



(19)

Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 831 176 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.03.1998 Bulletin 1998/13

(51) Int. Cl.⁶: D21H 17/01, D21H 19/38

(21) Application number: 97116484.3

(22) Date of filing: 22.09.1997

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC
NL PT SE

(30) Priority: 20.09.1996 IT VA960017

(71) Applicant: Geopolimeri S.r.l.
36028 Rossano Veneto, VI (IT)

(72) Inventors:
• Vaccari, Giuseppe
36028 Rossano Veneto VI (IT)
• Nicolucci, Clemente
36028 Rossano Veneto VI (IT)
• Mantovani, Giorgio
36028 Rossano Veneto VI (IT)
• Monegato, Achille
36028 Rossano Veneto VI (IT)
• Bonaguro, Giampaolo
36028 Rossano Veneto VI (IT)

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

(57) A process is disclosed allowing the use of muds from agriculture works, particularly from sugar-beet or from sugar-cane production, in the paper-making.

Description

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

According to this invention, the carbonatation 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.

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.

Card, board and sugar-cane residuals are therefore included in the scope of this invention.

Recently, some of the inventors prepared 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 application N.644293.

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.

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 European patent applications 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.

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.

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.

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.

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

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.

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.

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.

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.

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

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.

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.

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 possibility 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).

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

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 con-

sumed, which leads to the production of 10.5 kg of muds, having on average a dry-substance content of 50% in weight.

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.

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%.

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.

According to a fundamental characteristic of the invention, the carbonatation 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 carbonatation 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.

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.

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

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.

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.

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

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.

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).

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.

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.

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.

The paper-making process according to the present invention therefore comprises the following fundamental stages:

- 40 a) the lime solution used to purify the sugar extraction juices is made to react with the acid gases coming, from the heat decomposition of the limestone and from the combustion of organic fuels with the forming of a mud suspension having a pH of between 8 and 11;
- 45 b) this mud suspension is subjected to operations of sedimentation, filtering and/or thickening, giving muds with a dry-content of between 40 and 80% in weight;
- c) these muds are added as an additive to the cellulose fibre for converting into paper, in quantities of from 2% to 65% in weight with respect to the cellulose fibres.

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.

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.

55 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

500 KG of undried carbonatation 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
 5 which:

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

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

15 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 system (air cyclones) for separating the foreign particles as well as sifting. Dry sifting was carried out for production convenience and to guarantee quality.

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

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.

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

EXAMPLE 2

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

Diketene-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.

30 The outlet belt speed was adjusted to 72 metres per minute.

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

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

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

35 The paper was perfectly drawable, writable, photocopyable and printable.

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

Expancell 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. This behaviour was excellent.

40

45

50

55

TABLE 1

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

TABLE 2

Characteristics of papers obtained					
	DESCRIPTION	Unit	Reference	Example A	Example B
35	Grammage	g/m ²	90	90	90
40	Thickness	micron	105	117	149
45	Bulk	dm ³ /kg	1,17	1,30	1,65
50	Ash (525°C)	%	16	16	15
55	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 3,5	7,2 3,9	6,1 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 carbonatation muds deriving from the processing of sugar-beets, whereby:

5 a) the lime solution used to purify the sugar extraction juices is made to react with the acid gases coming from the heat decomposition of the limestone and from the combustion of organic fuels with the forming of a mud suspension having a pH of between 8 and 11;
10 b) this mud suspension is subjected to operations of sedimentation, filtering and/or thickening, giving muds with a dry-content of between 40 and 80% in weight;
15 c) these muds are added as an additive to the cellulose fibre for converting into paper, in quantities of from 2% to 65% in weight with respect to the cellulose fibres.

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).

15 3. Process as per claim 1. whereby before being mixed with cellulose fibres, 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.

20 4. Process as per claim 3. whereby the mud suspension mixed with these compounds is added to the cellulose fibres 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 mud suspension of point a) is dried and the solids obtained ground and sifted in order to obtain particles of average dimensions of less than 20 microns, suitable for use in the pulp.

25 6. Process as per claim 1. whereby the mud suspension of point a) is dried and the solids obtained ground and sifted in order to obtain particles of average dimensions of less than 5 microns, suitable for use in surfaces as coatings.

30

35

40

45

50

55



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	DE 39 22 310 A (HOELTER HEINZ) 10 January 1991 * the whole document * ----	1	D21H17/01 D21H19/38
A,D	EP 0 644 293 A (FAVINI CARTIERA SPA) 22 March 1995 -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			D21H C05F
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	8 December 1997	Songy, O	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			