FORM 25 (12) PATENT granted by (19) AP

AFRICAN REGIONAL INDUSTRIAL PROPERTY ORGANISATION (ARIPO) 939

(11) (A)

(21) Application Number: AP/P/98/01203
(22) Filing Date: 19971217
(24) Date of Grant & (45) Publication: 20010212

(30) Priority Data
(33) Country: DE
(31) Number: 196 53 957.9
(32) Date: 19961221

(84) Designated States:
BW GH GM KE LS MW
SD SZ UG ZM ZW

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(51) International Patent Classification (Int.Cl.7): C01C 3/08; C01C 3/10

(54) Title: Process For The Production Of Granulates From An Alkili Metal Or Alkaline Earth Metalcyanide

(57) Abstract:

This invention relates to a process for the production of granulates substantially comprising an alkali metal or alkaline earth metal cyanide from an aqueous solution of the cyanide by fluidised bed spray granulation.

According to the invention, superheated steam is used as the drying gas. Steam is preferably circulated in a closed circuit and only excess steam is discharged and condensed. The process produces little waste gas and results in high quality granulates.

(56) Documents Cited: EP 600282; CHEM. ABSTRA VOL 123, NO. 22

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Process for the production of granulates from an alkali metal or alkaline earth metal cyanide

Description

This invention relates to a process for the production of granulates substantially comprising an alkali metal or alkaline earth metal cyanide, in particular granulates substantially comprising sodium cyanide, potassium cyanide or calcium cyanide, by fluidised bed spray granulation, wherein an aqueous solution or suspension containing an alkali metal or alkaline earth metal cyanide is sprayed onto alkali metal cyanide nuclei located in a fluidised bed and water is vaporised by means of a stream of drying gas flowing through the fluidised bed.

Alkali metal cyanides, in particular sodium and potassium cyanide, are widely used in electroplating baths and as a raw material for the production of organic cyano compounds; sodium or calcium cyanide are used for obtaining gold by cyanide leaching of auriferous ores.

While solid NaCN and KCN have hitherto predominantly been handled as compressed pellets or low-dusting ground granulate, so-called fluidised bed spray granulates are attracting increasing interest. Such generally spherical fluidised bed spray granulates may be produced using the processes described in EP-A 0 600 211 and EP-A 0 600 282. In these processes, an alkali metal cyanide solution, conveniently such a solution having a content of 20 to 45 wt.%, is sprayed in a fluidised bed spray granulation

apparatus onto a fluidised bed of alkali metal cyanide nuclei. The introduced water is vaporised by means of a drying gas, which is simultaneously the fluidising gas. Once formed, the granulate is discharged from the apparatus, conveniently by means of a discharge apparatus having a classifying action. In both the cited processes, heated air is used as the drying gas.

One disadvantage of the process of EP-A 0 600 211 is the fact that it proposes to perform the process in two stages: a fluidised bed drier is required in addition to the fluidised bed spray granulation apparatus. Spray granulation is performed at a fluidised bed temperature of 60 to 90 °C. Further disadvantages include the unavoidable expense, due to the toxicity of alkali metal cyanides, of post-treating all the waste air and the consequential energy losses. As has been established by replication of the process, considerable operational problems occur under the stated operating conditions, and, moreover, the formation of irregularly shaped agglomerates cannot reliably be avoided.

The process according to EP-A 0 600 282, which, unlike the previously mentioned process, gives rise to perfect, spherical NaCN or KCN granulates having little tendency to cake, operates at a fluidised bed temperature of preferably 130 to 300°C, admittedly in two stages, but in this case there is no necessity to detoxify all the waste air.

The object of the present invention is accordingly to provide an improved process for the production of alkali metal and alkaline earth metal granulates by fluidised bed

spray granulation using a solution of the alkali metal or alkaline earth metal cyanide. According to preferred embodiments, it should be possible to operate the process while producing the smallest possible quantities of waste gas and, if possible, with a lower energy consumption than prior art processes. The quality of the granulate, in particular with regard to the range of secondary products, should not be degraded.

This object is achieved by a process for the production of granulates substantially comprising an alkali metal or alkaline earth metal cyanide, in particular NaCN, KCN and $Ca(CN)_2$ granulates, by fluidised bed spray granulation, wherein an aqueous solution or suspension containing an alkali metal or alkaline earth metal cyanide is sprayed in a fluidised bed spray granulation apparatus onto a fluidised bed of alkali metal or alkaline earth metal cyanide nuclei, the water is vaporised by means of a stream of drying gas flowing through the fluidised bed, the inlet temperature of which gas is 150 to 500 °C, at a fluidised bed temperature in the range from 110 to 350 °C and granulate is discharged from the apparatus in a known manner, which process is characterised in that superheated steam is used as the drying gas.

