

The Title of the invention is:

Alkali metal cyanide granulates and a process for their preparation

REPLACED SPACES		32
☒	Description : page 1 to page 16	16
☒	Claim(s) : page 16 to page 16	16
☐	Drawing(s) : page 1 to page 1	1
☒	Abstract : page 16 to page 16	16
TOTAL OF PAGES		32



Alkali metal cyanide granulates and a process for their preparation

5

Description

The invention relates to new alkali metal cyanide granulates based on sodium cyanide or potassium cyanide, whose
10 particles are essentially spherical and which are characterised by extraordinary properties as compared with previously known granulates, including minimal abrasion and a greatly reduced tendency to cake, and a process for preparing the granulates.

15

The two alkali metal cyanide salts sodium and potassium cyanide are used to prepare electrolytic baths and hardness salt baths as well as for the synthesis of organic compounds. In addition, sodium cyanide is used in large
20 amounts to recover gold by the cyanide leaching of ores.

Due to their toxicity, the alkali metal cyanides mentioned are preferably handled in the compressed form or as low-dust milling granulates. Sodium and potassium cyanide granulates
25 which are produced commercially on a large scale consist of irregularly shaped particles with a particle size spectrum which stretches between, for example, about 0.2 and 4 mm. Compressed products are produced using rotating roller presses or ram presses. The granulates are prepared by
30 crushing the pressed discs using a milling device. The irregular shape of this type of granulate is the reason for undesired dust formation during handling procedures.

Known NaCN and KCN commercially available compressed
35 products, milling granulates and powder have a strong tendency to agglomerate and cake on the internal surfaces of piping, fittings and equipment made of steel or stainless steel. The tendency to agglomerate and cake increases with decreasing particle size and in particular with increasing



humidity and applied load and makes handling procedures, such as storing in silos, weighing out and transporting, difficult and expensive.

- 5 Due to these difficulties, the applicant for the present application looked for a form of supply which did not tend to agglomerate and cake, or at least had a lower tendency to do so. Although NaCN filter cakes which were prepared by known methods could be converted into an approximately
10 spherical granulate and then dried, the resulting NaCN granulate had too low a bulk density, less than 600 g/dm^3 , and the resistance to abrasion was unsatisfactory.

A further disadvantage of the previously known sodium and
15 potassium cyanide granulates was the technically complicated process of preparation, which comprised several steps and which started with aqueous NaCN and KCN solution respectively. In the first step, the alkali metal cyanide is crystallised out of solution, this being performed, for
20 example, in a vacuum crystalliser. The crystallised product is separated from the mother liquor using known techniques. After a single- or multi-stage drying procedure, the alkali metal cyanide powder is compacted to give a compressed product, the latter being crushed to give the granulate
25 mentioned. Therefore the process requires not only a large investment in equipment and service personnel, but the evident tendency of NaCN and KCN to cake forces stoppages and reduces the availability of the whole plant.

- 30 Glatt Ingenieurtechnik GmbH, Weimar, describe a plant for continuous granulation and drying, in their company document Glatt® AGT (Feb. 92 - 3000 D (W)), which is based on the principle of the technique also known as fluidised bed spray granulation (see H. Uhlemann in Chem.-Ing. Technik 62 (1990)
35 no. 10, pp. 822-834) and describe its application to, inter alia, "carbonates and cyanides". However, it is not evident from the company document mentioned whether this refers to



alkali metal, alkaline earth metal or heavy metal cyanides or to complex cyanides. Also, neither data on the properties of the cyanide granulates nor the conditions of production of the same can be gathered from the company document.

5

The object of the invention is thus to provide alkali metal cyanide granulates based on sodium or potassium cyanide which have reduced disadvantages of the commercial granulates described above. A further object is directed at
10 providing a method which allows the new granulates to be produced in a simpler manner, in particular with less complicated apparatus and fewer staff, than was the case with the previously mentioned process.

15 Alkali metal cyanide granulates based on sodium or potassium cyanide were found which are characterised by

- (i) essentially spherical particles with smooth or raspberry-like surface structures,
20
- (ii) particle diameters in the range from at least 0.1 mm to 20 mm for at least 99% by wt. of the granulate,
- (iii) a bulk density of at least 600 g/dm³,
25
- (iv) an abrasion of less than 1% by wt., measured in the roller abrasion test (TAR abrasion tester from Erweka using 20 samples, 60 min, 20 rpm), and
- 30 (v) a caking index of at most 4, measured after applying a load of 10 kg to 100 g in a cylinder with an internal width of 5.5 cm for 14 days.

Alkali metal cyanide granulates according to the invention
35 have in general a content of at least 80% by wt., preferably at least 93% by wt. of sodium or potassium cyanide. In addition to residual moisture, which surprisingly may assume



a value of up to a maximum of 5% by wt., but is preferably less than 3% by wt, and in particular less than 1% by wt., the granulate may also contain, in addition to side products which depend on the raw materials and process, such as

5 alkali metal hydroxide, alkali metal formate and alkali metal carbonate, the side products mentioned in larger than customary amounts and/or other auxiliary substances, in order to modify certain properties of the granulate in a deliberate manner.

10

Production of alkali metal cyanide granulates with elevated water contents, from more than about 1% by wt. to 5% by wt., leads to a saving of drying energy. This type of granulate is of economic interest if the consumer dissolves the

15 granulate in water in any case. Contrary to expectations, granulates according to the invention with elevated water contents are also sufficiently resistant to caking.

In the mining industry, for example, it is of interest to
20 obtain sodium cyanide with a higher sodium hydroxide content than the customarily present 0.2 to 0.6% by wt. because sodium hydroxide is generally added during the production of dilute, aqueous solutions in mines. The production of sodium cyanide granulates with an NaOH content of up to a maximum
25 of 3% by wt. presents no problems.

The other auxiliary substances may be distributed uniformly in the individual granulate particles or they may be distributed uniformly on the surface of the granulate
30 particles. The auxiliary substances are, for instance, anti-caking agents, which are suitable for further reducing the tendency to cake of the alkali metal cyanide granulates according to the invention, which is already reduced as compared with the commercially available granulates. A
35 reduced tendency to cake of this type is of importance if the granulate has to be temporarily stored in silos, in particular in climatically humid areas. Anti-caking agents

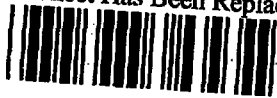


may be present in effective amounts in or on the granulates. Here, effective means that the caking index is lower due to the presence of the anti-caking agent than in its absence. Granulates which contain anti-caking agent preferably have a
5 caking index of at most 3.

Suitable anti-caking agents may be selected, for example, from the group of hydrophobic organic compounds such as Na or K salts of higher fatty acids. Another group consists of
10 natural and synthetic silicic acids and/or silicates. Although hydrophobic silicic acids and silicates are not excluded, hydrophilic substances are generally preferred, because there are then no wetting problems with the granulate in aqueous systems. Silicates which are alkaline
15 in aqueous dispersion are particularly preferred, in particular (Na, Ca) silicates and sodium aluminium silicates.

The amount used of the preferably hydrophilic silicates is
20 between 0.1 and 5% by wt. in the case of uniform distribution within the granulate particles. Provided one or more of the silicates is located essentially on the surface of the granulate, the amount used is generally between 0.01 and 4% by wt., in particular between 0.1 and 2% by wt.
25 Preferred silicates have a BET surface area (DIN 66131) of about 30 to 120 m²/g and a pH in a 5% strength aqueous suspension of 7 to 12, in particular 9 to 12. The major components are in the range 40 to 92% SiO₂, 0 to 36% Al₂O₃, 2 to 22% Na₂O, 0 to 6% CaO, particularly preferred silicates
30 consisting of 90 to 92% SiO₂, 5 to 7% CaO and about 2% Na₂O.

The amount of organic hydrophobic agent used, such as e.g. Na or K stearate, which are admixed with the final granulate and are thus located essentially on the surface of the
35 particles, is 0.1 to 4% by wt., in particular 0.1 to 2% by wt. This type of hydrophobic agent slows down the absorption



of moisture by hygroscopic alkali metal cyanides from the air and reduces the tendency to agglomerate.

5 The essentially spherical granulate particles have a smooth or raspberry-like surface structure. The expression "essentially" indicates that slight deviations from the spherical form, for example slightly ovoid shapes, are included.

10 The diameter of the particles of NaCN and KCN granulate according to the invention is essentially in the range from at least 0.1 mm to 20 mm. The expression "essentially" indicates that at least 99% by wt. of the granulate lies within the range. A preferred range is between 1 and 10 mm.

15 Granulates produced by the process according to the invention are further characterised in that the particle spectrum is very narrow. For an average particle diameter in the range from 2 to 9 mm, the diameter of the particles is essentially in the range of the average particle diameter
20 plus or minus less than 1 mm, preferably plus or minus less than 0.5 mm.

The bulk density of the granulate is of technical importance. Generally the bulk density is above 650.

25 Preferred granulates have a bulk density of greater than 700 g/l to 950 g/l. In view of the toxicity of alkali metal cyanides and thus the high investment in packaging which is required, specialists are interested in as high a bulk density as possible. As already explained above, it has
30 hitherto proved difficult to produce granulates which have the combination of properties in accordance with the Claims with respect to shape and size of particles, minimal abrasion and reduced tendency to cake and which at the same time have a high bulk density in the desired range.

35

The caking index of the granulates according to the invention is at most 4, preferably at most 3.



The caking index, also called the crushing strength, is determined by applying a load to the samples under specific conditions and is evaluated by using an assessment scale. To perform this procedure, 100 g samples are placed in a
5 tubular cylinder with de-airing holes ($\varnothing$ 1 mm) and an internal width of 55 mm, placed vertically on a base, and a 10 kg load is applied by means of a ram. The loading period is 14 days at room temperature (20 to 25°C) and atmospheric humidity (50 to 70% relative humidity). After removing the
10 ram, the cylinder is lifted off and the caking behaviour assessed.

	Index	Criterion
15		
	1	completely unchanged; smooth flowing
	2	some loose cohesion;
20		readily disintegrates into the original state
	3	loosely moulded: mostly disintegrates under slight finger pressure
25	4	loosely agglomerated: still disintegrates with moderate finger pressure
	5	semi-solid; no longer disintegrates under finger pressure
30		
	6	firmly moulded

Granulates according to the invention are essentially
35 resistant to abrasion, wherein particles smaller than 0.1 mm are understood to be the result of abrasion. The spherical shape of the granulates leads to virtually no abrasion.



Abrasion, measured in the roller abrasion test (TAR abrasion tester from Erweka Apparatebau GmbH, Heusenstamm, Germany, using a 20 g sample, 1 hour rotating at 20 rpm) is less than 1% by wt., generally less than 0.5% by wt. Abrasion of a commercially available granulate, sieved to give particles larger than 1mm, in contrast, is 2 to 3% by wt. If a granulate prepared according to the invention is compared with a comparable sieve fraction of a commercially available granulate, the abrasion of the granulates according to the invention is generally less than one tenth of the value of the corresponding fraction of the commercially available granulate. The good pourability of granulates according to the invention and the high resistance to abrasion contribute greatly to easier and safer handling.

15

As explained above, sodium cyanide granulate and potassium cyanide granulate according to the invention have much better material properties in several respects which are relevant in practical situations, as compared with commercially available granulates. Granulates according to the invention are pourable and form virtually no dust during handling, in contrast to commercially available granulates. The granulates can be stored in silos, due to their greatly reduced tendency to cake, and be withdrawn as needed, this being virtually impossible with previously known granulates. Silo vehicles can be readily emptied and the washing-out procedure which has hitherto been required is unnecessary. It could not have been predicted that the material properties in accordance with the Claims could be combined in one and the same granulate.

A process was found for preparing the alkali metal cyanide granulates based on sodium cyanide or potassium cyanide according to the invention which is characterised in that an aqueous solution or suspension containing at least 10% by wt. of alkali metal cyanide is sprayed onto a fluidised bed consisting of alkali metal cyanide nuclei in a device for



fluidised bed spray granulation, the water is evaporated off using a current of drying gas, whose temperature is 150 to 450°C, flowing through the fluidised bed, wherein the temperature of the fluidised bed is 90 to 350°C and
5 granulate is withdrawn from this device in a manner which is known per se and dust which is produced is returned thereto.

The structure and method of operation of a fluidised bed spray granulation device to be used according to the
10 invention can be found in the document cited at the beginning. The drying gas is generally air, and either compressed air or ambient air may be used. With regard to the ready formation of alkali metal carbonates from the alkali metal cyanide solution and carbon dioxide from the
15 air, the use of ambient air is preferred. The drying air emerging from the fluidised bed spray granulator is thus reheated, after drying, and used to operate the granulator. The initial temperature of the drying gas is generally in the range between 150 and 450°C, preferably above 200°C. The
20 drying gas leaves the granulator in general at a temperature between 70 and 300°C, preferably above 110°C.

