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(57) **Abrégé/Abstract:**

Shaped absorbent units suitable for use as chloride absorbents comprising a calcined intimate mixture of an alkali or alkaline earth, zinc and aluminium components having an alkali or alkaline earth metal to zinc atomic ratio in the range 0.5× to 2.5× and an alkali or alkaline earth metal to aluminium atomic ratio in the range 0.5× to 1.5×, where x is the valency of the alkali or alkaline earth metal, and containing from 5 to 20 % by weight of a binder. Preferred compositions are made from sodium carbonate or bicarbonate, basic zinc carbonate or zinc oxide and alumina or hydrated alumina.



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(21) International Application Number: PCT/GB99/00365 (22) International Filing Date: 3 February 1999 (03.02.99) (30) Priority Data: 9802439.1 6 February 1998 (06.02.98) GB (71) Applicant (for all designated States except US): IMPERIAL CHEMICAL INDUSTRIES PLC [GB/GB]; Imperial Chem- ical House, Millbank, London SW1P 3JF (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BAILEY, Stephen [GB/GB]; 3 Grange Road, Norton, Cleveland TS20 2NS (GB). WILLIAMS, Brian, Peter [GB/GB]; 31 St. Marys Street, Clitheroe, Lancashire BB7 2HH (GB). GRIZARD, Sebastien [FR/GB]; 52 Essex Close, Redcar, Cleveland TS10 4BZ (GB). DORAN, Mark, Sean [GB/GB]; 17 Allison Street, Guisborough, Cleveland TS14 6NX (GB). WILSON, Robert [GB/GB]; 58 Coleton Gardens, Ingleby Barwick, Stockton on Tees, Cleveland TS17 0YA (GB). (74) Agents: GRATWICK, Christopher et al.; ICI Group Intellectual Property, P.O. Box 11, The Heath, Runcorn, Cheshire WA7 4QE (GB).		(81) Designated States: CA, IN, JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: ABSORBENTS (57) Abstract Shaped absorbent units suitable for use as chloride absorbents comprising a calcined intimate mixture of an alkali or alkaline earth, zinc and aluminium components having an alkali or alkaline earth metal to zinc atomic ratio in the range 0.5x to 2.5x and an alkali or alkaline earth metal to aluminium atomic ratio in the range 0.5x to 1.5x, where x is the valency of the alkali or alkaline earth metal, and containing from 5 to 20 % by weight of a binder. Preferred compositions are made from sodium carbonate or bicarbonate, basic zinc carbonate or zinc oxide and alumina or hydrated alumina.		

Absorbents

This invention relates to absorbents, and to a process for their manufacture, in particular to absorbents suitable for removing halogen-containing contaminants such as hydrogen chloride or chlorine-containing organic compounds from gas streams.

5 Such absorbents are typically employed as a bed through which the gas stream to be treated is continuously passed: the contaminant is absorbed by the absorbent so that the effluent gas has a relatively low contaminant content. After a period of time, the absorbent becomes loaded with absorbed contaminant until the absorbent bed is unable to reduce the contaminant content to an acceptable level: typically it is desired to have an effluent gas containing less than a
10 specified amount, e.g. 0.1 ppm by volume, of contaminant. When the effluent gas contains an unacceptable proportion of contaminant, "break-through" is said to have occurred. It is normally found that, when break-through has occurred, the halide content of the bed is somewhat less than the theoretical maximum: thus while samples taken from bed inlet region may have a halogen content approaching the theoretical maximum, samples taken from the bed outlet region
15 are liable to have a halogen content significantly below the theoretical maximum.

Sodium and zinc compounds are effective absorbents for halogen-containing compounds. It has been proposed in US 3935295 to make absorbents from a composition comprising zinc oxide, a basic calcium compound and a binder. It has also been proposed in WO 95/22403 to make absorbents by granulating a mixture of sodium carbonate, or bicarbonate, alumina
20 trihydrate, and a binder followed by calcination at below 350°C. While such absorbents have a high halogen absorption capacity at low temperatures, e.g. below 150°C, at higher temperatures the absorption capacity decreases as a result of decomposition of the active species in the absorbent. It is thus desirable to produce an absorbent that is effective both at temperatures below 150°C and at higher temperatures, e.g. up to 300°C.

25 We have found that particularly effective absorbents can be made from a combination of alkali metal and zinc compounds.

