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Reactive composition and process for the purification of
a gas containing hydrogen chloride

The invention relates to the
purification of gases containing hydrogen chloride.

It relates more particularly to a
reactive composition based on sodium bicarbonate, which
5 can be employed for purifying a gas from hydrogen
chloride.

Burning is a technology which tends to
become a requirement for the disposal of household or
municipal waste. Burning of household waste is
10 accompanied by formation of smoke which generally
contains hydrogen chloride. It is imperative that
hydrogen chloride is removed from the smoke before the
latter is discharged into the atmosphere.

A known process for purifying a smoke
15 containing hydrogen chloride consists in treating the
smoke with sodium bicarbonate so as to decompose the
hydrogen chloride and to form sodium chloride.

More particularly, a process has been
proposed in which sodium bicarbonate is injected in the
20 form of a powder into the smoke leaving the incinerator
and the smoke thus treated is next conveyed onto a filter
(Solvay & Cie, pamphlet TR.895/5c-B-1-1290). In this
known process the smoke is at a temperature of 260°C at
the point of injection of the sodium bicarbonate. The
25 latter is used in the form of a size-graded powder
obtained by milling, in which 90 % by weight is in the
form of particles with a diameter smaller than 16 μ m.

In practice the sodium bicarbonate
powder used in this known process contains sodium
30 monocarbonate.

It has now been found that it is
possible to optimize the efficiency of the known process
which has just been described by selecting sodium
bicarbonate of well-defined quality.

35 The invention consequently relates to a
pulverulent, solid, reactive composition for the purifi-
cation of a gas containing hydrogen chloride, the said

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reactive composition including more than 98 % by weight of sodium bicarbonate and less than 2 % by weight of sodium monocarbonate and exhibiting a particle size distribution defined by a mean particle diameter smaller than 0.050 mm and a particle size slope lower than 5.

In the reactive composition according to the invention the sodium bicarbonate and the sodium monocarbonate are considered in the anhydrous state.

According to the invention the reactive composition includes more than 98 % (preferably at least 99 %) by weight of sodium bicarbonate and less than 2 % (preferably at most 1 %) by weight of sodium monocarbonate. It may possibly include other impurities usually accompanying commercial sodium bicarbonate, especially sodium chloride.

The reactive composition according to the invention is a pulverulent solid. An important characteristic of the reactive composition according to the invention lies in its particle size distribution, which is characterized by a mean particle diameter D_n smaller than 0.050 mm (preferably at most equal to 0.030 mm) and a particle size slope σ lower than 5 (preferably at most equal to 3).

In the reactive composition according to the invention the mean diameter D_n and the particle size slope σ are defined by the following relationships

$$D_n = \frac{\sum n_i \times D_i}{\sum n_i} , \sigma = \frac{D_{90} - D_{10}}{D_{50}}$$

in which n_i denotes the frequency (by weight) of the particles of diameter D_i , and D_{90} (or D_{50} and D_{10}) denotes the diameter at which 90 % (or 50 % and 10 %) of the particles of the reactive composition (expressed by weight) have a diameter smaller than D_{90} (or D_{50} and D_{10}). These particle size diameters are defined by the method of analysis by laser beam scattering employing a Sympatec model Helos 12LA measuring instrument manufactured by Sympatec GmbH.





The reactive composition according to the invention is especially intended for the purification of smokes originating from the furnaces for incinerating household waste. In addition to hydrogen chloride, these
5 smokes generally contain sulphur dioxide. It has been observed that the reactive composition according to the invention produces an effective purification of these smokes, both from hydrogen chloride and from sulphur dioxide.

10 In the reactive composition according to the invention the sodium bicarbonate forms the main active ingredient. The sodium carbonate content and the particle size distribution are, furthermore, two inter-
15 dependent parameters. On the one hand, it has been observed that, everything else being equal, an excessive sodium carbonate content tends to produce an agglomeration of the particles of the reactive
20 composition, reducing the effectiveness of the latter. On the other hand, the particle size distribution of the reactive composition must conform to a compromise, it being known that a fine particle size will promote the reaction with the hydrogen chloride in the gas being
25 treated, whereas a coarse particle size will promote the subsequent separation of the solid products of the reaction. In practice, reactive compositions which are especially recommended are those in the case of which the weight content of sodium bicarbonate is from 99 to 99.9
30 %, the weight content of sodium monocarbonate is from 0.1 to 1 %, the mean particle diameter is from 0.010 to 0.030 mm and the particle size slope is from 1 to 3. The optimum values of the particle size parameters are related to the means employed for separating the solid
35 products of the reaction of the reactive composition with the hydrogen chloride and, where applicable, the sulphur dioxide in the gas being treated. It has been found, in fact, that these reaction products have a particle size distribution that is directly related to that of the reactive composition.

