(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 1 967 649 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
10.09.2008 Bulletin 2008/37

(51) Int Cl.:
D21H 17/67 *(2006.01)*

(21) Application number: **08100527.4**

(22) Date of filing: **16.01.2008**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK RS

(30) Priority: **16.02.2007 IT VA20070018**

(71) Applicant: **Lamberti Spa**
21041 Albizzate (IT)

(72) Inventors:
- **Fumagalli, Stefano**
  21040, Carnago (VA) (IT)
- **Vago, Riccardo**
  20025, Legnano (MI) (IT)
- **Li Bassi, Giuseppe, Dr.**
  21026, Gavirate (VA) (IT)

(54) Concentrated aqueous gypsum suspensions and their use in paper production

(57) Process for the preparation of paper characterised by the fact that an aqueous gypsum suspension having Brookfield viscosity at 25°C and 100 rpm comprised between 100 and 1,000 mPa·s and containing from 60 to 85% by weight of gypsum in the form of calcium sulphate dihydrate ($Ca_2SO_4.2H_2O$) is added to the cellulose aqueous suspension used for the production of paper, the aqueous gypsum suspension containing from 0.1 to 2% by weight of an acrylic sulphonated polymer, or of an acrylic carboxylated polymer or of a polynaphthalene sulphonate, and from 0.1 to 1.0% by weight of an organic polyphosphonate.

EP 1 967 649 A1

Description

Technical Field

[0001] The present invention relates to stable, concentrated aqueous gypsum suspensions that are useful for the production of paper and cardboard and contain high amounts of gypsum.

[0002] In the present description, with the term stable, concentrated aqueous gypsum suspensions we mean suspensions having a $CaSO_4*2H_2O$ concentration comprised between 60% and 85% by weight.

[0003] In the following description we will use the term "paper" to include cardboard too.

Background Art

[0004] As it is known, many solutions have been proposed to make it possible to prepare stable, concentrated calcium sulphate suspensions, mainly based on the use of specific complexing agents and dispersants.

[0005] In particular, in our Italian patent Application VA2006A000044 a method providing highly concentrated aqueous gypsum suspensions having low viscosity is described, by adding gypsum in the form of hemi-hydrate or anhydrous salt to a basic aqueous solution containing a polyacrylic sulphonated dispersant and an organic polyphosphonate.

[0006] These low viscous, highly stable and highly concentrated gypsum suspensions are mixable with suspensions based on other pigments and they do not form foams, which would render troublesome their use.

[0007] While continuing our research on the compositions disclosed in the above said patent application, it was found that it is possible to use the suspensions described therein (modified in their particle size distribution) directly in the production of paper, to charge it with calcium sulphate as filler in the desired quantity.

[0008] As it is known, the use of calcium sulphate as additive in paper production is always looked at suspiciously in paper mills, despite its low cost among additives, because of its tendency to form solid masses that could stop the paper production plant.

[0009] In European patent EP 0056200 B1 a method was described allowing the use of aqueous calcium sulphate suspensions, which are directly prepared in a reactor located next to the paper production plant and introduced in diluted form (generally with concentration below 20%) directly in the paper production plant.

[0010] This method has a drawback: it also needs the preparation, directly next to the paper production plant, of the aqueous suspension of calcium sulphate, because it is economically disadvantageous to transport the large amounts of water of such suspensions.

Disclosure of Invention

[0011] The Applicant has now found that it is possible to use stable, concentrated aqueous suspensions of gypsum in the production of paper.

[0012] It is therefore a fundamental object of the present invention a process for the production of paper containing from 5 to 35% by weight of calcium sulphate dihydrate, characterised by the fact that a stable aqueous gypsum suspension having Brookfield viscosity at 25°C and 100 rpm comprised between 100 and 1,000 mPa*s and containing from 60 to 85% by weight of gypsum in the form of calcium sulphate dihydrate ($Ca_2SO_4.2H_2O$) is added to the cellulose aqueous suspension used for the production of paper.

[0013] In particular, said stable, aqueous gypsum suspension, which represents a further object of the present invention, contains from 0.1 to 2% by weight of an acrylic sulphonated polymer, or of an acrylic carboxylated polymer or of a polynaphthalene sulphonate, and from 0.1 to 1 % by weight of an organic polyphosphonate, and comprises gypsum in dihydrate form having particle size between 35% and 60% below 2 micron.

[0014] The use of an acrylic sulphonated polymer or of an acrylic carboxylated polymer or of a polynaphthalene sulphonate, acting as dispersing agent, and of the organic polyphosphonate allows to obtain stable, concentrated gypsum suspensions having rheological characteristics and stability which render them suitable for use in the method according to the invention.