The subordinate claims relate to preferred embodiments of the process according to the invention.

Although a fluidised bed operated with steam was known from other applications, such as coal drying (*c.f. Coal Handling and Utilization Conference*, Sydney, 19.-21.06.1990 pp. 184-188, C.J. Hamilton "*Steam Fluidized Bed Drying of Coal*"),

such a mode of operation had not hitherto been proposed for the production of granulates from alkali metal cyanides or alkaline earth metal cyanides from their solutions. The reason for this was the fear that it could result in increased formation of formate by hydrolysis of the cyanide, which is a notorious problem when crystallising NaCN, for example. Surprisingly, however, it has been found that, in the process according to the invention, the formate content of the alkali metal or alkaline earth metal cyanide granulates does not change during granulation. Since the process according to the invention uses superheated steam instead of air as the drying and fluidising gas, there is no CO_2 problem and thus no problem with an excessively high carbonate content. The composition of the granulates produced according to the invention substantially matches that of the substances dissolved in the solution used.

The superheated steam is preferably introduced into the spray granulator at a temperature in the range from 200 to 450 °C, in particular of 300 to 400 °C. The superheated steam here acts both as the drying gas and the fluidising gas. Superheated steam may additionally be used as a propellant for the solution to be sprayed by means of two-fluid nozzles and also as a classifying gas in a granulator having a granulate discharge with a classifying action.

According to a preferred embodiment, an aqueous alkali metal cyanide solution having a content of preferably 10 to 45 wt.%, in particular of 20 to 45 wt.% and particularly preferably of 40 to 45 wt.%, and superheated steam are

introduced into the granulator in a ratio such that a temperature in the range from 150 to 250 °, in particular from 180 to 220 °C, is maintained in the fluidised bed. The solution to be sprayed may also contain an effective quantity of additives and/or auxiliary substances in order to adjust properties to the intended application.

It has been found that the average granulate size of alkali metal cyanides may be controlled during fluidised bed spray granulation simply by adding an alkali metal hydroxide to the alkali metal cyanide solution to be sprayed in a quantity in the range from approx. 1 to 5 wt.%, in particular from 1.5 to 3 wt.%, relative to the alkali metal cyanide. Granulate size increases as the quantity of alkali metal hydroxide rises. In NaCN granulates having a granulate diameter of 1 to 2 mm, the granulate diameter rises to approx. 3 to 4 mm if the quantity of NaOH in the NaCN solution to be sprayed is raised from 1.5 wt.% to 2.5 wt.%, in each case relative to NaCN. It has furthermore been established that a lower content of alkali metal hydroxide, namely at least some 1 wt.%, relative to alkali metal cyanide, should be present in the alkali metal cyanide solution to be sprayed, in order to prevent discoloration (grey to black) of the granulate.

Reference is made to H. Uhlemann in *Chem.-Ing. Technik* 62 (1990), pp. 822-834 and to EP-A 0 600 282 with regard to the practical implementation of fluidised bed spray granulation. In order to achieve unproblematic formation of the granulate, the fluidised bed temperature, the spraying rate and the mass density of the nuclei in the fluidised bed must be adjusted relative to each other: these

parameters may be determined by optimisation. A stable fluidised bed is achieved if the number of nuclei remains substantially constant. If the number of nuclei is too low, it is increased by introducing finely divided material, such as dust, from a dust separator downstream from the granulator and/or produced within the granulator. Another possible method of control, namely by means of the alkali metal hydroxide content, has already been addressed. The granulator is preferably operated continuously, by granulate being continuously or at least periodically removed from the apparatus, preferably by means of a discharge apparatus with a classifying action integrated into the granulator or downstream therefrom.

According to a preferred embodiment of the process according to the invention, superheated steam is circulated in a closed circuit and substantially only that excess steam formed by vaporisation of the water introduced with the sprayed solution or suspension is discharged from the circuit. The circulated steam, once superheated again, is reintroduced into the spray granulator. The discharged steam may be further treated in the most varied manner, for example by means of a combination comprising a condenser and scrubber or a combination comprising a condenser and vacuum evaporator. In the embodiment with a closed steam circuit and variants thereof, not only is a high quality alkali metal cyanide or alkaline earth metal cyanide granulate obtained, since no formate and carbonate is formed, but the process produces particularly little waste gas and is also particularly favourable with regard to

energy consumption. Investment costs are additionally much lower than when drying air is used.

A particularly convenient embodiment of the above-stated process is illustrated by Figure 1/1, which shows essential components of a plant in diagrammatic form.