An embodiment of the reactive



composition according to the invention which is especially adapted to the particular case where an electrostatic filter is employed as means for separating the abovementioned reaction products is that in the case of which the mean particle diameter is from 0.020 to 0.030 mm and the particle size slope is from 1.25 to 2.50. A preferred alternative form of this embodiment of the invention is that in which at least 90 % by weight of the particles have a diameter equal to or smaller than 0.055 mm and at most 10 % by weight have a diameter smaller than 0.006 mm.

Another embodiment of the reactive composition according to the invention, which is especially adapted to the particular case where a filter of the type with filter fabrics is employed (for example a bag filter) as a means of mechanical separation of the abovementioned reaction products, is that in the case of which the mean particle diameter is from 0.010 to 0.020 mm and the particle size slope is from 1 to 3. A preferred alternative form of this other embodiment of the invention is that in which at least 90 % by weight of the particles have a diameter equal to or smaller than 0.035 mm and at most 10 % by weight have a diameter smaller than 0.005 mm.

The reactive composition according to the invention is generally obtained by milling a coarse powder of commercial sodium bicarbonate. The composition of the powder and its particle size play a significant part in the quality of the reactive composition according to the invention.

According to a specially recommended embodiment of the reactive composition according to the invention, the latter is obtained by milling a powder which includes more than 98 % (preferably at least 99 %) by weight of sodium bicarbonate and less than 2 % (preferably at most 1 %) by weight of sodium mon carbonate and which exhibits a particle size distribution such that at least 85 % by weight of its particles have a diameter smaller than 0.500 mm and that at most 25 % by



weight of its particles have a diameter smaller than 0.040 mm. In accordance with a preferred alternative form of this embodiment of the invention, the powder used in the milling exhibits a particle size distribution such that, per 100 weight units of its particles, 85 units have a diameter smaller than 0.250 mm, from 50 to 70 units have a diameter smaller than 0.125 mm, from 30 to 50 units have a diameter smaller than 0.090 mm and fewer than 25 units have a diameter smaller than 0.045 mm.

In the specially recommended embodiment which has just been described the milling conditions form an important parameter. In particular, it is important to control the milling in order to avoid an untimely or excessive thermal decomposition of the sodium bicarbonate in the powder under the effect of the heat released by the milling. The optimum milling parameters are directly related to other parameters such as the mill employed, the particle size of the powder subjected to the milling and its sodium bicarbonate and monocarbonate contents, the particle size distribution sought for the reactive composition according to the invention and its sodium bicarbonate and monocarbonate contents. In practice the optimum milling parameters can be easily determined in each particular case by routine laboratory work.

Everything else being equal, the reactive composition according to the invention exhibits an optimum effectiveness as reactant for the purification of a smoke from hydrogen chloride and, where appropriate, from sulphur dioxide. This effectiveness manifests itself in relation to the excess of reactive composition needed to decompose a defined fraction of the hydrogen chloride and sulphur dioxide in the gas, when compared with the stoichiometric quantity.

The reactive composition according to the invention finds an advantageous application for the purification of the residual smokes from the incineration of household waste.

The invention consequently also relates to a process for the purification of a smoke containing



hydrogen chloride, according to which a reactive composition in accordance with the invention, containing sodium bicarbonate, is introduced into the smoke at a temperature of 125 to 600°C and the smoke is next subjected to a dust removal operation.

In the process according to the invention the reactive composition is introduced in the solid state into the smoke. In general, the reactive composition is introduced into a stream of the smoke travelling inside a reaction chamber. In the latter the sodium bicarbonate decomposes the hydrogen chloride in the smoke, forming sodium chloride. The function of the removal of dust from the smoke is to extract from it the sodium chloride particles which are formed. This may be carried out by any appropriate known means, for example by mechanical separation in a cyclone, by filtration through a filter tissue or by electrostatic separation. In the implementation of the process according to the invention the sodium bicarbonate must be allowed a sufficient time for reacting with the hydrogen chloride in the smoke before the latter is subjected to dust removal. In practice it has been found advantageous for the dust removal to be performed more than 2 seconds (preferably within a period of 2.5 to 6 seconds) after the end of the introduction of the reactive composition into the smoke.

The process according to the invention finds an especially advantageous application for the purification of a smoke originating from the incineration of household waste. In this particular application of the process according to the invention the solid product collected from the dust removal operation generally includes, in addition to the sodium chloride, sodium sulphate, polyvalent metals in the metallic or combined state and sodium carbonate. This solid product may be treated in the way set out in the international patent application WO 93/04983 [[[sic] Solvay (Société Anonyme)]].