For problem-free granulate formation, it is essential to coordinate the fluidised bed temperature and the density of
25 the nuclei in the fluidised bed and the rate of spraying with each other. The person skilled in the art will determine these parameters in optimising tests. The temperature of the fluidised bed is preferably maintained between 130 and 300°C. To produce granulates with
30 predominantly a raspberry-like structure, the fluidised bed is generally operated at a lower temperature and higher spray rate than to produce granulates with smooth surfaces. If the density of nuclei is too high, particularly in the event of too high a spray rate, there is a risk of the
35 fluidised bed breaking down due to too great a formation of agglomerates.



The solution or suspension being sprayed onto or into the fluidised bed preferably has an NaCN or KCN content of 20 to 45% by wt., in particular 30 to 40% by wt. If desired, the solution or suspension also contains additives and/or
5 auxiliary substances for modifying the properties in appropriate effective amounts, these being selected in accordance with the intended application.

The solution being sprayed onto the nuclei may be sprayed
10 into the fluidised bed from below, from the side or even from above. It is advantageous to use one or more spray nozzles arranged inside the fluidised bed. Various structural types of nozzle may be used. If the nozzles are located above the fluidised bed, solid-cone nozzles or two-
15 fluid nozzles, for example, may be used, if the nozzles are located within the fluidised bed, two-fluid nozzles with external mixing are preferred. The amount of liquid to be sprayed is adjusted by the person skilled in the art in such a way that stability of the fluidised bed is maintained
20 during the spraying procedure. Here, stability is understood to mean that the number of nuclei remains constant. If the number of nuclei is too low, then it is increased by introducing finely divided material from a dust separator and/or a mill which is used to break up oversized particles,
25 for example. In the case of too high a rate of formation of nuclei, the desired particle size is no longer satisfactorily reached and the number of nuclei has to be decreased.

30 Fluidised bed spray granulation may be performed either batchwise or continuously. Appropriate units are obtainable commercially. In the case of batchwise operation, all of the granulate is withdrawn from the fluidised bed after reaching the desired particle size. A device for continuous fluidised
35 bed spray granulation normally also includes a device for inspecting the granulate. The inspection device may be

either integrated into the fluidised bed spray granulation device or arranged outside the same.

It could not have been predicted that alkali metal cyanide
5 granulates according to the invention with the set of
properties described would be obtained by the combination of
process features in accordance with the Claims. Furthermore,
a person skilled in the art would not have expected to be
able to prepare alkali metal cyanide granulates using
10 fluidised bed spray granulation without considerable
hydrolysis to give formate and ammonia taking place, even
though moist cyanide is subjected to an elevated temperature
for a long period of time (e.g. 0.5 to 4 hours). The rate of
dissolution of granulates prepared according to the
15 invention is in the range of commercially available
granulates. This was also surprising because when other
products are prepared by fluidised bed spray granulation,
such as sodium perborate monohydrate (DE-OS 28 13 326),
there is a distinct increase in time of dissolution.

20

The auxiliary substances for reducing the caking behaviour,
mentioned previously in the description of the alkali metal
cyanide granulates according to the invention, can be
incorporated in the granulates or deposited onto the surface
25 of the same in various ways. If the auxiliary substance is
intended to be uniformly distributed in the granulate
particles, it is expedient to introduce the auxiliary
substance to the fluidised bed spray granulator in the form
of an aqueous solution or suspension separated from or
30 already mixed with the aqueous solution which contains the
alkali metal cyanide. In the case of a batchwise operated
process, it is generally sufficient to spray the aqueous
solution or suspension containing auxiliary substance(s)
into the fluidised bed after granulate production has
35 largely finished, so that the auxiliary substance(s) is/are
essentially located on the surface of the granulate
particles. If the fluidised bed spray granulator is operated



continuously, incorporation of the auxiliary substance(s) in uniform distribution takes place in the same way as in the batchwise embodiment. In order to keep the amount of auxiliary substance(s), for instance anti-caking agent from
5 the silicate group, small, it is recommended that these substances be applied essentially to the surface of the granulate particles by spraying the granulate leaving the fluidised bed spray granulator with either an aqueous solution or suspension of the auxiliary substance(s) and
10 removing the water introduced in a subsequent drying step. This process may be performed, for example, in a second fluidised bed spray granulator or fluidised bed dryer with a spray device in the first zone. Alternatively, the auxiliary substance(s) may also be applied in the dry form to the
15 granulate withdrawn from the granulator, which has a residual moisture content of up to 5% by wt., by a simple mixing procedure for instance, followed by drying if required.

20 In addition to the advantageous properties of the granulates prepared according to the invention, the process has a number of advantages. To perform the process, only a fluidised bed spray granulator with the additive devices which are customary for this type of plant is required, thus
25 reducing the hitherto multi-step process in principle to a one-step process. The process according to the invention is also distinguished by a low staffing requirement. Shut down times due to repairs or caking up, and thus restrictions on the availability of the plant, are much shorter than has
30 been the case with the technique used in the prior art.



Examples 1 to 9

Preparation of sodium cyanide granulate

5 The fluidising chamber of a fluidised bed spray granulator consists of a quartz-UV glass vessel with an internal diameter of 150 mm and a length of 530 mm. The flow base is a screen cloth with a mesh of 144 μm . The nozzle (two-fluid nozzle with adjustable air valves) is mounted centrally over
10 the flow base. The distance between the flow base and the nozzle tip is 330 mm.

Upstream of the fluidising chamber is an air-heater with a temperature regulator and air-flow controller. Downstream of
15 the fluidising chamber is a settling zone made from stainless steel with a diameter of 300 mm. The current of air then has the dust removed in a stainless steel cyclone. The fine dust which separates out is returned to the fluidising chamber via a star wheel valve. A waste gas fan
20 with a maximum capacity of 500 m^3/h draws the air through the fluidising chamber and cyclone.

To produce an initial bed capable of being readily fluidised, NaCN nuclei with the particle sizes given in
25 Table 1 are used with the initial amount introduced being 500 g. During the start-up procedure for the plant, the fluidised bed is expanded, after exceeding the loosening point for the initial nuclei, by increasing the rate of flow of drying air (rate of flow with respect to the empty pipe
30 cross-section, ca. 3 m/s), in order to produce the requisite density (initial depth to start 330 to 400 mm). 40% by wt. strength aqueous NaCN solution (ca. 23°C) is sprayed onto the nuclei using a nozzle immersed in the fluidised bed (atomising pressure 2 bar). The spray droplets meet the
35 floating NaCN nuclei and are distributed onto these by spreading out. The intensive heat and material exchange in the fluidised bed brings about rapid solidification of the



liquid film due to drying. During growth of the particles, the fluidised bed is further expanded. After achieving a set diameter, fluidised bed granulation is discontinued and the granulates are removed from the fluidising chamber.

5

The operating parameters and material properties are given in Tables 1 and 2.

This Sheet Has Been Replaced





Table 1

Example No.	1	2	3	4	5	6	7	8*	9**
Operating parameter:									
Initial temp. of air (°C)	250	150	150	250	230	230	250	280	250
Amount of air (m ³ /h)	260	220	393	275	260	260	260	275	390
Temp. of fluidised bed (°C)	180	90	110	150	150	130	180	180	180
Exit temp. of air (°C)	146	79	82	124	122	100	146	157	150
Amount sprayed (l/h)	5.4	6.8	11.3	13.3	8.9	12.9	5.0	8.6	5.4
Diameter of nuclei (mm)	0.5	1.4	2	2	3	3	3	1.4	4.5-5
Spraying time (min.)	160-	55	72	50	41	28	75	97	60

Granulate:

Shape (R = raspberry) (S = smooth sphere)	S	R	S	R	R	R	S	S	S
Diameter (mm)	2	2	5-6	4-5	4.5-5	4.5-5	4.5-5	3	6
Bulk density (g/dm ³)	715	734	798	648	734	740	720	806	652

* 30% by wt. strength solution of NaCN sprayed in.

** A suspension containing 40% by wt. NaCN and 0.6% by wt. of a (Ca,Na) silicate (Extrusil, Degussa) sprayed onto nuclei from example 7.



Table 2

Material properties of the granulates

Example No.	2	3	4	5	6*	7	8	9	for comparison: milled granulate (commercial product 0.2-4 mm particle spectrum
Composition (% by wt.)									
NaCN	94.2	96.5	97.1	97.4	97.2	96.9	95.5	n.k.	>98.0
NaOH	0.5	0.7	0.7	0.3	0.7	0.3	0.3	n.k.	0.5
Na ₂ CO ₃	1.7	1.1	1.7	1.8	1.3	2.5	3.3	n.k.	0.4
Na formate	0.1	0.2	0.3	0.3	0.4	0.2	0.4	n.k.	0.3
Resid. moisture	3.7	1.7	0.2	0.2	0.2	0.05	0.05	n.k.	<0.1
Abrasion (%)	0.1	<0.05	0.4	0.3	<0.05**	<0.05	<0.05	<0.1	2-3
Caking index	4	4	3	4	1(2)	3(4)	n.k.	2	6(5)
Breaking strength (N)	n.k.	n.k.	n.k.	17	14	24	12	52	n.k.
Rate of dissolution (sec) to prepare a 0.1% strength solution at 20°C	50	105	85	75	75	70	50	n.k.	70 (particles >1 mm)

* Granulate was mixed with 2% silicate (Extrusil, Degussa) after withdrawal from the reactor.

** Measured using Si-free sample.

n.k. = not known.



Alkali metal cyanide granulates and a process for their preparation

Patent Claims

5

1. Alkali metal cyanide granulates based on sodium cyanide or potassium cyanide, characterised by

- 10 (i) essentially spherical particles with smooth or raspberry-like surface structure,
(ii) particle diameters in the range from at least 0.1 mm to 20 mm for at least 99% by wt. of the granulate,
(iii) a bulk density of at least 600 g/dm³,
15 (iv) an abrasion of less than 1% by wt. measured in a roller abrasion tester (TAR abrasion tester from Erweka, using 20 samples, 60 min., 20 rpm) and
(v) a caking index of at most 4, measured after
20 applying a load of 10 kg to 100 g in a cylinder of internal width 5.5 cm for 14 days.

2. Alkali metal cyanide granulates according to Claim 1,
25 characterised in that they have an alkali metal cyanide content of at least 93% by wt., a residual moisture content of up to a maximum of 5% by wt. and an alkali metal hydroxide content, wherein the alkali metal corresponds to that in the alkali metal cyanide, of at
30 most 3% by wt.

3. Alkali metal cyanide granulates according to Claim 1 or 2, characterised in that they also contain an anti-caking agent in effective amounts, uniformly
35 distributed in the granulate particles or essentially on the surface of the same, and that the caking index of the granulate is preferably a maximum of 3.





4. Alkali metal cyanide granulates according to Claim 3, characterised in that they contain, as anti-caking agent, a silicate which is alkaline in aqueous dispersion, preferably in an amount of 0.1 to 2% by wt., on the surface of the granulate particles.
5. Alkali metal cyanide granulates according to one or more of Claims 1 to 4, characterised in that the average diameter of the particles is in the range from 2 to 10 mm and the particle spectrum is in the range of the average particle diameter plus or minus a maximum of 1 mm.
6. A process for preparing alkali metal cyanide granulates according to Claims 1 to 5, characterised in that an aqueous solution or suspension containing at least 10% by wt. of alkali metal cyanide is sprayed onto a fluidised bed of alkali metal cyanide nuclei in a device for fluidised bed spray granulation, the water is evaporated by means of a current of drying gas, whose initial temperature is 150 to 450°C, flowing through the fluidised bed and the temperature of the fluidised bed is 90 to 350°C, and granulate is withdrawn from the device in a manner which is known per se and dust which is produced is returned thereto.
7. A process according to Claim 6 for preparing alkali metal cyanide granulates according to Claim 5, characterised in that an aqueous solution or suspension containing 20 to 45% by wt., preferably 30 to 40% by wt. of alkali metal cyanide is sprayed onto alkali metal cyanide nuclei with a particle diameter of at least 500 μm , wherein the temperature of the fluidised bed is in the range 130 to 300°C.