Accordingly the present invention provides shaped absorbent units comprising a calcined intimate mixture of

- 30 a) an alumina component selected from alumina and/or hydrated alumina,
b) a zinc component and an alkali metal component, said components being oxides, hydroxides, carbonates, bicarbonates and/or basic, and
c) a binder,

the alkali metal to zinc atomic ratio being in the range 0.8 to 2.5 and the alkali metal to aluminium atomic ratio being in the range 0.5 to 1.5, said shaped units containing from 5 to 20% by weight of
35 said binder.

AMENDED SHEET

Preferably the shaped units have an alkali metal content such that, after ignition of a sample of the units at 900°C, the sample has an alkali metal oxide content of at least 10%, particularly at least 15%, and more particularly at least 20%, by weight.

Alkali metal compounds that may be employed include compounds of lithium, sodium, and potassium. Preferred compounds are compounds of sodium. Particularly preferred alkali compounds are carbonates and/or bicarbonates. The zinc component is preferably zinc oxide, carbonate or, particularly, basic carbonate. The alkali metal and zinc components may be present at least partially as a mixed salt, such as sodium zinc carbonate and/or basic sodium zinc carbonate.

10 The shaped absorbent units preferably have an average size in the range 2-10 mm, and preferably at least about 3 mm as a bed of smaller units is liable to present an unacceptable resistance to flow of gas therethrough. Thus an unacceptably high pressure drop is experienced upon passage of the gas through a bed of small units.

The binder may be a suitable hydraulic cement, such as calcium aluminate cement.
15 Alternatively, and preferably, the binder comprises a clay, for example an acicular clay such as attapulgite or sepiolite.

The shaped absorbent units of the present invention may be made by granulating or extruding a mixture of alumina or a hydrated alumina such as alumina trihydrate, alkali metal component, zinc component and the binder, in the requisite proportions, and calcining the resultant mixture. Preferably the units are made from a mixture of hydrated alumina, sodium
20 bicarbonate, zinc oxide or basic zinc carbonate, and a clay binder.

Alternatively there may be used a preformed mixed alkali metal/zinc salt, e.g. sodium zinc carbonate or basic sodium zinc carbonate, e.g. as obtained by precipitation by the dropwise addition of a solution of sodium carbonate with a solution of a zinc compound such as zinc nitrate
25 under controlled conditions of pH in the range 7-8 and temperature of about 80°C, alone, or in admixture with additional zinc and/or sodium carbonates. This mixed alkali metal/zinc salt may be mixed with the alumina or hydrated alumina and binder to form the shaped absorbent units.

Where hydrated alumina is used as the alumina component, the calcination results in a substantial increase in the surface area of the absorbents. For these reasons the calcination is
30 preferably effected at temperatures in the range 200-450°C, particularly above 240°C, and most preferably above 300°C. Preferably the calcination temperature is below 500°C to minimise reaction of the alkali metal compound and the alumina: thus alkali metal aluminates have lower absorption capacity.

The shaped absorbent units preferably have a BET surface area of at least 10 m²/g,
35 particularly above 50 m²/g, and most preferably above 90 m²/g.

By the term granulation we mean mixing the powdered ingredients, including the binder, with a little wetting agent such as water, in an amount that is insufficient to form a slurry, and forming the resultant mixture into aggregates, generally of approximate spherical configuration. Such granulation techniques are well known in the art.

5 As an alternative to granulation, the composition may be formed into extrudates, for example using a pellet mill, for example of the type used for pelleting animal feedstuffs, wherein the mixture to be pelleted is charged to a rotating perforate cylinder through the perforations of which the mixture is forced by a bar or roller within the cylinder. The resulting extruded mixture is cut from the surface of the rotating cylinder by a doctor knife positioned to give pellets of the
10 desired length. It will be appreciated that other extrusion techniques may be employed.

It is preferred to employ alumina trihydrate, rather than alumina, since granulation or extrusion of alumina-containing compositions tends to present difficulties.

In order to make shaped units of adequate strength it is desirable to employ the ingredients in a finely divided form. Typically the ingredients have an average particle size in the range 1-
15 20 μm , preferably in the range 5-10 μm .

