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(54) Use of sugar-mill carbonatation muds in paper-making

Verwendung von Carbonatationsschlämmen aus Zuckerfabriken in der Papierherstellung

Utilisation de boues de carbonatation de fabrication de sucre dans la fabrication du papier

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Description

[0001] The present invention refers to the preparation and use of carbonatation muds deriving from sugar-beet processing.

[0002] According to this invention, the carbonated muds are the product of reaction between the lime solution used for purifying sugar extraction juices and acid gases, coming from the heat decomposition of limestone and from the combustion of organic fuels.

[0003] The following description refers particularly to paper and to beet-processing residuals, but the process described is equally useful for producing card or board and for using sugar-cane processing residuals.

[0004] Recently, some of the inventors provided a paper-making process that foresees the use of depleted sugar-beet pulp. This sugar production by-product is used in its integral form for making paper, as described in European patent N. 644293.

[0005] And still within the scope of the studies by some of the inventors of the present application; the use of seaweed in its integral form was studied, as described in European patent N. 565920.

[0006] Continuing in research for the potential use of low-cost materials in paper-making, and in particular waste materials coming from other productions, some of the inventors found and described in the European patents 645491 and 644293 a use for substances of agricultural-industrial origin to partly or totally replace the mineral fillers normally put in the paper, and even replacing part of the actual wood-pulp.

[0007] Particularly useful for paper making were found to be vegetable substances consisting in the wastes or residuals of several agricultural processes, such as integral straw, integral corn, corn-cobs, wheat bran, chaff of rice and other cereals, sugar-cane processing residuals, seed residuals after the extraction of oils, the residuals after the extraction of starch from corn, tapioca (kassava), grape residuals from the extraction of wine, the residuals of distillates and the vegetable residuals coming from agricultural-food processing.

[0008] According to a fundamental aspect of the processes prepared for using the above mentioned substances, these are dried at a temperature of not higher than 150°C and subsequently reduced to powder (flour) by means of micronizing mills and technologies commonly used to produce flours for food use.

[0009] During research for using the abovementioned flours in paper making, it was found that one of the very important characteristics is solubility in water, which must be reduced as much as possible in order to prevent the releasing of considerable amounts of solutes into the paper-making process waters.

[0010] Many solutes cause considerable worsening in the productiveness of quality paper and a considerable increase in pollution of the paper machine effluents.

[0011] Another consequence of solutes in the process waters is an increase in treatment costs for purifying the effluents with the need to reappraise and reorganize the antipollution plants.

[0012] Drops in yield consequent to the losses of colloids and salts in the process waters are the cause of web breakage with subsequent industrial losses.

[0013] In order to be industrially usable it is therefore essential that these flours are mixed with suitable colloids or agglomerating or their mixtures to reduce the water solubility of their soluble components.

[0014] The use of inorganic materials as filler or as coat in the paper-making industry is very widespread and mainly concerns kaolin and calcium carbonate.

[0015] These minerals are extracted from quarries and mines with subsequent problems to the environment and landscape, in addition to being non-renewable raw materials.

[0016] The replacing of minerals or part of these with industrial residuals which would otherwise be intended for elimination as wastes in dumps, is therefore a very important operation, not only from the economic standpoint but also from an environmental standpoint.

[0017] EP-A-0644293 discloses a process for manufacturing paper from sugar-beet pulp, comprising the steps of drying the integral sugar-beet pulp, grinding the dried pulp to a particle size of from 0.1 to 500µm, adding the pulp to cellulose mix to make paper and converting the mixture in paper in a papennaking machine. The present invention also relates to paper obtained from the above-described process.

[0018] DE 3922310 discloses the utilization of wastes from sugar production from beet comprising contacting the waste, under spray conditions, with chimney gas of a combustion plant, then using the product for soil improvement of growth media. The treatment removes SO₂ (and other acidic pollutants) from the gas and simultaneously lowers the pH of the waste material, making it suitable for neutralizing lightly over-acidified soils.