8. A process according to Claim 6 or 7, characterised in that the aqueous solution or suspension is sprayed onto the alkali metal cyanide nuclei by means of one or more spray nozzles, preferably two-fluid nozzles, placed inside the fluidised bed.
9. A process according to one or more of Claims 6 to 8, characterised in that the aqueous solution or suspension contains, in addition to the alkali metal cyanide, the relevant alkali metal hydroxide in an amount of up to 3% by wt., with reference to the relevant alkali metal cyanide, and/or an anti-caking agent in an effective amount, preferably a silicate which is alkaline in aqueous dispersion.
10. A process according to one or more of Claims 6 to 9, characterised in that the granulate withdrawn from the fluidised bed spray granulation device is subsequently treated with an anti-caking agent, preferably a silicate, by mixing the granulate withdrawn in the presence of up to 5% by wt. of moisture, with reference to the alkali metal cyanide, with the anti-caking agent which is added dry or in the form of an aqueous suspension, and, if required, subsequent drying.

This Sheet Has Been Replaced



Alkali metal cyanide granulates and a process for their preparation

5

Abstract

The invention relates to new alkali metal cyanide granulates based on sodium cyanide or potassium cyanide and a method
10 for their preparation.

Commercially available alkali metal cyanide granulates consist of irregular particles. Disadvantages are in particular the tendencies to form dust and to cake.

15

The alkali metal cyanide granulates according to the invention demonstrate virtually no abrasion and a reduced tendency to cake. The granulates are characterised by essentially spherical particles with particle diameters in
20 the range 0.1 to 20 mm, a bulk density of more than 600 g/dm³, an abrasion of less than 1% and a caking index of at most 4.

The granulates can be prepared by fluidised bed spray
25 granulation, by spraying an aqueous solution containing alkali metal cyanide onto alkali metal cyanide nuclei in a fluidised bed and evaporating the water.

This Sheet Has Been Replaced



Beschreibung

Die Erfindung betrifft neue Alkalicyanid-Granulate auf der Basis von Natriumcyanid oder Kaliumcyanid, deren Teilchen im wesentlichen kugelförmig sind und die sich gegenüber vorbekannten Granulaten durch außergewöhnliche Eigenschaften, darunter einen minimalen Abrieb und wesentlich verminderte Verbackungsneigung auszeichnen, sowie ein Verfahren zur Herstellung der Granulate.

Die beiden Alkalicyanid-Salze Natrium- und Kaliumcyanid werden zur Herstellung von galvanischen Bädern und von Härtesalzbädern sowie zur Synthese organischer Verbindungen verwendet. Darüber hinaus wird Natriumcyanid in großen Mengen zur Goldgewinnung durch Cyanidlaugung von Erzen eingesetzt.

Wegen ihrer Giftigkeit werden die genannten Alkalicyanide bevorzugt als Preßlinge oder staubarmes Mahlgranulat gehandelt. Handelsübliche, großtechnisch hergestellte Natrium- und Kaliumcyanid-Granulate bestehen aus unregelmäßig geformten Teilchen mit einem Teilchenspektrum, das sich beispielsweise zwischen etwa 0,2 und 4 mm erstreckt. Die Preßlinge werden mit rotierenden Walzenpressen oder mit Stempelpressen erzeugt. Die Granulate werden durch Zerkleinerung der Preßlinge mittels einer Mahlvorrichtung hergestellt. Die unregelmäßige Form derartiger Granulate ist die Ursache von unerwünschter Staubbildung während der Handhabung.

Die bekannten NaCN- und KCN-Handelsformen Preßlinge, Mahlgranulat und Pulver neigen stark zum Verdumpen und zum Anbacken an den Innenflächen von Rohrleitungen, Armaturen und Apparaten aus Stahl oder Edelstahl. Die Neigung zum Verdumpen und Anbacken nimmt mit abnehmender Korngröße und insbesondere zunehmender Feuchte und Belastung zu und macht die Handhabung, wie Lagern in Silos, Dosieren und Fördern, schwierig und aufwendig.

Wegen dieser Schwierigkeiten wurde von der Anmelderin der vorliegenden Anmeldung nach einer Lieferform gesucht, die nicht oder zumindest weniger zum Verdumpen und Anbacken neigt. NaCN-Filterkuchen, der nach bekannten Verfahren hergestellt wurde, konnte zwar in ein etwa kugelförmiges Granulat umgewandelt und anschließend getrocknet werden, das resultierende NaCN-Granulat lag jedoch beim Schüttgewicht mit unter 600 g/dm^3 zu niedrig und die Abriebfestigkeit war unbefriedigend.

Ein weiterer Nachteil der vorbekannten Natrium- und Kaliumcyanid-Granulate besteht in dem technisch aufwendigen, mehrere Stufen umfassenden Verfahren zu deren Herstellung, das von wäßriger NaCN- bzw. KCN-Lösung ausgeht: In der ersten Stufe wird das Alkalicyanid aus der Lösung auskristallisiert, dies läßt sich beispielsweise in einem Vakuumkristalliser durchführen. Das auskristallisierte Produkt wird mittels bekannter Techniken von der Mutterlauge abgetrennt. Nach einer ein- oder mehrstufigen Trocknung wird das Alkalicyanid-Pulver zu Preßlingen kompaktiert; letztere werden zu dem genannten Granulat zerkleinert. Das Verfahren erfordert somit nicht nur einen großen Aufwand an Apparaturen und Bedienungspersonal, sondern die aufgezeigte Neigung von NaCN und KCN zu Anbackungen zwingt zu Abstellungen und mindert die Verfügbarkeit der Gesamtanlage.

Die DE-A 38 32 883 richtet sich auf die Herstellung von festen teilchenförmigen Alkalicyaniden, insbesondere NaCN, wobei HCN kontinuierlich mit fein verteilten Tröpfchen einer wäßrigen Alkalihydroxidlösung in Kontakt gebracht wird. Das Schüttgewicht von nicht nachbehandeltem Natriumcyanid liegt meist im Bereich von 0,2 bis 0,4 kg/l. Das Produkt kann zwar in einem Wirbelbett granuliert werden, jedoch lehrt dieses Dokument weder Verfahrensparameter hierzu noch Stoffdaten des Granulats.

Aus dem US-Patent 4,107,274 ist bekannt, die Verbackungsneigung von Alkalimetallhalogeniden und solche enthaltenden Gemischen durch Zugabe eines hydrophilen und/oder hydrophoben Materials, beispielsweise eines Metallsilikats, in Verbindung mit einem komplexen Eisencyanid auf einen hydroxylgruppenhaltigen Träger zu mindern. Dieses Dokument lehrt nicht, die Verbackungsneigung von Alkalimetallcyaniden durch Zugabe von Metallsilikaten allein zu mindern.

In der Firmenschrift Glatt® AGT (Feb. 92 - 3000 D (W)) der Firma Glatt Ingenieurtechnik GmbH, Weimar erscheint als Anwendungszweck der dort beschriebenen Anlage zur kontinuierlichen Granulier-Trocknung, welche auf dem Prinzip der auch als Wirbelschicht-Sprühgranulation bezeichneten Technik (siehe H. Uhlemann in Chem.-Ing. Technik 62 (1990) Nr. 10, S. 822-834) beruht, unter anderem „Karbonate & Zyanide“. In der genannten Firmenschrift wird aber nicht offenbart, ob sich der Hinweis auf Alkalimetall-, Erdalkalimetall- oder Schwermetallcyanide oder auf komplexe Cyanide bezieht. Auch lassen sich der Firmenschrift keine Angaben zu den Eigenschaften von Cyanid-Granulaten entnehmen. Aus der genannten Firmenschrift wird ersichtlich, daß die Sprühdüse im Wirbelschichttrockner derart angeordnet ist, daß die zu versprühende Lösung von oben auf die Wirbelschicht gesprüht wird. Der Artikel von Uhlemann lehrt die Grundprinzipien der Sprühgranulation einschließlich der Verwendung von Zweistoffdüsen und verschiedene Möglichkeiten der Positionierung derselben in der Wirbelschicht-Sprühgranulationsvorrichtung.

Nach dem in der EP-A 0 600 211 offenbarten Verfahren läßt sich festes Natriumcyanid-Granulat mit einem Durchmesser des Granulats von 2 bis 6 mm in zwei Verfahrensstufen erzeugen, wobei in einer ersten Stufe eine wäßrige Natriumcyanidlösung in einen Wirbelschichtgranulator gesprüht und mittels warmer Luft aus einem nachgeschalteten zweiten Wirbelschichttrockner Granulat erzeugt wird; die der ersten Stufe zugeführte Luft wird in der Wirbelschicht der ersten Stufe auf eine Temperatur von 60 bis 90 °C abgekühlt. In der zweiten Stufe wird nachgetrocknet, wobei die Zuluft eine Temperatur von 150 bis 230 °C aufweist.

Aufgabe der Erfindung ist somit, Alkalicyanid-Granulate auf der Basis von Natrium- oder Kaliumcyanid zur Verfügung zu stellen, die die eingangs dargelegten Nachteile handelsüblicher Granulate in vermindertem Umfang aufweisen. Zudem sollten die Granulate durch eine spezifische Eigenschaftskombination gekennzeichnet sein. Eine weitere Aufgabe richtet sich darauf, ein Verfahren aufzuzeigen, das es gestattet, die neuen Granulate durch Wirbelschicht-Sprühgranulation herzustellen, wobei Verkrustungsprobleme, wie sie im vorbekannten Verfahren auftraten, vermieden werden sollten.

Gefunden wurden Alkalicyanid-Granulate auf der Basis von Natriumcyanid oder Kaliumcyanid mit

- ii) einem Teilchendurchmesser im Bereich von mindestens 0,1 bis 20 mm für mindestens 99 Gew.-% des Granulats,
 - (iii) einem Schüttgewicht von mindestens 600 g/dm³
 - (iv) einem Abrieb von weniger als 1 Gew.-%, gemessen im Roll-Abriebtest (Abriebtester TAR der Fa. Erweka mit 20 g Probe, 60 min 20 U/min),
 - (v) einem Verbackungsindex von maximal 4, gemessen nach 14-tägiger Belastung von 100 g in einem Zylinder der lichten Weite von 5,5 cm mit 10 kg,
- welche dadurch gekennzeichnet sind, daß sie
- (i) aus im wesentlichen kugelförmigen Teilchen mit glatter oder himbeerförmiger Oberflächenstruktur bestehen.

Erfindungsgemäße Alkalicyanid-Granulate weisen im allgemeinen einen Gehalt von mindestens 80 Gew.-%, vorzugsweise mindestens 93 Gew.-%, Natrium- bzw. Kaliumcyanid auf. Außer der Restfeuchte, welche überraschenderweise einen Wert bis maximal 5 Gew.-% annehmen kann, vorzugsweise aber unter 3 Gew.-% und insbesondere unter 1 Gew.-% liegt, kann das Granulat außer rohstoff- und verfahrensbedingten Nebenprodukten, wie Alkalihydroxid, Alkaliformiat und Alkalicarbonat, die genannten Nebenprodukte in größerer als üblicher Menge und/oder andere Hilfsstoffe enthalten, um bestimmte Eigenschaften der Granulate in gezielter Weise zu verändern.

Die Herstellung von Alkalicyanid-Granulaten mit erhöhtem Wassergehalt, etwa oberhalb 1 Gew.-% bis 5 Gew.-%, führt zu Einsparungen an Trocknungsenergie. Derartige Granulate sind von wirtschaftlichem Interesse, wenn der Verbraucher das Granulat ohnehin in Wasser auflöst. Entgegen den Erwartungen sind auch erfindungsgemäße Granulate mit erhöhtem Wassergehalt ausreichend verbackungsresistent.

Für die Minenindustrie ist es beispielsweise von Interesse, Natriumcyanid mit höherem Natriumhydroxid-Gehalt als den üblicherweise anwesenden 0,2 bis 0,6 Gew.-% zu beziehen, weil bei der Herstellung verdünnter, wäßriger Lösungen auf der Mine in der Regel Natriumhydroxid zugesetzt werden muß. Die Herstellung von Natriumcyanid-Granulat mit einem NaOH-Gehalt von bis maximal 3 Gew.-% bereitet keine Probleme.

Die anderen Hilfsstoffe können gleichförmig in den einzelnen Granulattellchen verteilt sein oder sich im wesentlichen gleichmäßig verteilt auf der Oberfläche der Granulattellchen befinden. Bei den Hilfsstoffen handelt es sich beispielsweise um Antibackmittel, welche geeignet sind, die Backneigung der erfindungsgemäßen Alkalicyanid-Granulate, welche bereits gegenüber handelsüblichen Granulaten vermindert ist, weiter zu reduzieren. Eine derart verminderte Backneigung ist dann von Wichtigkeit, wenn das Granulat in Silos, insbesondere in klimatisch feuchten Zonen, zwischengelagert werden muß. Antibackmittel können in wirksamer Menge in beziehungsweise auf den Granulaten anwesend sein. Wirksam bedeutet hierbei, daß der Verbackungsindex durch die Anwesenheit des Antibackmittels niedriger ist als in dessen Abwesenheit. Antibackmittel enthaltende Granulate weisen vorzugsweise einen Verbackungsindex von maximal 3 auf.