During the calcination step, it is believed that there is formed a highly dispersed alkali metal/zinc composite, probably an intimate mixture of alkali metal carbonate and zinc oxide, that is uniformly distributed over the alumina substrate. It appears that while zinc oxide is an effective chloride absorbent, alkali metal carbonates are less effective. For this reason the alkali metal to
20 zinc atomic ratio of the granules should be below 2.5. When employing sodium compounds as the alkali metal component and the absorbent is used for absorption of hydrogen chloride, we have observed that a sodium zinc chloride Na_2ZnCl_4 is formed: this species has been identified by X-ray diffractometry on absorbents that have been used for absorption of hydrogen chloride. It is evident by the dry, free-flowing nature of the fully chlorided shaped absorbent units that the
25 formation of this compound does not give rise to any of the deleterious effects associated with moisture absorption such as caking, pressure drop, and difficulties in discharge of spent absorbent. However, if the alkali metal to zinc ratio of the absorbent is too small, the granules become sticky during use, giving rise to caking of a the bed of absorbent units with the consequence of the bed exhibiting an unacceptable increase in the resistance of gas flow
30 therethrough. For this reason the alkali metal to zinc atomic ratio should be above 0.8. It is preferred that the alkali metal to zinc atomic ratio is in the range from about 0.8 to 2.2.

The absorbent granules of the invention may be used at temperatures ranging from 10 to 300°C and at any convenient pressure, for example atmospheric to 100 bar abs. They are of particular utility as guard beds to absorb chloride ions from gas streams, e.g. to avoid corrosion

problems during subsequent processing of the gas stream and/or to avoid poisoning of downstream catalysts, particularly copper containing catalysts such as low temperature shift catalysts or methanol synthesis catalysts. Thus the granules may be disposed as a bed adjacent the inlet of a bed of low temperature shift or methanol synthesis catalyst. They may also be of utility in removing

5 halogen-containing organic compounds from gas streams.

The invention is illustrated by the following examples.

Examples 1-5

Alumina trihydrate, basic zinc carbonate (hydrozincite - $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), sodium carbonate, and a clay binder, each in finely divided powder form having an average particle size in the range

10 5-10 μm , were dry mixed in the proportions specified in the table below. Part of the mixture (about 3kg) was charged to a Hobart mixer of 15l capacity and stirred therein. Water was slowly added while stirring until the mixture adhered to form small balls or agglomerates. Further amounts of the powder mixture and water were gradually added until all the powder mixture had formed into agglomerates. The agglomerates were then sieved to reject agglomerates having a size below

15 about 2.8mm or above about 4.8mm.

The remaining agglomerates were then calcined in air at 300°C for 2 hrs.

The hydrogen chloride absorption characteristics were assessed by passing hydrogen containing about 1% by volume of hydrogen chloride at atmospheric pressure and ambient temperature (20-25°C) down through a vertical bed of the pellets or granules of height 16cm and

20 height to diameter ratio of 7 at a space velocity of approximately 750h⁻¹. The time taken before the hydrogen chloride content of the exit gas reached 5ppm by volume was determined and is quoted in the following table as the "break-through time to 5ppm HCl". The granules were then carefully discharged from the bed and divided into 6 portions corresponding to 2.5cm bands of the bed depth. Each portion was analysed for the chloride content. The results are shown in the following table:

		Example				
		1	2	3	4	5
composition (parts by weight)	Al(OH) ₃	40	40	40	40	40
	Na ₂ CO ₃	20	25	30	35	40
	Zn ₃ (CO ₃) ₂ (OH) ₆	40	35	30	25	20
	binder	7	7	7	7	7
	Na/Zn atomic ratio	1.0	1.5	2.1	2.9	4.1
	Na/Al atomic ratio	0.7	0.9	1.1	1.3	1.5
Break-through time (hh:mm) to 5ppm HCl		13:00	11:00	13:30	6:15	<3:00
Chlorine content (% by weight of discharged absorbent)	Bed portion 1 (top)	21.8	19.2	21.7	11.4	5.3
	Bed portion 2	22.5	19.6	20.2	11.3	5.1
	Bed portion 3	nm	nm	19.1	nm	nm
	Bed portion 4	nm	nm	19.6	nm	nm
	Bed portion 5	nm	nm	18.2	nm	nm
	Bed portion 6 (bottom)	nm	nm	4.3	nm	nm

nm = not measured

It is seen that the absorption capacity deteriorates if the sodium to zinc ratio is too high.