[0019] Proceeding in research for alternative raw materials useful for making paper and board, the Applicant has now found a new process enabling the use of muds (commonly called sludge) deriving from the processing of sugar-beet and/or sugar cane, while at the same time recovering the carbon dioxide and other acid gases contained in the fumes coming from decomposition of limestone and from the combustion of traditional fuels used for producing sugar.

[0020] It appears immediately clear how the use of combustion fumes and depleted beet pulps, as foreseen in the present invention, represents a particularly advantageous process from the energy standpoint, considering the possi-

bility of using the muds merely filtered without drying them, and for the reduced consumption of non-renewable mineral substances (use of the carbon and sulphur contained in the combustion fumes).

[0021] A further advantageous characteristic of the invention's process is the fact that by using waste products such as depleted beet pulp and the carbonated muds deriving also from the combustion fumes of heating plants, substances directly usable in paper making are obtained.

[0022] Although the quantity of lime used in sugar mills varies according to the characteristics of the beets used it can be appraised that, on average, for every 100 kg of beets processed, 4.45 kg of limestone and 0.36 kg of coke are consumed, which leads to the production of 10.5 kg of muds, having on average a dry-substance content of 50% in weight.

[0023] The enormous amount of muds produced can be appraised by bearing in mind the quantity of beets that are processed yearly in the various countries. The composition of these muds is widely documented in the books.

[0024] Regarding the main components, given in grams per 100 grams of dry matter, the calcium carbonate content can be from 65% to 80%, the CaO from 35% to 45%, the MgO from 1% to 2%, the K₂O from 0.1% to 0.5%, the P₂O₅ from 1% to 2% and nitrogen from 0.2% to 0.8%.

[0025] The colour of these muds is potentially yellow-ivory, due to presence of coloured substances in the sugar-processing juices. During a long period of storage, this colour can undergo transformation due to organic substances present.

[0026] According to a fundamental characteristic of the invention, the carbonated muds deriving from sugar-beet processing are made to react with acid gases coming from the heat decomposition of the limestone and from the combustion of organic fuels. The reaction is done in such a way that the pH of the carbonation muds suspension reaches a value of between 8 and 11. The muds thus treated are therefore utilized in paper making, eventually after the addition of 1% to 30% in weight of colloids or agglomerating or their mixtures to reduce their solubility in the process water to values of less than 2% in weight.

[0027] Among the colloids and agglomerating useful for this purpose are the cationizing starches, partially micronized starches, aluminium salts, in particular the sulfate and polychloride, and iron sulfate.

[0028] The process according to the present invention offers an inorganic flour usable in paper making, both in pulp and in size press coating.

[0029] It is well-known that the muds deriving from sugar-production processes (sugar-beet or sugar-cane mills and refineries) constitute a serious ecological problem because of their difficult elimination and limited reutilization.

[0030] The muds can come from sugar mills using lime furnaces fed with limestone and fossil fuels or hydrocarbons of different origin, or by sugar mills using calcium oxide, which is saturated using the combustion gases.

[0031] Depending on the various types of systems, the dry-matter content of muds is normally between 40% and 80% in weight.

[0032] These muds can be pre-sifted with filters of 50/150 mesh per linear inch to obtain a product directly usable as pulp filler in paper making.

[0033] By sifting the same with nets of mesh 150/250 per linear inch it is possible to separate a fraction of flours usable also on the paper and board surfaces for their coating (surface application).

[0034] From an energy standpoint the use of fresh undried muds is advisable. These muds must be used within a short period of their being produced in order to prevent phenomena of biodegradation of the organic part with subsequent emission of bad-smelling volatile substances.

[0035] It is widely known how the elimination of these muds constitutes a big problem for the sugar industry. Even their use as an agricultural conditioner represents only a partial solution to the problem, bearing in mind the impossibility of this use for basic soils.