[0015] The use of a polynaphthalene sulphonate is preferred, because, advantageously, it can also be used in acid environments, that are typical of the paper production with acidic sizing, that is at pH about 4.5.

[0016] Preferably the Brookfield viscosity of the suspensions, at 25°C and 100 rpm, is comprised between 100 and 500 mPa*s.

[0017] The acrylic sulphonated polymers useful for the preparation of the suspensions of the present invention are obtained by polymerisation of acrylic and/or methacrylic acid, in acidic or salt form, with a monomer containing a sulphonic functional group and have a molecular weight from 5,000 to 40,000 dalton (measured with an acrylic acid standard); they are well known polymers, available on the market, and sold by way of example in the form of aqueous slurries by Lamberti SpA; they can be used in this form for the preparation of the gypsum suspensions of the invention.

[0018] Preferably the molar ratio between the total sum of acrylic and/or methacrylic acid and monomer containing a strongly acidic functional group is from 3 to 30, preferably from 3 to 10.

[0019] More preferably, the sulphonated acrylic polymer is a copolymer of acrylic acid, methacrylic acid and 2-acrylamido-2-methyl-1-propanesulphonic acid, where the molar ratio between acrylic and methacrylic acid is from 2 to 8.

[0020] The polynaphthalene sulphonates useful for the realisation of the present invention are condensation products of formaldehyde and sulphonated aromatics acting as dispersants, and are also normally available in the market; they are generally prepared by reacting an aromatic sulphonated compound (such as naphthalene sulphonic acids, naphthol sulphonic acids, alkylated naphthalene sulphonic acids, alkylated naphthol sulphonic acids, and also toluenesulphonic acid, benzenesulphonic acid, phenolsulphonic acid and similar compounds) with formaldehyde, to form a condensation product which is usually neutralised or alkalinised by adding a sodium hydroxide solution.

[0021] Among the sulphonated formaldehyde-aromatic condensation products which are commercially available as dispersants and are useful for the realisation of the present invention we cite TAMOL NN 9104, sold by BASF.

[0022] Among the acrylic carboxylated polymers useful for the realization of the present invention we cite the copolymers of acrylic, methacrylic, itaconic, fumaric, maleic acid, optionally copolymerized with acrylamide, having molecular weight from 1,000 to 10,000 dalton and obtained by using as initiators persulfate/metabisulfite or ipophosphite and as neutralising agents sodium or potassium hydroxides, or carbonates.

[0023] In the present text, with the term "organic polyphosphonate" we mean organic phosphonates containing two or more phosphonic groups, in the form of acid or salt thereof.

[0024] Polyphosphonates useful for the realisation of the present invention are: aminotri(methylene-phosphonic acid), aminotri(methylene-phosphonic acid)pentasodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid tetrasodium salt, diethylenetriamine penta(methylene phosphonic acid)pentasodium salt, diethylenetriamine penta(methylene phosphonic acid)trisodium salt, hexamethylene diamine tetra(methylene phosphonic acid), hexamethylene diamine tetra(methylene phosphonic acid)potassium salt, and mixtures thereof.

[0025] Other useful polyphosphonates are described in EP 1713568.

[0026] The aqueous gypsum suspensions of the present invention are repared by adding hemi-hydrate gypsum to an aqueous solution containing the dispersing agents and the organic polyphosphonate in a bead mill, gently grinding to homogenise the suspension.

[0027] The dihydrate gypsum which is obtained in these conditions has a particle size from 35% to 60% by weight below 2 microns.

[0028] The grinding avoids excessive sedimentation and compaction of the product, even in case no suspending agents are used.

[0029] According to a particularly advantageous aspect of this invention, it is observed that the possible presence of sedimentation in the suspension can be eliminated by simple mechanical stirring, even after months from its preparation.

[0030] The hemi-hydrate gypsum useful for the preparation of the aqueous suspensions of the present invention is commercially available and is normally obtained by calcinating dihydrate gypsum.

[0031] EXAMPLE 1

[0032] 3 gypsum suspensions are prepared with the following ingredients:

- Hemi-hydrate calcium sulphate
- Sequion 50 K33 (33% by weight hexamethylene diamine tetra(methylene phosphonic acid) potassium salt from Bozzetto SpA, Italy)
- AA= 45% aqueous solution of sodium acrylate homopolymer
- AA-MA-AMPS=30% aqueous slurry of acrylic acid, methacrylic acid and 2-acrylamido-2-methyl-1-propansulphonic acid sodium salt terpolymer (monomers molar ratio: 4: 1: 1)
- Tamol NN 0104, polynaphthalene sulphonate from BASF (Germany)

[0033] with the quantities reported in Table 1 and the following procedure:

[0034] The bead mill is charged with 400.6 g of water, 6.9 g of Sequion 50 K33 and 8.2 g of Tamol NN 0104.

