aryl; and any other individual member and subgroup subsumed therein.

[0036] It is also to be understood that any ranges and subranges relied upon in describing various embodiments of the present disclosure independently and collectively fall within the scope of the appended claims, and are understood to describe and contemplate all ranges including whole and/or fractional values therein, even if such values are not expressly written herein. The enumerated ranges and subranges sufficiently describe and enable various embodiments of the present disclosure, and such ranges and subranges may be further delineated into relevant halves, thirds, quarters, fifths, and so on. As just one example, a range "of 250 to 350" may be further delineated into a lower third, *i.e.*, from 250 to 283, a middle third, *i.e.*, from 284 to 317, and an upper third, *i.e.*, from 318 to 350, which individually and collectively are within the scope of the appended claims, and may be relied upon individually and/or collectively and provide adequate support for specific embodiments within the scope of the appended claims. In addition, with respect to the language which defines or modifies a range, such as "at least," "greater than," "less than," "no more than," and the like, it is to be understood that such language includes subranges and/or an upper or lower limit. As another example, a range of "up to 85%" inherently includes a subrange from 0.1% to 85%, a subrange from 30% to 50%, a subrange from 33% to 57%, and so on, and each subrange may be relied upon individually and/or collectively and provides adequate support for specific embodiments within the scope of the appended claims. Finally, an individual number within a disclosed range may be relied upon and provides adequate support for specific embodiments within the scope of the appended claims. For example, a range of "1 to 9" includes various individual integers, such as 3, as well as individual numbers including a decimal point (or fraction), such as 4.1, which may be relied upon and provide adequate support for specific embodiments within the scope of the appended claims.

[0037] The subject matter of all combinations of independent and dependent claims, both singly and multiply dependent, is expressly contemplated but is not described in detail for the sake of brevity. The disclosure has been described in an illustrative manner, and it is to be understood that the terminology which has been used is intended to be in the nature of words of description rather than of limitation. Many modifications and variations of the present disclosure are possible in light of the above teachings, and the disclosure may be practiced otherwise than as specifically described.

CLAIMS

1. A process for preparing a product comprising a monohydrogentrihalosilane of formula $HSiX_3$, where each X is independently a halogen atom, where the process comprises:

1) charging a reactor with a contact mass of fresh silicon and recycled contact mass, where the recycled contact mass is obtained during or after a production phase of an inorganic Direct Process reaction; and thereafter

2) feeding to the reactor a hydrogen halide of formula HX and additional fresh silicon, thereby forming the product.

2. The process of claim 1, where the contact mass in step 1) contains 50% to 95% silicon.

3. The process of claim 1 or claim 2, where the recycled contact mass is spent silicon.

4. The process of any one of claims 1 to 3, further comprising: step 3) feeding to the reactor additional hydrogen halide without fresh silicon after step 2).

5. The process of any one of claims 1 to 4, further comprising repeating steps 1) and 2), and, when present step 3), one or more times.

6. The process of any one of claims 1 to 5, where the reactor is a fluidized bed reactor.

7. The process of any one of claims 1 to 6, further comprising using the product to make fumed silica.

8. The process of any one of claims 1 to 6, further comprising recovering the monohydrogentrihalosilane from the product.

9. The process of any one of claims 1 to 8, where each X is chlorine.

10. The process of claim claim 8, further comprising using the monohydrogentrihalosilane as a reactant for producing polycrystalline silicon.

11. The process of claim 8, further comprising using the monohydrogentrihalosilane as a reactant for producing polysiloxane resin.

12. A process for preparing a product comprising a monohydrogentrihalosilane of formula $HSiX_3$, where each X is independently a halogen atom, the process comprises:

1) charging a reactor with a contact mass of fresh silicon and spent silicon, where the spent silicon is obtained no earlier than beginning a drop in overall selectivity of an inorganic Direct Process reaction campaign; and thereafter

2) feeding to the reactor a hydrogen halide of formula HX and additional fresh silicon, thereby forming the product.

13. The process of claim 12, where the contact mass in step 1) contains 50% to 95% silicon.

14. The process of claim 12 or claim 13, further comprising: step 3) feeding to the reactor additional hydrogen halide without fresh silicon after step 2).

15. The process of any one of claims 12 to 14, further comprising repeating steps 1) and 2), and, when present step 3), one or more times.