Special features and details of the



invention will emerge from the following description of the attached drawings.

Figure 1 shows diagrammatically a plant for the incineration of household waste making use of the process according to the invention;

Figures 2 and 3 are two diagrams reproducing the cumulative particle size distributions of two particular embodiments of the reactive composition according to the invention.

The incineration plant shown in Figure 1 includes an incineration furnace 1 (shown partially), a recovery boiler 2, a vertical tubular reaction chamber 3, a dust-removal device 4 and a stack 5. The dust-removal device 4 includes a cyclone 6 followed by a battery 7 of electrostatic filters. In an alternative form the plant may include a filter with filter fabrics, for example a bag filter, as a replacement for or downstream of the battery of electrostatic filters 7.

The reaction chamber 2 is equipped with an injector 8 connected to a device 14 for feeding a reactive composition.

When the plant in Figure 1 is being used, the incineration furnace 1 generates a smoke laden with hydrogen chloride, sulphur dioxide and various gaseous and solid impurities, including heavy metals. This smoke leaves the furnace 1, passes through the boiler 2 in which a proportion of its sensible heat is recovered, and then emerges, via a flue 9, into the lower part of the reaction chamber 3, below the injector 8. The injector 8 is, furthermore, fed with a pulverulent reactive composition in accordance with the invention, originating from the feeding device 14, the operation of which will be explained below. Thus, in the chamber 3 the smoke is treated with the reactive composition originating from the injector 8, the result of which is to decompose the hydrogen chloride and the sulphur dioxide in the smoke, with formation of sodium chloride and sodium sulphate particles. As it leaves the reaction chamber 3 the smoke passes through the dust-removal

device 4, where the solid matter which it contains, in particular the heavy metals and the sodium chloride and sulphate which are formed in the reaction chamber 3, are separated off. The purified smoke is next transferred as it is to the stack 5.

The reactive composition employed for feeding the injector 8 originates from the feeding device 14. The latter includes a silo 10 containing a commercial sodium bicarbonate powder and a mill 11 fed from the silo 10 by means of a vibrating dispenser 12. The mill 11 is of the attrition type, in which the energy of attrition is imparted to the material to be milled by a stream of air (Kirk Othmer, Encyclopedia of Chemical Technology, Volume 21, 1983, page 157). The mill incorporates a screening device. It is connected to the injector 8 by a conduit 13.

The following examples are used to illustrate the invention.

Example 1.

Domestic waste was incinerated in an industrial plant of the type described above with reference to Figure 1. As it left the incineration furnace the smoke had the following characteristics:

25

Weight composition (mg/Sm ³)	
HCl	: 1300
SO ₂	: 200
Temperature : 250°C	
Flow rate : 3500 Sm ³ /h	

A commercial sodium bicarbonate powder exhibiting the following characteristics was also used:

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Weight composition :	
NaHCO ₃ : > 99 %	
Na ₂ CO ₃ : < 1 %	
Particle size distribution :	
Diameter (mm)	Weight fraction (%)
< 0.250	> 85
< 0.125	50 - 70
< 0.088	30 - 50
< 0.044	< 25

5
10
15 This commercial sodium bicarbonate powder was milled in an RTM 300-S attrition mill manufactured by STM s.n.c.. The operation of the mill was controlled so as to obtain a reactive composition exhibiting the particle size distribution shown in Figure 2 and the following weight composition:

NaHCO₃ : > 99 %
Na₂CO₃ : < 1 %

20 Figure 2 reproduces the cumulative particle size distribution of the reactive composition collected from the mill. In this figure the abscissa scale represents the diameter of the particles, expressed in microns, and the ordinate scale represents the cumulative weight fraction, expressed in % undersize.

25 The reactive composition collected from the milling was immediately injected as it was into the smoke, with a flow rate corresponding appreciably to 1.6 moles of NaHCO₃ per mole of (HCl+SO₂) in the smoke. The treated smoke was next freed from dust on an electrostatic filter.

30 The composition of the smoke after the purification and dust removal treatment was analysed:
HCl : 200 mg/Sm³
SO₂ : 10 mg/Sm³
Example 2.