Geeignete Antibackmittel können beispielsweise ausgewählt sein aus der Gruppe hydrophobierender organischer Verbindungen, wie Na- oder K-Salze höherer Fettsäuren. Eine weitere Gruppe sind natürliche und synthetische Kieselsäuren und/oder Silikate. Obgleich hydrophobierte Kieselsäuren und Silikate nicht ausgeschlossen werden, werden im allgemeinen hydrophile Stoffe bevorzugt, weil es in wäßrigen Systemen damit zu keinen Benetzungsproblemen des Granulats kommt. Besonders bevorzugt werden in wäßriger Dispersion alkalisch wirkende Silikate, insbesondere (Na,Ca)-silikate und Natriumaluminiumsilikate.

Die Einsatzmenge der vorzugsweise hydrophilen Silikate liegt bei gleichförmiger Verteilung innerhalb des Granulatkorns zwischen 0,1 und 5 Gew.-%. Sofern sich eines oder mehrere der Silikate im wesentlichen auf der Oberfläche des Granulats befindet, liegt die Einsatzmenge im allgemeinen zwischen 0,01 und 4 Gew.-%, insbesondere zwischen 0,1 und 2 Gew.-%. Bevorzugte Silikate weisen eine BET-Oberfläche (DIN 66131) von etwa 30 bis 120 m²/g, einen pH-Wert einer 5 %igen wäßrigen Suspension von 7 bis 12, insbesondere 9 bis 12, auf; die Hauptbestandteile liegen im Bereich von 40 bis 92 % SiO₂, 0 bis 36 % Al₂O₃, 2 bis 22 % Na₂O, 0 bis 6 % CaO; besonders bevorzugt sind Silikate mit 90 bis 92 % SiO₂, 5 bis 7 % CaO und etwa 2 % Na₂O.

Die Einsatzmenge organischer Hydrophobierungsmittel, wie z. B. Na- oder K-Stearat, welche dem fertigen Granulat zugemischt werden und sich damit im wesentlichen auf der Oberfläche der Teilchen befinden, beträgt 0,1 bis 4 Gew.-%, insbesondere 0,1 bis 2 Gew.-%. Derartige Hydrophobierungsmittel verzögern die Feuchtigkeitsaufnahme der hygroskopischen Alkalicyanide an der Luft und reduzieren die Verklumpungsneigung.

Die im wesentlichen kugelförmigen Granulatlteilchen weisen eine glatte oder himbeerförmig strukturierte Oberfläche auf. Der Begriff "im wesentlichen" zeigt an, daß geringfügige Abweichungen von der Kugelgestalt, beispielsweise leichte Ovalformen, eingeschlossen sind.

Der Durchmesser der Teilchen des erfindungsgemäßen NaCN- und KCN-Granulats liegt im wesentlichen im Bereich von mindestens 0,1 mm bis 20 mm. Der Begriff "im wesentlichen" bedeutet, daß mindestens 99 Gew.-% des Granulats innerhalb des Bereichs liegen. Ein bevorzugter Bereich liegt zwischen 1 und 10 mm. Nach dem erfindungsgemäßen Verfahren hergestellte Granulate zeichnen sich ferner dadurch aus, daß das Teilchenspektrum sehr schmal ist; Bei einem mittleren Korndurchmesser im Bereich von 2 bis 9 mm liegt der Durchmesser der Teilchen im wesentlichen im Bereich des durchschnittlichen Teilchendurchmessers plus/minus weniger als 1 mm, vorzugsweise plus/minus weniger als 0,5 mm.

Von technischer Bedeutung ist das Schüttgewicht der Granulate; meist liegt das Schüttgewicht oberhalb 650; bevorzugte Granulate weisen ein Schüttgewicht von größer 700 g/l bis 950 g/l auf. In Anbetracht der Giftigkeit der Alkalicyanide und damit des erforderlichen hohen Verpackungsaufwands ist die Fachwelt an einem möglichst hohen Schüttgewicht interessiert. Wie bereits zuvor dargelegt, bereitete es bisher Schwierigkeiten, Granulate zu erzeugen, welche die anspruchsgemäße Eigenschaftskombination bezüglich der Form und Größe der Teilchen, des minimalen Abriebs und der verminderten Verbackungsneigung und gleichzeitig ein hohes Schüttgewicht im erwünschten Bereich aufweisen.

Der Verbackungsindex erfindungsgemäßer Granulate beträgt maximal 4, vorzugsweise maximal 3.

Der Verbackungsindex, auch als Druckfestigkeit bezeichnet, wird durch Belastung der Probe unter definierten Bedingungen ermittelt und anhand einer Bewertungsskala bewertet. Zur Durchführung werden 100 g Probe in einen senkrecht auf einer Unterlage gestellten, rohrförmigen, Entlüftungslöcher ($\varnothing$ 1 mm) aufweisenden Zylinder der lichten Weite von 55 mm gefüllt und mittels eines Stempels mit 10 kg belastet; Belastungsdauer 14 Tage bei Raumtemperatur (20 bis 25 °C) und Raumfeuchte (50 bis 70 % relative Feuchte). Nach Entfernen des Stempels wird der Zylinder hochgezogen und das Verbackungsverhalten bewertet.

Index	Kriterien
1	völlig unverändert; glatt rieselnd
2	teilweise lose zusammenhaftend; leicht in Originalzustand zerfallend
3	locker geformt; durch leichten Fingerdruck weitestgehend zerfallend
4	locker verbacken; mit mäßigem Fingerdruck noch zerfallend
5	halbfest verbacken; mit Fingerdruck nicht mehr zerfallend
6	fest geformt

Erfindungsgemäße Granulate sind im wesentlichen abriebfest, wobei als Abrieb Teilchen kleiner 0,1 mm verstanden werden. Die Kugelform der Granulate führt praktisch zu keinem Abrieb. Der Abrieb, gemessen im Roll-Abriebtest - Abriebtester TAR der Fa. Erweka Apparatebau GmbH, D-Heusenstamm anhand einer 20 g-Probe, 1 Stunde Umlauf bei 20 U/min - weniger als 1 Gew.-%, meist weniger als 0,5 Gew.-%. Der Abrieb handelsüblichen Granulats, abgeseibt auf Teilchen größer 1 mm, beträgt demgegenüber 2 bis 3 Gew.-%. Wird erfindungsgemäß hergestelltes Granulat mit einer vergleichbaren Siebfraction handelsüblichen Granulats verglichen, beträgt der Abrieb erfindungsgemäßer Granulate im allgemeinen weniger als ein Zehntel des Werts der jeweiligen Fraction des handelsüblichen Granulats. Die gute Rieselfähigkeit erfindungsgemäßer Granulate sowie die hohe Abriebbeständigkeit tragen wesentlich zur leichteren und sicheren Handhabung bei.

Wie zuvor dargelegt, weisen erfindungsgemäßes Natriumcyanid-Granulat und Kaliumcyanid-Granulat gegenüber handelsüblichen Granulaten in mehrfacher, für die Praxis relevanter Hinsicht wesentlich bessere Stoffeigenschaften auf. Erfindungsgemäße Granulate sind rieselfähig, und bei der Handhabung bildet sich im Gegensatz zu handelsüblichen Granulaten praktisch kein Staub. Die Granulate lassen sich wegen ihrer wesentlich reduzierten Verbackungsneigung in Silos lagern und nach Bedarf abziehen - dies war mit vorbekannten Granulaten praktisch nicht möglich. Silofahrzeuge lassen sich einfach entleeren und das bisher notwendige Auslaugen entfällt. Es war nicht vorhersehbar, daß sich die anspruchsgemäßen Stoffeigenschaften in ein und dem gleichen Granulat vereinen lassen.

Gefunden wurde ein Verfahren zur Herstellung erfindungsgemäßer Alkalicyanid-Granulate auf der Basis von Natriumcyanid oder Kaliumcyanid durch Aufsprühen einer mindestens 10 Gew.-% Alkalicyanid enthaltenden wäßrigen Lösung oder Suspension in einer Vorrichtung zur Wirbelschicht-Sprühgranulation auf Alkalicyanid-Keime, Verdampfen des Wassers mittels eines durch die Wirbelschicht strömenden Trocknungsgasstroms, dessen Eingangstemperatur

150 bis 450 °C beträgt und Austragen des Granulats in an sich bekannter Weise aus der Vorrichtung und Rückführen des anfallenden Staubs in diese, das dadurch gekennzeichnet ist, daß man die Temperatur der Wirbelschicht auf 110 bis 350 °C einstellt und die wäßrige Lösung oder Suspension mittels einer oder mehrerer innerhalb der Wirbelschicht angeordneter Sprühdüsen, vorzugsweise Zweistoffdüsen, auf die Alkalicyanid-Keime sprüht.

- 6 Der Aufbau und die Wirkungsweise einer erfindungsgemäß zu verwendenden Wirbelschicht-Sprühgranulationsvorrichtung ist den eingangs zitierten Dokumenten zu entnehmen. Bei dem Trocknungsgas handelt es sich im allgemeinen um Luft, welche als Durchluft oder Umluft schaltbar ist. Im Hinblick auf die leichte Bildung von Alkalicarbonaten aus der Alkalicyanid-Lösung mit Kohlendioxid der Luft wird eine Umluftschaltung bevorzugt: Die aus dem Wirbelschicht-Sprühgranulator austretende Trocknungsluft wird also nach Entwässerung wieder aufgeheizt und zum Betreiben des
- 10 Granulators genutzt. Die Eingangstemperatur des Trocknungsgases liegt meist im Bereich zwischen 150 und 450 °C, vorzugsweise oberhalb 200 °C. Das Trocknungsgas verläßt den Granulator im allgemeinen mit einer Temperatur zwischen 70 und 300 °C, vorzugsweise oberhalb 110 °C.

- Für eine problemlose Granulatbildung ist wesentlich, die Wirbelschichttemperatur sowie die Massendichte der Keime in der Wirbelschicht und die Sprührate aufeinander abzustimmen. Der Fachmann wird diese Größen in Optimierungsversuchen ermitteln. Die Temperatur der Wirbelschicht wird vorzugsweise zwischen 130 und 300 °C, gehalten.
- 15 Zur Erzeugung von Granulaten mit überwiegend himbeerförmiger Struktur wird im allgemeinen bei niedrigerer Wirbelschicht-Temperatur und höherer Sprührate gearbeitet als zur Erzeugung von Granulaten mit glatter Oberfläche. Bei zu hoher Massendichte der Keime besteht insbesondere im Falle einer zu hohen Sprührate die Gefahr des Zusammenbrechens der Wirbelschicht infolge zu großer Agglomeratbildung.

- 20 Die in die Wirbelschicht einzusprühende Lösung oder Suspension weist vorzugsweise einen NaCN-beziehungsweise KCN-Gehalt von 20 bis 45 Gew.-%, insbesondere 30 bis 40 Gew.-%, auf. Sofern erwünscht, enthält die Lösung beziehungsweise Suspension zusätzlich auf den Anwendungszweck gerichtete Zusatzstoffe und/oder Hilfsstoffe zur Beeinflussung der Eigenschaften in jeweils wirksamer Menge.

- Die wäßrige Lösung oder Suspension wird mittels einer oder mehrerer innerhalb der Wirbelschicht angeordneter
- 25 Sprühdüsen auf die Alkalicyanid-Keime gesprüht. Einsetzbar sind Düsen unterschiedlichster Bauart; Zweistoffdüsen mit Außenmischung werden bevorzugt. Die Menge der zu versprühenden Flüssigkeit wird der Fachmann derart einstellen, daß die Stabilität der Wirbelschicht während des Besprühens aufrechterhalten wird. Unter Stabilität wird hierbei verstanden, daß die Keimzahl im wesentlichen konstant bleibt. Bei zu geringer Keimzahl wird diese durch Zufuhr von feinteiligem Material, beispielsweise aus einem Staubabscheider und/oder einer Mühle, mittels welcher Überkorn gebrochen wird, erhöht. Im Falle einer zu hohen Keimbildungsrate läßt sich die Wunschkorngröße nicht mehr befriedi-
- 30 gend erreichen, so daß die Keimzahl erniedrigt werden muß.