Example 6

Example 3 was repeated but using different calcination temperatures. The BET surface area of the absorbent units was determined and was as set out in the following table.

Calcination temperature (°C)	BET surface area (m ² /g)
none	12
200	17
250	57
300	103
350	99
400	95

Example 7

Extrudates were made using the ingredients as employed for Example 3 by dry-mixing the powdered ingredients in a Kenwood mixer. The total weight of the dry ingredients used was 1000g. 200ml of distilled water was added and mixed in small aliquots to form a homogeneous mixture. The resulting paste was then extruded in a small pellet mill to give extrudates of 3.2mm diameter and about 6 mm long. The wet extrudates were calcined at 300°C for 2 hours. The procedure was repeated using 250ml of water giving a greater yield of extrudates of the requisite size. The procedure was also repeated using 2000g of the dry mixture and 550ml of water and using a pellet mill giving extrudates of 2mm diameter and length about 5mm. The yield of pellets of the requisite size and their properties are shown in the following table.

Feed weight (g)	Water (ml)	Weight of calcined product (g)	Bulk density (g/l)	BET surface area (m ² /g)
1000	200	371	-	89
1000	250	439	800	-
2000	550	1540	760	74

(The bulk density is the density of a bed of the extrudates).

The chloride contents of the extrudates when tested by the procedure employed in examples 1-5 were in the range 12.7-14.7% by weight.

Example 8

The material of Example 3 (hereinafter absorbent A) was tested as above but using a hydrogen chloride concentration of 0.1% by volume instead of 1%. The chlorine contents of the discharged portions of the bed were as follows:

	Chlorine content (% by weight of discharged absorbent)
Bed portion 1 (top)	20.9
Bed portion 2	20.4
Bed portion 3	20.1
Bed portion 4	20.6
Bed portion 5	20.2
Bed portion 6 (bottom)	8.5

Example 9

Absorbent A was tested as above using a hydrogen chloride concentration of 1% by volume but at differing temperatures. Since the space velocity (at NTP) was kept constant at 750h^{-1} , the contact time of the gas with the bed of absorbent units decreases as the temperature increases.

- 5 The approximate contact time and chlorine content of the top bed was as follows:

Test temperature (°C)	Approximate contact time (sec)	Chlorine content (% by weight of discharged absorbent)
25	4.8	20.0
50	4.3	19.7
100	3.8	19.0
200	3.0	16.1
300	2.5	11.9

Example 10

- A number of absorbents were tested for hydrogen chloride absorption using 500ml of the absorbent units disposed as a bed of height 45cm and diameter 4cm using a gas mixture of 80% by volume hydrogen and 20% natural gas containing 50ppm by volume of hydrogen chloride at a space velocity of 1756h^{-1} at a temperature of 35°C and a pressure of 20 barg. The absorbents used were as follows:

Absorbent A: (as described above)

- 15 Absorbent B: Granules of particle size within the range 3 to 5mm having a bulk density of about 0.9g/ml and a BET surface area of about $16\text{m}^2/\text{g}$ made by the procedure of Example 1 of WO 95/22403 using 50 parts by weight of sodium bicarbonate, 50 parts by weight of alumina trihydrate, and 10 parts by weight of attapulgite clay with the drying and calcining being effected in a single stage in a rotary drier at 145°C . Analysis of a sample of the granules that had been ignited at 900°C showed a sodium oxide, Na_2O , content of about 30% by weight.

- 20 Absorbent C: Commercially available alumina granules of about 3mm size impregnated with sodium carbonate and calcined at above 500°C to give granules of bulk density about 0.75g/ml and a BET surface area of about $113\text{m}^2/\text{g}$ which, after ignition at 900°C , had a sodium oxide, Na_2O , content of about 14% by weight.

- 25 Absorbent D: Commercially available activated alumina granules of about 3mm size having a bulk density of 0.83g/ml and a BET surface area of about $300\text{m}^2/\text{g}$.

