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(54) **METHOD FOR INCREASING THE DRY RESIDUE IN PROCESSED CYCLONE DUST**

(76) Inventors: **Hans-Jorg Bonath**, Oberkirch (DE); **Georg Bombeck**, Leverkusen (DE)

Correspondence Address:
Rodney T. Hodgson, Ph.D.
822 Pines Bridge Rd.
Ossining, NY 10562 (US)

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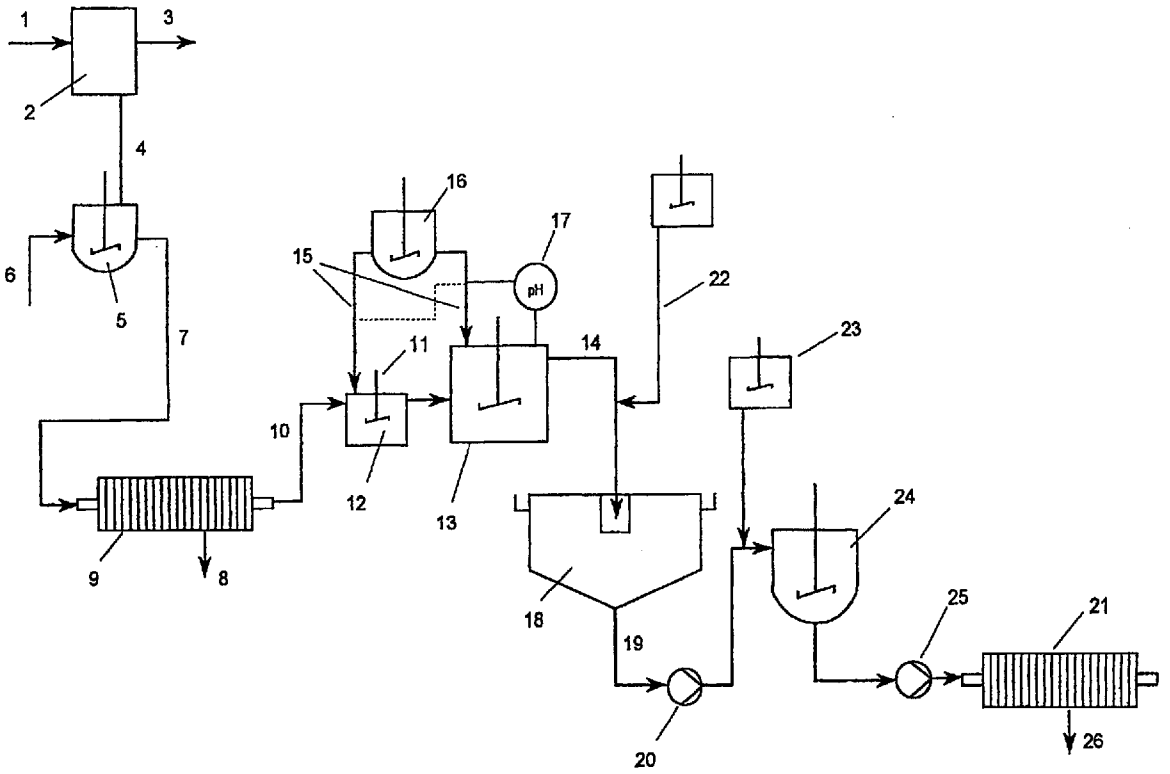
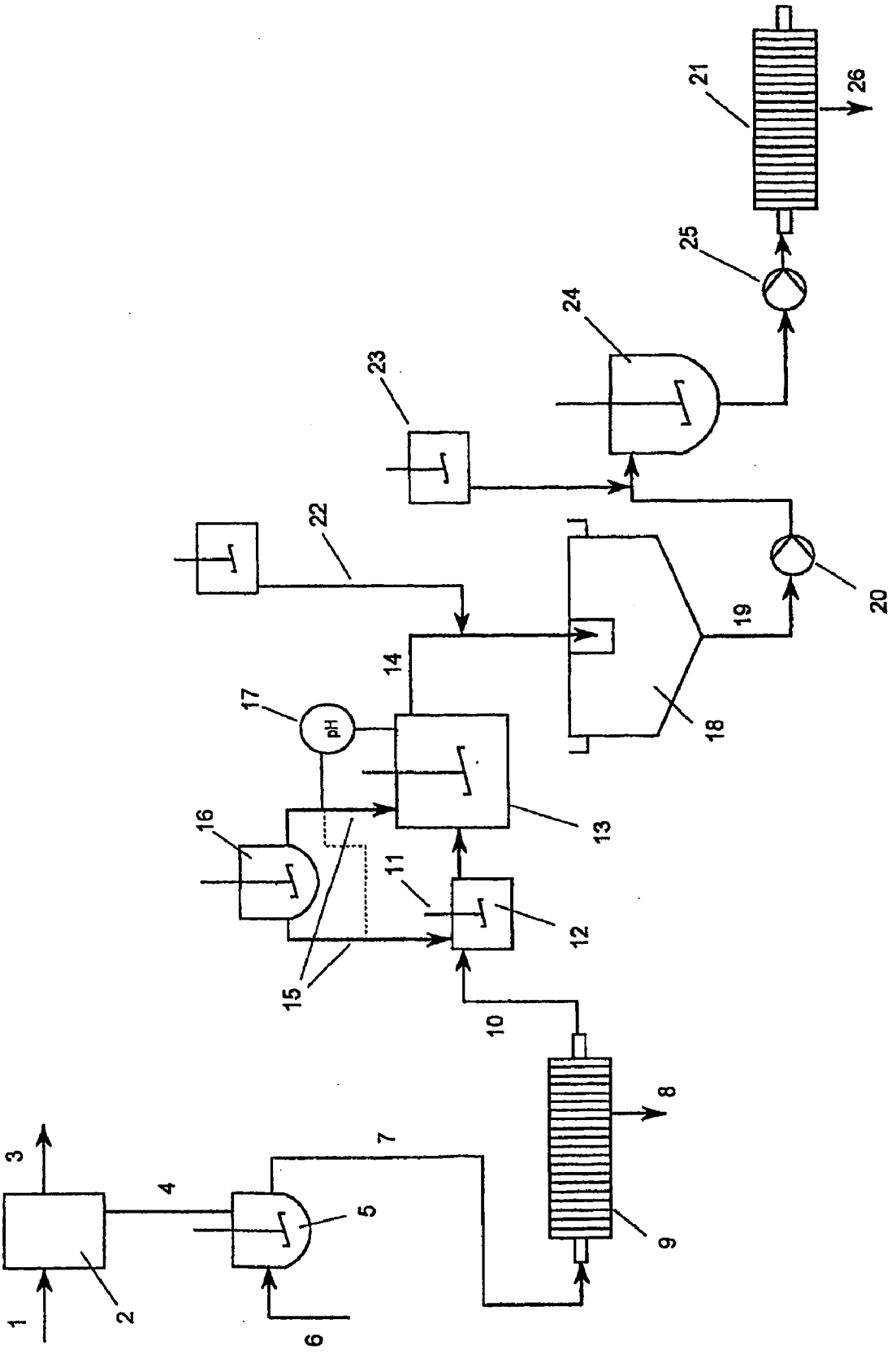
(57) **ABSTRACT**

