

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
23 September 2010 (23.09.2010)

(10) International Publication Number
WO 2010/106023 A1

PCT

(51) International Patent Classification:
D21H 9/62 (2006.01) **D21H 21/10** (2006.01)

(21) International Application Number:
PCT/EP2010/053301

(22) International Filing Date:
15 March 2010 (15.03.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
VA2009A000020 16 March 2009 (16.03.2009) IT

(71) Applicant (for all designated States except US): **LAMBERTI SPA** [IT/IT]; Ufficio Brevetti, via Piave 18, I-21041 Albizzate (VA) (IT).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **FEDERICI, Franco** [IT/IT]; Viale Stelvio, 49, I-21052 Busto Arsizio (VA) (IT). **COSTA, Gabriele** [IT/IT]; via Baranzate, 15, I-20026 Novate Milanese (IT). **BOSSI, Thierry** [IT/IT]; Via San Lorenzo, n. 50, I-21030 Orino (VA) (IT). **FU-MAGALLI, Stefano** [IT/IT]; Via Matteotti, 40, I-21040 Carnago (VA) (IT). **VAGO, Riccardo** [IT/IT]; Via Pio XI, 5, I-20025 Legnano (MI) (IT). **LI BASSI, Giuseppe** [IT/IT]; Via Stretti, 4, I-21026 Gavirate (VA) (IT).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- of inventorship (Rule 4.17(iv))

Published:

- with international search report (Art. 21(3))

(54) Title: PAPER COATING COMPOSITION

(57) Abstract: Paper coating compositions containing comb water soluble (hydrophilic) polyurethanes containing polyoxyethylene side-chains as deflocculants and water retention agents.



WO 2010/106023 A1

FIELD OF THE INVENTION

The present invention relates to paper coating compositions containing comb water soluble (hydrophilic) polyurethanes containing polyoxyethylene side-
5 chains as deflocculants and water retention agents.

BACKGROUND OF THE ART

It is well known that the surface of printing paper sheets is commonly coated with a paper coating formulation to improve the printability and to make it smooth and glossy.

10 Paper coating compositions generally comprise fillers or pigments dispersed in water, polymeric binders, rheology modifiers, water retention agents and dispersing agents.

Dispersing agents are indispensable to reduce the viscosity in the presence of the high solid contents which are typical of paper coating compositions and to
15 maintain a constant desired processing viscosity; examples of conventional dispersing agents are complex phosphates, salts of polyphosphoric acid and salts of polycarboxylic acids.

Water retention agents prevent dewatering of the coating composition upon contact with the surface of the paper sheet; a typical water retention agent for
20 paper coating composition is carboxymethyl cellulose.

Rheology modifiers are added to modulate the paper coating viscosity.

Binders are responsible for cohesion of the final coating and for its grafting to the paper sheet.

Some conventional paper coating additives are known to perform more than
25 one function; by way of example, carboxymethyl cellulose acts both as rheology modifier and water retention agent, polyvinyl alcohol acts as water retention agent and optical brightness enhancer.

WO 01/96007, WO 2004/044022, WO 2004/041883 and WO 2007/069037 describe the use of polyacrylic anionic copolymers in the paper industry, for making or coating paper; the polyacrylic anionic copolymers contain at least one anionic ethylenically unsaturated monomer having monocarboxylic
5 functionality and at least one non-ionic ethylenically unsaturated monomer having poly(C₂₋₄-alkylene oxide) functionalities. They are said to be useful as dispersing and/or grinding agents, as agents for improving the optical brightening activation, as water retention agents, as viscosity and gloss enhancers.

10 Unfortunately, when the known ionic substances are used in aqueous dispersions in accordance with the prior art, their effectiveness is dependent on the pH value of the dispersion.

It has now been found that specific hydrophilic comb polyurethanes are suitable as water retention agents and gloss enhancer for paper coating compositions;
15 the paper coating compositions of the invention are stable over a wide viscosity range irrespective of their pH value and impart good printability and gloss to coated paper.