35 The test of Example 1 was repeated with a smoke exhibiting the following characteristics on leaving the incineration furnace :

Weight composition (mg/Sm ³) :
HCl : 647
SO ₂ : 100
Temperature : 167°C
Flow rate : 36000 Sm ³ /h

5

The same commercial sodium bicarbonate powder as in Example 1 was employed. However, the powder milling conditions were modified so as to obtain a reactive composition exhibiting the cumulative particle size distribution shown in Figure 3 (the abscissa and ordinate scales are identical with those in Figure 2) and the following weight composition :

10

NaHCO₃ : > 99 %
Na₂CO₃ : < 1 %

15

The reactive composition collected from the milling was immediately injected as it was into the smoke, at a flow rate corresponding appreciably to 1.2 moles of NaHCO₃ per mole of HCl+SO₂ in the smoke. The treated smoke was next freed from dust on a filter with filter tissues.

20

The composition of the smoke after the purification and dust removal treatment was analysed :

HCl : 5 mg/Sm³
SO₂ : < 10 mg/Sm³

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CLAIMS

1. Pulverulent, solid, reactive composition for the purification of a gas containing hydrogen chloride, the said reactive composition including more than 98 % by weight of sodium bicarbonate and less than 2 % by weight of sodium monocarbonate and exhibiting a particle size distribution defined by a mean particle diameter smaller than 0.050 mm and a particle size slope lower than 5.
2. Reactive composition according to Claim 1, characterized in that the weight content of sodium bicarbonate is at least 99 %, the weight content of sodium monocarbonate is at most 1 %, the mean particle diameter is at most equal to 0.030 mm and the particle size slope is at most equal to 3.
3. Reactive composition according to Claim 2, characterized in that the weight content of sodium bicarbonate is from 99 to 99.9 %, the weight content of sodium monocarbonate is from 0.1 to 1 %, the mean particle diameter is from 0.010 to 0.030 mm and the particle size slope is from 1 to 3.
4. Reactive composition according to Claim 3, characterized in that the mean particle diameter is from 0.020 to 0.030 mm and the particle size slope is from 1.25 to 2.50.
5. Reactive composition according to Claim 4, characterized in that it consists of particles of which at least 90 % by weight have a diameter equal to or smaller than 0.055 mm and of which at most 10 % by weight have a diameter smaller than 0.006 mm.
6. Reactive composition according to Claim 4 or 5, exhibiting the cumulative particle size distribution shown in Figure 2.
7. Reactive composition according to Claim 3, characterized in that the mean particle diameter is from 0.010 to 0.020 mm and the particle size slope is from 1 to 3.
8. Reactive composition according to Claim 7, characterized in that it consists of particles of





which at least 90 % by weight have a diameter equal to or smaller than 0.035 mm and of which at most 10 % by weight have a diameter smaller than 0.005 mm.

9. Reactive composition according to Claim
5 7 or 8, exhibiting the particle size distribution shown in Figure 3.

10. Reactive composition according to any
one of Claims 1 to 9, which are obtained by milling a
powder which includes more than 98 % by weight of sodium
10 bicarbonate and less than 2 % by weight of sodium
monocarbonate and which exhibits a particle size
distribution such that at least 85 % by weight of its
particles have a diameter smaller than 0.500 mm and that
at most 25 % by weight of its particles have a diameter
15 smaller than 0.040 mm.

11. Reactive composition according to Claim
10, characterized in that the powder exhibits a particle
size distribution such that, per 100 weight units of par-
ticles, 85 units have a diameter smaller than 0.250 mm,
20 from 50 to 70 units have a diameter smaller than
0.125 mm, from 30 to 50 units have a diameter smaller
than 0.090 mm and fewer than 25 units have a diameter
smaller than 0.045 mm.

12. Reactive composition according to Claim
25 10 or 11, characterized in that the powder includes at
least 99 % by weight of sodium bicarbonate and at most 1
% by weight of sodium monocarbonate.

13. Reactive composition according to any
one of Claims 1 to 12, for the purification of a residual
30 smoke from the incineration of household waste.

14. Process for the purification of a smoke
containing hydrogen chloride, according to which a
reactive composition in accordance with any one of Claims
1 to 13 is introduced into the smoke at a temperature of
35 125 to 600°C and the smoke is next subjected to a dust
removal.

15. Process according to Claim 14,
characterized in that the dust removal includes an
electrostatic separation and in that the reactive



composition which is introduced into the smoke conforms to any one of Claims 4 to 6.

16. Process according to Claim 13, characterized in that the dust removal includes a filtration through a filter tissue and in that the reactive composition which is introduced into the smoke conforms to any one of Claims 7 to 9.

17. Process according to any one of Claims 14 to 16, characterized in that the dust removal from the smoke is performed more than 2 seconds after the end of the introduction of the reactive composition into the smoke.

18. Process according to Claim 17, characterized in that the time which elapses between the end of the introduction of the reactive composition into the smoke and the dust removal operation is from 2.5 to 6 seconds.

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