Nuclei of the granulate to be produced are introduced via a line (2) in a fluidised bed spray granulator (1). Once the fluidised bed has been generated in the reactor by means of superheated steam introduced beneath the fluidised bed floor (1.1), the alkali metal or alkaline earth metal cyanide solution to be sprayed is introduced via a line (3) into the spray apparatus (1.2), conventionally one- or two-fluid nozzles, arranged within or above the fluidised bed. Superheated steam, introduced via line (4) is preferably used as the propellant for spraying by means of two-fluid nozzles. Once formed, the granulate is discharged via a classifying apparatus (1.3) integrated within the reactor and a discharge line (20). Dust is removed from the steam leaving the granulator (1) in a dust separator (21), conventionally a filter or a cyclone. The steam then passes via a gas circulating blower (8) into a heating coil (6.1) arranged in a combustion chamber (6), wherein it is superheated and then returned to the fluidised bed spray granulator (1). The combustion chamber (6) is supplied via a line (5) with fuel gas and via a line (15) with combustion air, which is preheated by means of an air heater (16); flue gas leaves the combustion chamber via a line (7). In the embodiment illustrated in Figure 1/1, there is another heating coil (6.2) located within the combustion chamber to produce steam from condensate; this

steam is introduced into the classifier (1.3) as classifying gas (alternative to introduction via line (4)). Excess steam, which is drawn off from the closed circuit, is scrubbed and condensed in a combination of a condenser (10) and a scrubbing apparatus (9). The scrubber (9) is supplied with condensate or water via a line (11) and with sodium hydroxide solution via a line (12); sodium hydroxide solution acts as an absorbent for hydrogen cyanide. Scrubbing liquor is circulated via a pump (14) and a heat exchanger (22). The condensate containing cyanide is discharged from the scrubbing circuit via a line (13). Cooling water introduced via a line (18) passes through a cooler (17) and leaves the system through a line (19). A water circuit, which *inter alia* condenses the excess steam, comprises the preheater (16), the cooler (17), the heat exchanger (22) and the condenser (10).

The only waste gas from the process is flue gas, the energy content of which is used in the combustion chamber to superheat the circulating steam. If required, additional steam may be produced and used, for example, to operate a steam-jet blower for a vacuum evaporator. The energy consumption of the process may be further reduced by exploiting the heat of neutralisation from an apparatus, upstream from the spray reactor, for producing the alkali metal or alkaline earth metal cyanide solution from an aqueous solution or suspension of the corresponding hydroxide and gaseous or liquid hydrogen cyanide or a gas containing HCN. Thanks to operation with production of a small quantity of waste gas, the energy consumption and capital investment requirements of the process are

substantially reduced in comparison with prior art processes. The process furthermore does not give rise to an increase in secondary products, but instead results in granulates having excellent material characteristics.

Example

Sodium cyanide granulates are produced in a semi-technical plant according to Figure 1/1.

An NaCN solution having an NaCN content of 430 g/l was used. 7 g of NaOH/l was additionally initially added to this solution. The spraying rate was 120 kg/h.

The granulator was operated with superheated steam: inlet temperature 380 °C, quantity 1000 - 1200 m^3/h.

The steam leaving the granulator was at a temperature of approx. 200 °C; the temperature of the fluidised bed was between 200 and 220 °C (depending upon the position of the thermometer).

Colourless NaCN granulate was obtained, the formate and carbonate content of which were unchanged in comparison with the values of the solution used. Over 90 % of the granulate particles had a diameter of 1 to 2 mm.

By increasing the NaOH content in the NaCN solution to 10 g/l, the diameter of the particles rose to 3 to 4 mm.

New Patent claims

1. Process for the production of granulates substantially comprising an alkali metal or alkaline earth metal cyanide, in particular NaCN, KCN and $Ca(CN)_2$ granulates, by fluidised bed spray granulation, wherein an aqueous solution or suspension containing an alkali metal or alkaline earth metal cyanide is sprayed in a fluidised bed spray granulation apparatus onto a fludised bed of alkali metal or alkaline earth metal cyanide nuclei, the water is vaporised by means of a stream of drying gas flowing through the fluidised bed, the inlet temperature of which gas is 150 to 500 °C, at a fluidised bed temperature in the range from 110 to 350 °C and granulate is discharged from the apparatus in a known manner,
characterised in that,
superheated steam is used as drying gas whereby superheated steam is circulated in a closed circuit and substantially only the excess steam formed from vaporisation is discharged from the circuit.

2. Process according to claim 1,
characterised in that,
superheated steam having a temperture in the range from 200 to 450 °C is used.