[0036] Their use in paper making according to the present invention therefore represents not only an economical benefit for the paper industry but also helps solve a problem that for sugar mills is becoming more and more burdensome each year.

[0037] The present invention pertains to a process for making paper containing carbonated muds deriving from the processing of sugar-beets, whereby

- a) a lime solution deriving from sugar beet processing with lime, is made to react with carbon dioxide contained in acid gases coming from the heat decomposition of the limestone and from the combustion of organic fuels with the forming of a carbonated mud suspension having a pH of between 8 and 11;
- b) this carbonated mud suspension is subjected to operations of sedimentation, filtering and/or thickening, giving carbonated muds with a dry content of between 40 and 80% in weight, such mud suspension being dried and the solids obtained being ground and sifted in order to obtain particles of average dimensions of less than 20 microns;
- c) these carbonated muds are added as an additive to the cellulose fibre pulp for converting into paper, in quantities of from 2 to 65% in weight with respect to the cellulose fibre pulp.

[0038] Before undergoing stages b) and c) of the process, the mud suspension obtained as given in point a) can be mixed with other additives normally used in paper making, such as starch, kaolin, calcium carbonate, talc, barium sulfate, diatoms, zeolites, silicones, retentives, dyes, coagulants, fluidizers and bacteriostatics.

[0039] In the preferred forms of realizing the process according to the invention, the suspension muds given in point b) are dried, ground and sifted in order to have particles of average dimensions of less than 20 microns, suitable for use in the paper pulp, or of average dimensions of less than 5 microns, suitable for use as coatings on surfaces.

[0040] For the purpose of better illustrating the characteristics of the paper and the process according to the invention, several forms of realizing the same and of the products thus obtained will be given

EXAMPLE 1

[0041] 500 KG of undried carbonated muds obtained by blowing with combustion gas or limestone decomposition gas the lime solution used for purifying the sugar extraction juices up to a pH of 9, have the following characteristics of which:

moisture	28%
copper	15 mg/Kg
iron	750 mg/Kg
zinc	30 mg/Kg
total solubles	0.22%
total nitrogen	0.25%

[0042] This is a calcium carbonate precipitate at over 70%, with an attractive ivory colour.

[0043] These muds, for convenience of transport and storage, were firstly dried to approx. 97% dry content. 370 Kg were obtained. These dry muds were taken to the paper mill and micronized (elementarized separating, for the use, only those particles of dimensions of less than 20 microns), using a hammer mill used in the food flour sector and equipped with a suitable s system (air cyclones) for separating the foreign particles as well as sifting. Dry sifting was carried out for production convenience and to guarantee quality.

[0044] These inorganic fillers converted into flour can be used to make paper and card, just like traditional inorganic fillers.

[0045] These mud flours can be mixed with other substances and with other additives intended for use in paper making, such as cellulose, waste paper, starch, kaolin, calcium carbonate, talc.

[0046] The mud flour has a specific weight of 2.5 kg/dm³ and apparent specific weight of 1.5 kg/dm³.

EXAMPLE 2

[0047] Pulp having the composition given in Table 1 was put in paper machine of capacity of about 700 Kg/h of paper.

[0048] Diketenetic-type synthetic bonding agent (AKD) was added to the pulp to make the paper suitable for writing with watery inks, and cationic starch to retain the mineral fillers in the paper.

[0049] The outlet belt speed was adjusted to 72 metres per minute.

[0050] The paper machine was automatically controlled by an Accuray 1880 Micro Plus system.

[0051] This system measures and automatically controls substance (gr/m²), moisture (water %), thickness (microns) and controls opacity, whiteness and mineral content.

[0052] The paper was produced at 90 gr/m² and with respect to the white reference took on a natural ivory colour.

[0053] The paper was perfectly drawable, writable, photocopyable and printable.

[0054] Table 2 gives the main characteristics of the paper obtained compared with paper produced under the same operative conditions using traditional calcium carbonate.