Hydrophilic comb polyurethanes containing polyoxyethylene side-chains are known and have been described in the patent literature.

20 EP 60,430 discloses a process for making a polyurethane having polyalkylene oxide side-chains, but it does not mention the use of the polyurethane in paper coating compositions.

WO 03/046038 describes a broad family of polyurethane dispersants comprising from 35 to 90% by weight of poly(C₂₋₄-alkylene oxide) based on the
25 total weight of the polyurethane polymer, but it is silent about the possibility of using the polyurethanes in paper coating compositions.

SUMMARY OF THE INVENTION

The object of the invention is a paper coating composition comprising a) from 30 to 80% by weight of an inorganic pigment; b) from 0.05 to 3.0 parts by weight each 100 parts by weight of pigment of a water soluble comb
5 polyurethane containing polyoxyethylene side-chains having each molecular weight higher than 500, preferably from 2,000 to 20,000, and ethylene oxide content from 80 to 99.9% by weight; c) at least 15% by weight of water.

DETAILED DESCRIPTION

The paper coating compositions of the invention comprise: a) from 30 to 80%
10 by weight of inorganic pigment; b) from 0.05 to 3.0 parts by weight each 100 parts by weight of pigment of the above described comb polyurethane; c) at least 15% by weight of water, and have Brookfield® viscosity at 25°C and 100 rpm of less than 3,000 mPa*s, preferably from 500 to 2,000 mPa*s.

The paper coating compositions according to the present invention also
15 comprise from 0.01 to 3% by weight of a dispersing agent, because the comb polyurethane does not act per se as pigment dispersant; the compositions may also contain a specific rheology modifier.

Examples of useful dispersing agents are anionic un-crosslinked polyacrylate derivatives, such as sodium polyacrylate, having molecular weight from 5,000
20 to 40,000.

Typical useful rheology modifiers are carboxymethyl cellulose, hydroxypropyl guar, hydroxypropylmethyl cellulose, xanthan, ASA polymers (i.e. "Alkali Swellable Acrylic" polymers).

Dispersing agents, which are common ingredients of paper coating
25 compositions, are not generally able to prevent the flocculation of the finest particles, especially when the paper coating composition is being applied on the

paper sheet, i.e. under high stress conditions, and the particles flocculation is detrimental to smoothness and gloss of the resulting coated paper.

The comb polyurethanes containing polyoxyethylene side-chains having each molecular weight higher than 500, preferably from 2,000 to 20,000, and

5 ethylene oxide content from 80 to 99.9% by weight are particularly effective as deflocculants, avoiding the formation of clusters of fine particles, which may tend to settle, and they characterise the paper coating compositions of the present invention.

The inorganic pigments of the paper coating compositions, preferably having
10 from 40 to 90% of the particles finer than 2 microns, are those normally employed in the coating of paper, and are particularly kaolin, calcium carbonate, talc, titanium dioxide, barium sulfate, gypsum, and mixture thereof. The paper coating compositions of the invention normally also comprise from 1 to 15% by weight of a binder, preferably a polymeric acrylic binder.

15 Among the polymeric acrylic binder preferred for the realisation of the invention we cite the polymers of acrylic or methacrylic acid esters, the copolymers of acrylic ester monomers and vinyl acetate, styrene, butadiene or mixture thereof.

Other conventional additives, such as defoaming agents, biocides, optical
20 brighteners, may be present in the paper coating compositions.

The water soluble comb polyurethane useful for the realisation of the invention comprises a main chain (backbone) containing urethane and urea linkages with multiple trifunctional branch points (branch points) from each of which a polyoxyethylene side-chains emanates.

25 In the present text, with the expression "polyoxyethylene side-chains" we mean side chains containing $-(\text{CH}_2\text{CH}_2\text{O})_n-$ units with $n \geq 9$.