- Die Wirbelschicht-Sprühgranulation kann sowohl diskontinuierlich als auch kontinuierlich durchgeführt werden. Im Handel sind entsprechende Aggregate erhältlich. Bei diskontinuierlicher Fahrweise wird nach Erreichen der Wunschkorngröße das gesamte Granulat aus der Wirbelschicht entnommen. Eine Vorrichtung zur kontinuierlichen Wirbelschicht-Sprühgranulation umfaßt üblicherweise zusätzlich eine Vorrichtung zur Sichtung des Granulats. Die Sichtvorrichtung kann sowohl in die Wirbelschicht-Sprühgranulationsvorrichtung integriert oder außerhalb derselben angeordnet sein.
- 35

- Es war nicht vorhersehbar, daß durch die Kombination der anspruchsgemäßen Verfahrensmerkmale erfindungsgemäße Alkalicyanid-Granulate mit dem beschriebenen Eigenschaftsbild erhältlich sind. Es war ferner für den Fachmann nicht zu erwarten, daß sich mittels Wirbelschicht-Sprühgranulation Alkalicyanid-Granulate herstellen lassen, ohne daß es zu nennenswerter Hydrolyse des Cyanids zu Formiat und Ammoniak kommt, obgleich feuchtes Cyanid über einen langen Zeitraum (z. B. 0,5 bis 4 Std.) hoher Temperatur ausgesetzt ist. Die Lösegeschwindigkeit erfindungsgemäß hergestellter Granulate liegt im Bereich handelsüblicher Granulate. Auch dies war überraschend, weil es bei der Herstellung anderer Produkte durch Wirbelschicht-Sprühgranulation, wie etwa Natriumperboratmonohydrat (DE-OS 28
- 40 13 326), zu einer wesentlichen Verlängerung der Lösezeit kommt.

- Die zuvor bei der Beschreibung der erfindungsgemäßen Alkalicyanid-Granulate genannten Hilfsstoffe zur Verminderung des Backverhaltens lassen sich in unterschiedlicher Weise in die Granulate einbringen oder auf der Oberfläche derselben abscheiden. Sofern der Hilfsstoff gleichförmig in dem Granulatkorn verteilt sein soll, ist es zweckmäßig, den Hilfsstoff in Form einer wäßrigen Lösung oder Suspension getrennt oder bereits mit der Alkalicyanid enthaltenden wäß-
- 50 rigen Lösung gemischt dem Wirbelschicht-Sprühgranulator zuzuführen. Im Falle diskontinuierlicher Verfahrensführung reicht es im allgemeinen aus, eine den oder die Hilfsstoffe enthaltende wäßrige Lösung oder Suspension nach weitgehend beendeten Granulataufbau in die Wirbelschicht einzusprühen, so daß sich der/die Hilfsstoffe im wesentlichen auf der Oberfläche des Granulatkorns befindet. Bei kontinuierlicher Wirbelschicht-Sprühgranulation erfolgt die Einbringung des/der Hilfsstoffe in gleichmäßiger Verteilung in das Granulatkorn in gleicher Weise wie bei diskontinuierlicher Ausführungsform. Um die Menge an dem oder den Hilfsstoffen, etwa Antbackmittel aus der Reihe der Silikate, niedrig zu halten, ist es empfehlenswert, diese Stoffe im wesentlichen auf die Oberfläche des Granulatkorns aufzubringen, indem aus dem Wirbelschicht-Sprühgranulator ausgetragenes Granulat entweder mit einer wäßrigen Lösung oder Suspension des beziehungsweise der Hilfsstoffe besprüht und eingetragenes Wasser in einer Nachtrocknungsstufe entfernt
- 55

wird; diese Maßnahmen können beispielsweise in einem zweiten Wirbelschicht-Sprühgranulator oder Fließbettrockner mit Sprühvorrichtung in einer ersten Zone durchgeführt werden. Alternativ können der/die Hilfstoffe auch in trockener Form auf das mit einer Restfeuchte bis zu 5 Gew.-% aus dem Granulator abgezogene Granulat, beispielsweise durch einfaches Mischen, aufgebracht werden; falls erforderlich, wird nachgetrocknet.

Außer den vorteilhaften Eigenschaften der erfindungsgemäß hergestellten Granulate weist das Verfahren eine Reihe von Vorteilen auf. Zur Durchführung des Verfahrens ist lediglich ein Wirbelschicht-Sprühgranulator mit den für derartige Anlagen üblichen Zusatzeinrichtungen erforderlich; damit reduziert sich das bisher mehrstufige Verfahren auf im wesentlichen eine einzige Stufe. Das erfindungsgemäße Verfahren zeichnet sich zudem durch einen geringen Personalaufwand aus. Reparatur- oder verdeckungsbedingte Stillstandszeiten und damit Limitierung der Verfügbarkeit der Anlage sind wesentlich geringer als dies bei dem in der Technik benutzten Verfahren der Fall war.

Beispiele 1 bis 9

Herstellung von Natriumcyanid-Granulat

Der Wirbelraum eines Wirbelschicht-Sprühgranulators besteht aus einem QVF-Glasschuß mit einem Innendurchmesser von 150 mm und einer Länge von 530 mm. Als Anströmboden wird ein Siebgewebe mit einer Maschenweite von 144 µm verwendet. Die Düse (Zweistoffdüse mit verstellbarer Luftklappe) ist zentral über dem Anströmboden angebracht; der Abstand zwischen Anströmboden und Düsen Spitze beträgt 330 mm.

Vor dem Wirbelraum befindet sich der Lufterhitzer mit Temperaturregelung und Luftmengendrosselung. Hinter dem Wirbelraum befindet sich eine Beruhigungszone aus Edelstahl mit einem Durchmesser von 300 mm. Der Luftstrom wird danach zur Entstaubung durch einen Edelstahlzyklon geführt. Der abgeschiedene Feinstaub wird über eine Zellenradschleuse wieder in den Wirbelraum zurückgeführt. Ein Abluftventilator mit einer maximalen Leistung von 500 m³/h zieht die Luft durch den Wirbelraum und Zyklon.

Zur Erzielung einer gut fluidisierbaren Start-Wirbelschicht werden NaCN-Keime mit der in Tabelle 1 angegebenen Korngröße eingesetzt; Start-Füllmenge 500 g. Bei der Inbetriebnahme der Anlage wird nach Überschreiten des Lockerungspunktes der Start-Keime die Wirbelschicht durch Steigerung der Anströmgeschwindigkeit der Trocknungsluft (Anströmgeschwindigkeit bezogen auf den Leerrohrquerschnitt ca. 3 m/s) expandiert, um die geforderte Massendichte zu erzielen (Starthöhe zu Beginn 330 bis 400 mm). 40 gew.-%ige wäßrige NaCN-Lösung (ca. 23 °C) wird mittels der in die Wirbelschicht eingetauchten Düse (Zerstäubungsdruck 2 bar) auf die Keime gesprüht. Die Sprühtropfen treffen die schwebenden NaCN-Keime und verteilen sich auf diesen durch Spreitung. Der intensive Wärme- und Stoffaustausch in der Wirbelschicht bewirkt eine rasche Verfestigung des Flüssigkeitsfilmes durch Trocknung. Während des Wachstums der Partikel wird die Wirbelschicht weiter expandiert. Nach Erreichen des Solldurchmessers wird die Wirbelschichtgranulation abgebrochen und die Granulate werden aus dem Wirbelraum entnommen.

Die Betriebsparameter sowie Stoffeigenschaften folgen aus den Tabellen 1 und 2.

Tabelle 1

Beispiel-Nr.	1	2	3	4	5	6	7	8 *)	9 **)
Betriebsparameter:									
Lufteingangstemperatur (°C)	250	150	150	250	230	230	250	280	250
Luftmenge (m³/h)	260	220	398	275	260	260	260	275	390
Wirbelschichttemperatur (°C)	180	90	110	150	150	130	180	180	180
Luftaustrittstemperatur (°C)	146	79	82	124	122	100	146	157	150
Einsprühmenge (l/h)	5,4	6,8	11,3	13,3	8,9	12,9	5,0	8,6	5,4
Keimdurchmesser (mm)	0,5	1,4	2	2	3	3	3	1,4	4,5-5
Sprühdauer (min)	160	55	72	50	41	28	75	97	80
Granulat:									
Form (H=Himbeere) (K=glatte Kugel)	K	H	K	H	H	H	K	K	K
Durchmesser (mm)	2	2	5-6	4-5	4,5-5	4,5-5	4,5-5	3	6
Schüttgewicht (g/dm³)	715	734	798	648	734	740	720	806	652

*) eingespritzt wurde 30 gew.-%ige NaCN-Lösung

**) Gespritzt wurde eine 40 Gew.-% NaCN und 0,8 Gew.-% eines (Ca,Na)-silikats (Extrusil Fa. Degussa) enthaltende Suspension auf Keime aus Beispiel 7.

T a b e l l e 2

Stoffeigenschaften der Granulate

Beispiel-Nr.	2	3	4	5	6 a)	7	8	9	zum Vergleich: Mahlgranulat (Handelsprodukt: 0,2-4 mm Korn- spektrum)
Gehalt (Gew.-%)									
NaCN	94,2	96,5	97,1	97,4	97,2	96,9	95,5	n.b.	>96,0
NaOH	0,5	0,7	0,7	0,3	0,7	0,3	0,3	n.b.	0,5
Na ₂ CO ₃	1,7	1,1	1,7	1,8	1,3	2,5	3,3	n.b.	0,4
Na-formiat	0,1	0,2	0,3	0,3	0,4	0,2	0,4	n.b.	0,3
Restfeuchte	3,7	1,7	0,2	0,2	0,2	0,05	0,05	n.b.	<0,1
Abrieb (Z)	0,1	<0,05	0,4	0,3	<0,05 ^{*)}	<0,05	<0,05	<0,1	2-3
Verpackungs- index	4	4	3	4	1(2)	3(4)	n.b.	2	6(5)
Bruchfestigkeit (N)	n.b.	n.b.	n.b.	17	14	24	12	52	n.b.
Lösegeschwindig- keit (sac) zur Herst. einer 0,1 %igen Lösung bei 20 °C	50	105	85	75	75	70	50	n.b.	70 (Korn > 1 mm)

a) Granulat wurde nach dem Austrag aus dem Reaktor mit 2 % Silikat
(Extrusil, Fa. Degussa) gemischt.

*) Messung an Silikat-freier Probe

n.b. = nicht bekannt

Patentansprüche

1. Alkalicyanid-Granulate auf der Basis von Natriumcyanid oder Kaliumcyanid mit

(i) einem Teilchendurchmesser im Bereich von mindestens 0,1 bis 20 mm für mindestens 99 Gew.-% des Granulats,

(ii) einem Schüttgewicht von mindestens 600 g/dm³

(iv) einem Abrieb von weniger als 1 Gew.-%, gemessen im Roll-Abriebtest (Abriebtester TAR der Fa. Erweka mit 20 g Probe, 60 min 20 U/min),

(v) einem Verbackungsindex von maximal 4, gemessen nach 14-tägiger Belastung von 100 g in einem Zylinder der lichten Weite von 5,5 cm mit 10 kg, dadurch gekennzeichnet, daß sie

(i) aus im wesentlichen kugelförmigen Teilchen mit glatter oder himbeerförmiger Oberflächenstruktur bestehen.

2. Alkalicyanid-Granulate nach Anspruch 1, dadurch gekennzeichnet,

daß sie einen Alkalicyanidgehalt von mindestens 93 Gew.-%, eine Restfeuchte bis maximal 5 Gew.-% und einen Alkalihydroxidgehalt, wobei das Alkalimetall demjenigen des Alkalicyanids entspricht, von maximal 3 Gew.-% aufweisen.

3. Alkalicyanid-Granulate nach Anspruch 1 oder 2, dadurch gekennzeichnet,

daß sie zusätzlich ein Antibackmittel in wirksamer Menge, in den Granulatteilchen oder im wesentlichen auf der Oberfläche derselben gleichmäßig verteilt enthalten und der Verbackungsindex des Granulats vorzugsweise maximal 3 beträgt.

4. Alkalicyanid-Granulate nach Anspruch 3, dadurch gekennzeichnet,

daß sie als Antibackmittel ein in wäßriger Dispersion alkalisch wirkendes Silikat, vorzugsweise in einer Menge von 0,1 bis 2 Gew.-% auf der Oberfläche der Granulatteilchen, enthalten.

5. Alkalicyanid-Granulate nach einem oder mehreren der Ansprüche 1 bis 4, dadurch gekennzeichnet,

daß der mittlere Durchmesser der Teilchen im Bereich von 2 bis 10 mm und das Teilchenspektrum im Bereich des mittleren Teilchendurchmessers plus/minus maximal 1 mm liegt.