[0055] Expacell P-50 was added in example B to verify the behaviour of a fibre panel containing carbonatation muds in products having a high air-content.

[0056] This behaviour was excellent.

TABLE 1:

Paper pulp composition				
DESCRIPTION	Unit	Reference	Example A	Example B
Bleached chemical pulp (70% Eucaplyptus 30% Fir)	Kg.	640	640	640
	%	79,5	79,5	78,4
CaCO ₃ micronized	Kg.	130	0	0
	%	16,1	0	0
Carbonatation mud flour	Kg.	0	130	130
	%	0	16,1	16
Methyletilketene dimer (AKD bonding agent)	Kg.	10	10	10
	%	1,2	1,2	1,2
Cationic starch	Kg.	6	6	6
	%	0,7	0,7	0,7
Expancell P 50	Kg.	0	0	10
	%	0	0	1,2
Surface starch (size press)	Kg.	20	20	20
	%	2,5	2,5	2,5
TOTAL	Kg.	806	806	816
	%	100	100	100

TABLE 2:

Characteristics of papers obtained				
DESCRIPTION	Unit	Reference	Example A	Example B
Grammage	g/m ²	90	90	90
Thickness	micron	105	117	149
Bulk	dm ³ /kg	1,17	1,30	1,65
Ash (525°C)	%	16	16	15
Ink flotation (Pelikan 4001)	min	4	5	2
Cobb (60 sec)	g/m ²	32	33	40
Smoothness (Gurley 100 ml)	sec	150	100	90
Air permeability (Gurley 100 ml)	sec	45	13	4
Dennison waxes	N	16/18	16/18	14/16
Breaking lenght long./cross	Km	7,0	7,2	6,1
		3,5	3,9	3,3
Dust-free rating (400 sheets)		good	good	fair
Absolute humidity	%	7,0	6,7	6,9

Claims

1. Process for making paper containing carbonated muds deriving from the processing of sugar-beets, whereby

a) a lime solution deriving from sugar beet processing with lime, is made to react with carbon dioxide contained in acid gases coming from the heat decomposition of the limestone and from the combustion of organic fuels with the forming of a carbonated mud suspension having a pH of between 8 and 11;

b) this carbonated mud suspension is subjected to operations of sedimentation, filtering and/or thickening, giving carbonated muds with a dry content of between 40 and 80% in weight, such mud suspension being dried and the solids obtained being ground and sifted in order to obtain particles of average dimensions of less than 20 microns;

c) these carbonated muds are added as an additive to the cellulose fibre pulp for converting into paper, in quantities of from 2 to 65% in weight with respect to the cellulose fibre pulp.

2. Process as per claim 1. whereby before undergoing stages b) and c), fluidizers and bacteriostatics are added to the mud suspension of point a).

3. Process as per claim 1. whereby before being mixed with cellulose fibre pulp, the mud suspension obtained of point a) is mixed with one or more compounds such as starch, kaolin, calcium carbonate, talc, barium sulfate, diatoms, zeolites, silicones, retentives, dyes, coagulants.

4. Process as per claim 3. whereby the mud suspension mixed with these compounds is added to the cellulose fibre pulp for converting into paper, in quantities of from 1 to 40% in weight with respect to the paper.

5. Process as per claim 1, whereby the solids are sifted in order to obtain particles of an average dimensions of less than 5 microns.

Patentansprüche

1. Verfahren zur Herstellung von Papier, umfassend karbonisierte Schlämme, die sich von der Verarbeitung von Zuckerrüben ableiten, wobei

a) eine Kalklösung, die aus der Zuckerrübenbehandlung mit Kalk stammt, zur Reaktion gebracht wird mit Kohlendioxid, welches in sauren Gasen enthalten ist, die aus der Wärmezersetzung von Kalkstein und aus der Verbrennung von organischen Brennstoffen stammen, unter Bildung einer karbonisierten Schlammsuspension mit einem pH zwischen 8 und 11;