The main chain containing urethane and urea linkages has uniformly spaced branch points, whose distribution can be predicted from the molar ratios and chemical nature of reactants and does not depend from the reaction conditions or catalysts used. Therefore, the fine structure of the comb polyurethane can
5 be advantageously reproduced and possibly modulated as desired.

The polyurethane backbone shall be per se insoluble in water and preferably it does not contain any internal or terminal polyoxyethylene chain.

In the comb polyurethane the total ethylene oxide content, i.e. the sum of the $-(CH_2CH_2O)-$ units, is preferably higher than 50% by weight, more preferably
10 higher than 70% by weight.

The preferred comb polyurethanes have molecular weight higher than 100.000, more preferably from 300.000 to 3.000.000, and polyoxyethylene side-chains having molecular weight from 2,000 to 20,000 and ethylene oxide content from 90 to 99.9% by weight.

15 The polyoxyethylene side-chains of the comb polyurethane are distributed along the backbone at intervals of less than 100, preferably of less than 50, covalent bonds.

The high molecular weight hydrophilic comb polyurethanes may be prepared by any method known in the art.

20 The polyoxyethylene side-chains of the comb polyurethane are introduced by reacting in one of the preparation steps an organic isocyanate group with at least one compound having molecular weight higher than 500, preferably from 2,000 to 20,000, more preferably from 4000 to 6000, ethylene oxide content from 80 to 99.9% by weight, preferably from 90 to 99.9% by weight, and
25 having one group which reacts with isocyanates.

Comb polyurethanes having polyoxyethylene side-chains with molecular weight from 2,000 to 20,000 and ethylene oxide content from 90 to 99.9% by

weight are preferred for use in paper coating compositions, because they impart better water retention, with only slight loss on gloss values.

Any compound having molecular weight higher than 500, ethylene oxide content from 80 to 99.9% by weight and having one group which reacts with isocyanates may be used to introduce the polyoxyethylene side-chains in the comb polyurethane.

Convenient examples of such compounds are C₁-C₄ poly(ethylene oxide) monoalkyl ether, such as poly(ethylene oxide) monomethyl ether and poly(ethylene oxide) monobutyl ether, poly(ethylene oxide) monomethyl ether having molecular weight from 4,000 to 6,000 being the most preferred compound.

The term molecular weight used in this text means the number average molecular weight, when polymers are concerned.

The methods of preparation of the comb polyurethanes of the invention comprise, as key intermediate, a bifunctional isocyanate containing polyoxyethylene side-chains having each molecular weight higher than 500, preferably from 2,000 to 20,000, and ethylene oxide content from 80 to 99.9% by weight which is reacted with one or more compounds having molecular weight from 34 to 300 and two groups which react with isocyanates, in order to chain extend the backbone, to increase the molecular weight of the bifunctional isocyanate and to obtain a comb polyurethane having high molecular weight.

According to one preferred method of preparation (Method A), the comb polyurethane is obtained by reacting in a first step about one mole of a compound having molecular weight from 92 to 1,200 and having three groups which react with isocyanates with about 3 moles of a diisocyanate (step a1); in a second step, the thus obtained trifunctional isocyanate is reacted with equimolar amounts of one or more compounds having molecular weight higher

than 500, preferably from 2,000 to 20,000, ethylene oxide content from 80 to 99.9% by weight and having one group which reacts with isocyanates (step a2); in a third step, the thus obtained bifunctional isocyanate is reacted with one or more compounds having molecular weight from 34 to 300 and having
5 two groups which react with isocyanates (step a3).

According to another preferred method of preparation (Method B) the comb polyurethane is obtained by reacting in a first step a polyisocyanate with one or more compounds having molecular weight higher than 500, preferably from 2,000 to 20,000, ethylene oxide content from 80 to 99.9% by weight and
10 having one group which reacts with isocyanates (step b1) in order to obtain, in the average, a bifunctional isocyanate; in a second step, the thus obtained isocyanate is reacted with one or more compounds having molecular weight from 34 to 300 and having two groups which react with isocyanates (step b2).