6. Verfahren zur Herstellung von Alkalicyanid-Granulaten gemäß den Ansprüchen 1 bis 5 durch Aufsprühen einer mindestens 10 Gew.-% Alkalicyanid enthaltenden wäßrigen Lösung oder Suspension in einer Vorrichtung zur Wirbelschicht-Sprühgranulation auf Alkalicyanid-Keime, Verdampfen des Wassers mittels eines durch die Wirbelschicht strömenden Trocknungsgasstromes, dessen Eingangstemperatur 150 bis 450 °C beträgt, und Austragen des Granulats in an sich bekannter Weise aus der Vorrichtung und Rückführen des anfallenden Staubs in diese, dadurch gekennzeichnet,

daß man die Temperatur der Wirbelschicht auf 110 bis 350 °C einstellt und die wäßrige Lösung oder Suspension mittels einer oder mehrerer innerhalb der Wirbelschicht angeordneter Sprühdüsen, vorzugsweise Zweistoffdüsen auf die Alkalicyanid-Keime sprüht.

7. Verfahren nach Anspruch 6 zur Herstellung von Alkalicyanid-Granulaten nach Anspruch 5, dadurch gekennzeichnet,

daß man eine 20 bis 45 Gew.-%, vorzugsweise 30 bis 40 Gew.-%, Alkalicyanid enthaltende wäßrige Lösung oder Suspension auf Alkalicyanid-Keime mit einem Korndurchmesser von mindestens 500 µm sprüht, wobei die Temperatur der Wirbelschicht im Bereich von 130 bis 300 °C liegt.

8. Verfahren nach einem oder mehreren der Ansprüche 6 bis 7, dadurch gekennzeichnet, daß die wäßrige Lösung oder Suspension außer dem Alkalicyanid das jeweilige Alkalihydroxid in einer Menge bis 3 Gew.-%, bezogen auf das jeweilige Alkalicyanid, oder/und ein Antibackmittel in wirksamer Menge, vorzugsweise ein in wäßriger Dispersion alkalisch wirkende Silikat enthält.
9. Verfahren nach einem oder mehreren der Ansprüche 6 bis 8, dadurch gekennzeichnet, daß man aus der Wirbelschicht-Sprühgranulationsvorrichtung ausgetragenes Granulat mit einem Antibackmittel, vorzugsweise einem Silikat, nachbehandelt, indem man das ausgetragene Granulat in Gegenwart von bis zu 5 Gew.-% Feuchte, bezogen auf Alkalicyanid, mit dem Antibackmittel, das trocken oder in Form einer wäßrigen Suspension zugegeben wird, mischt und, soweit erforderlich, nachtrocknet.

Claims

1. Alkali metal cyanide granules based on sodium cyanide or potassium cyanide with

(i) a particle diameter in the range from at least 0.1 to 20 mm for at least 99 wt.% of the granules,

(ii) a bulk density of at least 600 g/dm³,

(iv) an abrasion of less than 1 wt.% measured in a roller abrasion tester (TAR abrasion tester from Erweka, using 20 g samples, 60 min., 20 rpm),

(v) a caking index of at most 4, measured after applying a load of 10 kg to 100 g in a cylinder with an internal width of 5.5 cm for 14 days, characterised in that it comprises

(i) substantially spherical particles with a smooth or raspberry-like surface structure,

2. Alkali metal cyanide granules according to Claim 1, characterised in that they have an alkali metal cyanide content of at least 93 wt.%, a residual moisture content of up to a maximum of 5 wt.% and an alkali metal hydroxide content, wherein the alkali metal corresponds to that in the alkali metal cyanide, of at most 3 wt.%.

3. Alkali metal cyanide granules according to Claim 1 or 2, characterised in that they also contain an anti-caking agent in effective amounts, uniformly distributed in the granular particles or substantially on the surface of the same, and that the caking index of the granules is preferably a maximum of 3.

4. Alkali metal cyanide granules according to Claim 3, characterised in that they contain, as anti-caking agent, a silicate which is alkaline in aqueous dispersion, preferably in an amount of 0.1 to 2 wt.%, on the surface of the granules.

5. Alkali metal cyanide granules according to one or more of Claims 1 to 4, characterised in that the average diameter of the particles is in the range 2 to 10 mm and the particle size distribution is in the range comprising the average particle diameter plus or minus a maximum of 1 mm.

6. A process for preparing alkali metal cyanide granules according to Claims 1 to 5 by spraying an aqueous solution or suspension containing at least 10 wt.% of alkali metal cyanide onto alkali metal cyanide nuclei in a device for fluidised bed spray-granulation, evaporating the water by means of a current of drying gas, whose inlet temperature is 150 to 450°C, flowing through the fluidised bed and discharging the granules from the device in a manner known per se and returning thereto any dust which arises, characterised in that the temperature of the fluidised bed is adjusted to 110 to 350°C and the aqueous solution or suspension is sprayed onto the alkali metal nuclei by means of one or more spray-nozzles, preferably two-fluid nozzles, located within the fluidised bed.

7. A process according to Claim 6 for preparing alkali metal cyanide granules according to Claim 5, characterised in that an aqueous solution or suspension containing 20 to 45 wt.%, preferably 30 to 40 wt.%, of alkali metal cyanide is sprayed onto alkali metal cyanide nuclei with a particle diameter of at least 500 µm, wherein the temperature of the fluidised bed is in the range 130 to 300°C.

8. A process according to one or more of Claims 6 to 7, characterised in that the aqueous solution or suspension contains, in addition to the alkali metal cyanide, the relevant alkali metal hydroxide in an amount of up to 3 wt.%, with reference to the relevant alkali metal cyanide, and/or an anti-caking agent in an effective amount, preferably a silicate which is alkaline in aqueous dispersion.

9. A process according to one or more of Claims 6 to 8, characterised in that the granular material discharged from the fluidised bed spray-granulation device is subsequently treated with an anti-caking agent, preferably a silicate, by mixing the discharged granular material, in the presence of up to 5 wt.% of moisture, with reference to the alkali metal cyanide, with the anti-caking agent which is added dry or in the form of an aqueous suspension, and, if required, subsequently drying the product.

Revendications

1. Granulés de cyanure alcalin à base de cyanure de sodium ou de cyanure de potassium, présentant:

- (ii) un diamètre particulaire dans la plage d'au moins 0,1 à 20 mm pour au moins 99 % en poids du granulé,
 - (iii) un poids spécifique apparent d'au moins 600 g/dm³,
 - (iv) une abrasion de moins de 1 % en poids, mesurée par le test d'abrasion au rouleau (appareil d'essai d'abrasion TAR de la société Erweka avec un échantillon de 20 g, à 20 tours/min, pendant 60 minutes),
 - (v) un indice d'agglutination de 4 au maximum, mesuré après sollicitation pendant 14 jours de 100 g dans un cylindre d'un diamètre intérieur de 5,5 cm avec 10 kg,
- caractérisés en ce :
- (i) qu'ils sont constitués de particules sensiblement sphériques de structure superficielle lisse ou en forme de framboise.

2. Granulés de cyanure alcalin selon la revendication 1, caractérisés en ce qu'ils présentent une teneur en cyanure alcalin d'au moins 93 % en poids, une humidité résiduaire allant au maximum jusqu'à 5 % en poids et une teneur en hydroxyde alcalin, dont le métal alcalin correspond à celui du cyanure alcalin, de 3 % en poids au maximum.

3. Granulés de cyanure alcalin selon la revendication 1 ou 2, caractérisés en ce qu'ils contiennent en outre un agent antiagglutinant en quantité efficace, réparti uniformément dans les particules ou sensiblement à leur surface, et l'indice d'agglutination du granulé est de préférence de 3 au maximum.

4. Granulés de cyanure alcalin selon la revendication 3, caractérisés en ce qu'ils contiennent comme agent antiagglutinant un silicate à effet alcalin en dispersion aqueuse, de préférence en quantité de 0,1 à 2 % en poids, à la surface des particules de granulés.

5. Granulés de cyanure alcalin selon une ou plusieurs des revendications 1 à 4, caractérisés en ce que le diamètre moyen des particules se situe dans la plage de 2 à 10 mm et le spectre de particules se situe dans la plage du diamètre moyen des particules plus ou moins 1 mm au maximum.

6. Procédé de production de granulés de cyanure alcalin selon les revendications 1 à 5 par pulvérisation sur des germes de cyanure alcalin d'une solution ou d'une suspension aqueuse contenant au moins 10 % en poids de cyanure alcalin, dans un dispositif de granulation par pulvérisation à lit tourbillonnant, évaporation de l'eau au moyen d'un courant de gaz de séchage s'écoulant à travers le lit tourbillonnant, courant dont la température d'entrée est de 150 à 450°C, et extraction du granulé du dispositif de manière connue en soi et recyclage de la poussière produite à ce dispositif, caractérisé en ce qu'on règle la température du lit tourbillonnant à 110 à 350°C et on pulvérise la solution ou la suspension aqueuse sur les germes de cyanure alcalin au moyen d'une ou plusieurs buses de pulvérisation, de préférence de buses doubles, agencées à l'intérieur du lit tourbillonnant.

7. Procédé selon la revendication 6 pour la production de granulés de cyanure alcalin selon la revendication 5, caractérisé en ce qu'on pulvérise une solution ou une suspension aqueuse contenant 20 à 45 % en poids, de préférence 30 à 40 % en poids, de cyanure alcalin sur des germes de cyanure alcalin ayant un diamètre particulaire d'au moins 500 µm, la température du lit tourbillonnant se situant dans la plage de 130 à 300°C.

8. Procédé selon une ou plusieurs des revendications 6 et 7, caractérisé en ce que la solution ou la suspension aqueuse contient, en-dehors du cyanure alcalin, l'hydroxyde alcalin respectif en quantité allant jusqu'à 3 % en poids, par rapport au cyanure alcalin respectif, ou/et un agent antiagglutinant en quantité efficace, de préférence

EP 0 600 282 B1

un silicate à effet alcalin en dispersion aqueuse.

9. Procédé selon une ou plusieurs des revendications 6 à 8, caractérisé en ce qu'on traite le granulé extrait du dispositif de granulation par pulvérisation à lit tourbillonnant par un agent antiagglutination, de préférence, un silicate, en mélangeant le granulé extrait, en présence d'une proportion jusqu'à 5 % en poids d'humidité, par rapport au cyanure alcalin, avec l'agent antiagglutinant, qui est ajouté à l'état sec ou sous la forme d'une suspension aqueuse, et, pour autant que cela soit nécessaire, en séchant.

23 AUG 1999

- 1 -

REPLACEMENT SHEET

ALKALI CYANIDE GRANULES AND PROCESS FOR THE PREPARATION THEREOF

The invention relates to new alkali metal cyanide granules based on sodium cyanide or potassium cyanide, whose particles are substantially spherical and which are characterised by extraordinary properties as compared with previously known granules, including minimal abrasion and a greatly reduced tendency to cake, and a process for preparing the granules.

The two alkali metal cyanide salts sodium and potassium cyanide are used to prepare electrolytic baths and hardening salt baths as well as for the synthesis of organic compounds. In addition, sodium cyanide is used in large amounts to recover gold by cyanide leaching from ores.

Due to their toxicity, the alkali metal cyanides mentioned are preferably handled in the compressed form or as low-dust milling granules. Sodium and potassium cyanide granules which are produced commercially on a large scale consist of irregularly shaped particles with a particle size spectrum which extends, for example, from about 0.2 to about 4 mm. Compressed products are produced using rotating roller presses or ram presses. The granules are prepared by crushing the pressed discs using a milling device. The irregular shape of this type of granule is the reason for undesired dust formation during handling procedures.

Known NaCN and KCN commercially available compressed products, milling granules and powder have a strong tendency to agglomerate and cake on the internal surfaces of piping, fittings and equipment made of steel or stainless steel. The tendency to agglomerate and cake increases with decreasing particle size and in particular with increasing humidity and applied load and makes handling procedures, such as storing in silos, weighing out and transporting, difficult and expensive.

✓ 1. to page 17.
✓ 2. to page 20.
✓ 3. to page 24.
✓ 4. to page 27.

23/8/99

23 AUG 1999

Due to these difficulties, the applicant for the present application looked for a form of supply which did not tend to agglomerate and cake, or at least had a lower tendency to do so. Although NaCN filter cakes which were prepared by known methods could be converted into approximately spherical granules and then dried, the resulting NaCN granules had too low a bulk density, less than 600 g/dm^3 , and the resistance to abrasion was unsatisfactory.

A further disadvantage of the previously known sodium and potassium cyanide granules is the technically complicated process of preparation, which comprises several steps and which starts with aqueous NaCN and KCN solution respectively. In the first step, the alkali metal cyanide is crystallised out of solution, this being performed, for example, in a vacuum crystalliser. The crystallised product is separated from the mother liquor using known techniques. After a single- or multi-stage drying procedure, the alkali metal cyanide powder is compacted to give a compressed product, the latter being crushed to give the granules mentioned. Therefore the process requires not only a large investment in equipment and service personnel, but the evident tendency of NaCN and KCN to cake forces stoppages and reduces the availability of the whole plant.