3. Process according to claim 1 or 2,
characterised in that,
spray granulation is performed at a fluidised bed temperature in the range from 150 to 250 °C, in particular from 180 to 220 °C.

4. Process according to one of claims 1 to 3, characterised in that, once the steam leaving the fluidised bed has passed through a dust separator, it is divided into two sub-streams, the first sub-stream is passed through a combustion chamber and the resultant superheated steam is reused as a drying gas, and the second sub-stream, substantially corresponding to the quantity of the excess steam, is discharged from the circuit and scrubbed and/or condensed.

5. Process according to one of claims 1 to 4, characterised in that, 1 to 5 wt.%, preferably 1.5 to 3 wt.%, of alkali metal hydroxide, relative to alkali metal cyanide, is added to the alkali metal cyanide solution to be sprayed in order to produce an alkali metal cyanide granulate.

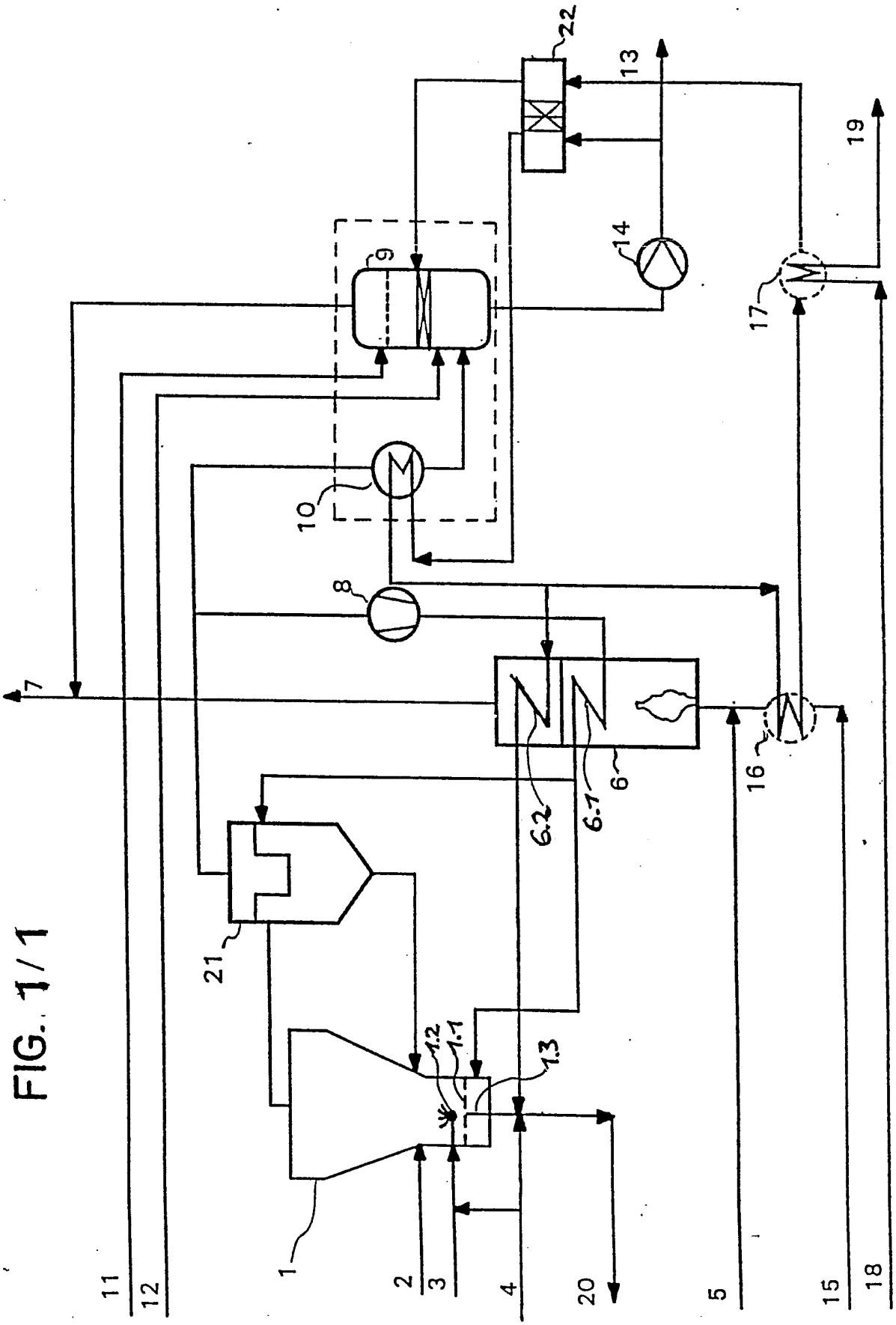

FIG. 1/1

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