According to still another preferred method of preparation (Method C) the comb
15 polyurethane is obtained by reacting in a first step a diisocyanate with equimolar amounts of one or more compounds having molecular weight higher than 500, preferably from 2,000 to 20,000, ethylene oxide content from 80 to 99.9% by weight and having one group which reacts with isocyanates (step c1); in a second step, the thus obtained monofunctional isocyanate is reacted
20 with equimolar amounts of one or more compounds having molecular weight from 34 to 300 and having at least one -NH- group which reacts with isocyanates and at least two hydroxyl groups which react with isocyanates (step c2); in a third step, the thus obtained compound having two groups which react with isocyanates is reacted with diisocyanates in order to obtain an
25 intermediate compound capped by two lateral isocyanate groups (step c3); in a fourth step, the thus obtained bifunctional isocyanate is reacted with one or

more compounds having molecular weight from 34 to 300 and having two groups which react with isocyanates (step c4).

The compound of step a1 having molecular weight from 92 to 1,200 and having three groups which react with isocyanates is preferably a trifunctional alcohol.

- 5 Examples of utilizable trifunctional alcohols are glycerin, polypropylene glycol triol, trimethylolpropane, trimethylolethane,

Any organic diisocyanate having molecular weight below 500 and average –NCO functionality from 2.0 to 2.1 may be used in step a1 and c1 as the diisocyanate.

- 10 Examples of useful diisocyanates are 1,6-hexamethylene diisocyanate (HDI), tetramethylene diisocyanate, 1-isocyanate-3-isocyanate-methyl-3,5,5-trimethyl-cyclohexane (or isophoronediiisocyanate) (IPDI), 4,4'-dicyclohexylmethanediisocyanate, 2,4- toluenediisocyanate either alone or in admixture with 2,6-toluenediisocyanate (TDI), 4,4'-diphenyl-methanediisocyanate (MDI),
15 meta-tetramethylxilylenediisocyanate (TMXDI), 1,5-naphthalene diisocyanate, and mixtures thereof; cycloaliphatic and aliphatic diisocyanate are preferred, the most preferred being IPDI.

The compounds having molecular weight from 34 to 300 and two groups which react with isocyanates used in steps a3, b2 and c4 are preferably diamines.

- 20 Examples of utilizable diamines are hydrazine, ethylenediamine, piperazine, 1,5-pentanediamine, 1,6-dihexanediamine, isophoronediamine, diethylenetriamine.

- Steps a3, b2 and c4 are preferably carried out by dispersing the bifunctional isocyanate in water and adding to the dispersion the diamine, possibly
25 dissolved in water.

The compound having molecular weight from 34 to 300 of step c2 is preferably diethanolamine.

Any organic polyisocyanates with average -NCO functionality from 2,4 to 3,8 (trifunctional isocyanate), and having molecular weight below 800 may be used in step b1.

Examples of trifunctional isocyanates are the compounds obtained from
5 trimerization, biurethization, urethanization or allophanation of difunctional isocyanates, such as those mentioned above, and mixtures thereof.

Useful trifunctional isocyanates are HDI biuret, HDI isocyanurate, IPDI trimers and the combination of the above trifunctional isocyanates with diisocyanates.

The preferred trifunctional isocyanates are the isocyanurate and biuret obtained
10 from hexamethylenediisocyanate, for example HDI isocyanurate in asymmetrical form, HDI biuret in low viscous form, and those obtained by the combinations of IPDI trimers and HDI trimers.

For purpose of the present invention, in order to obtain the desired high molecular weight comb polyurethane, it is preferred to minimize the quantity of
15 diisocyanate that may be present together with the trifunctional isocyanates during the step b1, as it is well known to person skilled in the art.

For the purpose of the present invention, the ratio between the equivalents of isocyanate groups and the equivalent of groups which react with isocyanate during the step c3 is between 1.1 and 2.3.

20 The water soluble comb polyurethanes are preferably non-ionic compounds, devoid of acid groups, such as carboxylic and sulphonic acid groups.