DE-A 38 32 883 provides the preparation of solid particulate alkali metal cyanides, in particular NaCN, wherein HCN is continuously brought into contact with finely divided droplets of an alkali metal hydroxide solution. The bulk density of non post-treated sodium cyanide is generally in the range 0.2 to 0.4 kg/l. Although the product can be granulated in a fluidised bed, this document does not disclose either the process parameters for this or the materials characteristics of the granular material.

23 AUG 1999

3

REPLACEMENT SHEET

US patent 4,107,274 discloses reducing the tendency to cake of alkali metal halides and mixtures containing these by adding a hydrophilic and/or hydrophobic material, for example a metal silicate, in combination with a complex iron cyanide on a hydroxyl group-containing support. This document does not disclose reducing the tendency to cake of alkali metal cyanides by adding only metal silicates.

Glatt Ingenieurtechnik GmbH, Weimar, describe a plant for continuous granulation and drying, in their company document Glatt® AGT (Feb. 92 - 3000 D (W)), which is based on the principle of the technique also known as fluidised bed spray granulation (see H. Uhlemann in Chem.-Ing. Technik 62 (1990) no. 10, pp. 822-834) and describe its application to, inter alia, "carbonates and cyanides". However, it is not evident from the company document mentioned whether this refers to alkali metal, alkaline earth metal or heavy metal cyanides or to complex cyanides. Also, no data relating to the properties of the cyanide granules can be gathered from the company document. It is evident from the company document mentioned above that the spray nozzles in the fluidised bed dryer are arranged in such a way that the solution to be sprayed is sprayed onto the fluidised bed from above. The article by Uhlemann discloses the basic principles of spray granulation, including the use of two-material nozzles and a variety of possibilities for positioning the same in the fluidised bed spray granulation device.

According to the process disclosed in EP-A 0 600 211, solid sodium cyanide granules with a diameter of 2 to 6 mm can be produced in two process steps, wherein in a first step an aqueous sodium cyanide solution is sprayed into a fluidised bed granulator and granules are produced using warm air
35 from a second fluidised bed granulator connected in series; the air supplied to the first step is cooled to a temperature of 60 to 90°C in the fluidised bed in the first -

step. The material is then dried in the second step, wherein the air supply has a temperature of 150 to 230°C.

The object of the invention is thus to provide alkali metal cyanide granules based on sodium or potassium cyanide in which the disadvantages of the commercial granules described above are greatly reduced. In addition, the granules are characterised by a specific combination of properties. A further object is directed at providing a method which allows the new granules to be produced by fluidised bed spray granulation, wherein problems with incrustations, such as those which occur in previously disclosed processes, are intended to be avoided.

Alkali metal cyanide granules based on sodium or potassium cyanide were found with

- (ii) a particle diameter in the range from at least 0.1 mm to 20 mm for at least 99 wt.% of the granules,
- (iii) a bulk density of at least 600 g/dm³,
- (iv) an abrasion of less than 1 wt.%, measured in the roller abrasion test (TAR abrasion tester from Erweka using 20 g samples, 60 min, 20 rpm),
- (v) a caking index of at most 4, measured after applying a load of 10 kg to a mass of 100 g in a cylinder with an internal width of 5.5 cm for 14 days,

which are characterised in that they comprise

- (i) substantially spherical particles with a smooth or raspberry-like surface structure.

Alkali metal cyanide granules according to the invention have in general a content of at least 80 wt.%, preferably

at least 93 wt.% of sodium or potassium cyanide. In addition to residual moisture, which surprisingly may assume a value of up to a maximum of 5 wt.%, but is preferably less than 3 wt.%, and in particular less than 1 wt.%, the granules may also contain, in addition to side products which depend on the raw materials and process, such as alkali metal hydroxide, alkali metal formate and alkali metal carbonate, the side products mentioned in larger than customary amounts and/or other auxiliary substances, in order to modify certain properties of the granules in a deliberate manner.

Production of alkali metal cyanide granules with elevated water contents, from more than about 1 wt.% to 5 wt.%, leads to a saving of drying energy. This type of granule is of economic interest if the consumer dissolves the granules in water in any case. Contrary to expectations, granules according to the invention with elevated water contents are also sufficiently resistant to caking.

In the mining industry, for example, it is of interest to obtain sodium cyanide with a higher sodium hydroxide content than the customarily present 0.2 to 0.6 wt.% because sodium hydroxide generally has to be added during the production of dilute, aqueous solutions in mines. The production of sodium cyanide granules with an NaOH content of up to a maximum of 3 wt.% presents no problems.

The other auxiliary substances may be distributed uniformly in the individual granules or they may be distributed uniformly on the surface of the granules. The auxiliary substances are, for instance, anti-caking agents, which are suitable for further reducing the tendency to cake of the alkali metal cyanide granules according to the invention, which is already reduced as compared with the commercially available granules. A reduced tendency to cake of this type is of importance if the granules have to be temporarily

23 AUG 1999

stored in silos, in particular in areas with humid climates. Anti-caking agents may be present in effective amounts in or on the granules. Here, effective means that the caking index is lower due to the presence of the anti-caking agent than in its absence. Granules which contain anti-caking agent preferably have a caking index of at most 3.

Suitable anti-caking agents may be selected, for example, from the group of hydrophobic organic compounds such as Na or K salts of higher fatty acids. Another group consists of natural and synthetic silicas and/or silicates. Although hydrophobic silicas and silicates are not excluded, hydrophilic substances are generally preferred, because there are then no wetting problems with the granules in aqueous systems. Silicates which are alkaline in aqueous dispersion are particularly preferred, in particular (Na, Ca) silicates and sodium aluminium silicates.

The amount used of the preferably hydrophilic silicates is between 0.1 and 5 wt.% in the case of uniform distribution within the granules. If one or more of the silicates is located substantially on the surface of the granules, the amount used is generally between 0.01 and 4 wt.%, in particular between 0.1 and 2 wt.%. Preferred silicates have a BET surface area (DIN 66131) of about 30 to 120 m²/g and a pH in a 5 % strength aqueous suspension of 7 to 12, in particular 9 to 12. The major components are in the range 40 to 92 % SiO₂, 0 to 36 % Al₂O₃, 2 to 22 % Na₂O, 0 to 6 % CaO, silicates with 90 to 92 % SiO₂, 5 to 7 % CaO and about 2 % Na₂O being particularly preferred.

The amount of organic hydrophobic agent used, such as e.g. Na or K stearate, which is admixed with the final granules and is thus located substantially on the surface of the particles, is 0.1 to 4 wt.%, in particular 0.1 to 2 wt.%. This type of hydrophobic agent slows down the absorption of

moisture by hygroscopic alkali metal cyanides from the air and reduces the tendency to agglomerate.

The substantially spherical granulate particles have a smooth or raspberry-like surface structure. The expression "substantially" indicates that slight deviations from the spherical form, for example slightly ovoid shapes, are included.

The diameter of the particles comprising NaCN and KCN granules according to the invention is substantially in the range from at least 0.1 mm to 20 mm. The expression "substantially" indicates that at least 99 wt.% of the granules lies within the range. A preferred range is between 1 and 10 mm. Granules produced by the process according to the invention are further characterised in that the particle spectrum is very narrow. For an average particle diameter in the range from 2 to 9 mm, the diameter of the particles is substantially within the range of the average particle diameter plus or minus less than 1 mm, preferably plus or minus less than 0.5 mm.

The bulk density of the granules is of technical importance. Generally the bulk density is above 650. Preferred granules have a bulk density of greater than 700 g/l to 950 g/l. In view of the toxicity of alkali metal cyanides and thus the high investment in packaging which is required, specialists are interested in as high a bulk density as possible. As already explained above, it has hitherto proved difficult to produce granules which have the combination of properties in accordance with the Claims with respect to shape and size of particles, minimal abrasion and reduced tendency to cake and which at the same time have a high bulk density in the desired range.

The caking index of the granules according to the invention is at most 4, preferably at most 3.

The caking index, also called the crushing strength, is determined by applying a load to the samples under specific conditions and is evaluated by using an assessment scale. To perform this procedure, 100 g samples are placed in a tubular cylinder with holes ($\varnothing$ 1 mm) to allow air to escape and an internal width of 55 mm, placed vertically on a base, and a 10 kg load is applied by means of a ram. The loading period is 14 days at room temperature (20 to 25°C) and atmospheric humidity (50 to 70% relative humidity). After removing the ram, the cylinder is lifted off and the caking behaviour assessed.

Index

Criteria

-
- | | |
|---|--|
| 1 | completely unchanged; free-flowing |
| 2 | some loose cohesion;
readily disintegrates into the original
state |
| 3 | loosely moulded: largely disintegrates under
slight finger pressure |
| 4 | loosely agglomerated: still disintegrates
with moderate finger pressure |
| 5 | semi-solid; no longer disintegrates under
finger pressure |
| 6 | firmly moulded |

Granules according to the invention are substantially resistant to abrasion, wherein particles smaller than

23 AUG 1999

9

REPLACEMENT SHEET

0.1 mm are understood to be the result of abrasion. The spherical shape of the granules leads to virtually no abrasion. Abrasion, measured in the roller abrasion test (TAR abrasion tester from Erweka Apparatebau GmbH, Heusenstamm, Germany, using a 20 g sample, rotation for 1 hour at 20 rpm) is less than 1 wt.%, generally less than 0.5 wt.%. Abrasion of commercially available granules, sieved to give particles larger than 1 mm, in contrast, is 2 to 3 wt.%. If granules prepared according to the invention are compared with a comparable sieve fraction from commercially available granules, the abrasion of the granules according to the invention is generally less than one tenth of the value of the corresponding fraction of the commercially available granules. The good flow properties of granules according to the invention and the high resistance to abrasion contribute greatly to easier and safer handling.

As explained above, sodium cyanide granules and potassium cyanide granules according to the invention have much better material properties in several respects which are relevant in practical situations, as compared with commercially available granules. Granules according to the invention are free-flowing and form virtually no dust during handling, in contrast to commercially available granules. The granules can be stored in silos, due to their greatly reduced tendency to cake, and be withdrawn as needed, this being virtually impossible with previously known granules. Silo vehicles can be readily emptied and the washing-out procedure which has hitherto been required is unnecessary. It could not have been predicted that the material properties in accordance with the Claims could be combined in one and the same granular material.

A process was found for preparing the alkali metal cyanide granules based on sodium cyanide or potassium cyanide according to the invention by spraying an aqueous solution

23 AUG 1999

REPLACEMENT SHEET

10

or suspension containing at least 10 wt.% of alkali metal cyanide onto a fluidised bed consisting of alkali metal cyanide nuclei in a device for fluidised bed spray granulation, evaporating the water by means of a current of drying gas, whose inlet temperature is 150 to 450°C, flowing through the fluidised bed and discharging the granules from the device in a manner known per se and returning thereto any dust which arises, characterised in that the temperature of the fluidised bed is adjusted to 110 to 350°C and the aqueous solution or suspension is sprayed onto the alkali metal cyanide nuclei by means of one or more spray-nozzles, preferably two-fluid nozzles, located within the fluidised bed.

The structure and method of operation of a fluidised bed spray granulation device to be used according to the invention can be found in the document cited at the beginning. The drying gas is generally air, and either throughput air or circulating air may be used. With regard to the ready formation of alkali metal carbonates from the alkali metal cyanide solution and carbon dioxide from the air, the use of circulating air is preferred. The drying air emerging from the fluidised bed spray granulator is thus reheated, after drying, and used to operate the granulator. The initial temperature of the drying gas is generally in the range between 150 and 450°C, preferably above 200°C. The drying gas leaves the granulator in general at a temperature between 70 and 300°C, preferably above 110°C.

For problem-free granule formation, it is essential to coordinate the fluidised bed temperature with the density of the nuclei in the fluidised bed and the rate of spraying. A person skilled in the art will determine these parameters in optimising tests. The temperature of the fluidised bed is preferably maintained between 130 and 300°C. To produce granules with predominantly a raspberry-

23 AUG 1999

like structure, the fluidised bed is generally operated at a lower temperature and higher spray rate than to produce granules with smooth surfaces. If the density of nuclei is too high, particularly in the event of too high a spray rate, there is a risk of the fluidised bed breaking down due to too great a formation of agglomerates.

The solution or suspension being sprayed into the fluidised bed preferably has an NaCN or KCN content of 20 to 45 wt.%, in particular 30 to 40 wt.%. If desired, the solution or suspension also contains suitable effective amounts of additives and/or auxiliary substances for modifying the properties, these being selected in accordance with the intended application.