During processing of cyclone dust **(4)** resulting from the chlorination of titanium ore, a disposable filter cake **(26)** having a dry residue of greater than 40% (without inert portions serving as a supporting structure), regardless of whether ilmenite, slag or natural or artificial rutile or mixtures thereof were used as a raw material, is obtained when one or a combination of the following method steps is carried out: before increasing to a pH value ranging from 9 to 12 in a neutralization tank **(13)**, a rapid neutralization step **(12)** is conducted whereby for all volume elements of the liquid, the same precipitation conditions can be maintained in a pH range of 6 to 9; a (preferably anionic) flocculation aid **(22)** is added before thickening, and; a (preferably cationic) second flocculation aid is mixed into the slurry after thickening. All measures improve the flocculation and render the processing more economical.

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METHOD FOR INCREASING THE DRY RESIDUE IN PROCESSED CYCLONE DUST

[0001] The invention relates to a method for processing, in a manner suitable for landfilling, heavy-metal chlorides obtained in the form of cyclone dust during the manufacture of titanium dioxide by the chloride process, where insoluble constituents are first separated from the cyclone dust slurried with water or acids, after which the pH value of the solution is raised to a pH ranging from 9 to 12 by adding a neutralising agent, the heavy metals are precipitated in the form of hydroxides, and the hydroxides are thickened in the form of sludge and further dewatered.