16. The process of any one of claims 12 to 15, where the reactor is a fluidized bed reactor.

17. The process of any one of claims 12 to 16, further comprising using the product to make fumed silica.

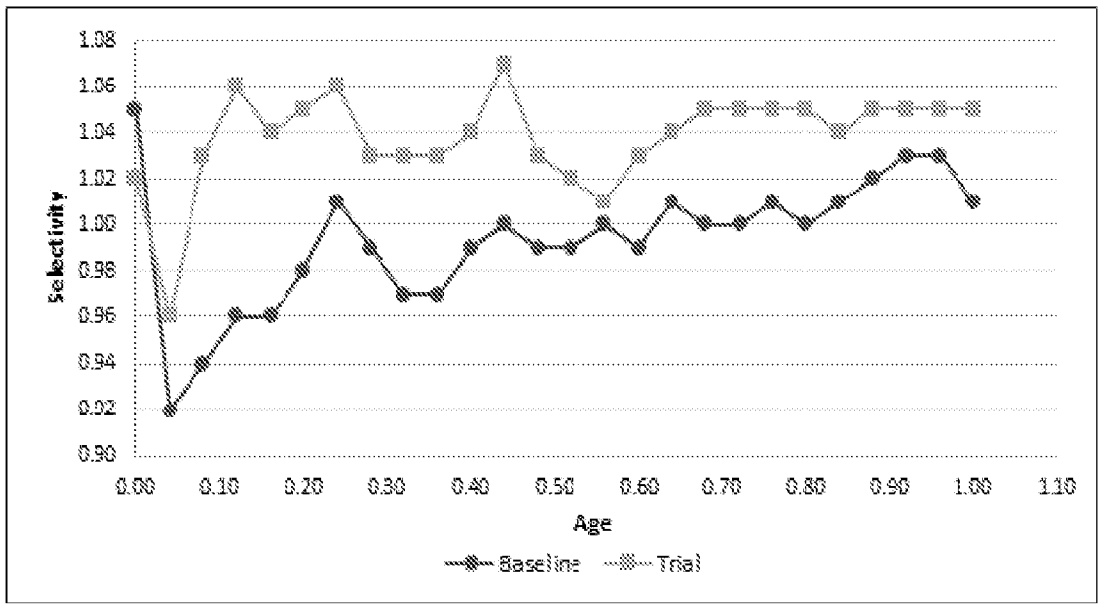
18. The process of any one of claims 12 to 16, further comprising recovering the monohydrogentrihalosilane from the product.

19. The process of any one of claims 12 to 18, where each X is chlorine.

20. The process of claim 18, further comprising using the monohydrogentrihalosilane as a reactant for producing polycrystalline silicon.

21. The process of claim 18, further comprising using the monohydrogentrihalosilane as a reactant for producing polysiloxane resin.

FIGURE 1


1.08
1.06
1.04
1.02
1.00
0.98
0.96
0.94
0.92
0.90
Selectivity
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
0.90
1.00
1.10
Age
Baseline
Trial

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/062569

A. CLASSIFICATION OF SUBJECT MATTER

C01B 33/107(2006.01)i, C03B 29/06(2006.01)i, C08G 77/04(2006.01)i

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)
C01B 33/107; C01B 33/04; B01J 19/24; C01B 33/08; C03B 29/06; C08G 77/04

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: monohydrogentrihalosilane, inorganic Direct Process reaction, recycled contact mass, spent silicon, hydrogen halide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4390510 A (RITZER, ALAN et al.) 28 June 1983 See abstract; column 4, lines 27-43; column 13, lines 3-7; column 13, lines 50-58; and table 1.	1-3,12-14
A	US 2007-0086936 A1 (HOEL, JAN-OTTO et al.) 19 April 2007 See abstract; claims 1-11; and figures 1-5.	1-3,12-14
A	US 2013-0156676 A1 (KATSOULIS, DIMITRIS et al.) 20 June 2013 See abstract; and claims 1-20.	1-3,12-14
A	US 2013-0156675 A1 (BRENEMAN, WILLIAM C.) 20 June 2013 See abstract; claims 6-14; and figure 1.	1-3,12-14
A	WO 2013-138461 A1 (CENTROTHERM PHOTOVOLTAICS USA, INC.) 19 September 2013 See abstract; and claims 1-10.	1-3,12-14

☐ 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	Date of mailing of the international search report
02 February 2016 (02.02.2016)	**03 February 2016 (03.02.2016)**

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/062569

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 10, 11, 20, 21
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 10, 11, 20 and 21 are unclear because they refer to multiple claims which are not drafted in accordance with PCT Rule 6.4(a).

3. ☒ Claims Nos.: 4-9, 15-19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required addtional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/US2015/062569

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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US 2007-0086936 A1	19/04/2007	AT 409678 T	15/10/2008
		CN 100349797 C	21/11/2007
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		EP 2825506 A1	21/01/2015
		EP 2825506 A4	02/12/2015
		KR 10-2014-0136985 A	01/12/2014
		US 2015-0030520 A1	29/01/2015