[0035] Stirring is started and 584.3 g of calcium sulphate hemi-hydrate are added with 300ml of beads having diameter 1.5-2.0 mm.

[0036] After 30 minutes stirring the product is discharged.

[0037] The next samples were prepared using the same procedure and substituting Tamol NN 0104 with AA-MA-AMPS (Suspension 2) or with AA (Suspension 3).

[0038]

Table 1

Calcium sulfate dihydrate suspensions						
Sample No.	Susp. Conc. %	Tamol NN 9104 %	AA-MA-AMPS %	AA %	Brookfiel d Viscosity 100 rpm (mPa*s)	Particle size % < 2 μm
1	70,0	1,2%	/	/	270	42,8
2	70,0	/	1,0	/	215	40,1
3	70,0	/	/	1,0	310	43,5

[0039] EXAMPLE 2

[0040] Use of the calcium sulphate dihydrate suspensions as fillers in the production of paper sheets.

[0041] Ingredients:

- Calcium sulphate dihydrate suspension prepared as Sample No 1 of Example 1
- Calcium sulphate dihydrate suspension prepared according to the method of patent EP 0056200 B1
- Cellulose paste (3% in water)
- Colloidal silica (Nalco 8694, from Nalco, USA, 0.01 % solution)
- Retention agent (Nalco 74648, anionic polyacrylamide from Nalco, USA, 0.01 % solution)

[0042] Two series of sheets are prepared having different fillers, the first with calcium sulphate dihydrate prepared as sample No. 1 of Example 1, the second with calcium sulphate dihydrate prepared according to the method of patent EP 0056200 B1.

[0043] To obtain 80 g/m^2 sheets, 65 g of cellulose fibre paste are taken and 0.93 g of calcium sulphate dihydrate prepared as sample No. 1 of Example 1 are added into it (1st series), diluting with water saturated with calcium sulphate dihydrate to 500 g total weight.

[0044] 7.8 g of colloidal silica Nalco 8694 (0.01 % solution) and 0.5 g of retention agent Nalco 74648 (0.01 % solution) are then added.

[0045] The paste is then inserted in the sheet-maker machine and the sheet is prepared.

[0046] The 2nd series is prepared in the same conditions.

[0047] For each series, 6 sheets having grammage of 80 g/m^2 were prepared.

[0048] The sheets are conditioned for 24 hours in a room at 21°C and 50 % r.h.

[0049] Example 2.1

[0050] The sheets prepared as in Example 2 were characterised by taking the following measurements, and reporting the results in Table 2:

- Grammage - Tappi method T410
- Opacity - Tappi method T425
- Ash at 500 and 900°C - Tappi method T211
- Charge
- Tensile breaking - Tappi method T494

[0051]

Table 2

		1ST SERIES	2ND SERIES
ASH %	500°C	22.61	20.77
	900°C	20.56	18.15
CHARGE %		28.26	25.96
Opacity		93.83	93.64
Tensile breaking (m)		3465	3563

[0052] The charge is calculated by multiplying the ash value at 500°C per 1.25 (conversion factor from $CaSO_4$ to

$CaSO_4*2H_2O$).

Claims

1. A process for the preparation of paper containing from 5 to 35% by weight of calcium sulphate dihydrate, **characterised by** the fact that an aqueous gypsum suspension having Brookfield viscosity at 25°C and 100 rpm comprised between 100 and 1,000 mPa*s and containing from 60 to 85% by weight of gypsum in the form of calcium sulphate dihydrate ($Ca_2SO_4.2H_2O$) is added to the cellulose aqueous suspension used for the production of paper, the aqueous gypsum suspension containing from 0.1 to 2% by weight of an acrylic sulphonated polymer, or of an acrylic carboxylated polymer or of a polynaphthalene sulphonate, and from 0.1 to 1.0% by weight of an organic polyphosphonate.

2. The process as claimed in 1 further **characterised by** the fact that from 35% to 60% of the gypsum contained in the suspension has particle size below 2 micron.

3. The process as claimed in 1 or 2 where the gypsum aqueous suspension contains from 0.1 to 2.0% by weight of a polynaphthalene sulphonate.

4. The process as claimed in 3 where the gypsum aqueous suspension has Brookfield viscosity, at 25°C and 100 rpm, between 100 and 500 mPa*s.

