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Canadian Intellectual Property Office

CA 2991680 C 2023/09/26

(11)(21) 2 991 680

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(86) Date de dépôt PCT/PCT Filing Date: 2016/07/12
(87) Date publication PCT/PCT Publication Date: 2017/02/09
(45) Date de délivrance/Issue Date: 2023/09/26
(85) Entrée phase nationale/National Entry: 2018/01/08
(86) N° demande PCT/PCT Application No.: GB 2016/052099
(87) N° publication PCT/PCT Publication No.: 2017/021684
(30) Priorité/Priority: 2015/08/05 (GB1513836.5)

(51) Cl.Int./Int.Cl. *B01J 20/08* (2006.01),
B01D 15/00 (2006.01), *B01D 53/68* (2006.01),
B01J 20/02 (2006.01), *B01J 20/04* (2006.01),
B01J 20/28 (2006.01), *B01J 20/30* (2006.01)

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(54) Titre : COMPOSITION ABSORBANT DES PRODUITS CHIMIQUES
(54) Title: CHEMICAL ABSORBENT COMPOSITION

(57) Abrégé/Abstract:
A particulate composition said composition comprises a metal carbonate and/or a metal bicarbonate and a compound of aluminium, characterised in that the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 3: 1. The composition is useful for removing halogenated compounds from a hydrocarbon-containing process stream.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 February 2017 (09.02.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/021684 A1

(51) International Patent Classification:
B01J 20/04 (2006.01) ***B01J 20/30*** (2006.01)
B01D 15/00 (2006.01) ***B01D 53/68*** (2006.01)
B01J 20/08 (2006.01) ***B01J 20/02*** (2006.01)
B01J 20/28 (2006.01)

(21) International Application Number:
PCT/GB2016/052099

(22) International Filing Date:
12 July 2016 (12.07.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
1513836.5 5 August 2015 (05.08.2015) GB

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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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

— *of inventorship (Rule 4.17(iv))*

Published:

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

WO 2017/021684 A1

(54) Title: CHEMICAL ABSORBENT COMPOSITION

(57) Abstract: A particulate composition said composition comprises a metal carbonate and/or a metal bicarbonate and a compound of aluminium, characterised in that the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 3: 1. The composition is useful for removing halogenated compounds from a hydrocarbon-containing process stream.

Chemical Absorbent Composition

The present invention concerns absorbent compositions which may be useful for removing halide species from hydrocarbon process streams.

Absorbents for use as halide guards have been widely used for many years. US 5,897,845 describes absorbent granules comprising an intimate mixture of particles of alumina trihydrate, 0.5 to 2 parts by weight of particles of a sodium component selected from the group consisting of sodium carbonate, sodium bicarbonate and mixtures thereof per part by weight of said alumina trihydrate and from 5 to 20% by weight of a binder, said alumina trihydrate, sodium component and binder being present in such proportions that, after ignition of a sample of the granules at 900 °C, the sample has a sodium oxide, Na_2O, content of at least 20% by weight. Processes for manufacturing and using such absorbent granules are also described. WO2007061607 describes a composite sorbent which is the reaction product of a solid alkali metal carbonate, rehydratable alumina and water or an aqueous solution of a metal salt. The reaction between the components occurs while forming particulates followed by curing and activation at high temperatures. The composite sorbent comprises 10 – 25 mass% of Na_2O. There is a need for improved absorbent compositions which exhibit high capacity for chloride absorption and stability in use.

According to the invention we provide a particulate composition for use in removing halogenated compounds from a hydrocarbon-containing process stream, said composition comprising a metal carbonate and/or a metal bicarbonate and a compound of aluminium, characterised in that the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 3 : 1.

The weight ratio of metal carbonate plus metal bicarbonate compounds to the compound of aluminium may be at least 4 : 1. The metal carbonate and/or bicarbonate compounds are present and calculated as solid compounds. The ratio of metal carbonate/ bicarbonates to aluminium compounds is particularly high compared with the prior art absorbents and is very effective in providing a high capacity for chloride. It is surprising that the relative proportion of carbonate and bicarbonate may be so high, since it would be expected that the strength of the material would prove to be too low for practical uses. We have found that the compositions provide absorbent particles which are at least as strong and resistant to attrition as some prior commercial absorbents.