b) diese karbonisierte Schlammsuspension einer Sedimentationsbehandlung, einer Filtration und/oder Verdickungsbehandlung unterworfen wird, welche karbonisierte Schlämme mit einem Feststoffgehalt zwischen 40 und 80 Gew.-% ergeben, wobei diese Schlammsuspension getrocknet wird und die erhaltenen Feststoffe gemahlen und gesiebt werden, um Partikel mit mittleren Abmessungen von weniger als 20 µm zu erhalten;

c) diese karbonisierten Schlämme als ein Additiv zu einem Zellulosefaserbrei zur Umwandlung in Papier zugegeben werden und zwar in Mengen von 2 bis 65 Gew.-%, bezogen auf den Zellulosefaserbrei.

2. Verfahren nach Anspruch 1, wobei vor der Durchführung der Schritte b) und c) Fluidisierungsmittel und bakterienwachstumshemmende Mittel zu der Schlammsuspension des Schrittes a) zugegeben werden.

3. Verfahren nach Anspruch 1, wobei vor dem Mischen mit dem Zellulosefaserbrei die Schlammsuspension, die in Schritt a) erhalten wurde, mit einem oder mehreren der Verbindungen wie z.B. Stärke, Kaolin, Kalziumkarbonat, Talkum, Bariumsulfat, Diatomee, Zeoliten, Silikonen, Rückhaltemitteln, Farbstoffen, Coagulantien gemischt wird.

4. Verfahren nach Anspruch 3, worin die Schlammsuspension, die mit diesen Verbindungen vermischt ist, dem Zellulosefaserbrei zur Umwandlung in Papier in Mengen von 1 bis 40 Gew.-%, bezogen auf das Papier, zugegeben wird.

5. Verfahren nach Anspruch 1, worin die Feststoffe gesiebt werden, um Partikel zu erhalten mit mittleren Abmessungen von weniger als 5 µm.

Revendications

1. Procédé pour fabriquer du papier contenant des boues carbonatées dérivées du traitement de betteraves sucrières, dans lequel :

a) une solution de chaux dérivée du traitement de betteraves sucrières avec de la chaux, est mise à réagir avec le dioxyde de carbone contenu dans des gaz acides provenant de la décomposition thermique de pierre à chaux et de la combustion de combustibles organiques, avec formation d'une suspension de boues carbonatées ayant un pH compris entre 8 et 11 ;

b) cette suspension de boues carbonatées est soumise à des opérations de sédimentation, filtrage et/ou épaissement, pour obtenir des boues carbonatées ayant une siccité comprise entre 40 et 80 % en poids, ladite suspension de boues étant séchée et les matières solides obtenues étant broyées et tamisées afin d'obtenir des particules de dimensions moyennes de moins de 20 microns ;

c) ces boues carbonatées sont ajoutées en tant qu'additif à la pâte de fibres de cellulose pour transformation en papier, en des quantités de 2 à 65 % en poids par rapport à la pâte de fibres de cellulose.

2. Procédé selon la revendication 1, dans lequel, avant de subir les étapes b) et c), des fluidiseurs et des bactériostatiques sont ajoutés à la suspension de boues de l'étape a).

3. Procédé selon la revendication 1, dans lequel, avant d'être mélangée avec la pâte de fibres de cellulose, la suspension de boues obtenue à l'étape a) est mélangée avec un ou plusieurs composés tels que l'amidon, le kaolin, le carbonate de calcium, le talc, le sulfate de baryum, des diatomées, des zéolites, des siliciums, des agents de rétention, des colorants, des coagulants.

4. Procédé selon la revendication 3, dans lequel la suspension de boues mélangée avec ces composés est ajoutée à la pâte de fibres de cellulose pour transformation en papier, en des quantités de 1 à 40 % en poids par rapport au papier.

5. Procédé selon la revendication 1, dans lequel les matières solides sont tamisées afin d'obtenir des particules d'une dimension moyenne de moins de 5 microns.