5. The process as claimed in 4 where the polyphosphonate is selected among: aminotri(methylene-phosphonic acid), aminotri(methylene-phosphonic acid)pentasodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid tetrasodium salt, diethylenetriamine penta(methylene phosphonic acid)pentasodium salt, diethylenetriamine penta(methylene phosphonic acid)trisodium salt, hexamethylene diamine tetra(methylene phosphonic acid), hexamethylene diamine tetra(methylene phosphonic acid)potassium salt, and mixtures thereof.

6. A gypsum aqueous suspension having Brookfield viscosity at 25°C and 100 rpm comprised between 100 and 1,000 mPa*s containing: a. from 60 to 85% by weight of calcium sulphate dihydrate ($Ca_2SO_4.2H_2O$) having particle size between 35 and 60% by weight below 2 micron; b. from 0.1 to 2.0% by weight of an acrylic sulphonated polymer, or of an acrylic carboxylated polymer or of a polynaphthalene sulphonate; c. from 0.1 to 1.0% by weight of an organic polyphosphonate.

7. The gypsum aqueous suspension according to claim 6 having Brookfield viscosity, at 25°C and 100 rpm, between 100 and 500 mPa*s.

8. The gypsum aqueous suspension according to claim 6 or 7 containing from 0.1 to 2.0% by weight of a polynaphthalene sulphonate.

9. The gypsum aqueous suspension of claim 8 where the polyphosphonate is selected among: aminotri(methylene-phosphonic acid), aminotri(methylene-phosphonic acid)pentasodium salt, 1-hydroxyethylidene-1,1-diphosphonic acid, 1-hydroxyethylidene-1,1-diphosphonic acid tetrasodium salt, diethylenetriamine penta(methylene phosphonic acid)pentasodium salt, diethylenetriamine penta(methylene phosphonic acid)trisodium salt, hexamethylene diamine tetra(methylene phosphonic acid), hexamethylene diamine tetra(methylene phosphonic acid)potassium salt, and mixtures thereof.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 08 10 0527

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,Y	US 2004/187741 A1 (LIU QINGXIA [US] ET AL) 30 September 2004 (2004-09-30) * claims 1-41 *	1	INV. D21H17/67
Y	DE 40 27 237 A1 (GYPSUM RESEARCH [CH]) 5 March 1992 (1992-03-05) * claims 1-4 *	1	
A	DE 32 03 067 A1 (KEMIRA OY [SE]) 26 August 1982 (1982-08-26) * the whole document *	1-9	
A	US 3 645 677 A (AKAZAWA HAKUICHI ET AL) 29 February 1972 (1972-02-29) * the whole document *	1-9	
A	GB 2 173 781 A (BEROL KEMI AB) 22 October 1986 (1986-10-22) * the whole document *	1-9	
A	US 5 236 989 A (BROWN ALAN J [US] ET AL) 17 August 1993 (1993-08-17) * the whole document *	1-9	TECHNICAL FIELDS SEARCHED (IPC) D21H
A	WO 92/08755 A (ECC AMERICA INC [US]) 29 May 1992 (1992-05-29) * the whole document *	1-9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	31 July 2008	Karlsson, Lennart

CATEGORY OF CITED DOCUMENTS

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

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

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 10 0527

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-07-2008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2004187741 A1	30-09-2004	AU 2004225955 A1	14-10-2004
		CA 2514322 A1	14-10-2004
		EP 1606228 A2	21-12-2005
		JP 2006521276 T	21-09-2006
		MX PA05009335 A	04-11-2005
		NZ 541536 A	30-05-2008
		WO 2004087604 A2	14-10-2004
DE 4027237 A1	05-03-1992	NONE	
DE 3203067 A1	26-08-1982	FI 810311 A	05-08-1982
		SE 460672 B	06-11-1989
		SE 8200586 A	05-08-1982
US 3645677 A	29-02-1972	NONE	
GB 2173781 A	22-10-1986	DE 3612087 A1	23-10-1986
		DK 161586 A	12-10-1986
		FI 861530 A	12-10-1986
US 5236989 A	17-08-1993	NONE	
WO 9208755 A	29-05-1992	AU 659815 B2	01-06-1995
		AU 9059191 A	11-06-1992
		BR 9107068 A	09-11-1993
		CA 2095541 C	15-07-1997
		EP 0556311 A1	25-08-1993
		FI 932054 A	06-05-1993
		JP 7503027 T	30-03-1995

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- IT VA20060044 A **[0005]**
- EP 0056200 B1 **[0009] [0041] [0042]**
- EP 1713568 A **[0025]**