By “metal carbonate” we mean a metal compound in which the anion is a carbonate (CO_3) anion. By “metal bicarbonate” we mean a metal compound in which the anion is a hydrogen carbonate (HCO_3) anion. The metal carbonate may be an alkali metal carbonate or an alkaline earth metal carbonate, in particular potassium carbonate, calcium carbonate or sodium carbonate (Na_2CO_3), including hydrated forms such as sodium carbonate

decahydrate, heptahydrate and monohydrate. Highly hydrated sodium carbonate tends to have a significantly lower melting point than monohydrate or anhydrous sodium carbonate and therefore these less hydrated forms may be preferred because they are easier to handle. The metal bicarbonate may be an alkali metal bicarbonate or an alkaline earth metal bicarbonate, in particular potassium bicarbonate or sodium bicarbonate ($NaHCO_3$). The composition may contain a mixture of a metal bicarbonate and a metal carbonate. When the composition comprises both sodium carbonate and sodium bicarbonate, the sodium compounds may be present in the form of sodium sesquicarbonate, which is a natural material containing approximately equal amounts of carbonate and bicarbonate. Other forms of carbonate and bicarbonate materials may be used, including other naturally occurring materials and hydroxycarbonate materials. The amount of metal carbonate in the total amount of metal carbonate plus metal bicarbonate may be 0 – 75% by weight. In certain embodiments of the invention, the amount of metal carbonate in the total amount of metal carbonate plus metal bicarbonate may be 30 – 60% by weight. The composition, after ignition of a sample at 900 °C, may have a sodium oxide, Na_2O, content of at least 20% by weight, and may be at least 25% by weight, especially at least 30% by weight.

The compound of aluminium is preferably an oxide or hydroxide of aluminium, such as an alumina, including a transition alumina, or a hydrated alumina. The compound of aluminium may be hydrated alumina, for example alumina trihydrate ($Al(OH)_3$) or $Al_2O_3 \cdot 3H_2O$ or aluminium oxide-hydroxide ($AlO(OH)$) or $Al_2O_3 \cdot H_2O$. Hydrated alumina is available in different forms, for example boehmite, Gibbsite, hydrargillite, bayerite, and known by different nomenclatures such as γ-$AlO(OH)$, α-$Al(OH)_3$, β-$Al(OH)_3$ and γ-$Al(OH)_3$. Optionally a transition form of alumina may be present. Transition aluminas are formed by the partial dehydration of alumina trihydrate or boehmite; different transition aluminas being formed at different stages of dehydration.

The composition may further comprise a binder. Suitable binders include clay materials, for example sepiolite or attapulgite, and cements such as calcium aluminate cement. The amount of binder in the composition, if present, may be such as to give a weight ratio of aluminium compound to binder of 0.5 – 2 : 1.

As an example of the composition of the invention, we have found that a composition comprising about 75%wt sodium bicarbonate, 12.5%wt alumina trihydrate and 12.5%wt of attapulgite clay provides a high capacity for chloride removal. Such a composition has a sodium oxide content of at least 45%wt by weight after ignition of a sample at 900 °C.

As a further example of the composition of the invention, we have found that a composition comprising about 50%wt sodium bicarbonate, about 25%wt sodium carbonate, about 16.7%wt alumina trihydrate and about 8.3%wt of attapulgite clay provides a high capacity for chloride removal.

The absorbent composition preferably has a surface area, as measured by B.E.T. methods, of at least 5 m^2g^{-1}, more preferably at least 10 m^2g^{-1}.

The composition is preferably provided in the form of particles having an average size (diameter or equivalent dimension) of at least 0.2mm, preferably 0.8mm, more preferably at least 1mm. The particle size range is preferably 0.2mm to 10mm, more preferably 2 to 5mm. The particles typically have a minimum dimension which is < 10mm, particularly < 5mm. The particle size may be determined using conventional methods. The particles may be in the form of granules, agglomerates, spheres, cylinders, rings, saddles or another shape. The particles may be formed by granulation, tabletting or extrusion. When we refer to a particulate absorbent composition, we mean that the particles of absorbent include all of the ingredients of the composition, and not that particles of each of the ingredients is used separately.

In one embodiment, the ingredients of the composition, i.e. the solid metal carbonate and/or metal bicarbonate compounds, the compound of aluminium and the binder, if present, are mixed together in the presence of a liquid such as water to form granules. The granules are then dried at a temperature which is less than 120 °C, usually in the range 25 - 90 °C, especially 30 – 65 °C. The dried granules may be classified, e.g. by sieving, to remove fines and over-sized particles. The dried particles may be subjected to a heat treatment, or calcination. Such calcination may decompose the metal carbonate or metal bicarbonate to form the oxide. If this step is carried out, the calcination temperature is usually less than 600 °C, for example 300 – 550 °C.