Suitable solvents may be used in the preparation steps, but it is also possible to perform all the preparation steps with the neat reactants, without the use of water or organic solvents.

25 The water soluble comb polyurethanes according to the invention are useful as water retention agents, deflocculant and viscosity stabilizer for paper coating

compositions and provide coated paper with excellent printability, brightness and gloss.

Another advantageous characteristic of the polyurethanes of the invention is the fact that they act as rheology and water retention buffers over different batches of industrial paper coating compositions having same recipe; this means that, in the industrial coating process, the usual deviations from the theoretical amounts of paper coating ingredients does not affect the rheology and water retention characteristics.

10 EXAMPLES

In the examples the following materials were used:

TRIOL1: polypropylene glycol triol, molecular weight 1000 g/mol, Voranol CP 1055, from Dow Chemical Company

ETHOXY1: butanol polyethoxylated, molecular weight 3000 g/mol

15 ETHOXY2: methanol polyethoxylated, molecular weight 5000 g/mol

ETHOXY3: butanol polyethoxylated, molecular weight 5000 g/mol

ETHOXY4: methanol polyethoxylated, molecular weight 750 g/mol

DIISOCYANATE1: isophoronediiisocyanate, molecular weight 222.3 g/mol, Desmodur I from Bayer Material Science.

20 TRIISOCYANATE1: hexamethylene diisocyanate trimer, NCO content 24,0%, NCO functionality 3,1, Desmodur XP2410 from Bayer Material Science.

AMINE1: isophorone diamine, molecular weight 170.3 g/mol, from Sigma Aldrich

AMINE2: diethanolamine, molecular weight 105,14 g/mol, from Sigma Aldrich

25 AMINE3: ethylendiamine, molecular weight 60,10 g/mol, from Sigma Aldrich

AMINE4: 24% hydrazine hydrate solution, molecular weight 32.3 g/mol, from Sigma Aldrich.

EXAMPLE I

Preparation of a comb polyurethane with Method A

A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 100.0 g of

5 TRIOL1 and 300.0 g of ETHOXY1. The mixture was heated under stirring condition to 85°C and 0.15 g of 85% phosphoric acid were added. At 85°C 69.0 g of DIISOCYANATE1 were charged to the homogeneous mixture, under stirring; after 20 minutes 0.3 g of dibutyltindilaurate (DBTL) were added. The reaction temperature was kept at 85°C until the titrimetric determination of the
10 free

–NCO groups still present gave a calculated value of 1,7% (value determined in this example as well as in the other examples according to the standard method ASTM D2572),

300 g of the obtained product were dispersed by vigorous stirring into 890 g of
15 water cooled at 18°C. After 20 minutes 9.7 g of AMINE1 dissolved in 39.3 g of water were dropped in.

The obtained product had 25.55% solid content, viscosity 48 mPa·s (measured by Brookfield® viscometer at 20 rpm) and pH 6.5.

EXAMPLE II

20 Preparation of a comb polyurethane with Method A

A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 50.0 g of

TRIOL1 and 250.0 g of ETHOXY2. The mixture was heated under stirring to 85°C and 0.11 g of 85% phosphoric acid were added . At 85°C, 34.5 g of
25 DIISOCYANATE1 were charged to the homogeneous mixture under stirring condition; after 20 minutes 0.3 g of dibutyltindilaurate (DBTL) were added. The

reaction temperature was kept at 85°C until the titrimetric determination of the free –NCO groups still present gave a calculated value of 1.26%.

300 g of the obtained product were dispersed by vigorous stirring into 893.1 g of water cooled at 18°C. After 20 minutes 6.9 g of AMINE1 dissolved in 27.4 g of water were dropped in.

The obtained product had solid content 26.15%, viscosity 62 mPa*s (measured by Brookfield® viscometer at 20 rpm) and pH 6.4.