The aqueous solution or suspension is sprayed onto the alkali metal cyanide nuclei by means of one or more spray nozzles located within the fluidised bed. A wide variety of types of nozzle may be used; two-fluid nozzles with external mixing are preferred. The amount of liquid to be sprayed is adjusted by a person skilled in the art in such a way that stability of the fluidised bed is maintained during the spraying procedure. Here, stability is understood to mean that the number of nuclei remains substantially constant. If the number of nuclei is too low, then it is increased by introducing finely divided material, for example from a dust separator and/or a mill which is used to break up oversized particles. In the case of too high a rate of formation of nuclei, the desired particle size is no longer satisfactorily reached and the number of nuclei has to be decreased.

Fluidised bed spray granulation may be performed either batchwise or continuously. Appropriate units are obtainable commercially. In the case of batchwise operation, all of the granular material is withdrawn from the fluidised bed after reaching the desired particle size. A device for

23 AUG 1999

continuous fluidised bed spray granulation normally also includes a device for inspecting the granules. The inspection device may be either integrated into the fluidised bed spray granulation device or arranged outside the same.

It could not have been predicted that alkali metal cyanide granules according to the invention with the set of properties described would be obtained by the combination of process features in accordance with the Claims. Furthermore, a person skilled in the art would not have expected to be able to prepare alkali metal cyanide granules using fluidised bed spray granulation without considerable hydrolysis of the cyanide taking place to give formate and ammonia, even though moist cyanide is subjected to an elevated temperature for a long period of time (e.g. 0.5 to 4 hours). The rate of dissolution of granules prepared according to the invention is within the range for commercially available granules. This was also surprising because when other products are prepared by fluidised bed spray granulation, such as sodium perborate monohydrate (DE-OS 28 13 326), there is a distinct increase in time of dissolution.

The auxiliary substances for reducing the caking behaviour, mentioned previously in the description of the alkali metal cyanide granules according to the invention, can be incorporated in the granules or deposited onto the surface of the same in various ways. If the auxiliary substance is intended to be uniformly distributed in the granules, it is expedient to introduce the auxiliary substance to the fluidised bed spray granulator in the form of an aqueous solution or suspension separated from or already mixed with the aqueous solution which contains the alkali metal cyanide. In the case of a batchwise operated process, it is generally sufficient to spray the aqueous solution or suspension containing auxiliary substance(s) into the

23 AUG 1999

REPLACEMENT SHEET

13

REPLACEMENT SHEET

fluidised bed after granule production has largely finished, so that the auxiliary substance(s) is/are substantially located on the surface of the granules. If the fluidised bed spray granulator is operated continuously, incorporation of the auxiliary substance(s) in uniform distribution into the granules takes place in the same way as in the batchwise embodiment. In order to keep the amount of auxiliary substance(s), for instance anti-caking agent from the silicate group, small, it is recommended that these substances be applied substantially to the surface of the granules by spraying the granules being discharged from the fluidised bed spray granulator with either an aqueous solution or suspension of the auxiliary substance(s) and removing the water introduced in a subsequent drying step. This process may be performed, for example, in a second fluidised bed spray granulator or fluidised bed dryer with a spray device in the first zone. Alternatively, the auxiliary substance(s) may also be applied in the dry form to the granules withdrawn from the granulator, which has a residual moisture content of up to 5 wt.%, for instance by a simple mixing procedure, followed by drying if required.

In addition to the advantageous properties of the granules prepared according to the invention, the process has a number of advantages. To perform the process, only a fluidised bed spray granulator with the additional devices which are customary for this type of plant is required, thus reducing the hitherto multi-step process in principle to a one-step process. The process according to the invention is also distinguished by a low staffing requirement. Shut down times due to repairs or caking up, and thus restrictions on the availability of the plant, are much shorter than has been the case with the process used hitherto in industry.

23 AUG 1969
REPLACEMENT SHEET**Examples 1 to 9****Preparation of sodium cyanide granules**

The fluidising chamber of a fluidised bed spray granulator consists of a quartz-UV glass vessel with an internal diameter of 150 mm and a length of 530 mm. The feeding base is a screen cloth with a mesh of 144 μm . The nozzle (two-fluid nozzle with adjustable air valves) is mounted centrally over the feeding base. The distance between the feeding base and the nozzle tip is 330 mm.

Upstream of the fluidising chamber is an air-heater with a temperature regulator and air-flow controller. Downstream of the fluidising chamber is a settling zone made from stainless steel with a diameter of 300 mm. The current of air then has the dust removed in a stainless steel cyclone. The fine dust which separates out is returned to the fluidising chamber via a star wheel valve. A waste gas fan with a maximum capacity of 500 m^3/h draws the air through the fluidising chamber and cyclone.

To produce an initial bed capable of being readily fluidised, NaCN nuclei with the particle sizes given in Table 1 are used with the initial amount introduced being 500 g. During the start-up procedure for the plant, the fluidised bed is expanded, after exceeding the loosening point for the initial nuclei, by increasing the rate of flow of drying air (rate of flow with respect to the empty pipe cross-section, ca. 3 m/s), in order to produce the requisite density of material (initial depth to start 330 to 400 mm). 40 wt.% strength aqueous NaCN solution (ca. 23°C) is sprayed onto the nuclei using a nozzle immersed in the fluidised bed (atomising pressure 2 bar). The spray droplets meet the floating NaCN nuclei and are distributed onto these by spreading out. The intensive heat and material exchange in the fluidised bed brings about rapid

solidification of the liquid film due to drying. During growth of the particles, the fluidised bed is further expanded. After achieving a set diameter, fluidised bed granulation is discontinued and the granules are removed from the fluidising chamber.

The operating parameters and material properties are given in Tables 1 and 2.

Table 1

Example No.	1	2	3	4	5	6	7	8*	9**
Operating parameter:									
Initial temp. of air (°C)	250	150	150	250	230	230	250	280	250
Amount of air (m ³ /h)	260	220	393	275	260	260	260	275	390
Temp. of fluidised bed (°C)	180	90	110	150	150	130	180	180	180
Exit temp. of air (°C)	146	79	82	124	122	100	146	157	150
Amount sprayed (l/h)	5.4	6.8	11.3	13.3	8.9	12.9	5.0	8.6	5.4
Diameter of nuclei (mm)	0.5	1.4	2	2	3	3	3	1.4	4.5-5
Spraying time (min.)	160	55	72	50	41	28	75	97	60

16

Granules:

Shape (R = raspberry) (S = smooth sphere)	S	R	S	R	R	R	S	S	S
Diameter (mm)	2	2	5-6	4-5	4.5-5	4.5-5	4.5-5	3	6
Bulk density (g/dm ³)	715	734	798	648	734	740	720	806	652

* 30 wt.% strength solution of NaCN sprayed in.

** A suspension containing 40 wt.% NaCN and 0.6 wt.% of a (Ca,Na) silicate (Extrasil, Degussa) sprayed onto nuclei from example 7.

23 AUG 1999
REPLACEMENT SHEET

Table 2

Material properties of the granules

Example No.	2	3	4	5	6*	7	8	9	for comparison: milled granules (commercial product 0.2-4 mm particle spectrum
Composition (wt.%)									
NaCN	94.2	96.5	97.1	97.4	97.2	96.9	95.5	n.k.	>98.0
NaOH	0.5	0.7	0.7	0.3	0.7	0.3	0.3	n.k.	0.5
Na ₂ CO ₃	1.7	1.1	1.7	1.8	1.3	2.5	3.3	n.k.	0.4
Na formate	0.1	0.2	0.3	0.3	0.4	0.2	0.4	n.k.	0.3
Resid. moisture	3.7	1.7	0.2	0.2	0.2	0.05	0.05	n.k.	<0.1
Abrasion (%)	0.1	<0.05	0.4	0.3	<0.05**	<0.05	<0.05	<0.1	2-3
Caking index	4	4	3	4	1(2)	3(4)	n.k.	2	6(5)
Breaking strength (N)	n.k.	n.k.	n.k.	17	14	24	12	52	n.k.
Rate of dissolution (sec) to prepare a 0.1% strength solution at 20°C	50	105	85	75	75	70	50	n.k.	70 (particles >1 mm)

* Granules were mixed with 2% silicate (Extrusil, Degussa) after withdrawal from the reactor.

** Measured using Si-free sample.

n.k. = not known.



23 AUG 1999

REPLACEMENT SHEET

18

Claims

1. Alkali metal cyanide granules based on sodium cyanide or potassium cyanide with
 - (ii) a particle diameter in the range from at least 0.1 to 20 mm for at least 99 wt.% of the granules,
 - (iii) a bulk density of at least 600 g/dm³,
 - (iv) an abrasion of less than 1 wt.% measured in a roller abrasion tester (TAR abrasion tester from Erweka, using 20 g samples, 60 min., 20 rpm),
 - (v) a caking index of at most 4, measured after applying a load of 10 kg to a mass of 100 g in a cylinder with an internal width of 5.5 cm for 14 days,characterised in that they comprise
 - (i) substantially spherical particles with a smooth or raspberry-like surface structure,
2. Alkali metal cyanide granules according to Claim 1, characterised in that they have an alkali metal cyanide content of at least 93 wt.%, a residual moisture content of up to a maximum of 5 wt.% and an alkali metal hydroxide content, wherein the alkali metal corresponds to that in the alkali metal cyanide, of at most 3 wt.%.
3. Alkali metal cyanide granules according to Claim 1 or 2, characterised in that they also contain an anti-



23 AUG 1999
REPLACEMENT SHEET

19

- caking agent in effective amounts, uniformly distributed in the granular particles or substantially on the surface of the same, and that the caking index of the granules is preferably a maximum of 3.
4. Alkali metal cyanide granules according to Claim 3, characterised in that they contain, as anti-caking agent, a silicate which is alkaline in aqueous dispersion, preferably in an amount of 0.1 to 2 wt.%, on the surface of the granules.
 5. Alkali metal cyanide granules according to one or more of Claims 1 to 4, characterised in that the average diameter of the particles is in the range 2 to 10 mm and the particle size distribution is in the range comprising the average particle diameter plus or minus a maximum of 1 mm.
 6. A process for preparing alkali metal cyanide granules according to Claims 1 to 5 by spraying an aqueous solution or suspension containing at least 10 wt.% of alkali metal cyanide onto alkali metal cyanide nuclei in a device for fluidised bed-spray-granulation, evaporating the water by means of a current of drying gas, whose inlet temperature is 150 to 450°C, flowing through the fluidised bed and discharging the granules from the device in a manner known per se and returning thereto any dust which arises, characterised in that the temperature of the fluidised bed is adjusted to 110 to 350°C and the aqueous solution or suspension is sprayed onto the alkali metal cyanide nuclei by means of one or more spray-nozzles, preferably two-fluid nozzles, located within the fluidised bed.
 7. A process according to Claim 6 for preparing alkali metal cyanide granules according to Claim 5, characterised in that an aqueous solution or



23 AUG 1999

REPLACEMENT SHEET

20

suspension containing 20 to 45 wt.%, preferably 30 to 40 wt.%, of alkali metal cyanide is sprayed onto alkali metal cyanide nuclei with a particle diameter of at least 500 μm , wherein the temperature of the fluidised bed is in the range 130 to 300°C.

8. A process according to one or more of Claims 6 to 7, characterised in that the aqueous solution or suspension contains, in addition to the alkali metal cyanide, the relevant alkali metal hydroxide in an amount of up to 3 wt.%, with reference to the relevant alkali metal cyanide, and/or an anti-caking agent in an effective amount, preferably a silicate which is alkaline in aqueous dispersion.
9. A process according to one or more of Claims 6 to 8, characterised in that the granular material discharged from the fluidised bed spray-granulation device is subsequently treated with an anti-caking agent, preferably a silicate, by mixing the discharged granular material, in the presence of up to 5 wt.% of moisture, with reference to the alkali metal cyanide, with the anti-caking agent which is added dry or in the form of an aqueous suspension, and, if required, subsequently drying the product.

23 AUG 1999

REPLACEMENT SHEET

- 21 -

ALKALI CYANIDE GRANULES AND PROCESS FOR THE PREPARATION THEREOF

Abstract

The invention relates to new alkali metal cyanide granulates based on sodium cyanide or potassium cyanide and a method for their preparation.

Commercially available alkali metal cyanide granulates consist of irregular particles. Disadvantages are in particular the tendencies to form dust and to cake.

The alkali metal cyanide granulates according to the invention demonstrate virtually no abrasion and a reduced tendency to cake. The granulates are characterised by essentially spherical particles with particle diameters in the range 0.1 to 20 mm, a bulk density of more than 600 g/dm³, an abrasion of less than 1% and a caking index of at most 4.

The granulates can be prepared by fluidised bed spray granulation, by spraying an aqueous solution containing alkali metal cyanide onto alkali metal cyanide nuclei in a fluidised bed and evaporating the water.