[0002] A method of this kind is known from DE 41 31 577 A1, which describes that the (heavy) metal chlorides—except iron chloride—inevitably occurring during the manufacture of titanium dioxide by the chloride process have to be converted into products suitable for landfilling and that a filter cake suitable for landfilling is obtained if the inert constituents also contained in the cyclone dust are not separated prior to neutralisation of the dust, thereby accepting that the volume for landfilling becomes substantially larger and the re-usable, inert components of the cyclone dust are dispensed with. If the teaching given in DE 41 31 577 A1 is applied, it is also possible to obtain a filter cake suitable for landfilling with a dry residue of less than 40%, usually in the region of 35%, without inert materials as a filter aid when using slag or slag/rutile blends consisting predominantly of slag as the raw material. However, when using natural or synthetic rutile in the chloride process, the known method of reprocessing causes the dry residue to drop below the thixotropy limit during sludge dewatering. A filter cake of this kind cannot be handled and is not suitable for landfilling.

[0003] The object of the invention is a method for the economical, industrial-scale reprocessing of heavy-metal chlorides occurring during the chlorination of titanium ore; in particular, a product suitable for landfilling with a dry residue of more than 40% is to be obtained from the cyclone dust following separation of the inert constituents, regardless of the raw material used.

[0004] The object is solved in that a readily filterable floccule is produced in the course of the process, this being achieved by one—or preferably a combination—of the following process improvements: Rapid, homogeneous pre-neutralisation to a pH value in the range from 6 to 9 is carried out prior to adjusting the pH value to between 9 and 12 in the neutralisation stage.

[0005] A (preferably anionic) flocculant is mixed into the suspension containing the precipitated heavy-metal hydroxides prior to thickening.

[0006] A (preferably cationic) flocculant is mixed into the thickened sludge.

[0007] It is advantageous to dewater the sludge in a membrane filter press, the filter pressure preferably being above 4 bar and the repressing pressure above 10 bar. Each of these individual measures—and certainly any combination—results in a filter cake suitable for landfilling with a dry residue of over 40% by weight without inert materials as a filter aid, regardless of the raw material fed into the chlorinator.

[0008] The invention is illustrated in the drawing, and an example is described in further detail below. The Figure shows a diagram of the process for reprocessing cyclone dust.

[0009] When manufacturing titanium dioxide by the chloride process, the volatile metal chlorides **(1)** formed in the chlorinator are cooled to such an extent that, apart from titanium tetrachloride, they are all separated in a cyclone **(2)** in condensed form along with the inert constituents—mainly unreacted ore and coke particles. The titanium tetrachloride **(3)**, which is still gaseous at this temperature, is subsequently condensed (not shown here) and the remaining chlorinator off-gases are passed to a gas scrubber. The solids mixture separated in the cyclone is referred to as cyclone dust **(4)**.

[0010] Slurrying of the cyclone dust **(4)** in a tank **(5)** by adding water and/or acidic process waste water **(6)**, which occurs in the plant and need not be expensively purified due to being used in this way, produces an acidic suspension **(7)**: all metal chlorides are dissolved, while the inert solid particles **(8)**, coke and unreacted ore, remain unchanged and can be put to further use. They can easily be separated in a filter **(9)**.

[0011] The Figure outlines a method according to the invention, by which none of the heavy metals present in the solution **(10)** are to be selectively recovered; all heavy-metal ions are to be landfilled as unserviceable material. They are converted into metal hydroxides by neutralisation. It would be perfectly possible to selectively separate individual ions or ion groups (such as iron or vanadium) at this point and subject them to reprocessing. Process steps of this kind, which are familiar in themselves, do not disrupt or alter the method according to the invention and will therefore not be discussed further.

[0012] It has proven particularly favourable for the dewatering necessary at the end of the process to divide neutralisation into two stages: "rapid" pre-neutralisation and subsequent adjustment. Rapid pre-neutralisation is performed in a stirred **(11)**, small pre-mixing tank **(12)**, this achieving a rapid and, above all, spatially and temporally uniform rise in the pH value, thereby ensuring that, even in the event of fluctuations in the operating cycle, no partial volumes occur in which nucleation and flocculation are spatially and temporally sub-optimum. The pH value increases to between 6 and 9 during pre-neutralisation. A second (larger) neutralisation tank **(13)** is provided for stabilisation and precision adjustment; the suspension **(14)** discharged from there has a uniform pH value of between 9 and 12, preferably in the region of 10. Neutralisation is preferably performed using milk of lime **(15)** from a tank **(16)**. A pH value controller **(17)** is indicated.