EXAMPLE III

Preparation of a comb polyurethane with Method B

10 A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 300.0 g of ETHOXY1 and 0.11 g of 85% phosphoric acid. The mixture was heated under stirring condition to 85°C and 56.6 g of TRIISOCYANATE1 were charged; after 20 minutes 0.3 g of dibutyltindilaurate (DBTL) were added. The reaction
15 temperature was kept at 85°C until the titrimetric determination of the free –NCO groups still present gave a calculated value of 2.5%.

300 g of the obtained product were dispersed by vigorous stirring into 862.6 g of water cooled at 18°C. After 20 minutes 12.8 g of AMINE1 dissolved in 51.5 g of water were dropped in.

20 The obtained product had solid content 25.98%, viscosity 196 mPa*s (measured by Brookfield® viscometer at 20 rpm) and pH 6.6.

EXAMPLE IV

Preparation of a comb polyurethane with Method B

A reaction vessel, equipped with internal thermometer, stirrer and cooler, was
25 filled, under nitrogen atmosphere and at room temperature, with 274.5 g of ETHOXY 2 and 0.11 g of 85% phosphoric acid. The mixture was heated under stirring to 85°C and 31.1 g of TRIISOCYANATE1 were charged; after 20

minutes 0.3 g of dibutyltindilaurate (DBTL) were added. The reaction temperature was kept at 85°C until the titrimetric determination of the free –NCO groups still present gave a calculated value of 1.6%.

275 g of the obtained product were dispersed by vigorous stirring into 795.3 g of water cooled at 18°C. After 20 minutes 7.6 g of AMINE1 dissolved in 30.2 g of water were dropped in.

The obtained product had solid content 25.51%, viscosity 246 mPa*s (measured by Brookfield® viscometer at 20 rpm) and pH 5.5.

EXAMPLE V

10 Preparation of a comb polyurethane with Method B

A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 300.0 g of ETHOXY3 and 0.11 g of 85% phosphoric acid. The mixture was heated under stirring to 85°C and 22.0 g of TRIISOCYANATE1 and 10.1 g of DIISOCYANATE1 were charged; after 20 minutes 0.3 g of dibutyltindilaurate (DBTL) were added. The reaction temperature was kept at 85°C until the titrimetric determination of the free –NCO groups still present gave a calculated value of 1.8%.

280 g of the obtained product was dispersed by vigorous stirring into 826.4 g of water cooled at 18°C. After 20 minutes 9.4 g of AMINE4 dissolved in 9.8 g of water were dropped in.

The obtained product had solid content 26.07%, viscosity 412 mPa*s (measured by Brookfield® viscometer at 20 rpm) and pH 6.8.

EXAMPLE VI

Preparation of a comb polyurethane with Method B

25 A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 300.0 g of ETHOXY3 and 0.11 g of 85% phosphoric acid. The mixture was heated under

stirring to 85°C and 22.0 g of TRIISOCYANATE1 and 10.1 g of DIISOCYANATE1 were charged; after 20 minutes 0.3 g of dibutyltindilaurate (DBTL) were added. The reaction temperature was kept at 85°C until the titrimetric determination of the free –NCO groups still present gave a calculated value of 1.8%.

- 5 280 g of the obtained product were dispersed by vigorous stirring into 838.1 g of water cooled at 18°C. After 20 minutes 2.7 g of AMINE3 dissolved in 10.0 g of water were dropped in.

The obtained product had solid content 25.84%, viscosity 256 mPa*s (measured by Brookfield® viscometer at 20 rpm) and pH 6.8.