The absorbent composition is useful for removing halogenated compounds from a hydrocarbon-containing process stream. The halogenated compounds may be organic halides such as alkyl-halides (RCl, where R is a hydrocarbon), or inorganic halides such as hydrogen chloride, HCl. In particular the absorbent may be used for the removal or organic chlorides and/or HCl. The removal of organic halides and/or inorganic halides from hydrocarbons is practiced in particular in petroleum refineries. Therefore a preferred hydrocarbon stream is a refinery process stream. The hydrocarbon stream may be in the liquid or the gas phase.

The invention will be further described in the following examples.

Example 1

Granules of a composition according to the invention were prepared by mixing powders of sodium bicarbonate, alumina trihydrate (gibbsite) and a binder (attapulgite clay) in the weight ratio 6:1:1. The powders were formed into granules using a planetary (Hobart) mixer by adding water. The resulting granular material was dried in air in an oven at 25°C (or at 90°C – see Table 1). The granules were then sieved to a size fraction of 2 - 4.8 mm and tested for chloride capacity as described in Example 4 below.

Example 2

Granules of a composition according to the invention were prepared by mixing powders of sodium bicarbonate, sodium carbonate, alumina trihydrate (gibbsite) and a binder (attapulgite clay) in the weight ratio 6:3:2:1. The powders were formed into granules using a planetary (Hobart) mixer by adding water. The resulting granular material was dried in air in an oven at 30°C (or at 90°C – see Table 1). The granules were then sieved to a size fraction of 2.8 - 4.8 mm and tested for chloride capacity as described in Example 4 below.

Example 3 (comparative)

Granules of a composition according to the invention were prepared by mixing powders of sodium bicarbonate, alumina trihydrate and a binder in the ratio 55:45:11. The powders were formed into granules using a Hobart mixer and adding water. The resulting granular material was dried in air in an oven at 25°C (or at 90°C – see Table 1). The granules were then sieved to a size fraction of 2 – 4.8 mm and tested for chloride capacity as described in Example 4 below.

Example 4: Chloride saturation test

10 ml samples of each of the absorbent granules made in Examples 1 and 2 were tested separately for HCl absorption characteristics by passing hydrogen containing 1% HCl by volume at atmospheric pressure and about 20 °C for 22 hours through the sample. The gas flow rate was set to 45 litres/hour, giving a GHSV of 4,500 hr^{-1}. The samples are then ground up and tested for chloride content using a commercially available chloride analyser (Sherwood Scientific Ltd). Prior to analysis the ground samples are reacted in nitric acid/water mixture to prevent the formation of Ag salts which would otherwise interfere with the chloride analysis.

Table 1

Sample	Drying T (°C)	Cl^- (%)
Example 1	25	40.4
Example 1	90	28.3
Example 2	30	39.1
Example 2	90	33.6
Example 3 (comp)	25	26.3
Example 3 (comp)	90	12.7

Claims

1. A particulate composition for use in removing halogenated compounds from a hydrocarbon-containing process stream, said composition comprising

   a metal carbonate which is an alkali metal carbonate or an alkaline earth metal carbonate, a metal bicarbonate which is an alkali metal bicarbonate or an alkaline earth metal bicarbonate, or a combination of the metal carbonate and the metal bicarbonate; and

   a compound of aluminium which is an alumina or a hydrated alumina,

   wherein the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 3 : 1, and wherein the amount of metal carbonate in the total amount of metal carbonate plus metal bicarbonate is 0 – 75% by weight.

2. The particulate composition for the use as claimed in claim 1, wherein the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 4 : 1.

3. The particulate composition for the use as claimed in claim 1 or claim 2, wherein the metal carbonate is potassium carbonate, calcium carbonate or sodium carbonate.

4. The particulate composition for the use as claimed in any one of claims 1 to 3, wherein the metal bicarbonate is potassium bicarbonate or sodium bicarbonate.

5. The particulate composition for the use as claimed in any one of claims 1 to 4, wherein the composition contains a mixture of the metal bicarbonate and the metal carbonate.

6. The particulate composition for the use as claimed in any one of claims 1 to 5, wherein the amount of metal carbonate in the total amount of metal carbonate plus metal bicarbonate is 20 – 60% by weight.

7. The particulate composition for the use as claimed in any one of claims 1 to 6 further comprising a binder.

8. A method of forming the particulate composition as claimed in any one of claims 1 to 6 comprising the steps of mixing together
   a. the metal carbonate and/or the metal bicarbonate compounds,
   b. the compound of aluminium and
   c. optionally a binder,

   in the presence of water and forming the mixture into particles.