The results are shown in the following table

Absorbent	Chlorine content of discharged absorbent (% by weight)					
	Bed 1	Bed 2	Bed 3	Bed 4	Bed 5	Bed 6
A	28.0	27.9	26.6	23.4	18.8	7.6
B	21.3	19.9	19.7	18.2	14.8	6.6
C	14.2	12.8	12.5	12.4	10.8	6.8
D	8.8	7.5	6.7	5.5	5.5	4.4

Example 11

30 parts by weight of alumina trihydrate, 35 parts by weight of sodium bicarbonate, 35 parts by weight of zinc oxide and 7 parts by weight of a clay binder, each in finely divided powder form having an average particle size in the range 5-10 μ m, were dry mixed, granulated, dried and calcined, by the procedure described in Examples 1-5. The sodium to zinc atomic ratio was about 1.0 and the sodium to aluminium atomic ratio was about 1.1. The BET surface area of the absorbent granules was 95m²/g. The resulting agglomerates were then tested for hydrogen chloride absorption by the procedure described in Examples 1-5. The break-through time was 14:55 (hh:mm) and the chloride content of the top portion of the absorbent bed was 32.3% by weight.

When a calcium aluminate cement was used in place of the clay as the binder, lower chloride absorption was achieved.

Granules made by a similar procedure but with sodium to zinc ratios below 0.8 became sticky and formed into a solid lump during the chloride absorbency test.

Example 12

The procedure of Example 11 was repeated using basic zinc carbonate in place of zinc oxide and 10 parts of the clay binder. The resultant absorbent was designated Absorbent E and had a sodium to zinc atomic ratio of 1.3 and a sodium to aluminium atomic ratio of 1.1. Absorbents E, B and C were tested for their ability to absorb chlorine-containing organic compounds by passing hydrogen containing about 1% by volume of 1,2 dichloropropane at atmospheric pressure and ambient temperature (20-25°C) down through a vertical bed of the absorbent of height 16cm and height to diameter ratio of 7 at a space velocity of approximately 750h⁻¹. The bed inlet and outlet 1,2 dichloropropane concentrations were monitored over a period of time and the ratio of the outlet to inlet concentrations used to give an indication of the performance of the absorbent. The results are shown in the following table.

Time (min)	1,2 dichloropropane concentration: outlet/inlet (%)		
	Absorbent B	Absorbent C	Absorbent E
0	0	0	0
30	50	5	2
60	71	42	3
90	92	76	5
120	100	93	11
150		100	86
180			93
210			100

It is seen that the absorbent in accordance with the invention, viz. absorbent E, was far more effective in absorbing 1,2-dichloropropane than the prior art absorbents.

When tested for hydrogen chloride absorption capacity by the procedure employed in Examples 1-5, the absorbent E gave a performance very similar to the absorbent of Example 11; the chloride content of the top portion of the absorbent bed at hydrogen chloride breakthrough was 32.5% by weight.

Claims.

1. Shaped absorbent units comprising a calcined intimate mixture of
 - a) an alumina component selected from alumina and/or hydrated alumina,
 - b) a zinc component and an alkali metal component, said components being oxides, hydroxides, carbonates, bicarbonates, and/or basic carbonates, and
 - c) a binder,the alkali metal to zinc atomic ratio being in the range 0.8 to 2.5 and the alkali metal to aluminium atomic ratio being in the range 0.5 to 1.5, said shaped units containing from 5 to 20% by weight of said binder.
2. Shaped absorbent units according to claim 1 having an alkali metal content such that, after ignition of a sample of the shaped units at 900°C, the sample has a alkali metal oxide content of at least 10% by weight.
3. Shaped absorbent units according to claim 1 or claim 2 having a BET surface area above 50 m²/g.
4. Shaped absorbent units according to any one of claims 1 to 3 wherein the alkali metal to zinc atomic ratio is in the range from about 0.8 to 2.2.
5. A process for the manufacture of shaped absorbent units according to any one of claims 1 to 4 comprising forming granules or extrudates from a mixture of (i) alumina trihydrate, (ii) an alkali metal carbonate or bicarbonate, (iii) basic zinc carbonate or zinc oxide, and (iv) a binder in such proportions that the alkali metal to zinc atomic ratio is in the range 0.8 to 2.5, the alkali metal to aluminium atomic ratio is in the range 0.5 to 1.5, and the binder forms from 5 to 20% by weight of the granules or extrudates, and then calcining the granules or extrudates at a temperature in the range 200 to 450°C.
6. A process for the removal of halogen-containing contaminants from a gas stream, comprising passing the gas stream through a bed of shaped absorbent units according to any one of claims 1 to 4 or made according to a process according to claim 5.