[0013] All heavy-metal ions from the cyclone dust are precipitated in the form of hydroxides as a result of this neutralisation. The intermediate connection of the stirred pre-mixing tank **(12)** has an influence on flocculation, appearing primarily to have a positive effect on the uniformity of the floccules.

[0014] Sludge **(19)** settles from the suspension **(14)** in a thickener **(18)** and is conveyed to a filter press **(21)** by a pump **(20)**, via a tank **(24)** and a pump **(25)**.

[0015] Two further measures are capable of exerting a favourable influence on flocculation, with an impact on filterability:

[0016] A first flocculant (22), preferably an anionic flocculant, can be added upstream of the settling tank (18). The anionic flocculants open to consideration include, for example, copolymers of acrylamide and sodium acrylate, the preferred quantity being in the range from 5 to 30 ppm, referred to the total quantity of suspension.

[0017] Also, a second flocculant (23), preferably a cationic flocculant, can be added after thickening (18). The cationic flocculants open to consideration include, for example, cationic acrylamide copolymers, the preferred quantity being in the range from 5 to 30 ppm, referred to the quantity of thickened sludge.

[0018] Also of influence as regards the dry residue of the filter cake (26) to be landfilled is dewatering, which is preferably performed using a membrane filter press (21). The filter pressure should be greater than 4 bar, preferably 10 to 15 bar. Repressing of the sludge is preferably performed at 10 to 15 bar.

[0019] Using these exemplary methods, the dry residue in the filter cake can be increased to more than 45%. This value is achieved regardless of the raw material used. It has been found with the methods presented that the use of both natural and synthetic rutile as the ore to be chlorinated yields a non-thixotropic filter cake suitable for landfilling. With ilmenite or with slag/rutile blends as the starting material, either with or without selective reprocessing of the iron chloride, the advantage lies solely in the high dry solids content of the filter cake obtained during the neutralisation and reprocessing of the metal chlorides.

[0020] The following are the achievable dry residues and quantities for landfilling when using pure rutile:

Method A (Prior Art)

[0021] When neutralising the original suspension without separation of the inert constituents, the filter cake is non-thixotropic; the dry residue reaches 46.5% and the quantity to be landfilled is 1,115 kg per metric ton TiO_2.

Method B (Prior Art)

[0022] If the inert components are removed from the suspension in Method A, the filter cake is thixotropic (not suitable for landfilling); the dry residue reaches only 26.9% and the quantity to be landfilled is 1,270 kg per metric ton TiO_2.

Method C (Prior Art)

[0023] When treating the suspension in accordance with Method III described in DE 41 31 577 A1, the filter cake is non-thixotropic; the dry residue is 38.6% and the quantity to be landfilled is 627 kg per metric ton TiO_2.

Method D

[0024] The method according to the invention produces a non-thixotropic filter cake with 45% dry residue. The quantity to be landfilled is only 538 kg per metric ton TiO_2.

1. Method for reprocessing, in a manner suitable for landfilling, heavy-metal chlorides obtained in the form of cyclone dust during the manufacture of titanium dioxide by the chloride process, where insoluble constituents are first separated from the cyclone dust slurried with water or acids, after which the pH value of the solution is raised into the pH range from 9 to 12 by adding a neutralising agent, the heavy metals are precipitated in the form of hydroxides, and the hydroxides are thickened in the form of sludge and further dewatered, characterised in that the dry residue of the sludge to be landfilled is increased to over 40% by weight as a result of improved flocculation.

2. Method according to claim 1, characterised in that the improved flocculation is promoted by rapidly increasing the pH value to pH 9 prior to precision adjustment of the pH value, this resulting in uniform and rapid adjustment of the pH value in all volume elements of the solution.

3. Method according to claim 1, characterised in that the improved flocculation is promoted by adding a first flocculant prior to thickening in the settling tank.

4. Method according to claim 1, characterised in that the improved flocculation is promoted by adding a second flocculant prior to dewatering of the sludge.

5. Method according to claim 1, characterised in that the improved flocculation is promoted by combining two, or all three, of the measures according to claims 2 to 4.

6. Method according to claim 3, characterised in that an anionic flocculant is used as the first flocculant.

7. Method according to claim 4, characterised in that a cationic flocculant is used as the second flocculant.

8. Method according to one or more of claims 1 to 7, characterised in that the sludge is dewatered with a membrane filter press.

9. Method according to claim 8, characterised in that the filter pressure in the membrane filter pressure is greater than 4 bar.

10. Method according to claim 8 or 9, characterised in that the repressing pressure in the membrane filter press is greater than 10 bar.

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