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9. The method as claimed in claim 8, further comprising the step of drying the formed particles at less than 120 °C.

10. The method as claimed in claim 9, wherein the drying is carried out a temperature in the range 25 - 90 °C.

11. The method as claimed in any one of claims 8 to 10, wherein the mixture is formed into particles by granulation, tabletting or extrusion.

12. A process for removing halogenated compounds from a hydrocarbon-containing process stream using the particulate composition as claimed in any one of claims 1 to 7 or as prepared by the method of any one of claims 8 to 11.

13. A particulate composition for use in removing halogenated compounds from a hydrocarbon-containing process stream, said composition comprising

a metal carbonate which is an alkali metal carbonate ,a metal bicarbonate which is an alkali metal bicarbonate, or a combination of the metal carbonate and the metal bicarbonate; and

a compound of aluminium which is an alumina or a hydrated alumina,

wherein the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 3 : 1, and wherein the amount of metal carbonate in the total amount of metal carbonate plus metal bicarbonate is 0 – 75% by weight.

14. The particulate composition for the use as claimed in claim 13, wherein the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 4 : 1.

15. The particulate composition for the use as claimed in claim 13 or claim 14, wherein the metal carbonate is potassium carbonate or sodium carbonate.

16. The particulate composition for the use as claimed in any one of claims 13 to 15, wherein the metal bicarbonate is potassium bicarbonate or sodium bicarbonate.

17. The particulate composition for the use as claimed in any one of claims 13 to 16, wherein the composition contains a mixture of the metal bicarbonate and the metal carbonate.

18. The particulate composition for the use as claimed in any one of claims 13 to 17, wherein the amount of metal carbonate in the total amount of metal carbonate plus metal bicarbonate is 20 – 60% by weight.

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19. The particulate composition for the use as claimed in any one of claims 13 to 18 further comprising a binder.

20. A method of forming a particulate composition as claimed in any one of claims 13 to 18, comprising the steps of mixing together
    a. the metal carbonate and/or the metal bicarbonate compounds,
    b. the compound of aluminium and
    c. optionally a binder,

    in the presence of water and forming the mixture into particles.

21. The method as claimed in claim 20, further comprising the step of drying the formed particles at less than 120 °C.

22. The method as claimed in claim 21, wherein the drying is carried out a temperature in the range 25 - 90 °C.

23. The method as claimed in any one of claims 20 to 22, wherein the mixture is formed into particles by granulation, tabletting or extrusion.

24. A process for removing halogenated compounds from a hydrocarbon-containing process stream using the particulate composition as claimed in any one of claims 13 to 19 or prepared by the method of any one of claims 20 to 23.

25. A particulate composition for use in removing halogenated compounds from a hydrocarbon-containing process stream, said composition comprising a metal carbonate which is an alkali metal carbonate and a metal bicarbonate which is an alkali metal bicarbonate and a compound of aluminium which is a hydrated alumina, wherein the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 3 : 1, and wherein the amount of metal carbonate in the total amount of metal carbonate plus metal bicarbonate is 20 – 60% by weight.

26. The particulate composition for the use as claimed in claim 25, wherein the weight ratio of metal carbonate plus metal bicarbonate compounds to said compound of aluminium is at least 4 : 1.

27. The particulate composition for the use as claimed in claim 25 or claim 26, wherein the metal carbonate is potassium carbonate or sodium carbonate.

28. The particulate composition for the use as claimed in any one of claims 25 to 27, wherein the metal bicarbonate is potassium bicarbonate or sodium bicarbonate.

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29. The particulate composition for the use as claimed in any one of claims 25 to 28 further comprising a binder.

30. A method of forming a particulate composition as claimed in any one of claims 25 to 28 comprising the steps of mixing together

    a. the metal carbonate and the metal bicarbonate compounds,
    b. the compound of aluminium and
    c. optionally a binder,

    in the presence of water and forming the mixture into particles.

31. The method as claimed in claim 30, further comprising the step of drying the formed particles at less than 120 °C.

32. The method as claimed in claim 31, wherein the drying is carried out a temperature in the range 25 - 90 °C.

33. The method as claimed in any one of claims 30 to 32, wherein the mixture is formed into particles by granulation, tabletting or extrusion.

34. A process for removing halogenated compounds from a hydrocarbon-containing process stream using a particulate composition as claimed in any one of claims 25 to 29 or prepared by the method of any one of claims 30 to 33.

Date reçue/Date received 2023-05-15