10 EXAMPLE VII

Preparation of a comb polyurethane with Method C

- A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 300.0 g of ETHOXY2 and 0.11 g of 85% phosphoric acid. The mixture was heated under
- 15 stirring to 85°C and 15.3 g of DIISOCYANATE1 were charged; after 10 minutes 0.3 g of dibutyltindilaurate (DBTL) were added. The reaction temperature was brought to 85°C until the titrimetric determination of the free –NCO groups still present gave a calculated value of 0.9%. The mixture was then cooled to 55°C and 6.6 of AMINE2 dissolved in 6.6 g of N-methylpyrrolidone were charged
- 20 dropwise. After 20 minutes the titrimetric determination of the free –NCO groups gave a calculated value of 0.0%. The reaction temperature was then brought to 85°C and 28.5 g of DIISOCYANATE1 was charged and it was reacted until the titrimetric determination of the free –NCO groups gave a calculated value of 1.5%.
- 25 300 g of the obtained product were dispersed by vigorous stirring into 898.0 g of water cooled at 18°C. After 20 minutes 2.9 g of AMINE3 dissolved in 10.7 g of water were dropped.

The obtained product had solid content 24.99%, viscosity 194 mPa*s (measured by Brookfield® viscometer at 20 rpm) and pH 6.3.

EXAMPLE VIII

Preparation of a comb polyurethane with Method B

- 5 A reaction vessel, equipped with internal thermometer, stirrer and cooler, was filled, under nitrogen atmosphere and at room temperature, with 300.0 g of ETHOXY4 and 0.11 g of 85% phosphoric acid. The mixture was heated under stirring to 85°C and 226.2 g of TRIISOCYANATE1 were charged; after 10 minute 0.3 g of dibutyltindilaurate (DBTL) were added. The reaction
- 10 temperature was kept at 85°C until the titrimetric determination of the free – NCO groups still present gave a calculated value of 5.9%. 470 g of the obtained product was dispersed by vigorous stirring into 1360 g of water cooled at 18°C. After 20 minutes 16.7 g of AMINE3 dissolved in 62.1 g of water were dropped in.
- 15 The obtained product had solid content 25.1%.

Application Examples

Paper coating compositions based on 100% carbonate (Hydrocarb 90, from Omya, CH) were prepared using the comb polyurethanes from Examples I-VIII and with a water retention agent of the prior art.

- 20 The compositions of the paper coating compositions are reported in Table 1; the amounts of the ingredients are parts by weights.
- The paper coating compositions were characterized by performing the following measurements:
- pH
 - 25 • Brookfield® viscosity, 100 rpm
 - Dry matter
 - Water retention –Tappi Method T710

The data obtained are also reported in Table 1.

The paper coating compositions were applied (13 g/m^2) on offset sheets (80 g/m^2); the sheets were conditioned for 24h at 21°C and 50% r.h. and calendared (cylinders temperature 55°C , pressure 67.5 Kg/cm ; 4 nips).

- 5 Brightness and gloss were measured and are reported in Table 2.

Table 1

PAPER COATING COMPOSITIONS:	1	2	3	4	5	6	7	8	9 ⁶⁾
HYDROCARB 90	100	100	100	100	100	100	100	100	100
DOW LATEX 935 ¹⁾	10	10	10	10	10	10	10	10	10
REOTAN A ²⁾	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045	0.045
DEFOMEX 108 ³⁾	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
TINOPAL ABP-Z ⁴⁾	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Ex. 1	0.45	/	/	/	/	/	/	/	/
Ex. 2	/	0.45	/	/	/	/	/	/	/
Ex. 3	/	/	0.45	/	/	/	/	/	/
Ex. 4	/	/	/	0.45	/	/	/	/	/
Ex. 5	/	/	/	/	0.45	/	/	/	/
Ex. 6	/	/	/	/	/	0.45	/	/	/
Ex. 7	/	/	/	/	/	/	0.45	/	/
Ex. 8	/	/	/	/	/	/	/	0.45	/
Viscolam GP37 ⁵⁾	/	/	/	/	/	/	/	/	0.15
CHARACTERISTICS OF THE PAPER COATING COMPOSITIONS									
Dry matter (%)	70.32	70.40	70.18	70.16	69.95	69.95	69.97	70.21	70.18
pH	8.85	9.02	8.85	8.91	8.97	9.08	9.06	8.87	8.95
Viscosity (mPa*s)	550	655	570	650	600	770	650	450	960
Water retention (g/m^2)	150	140	155	145	130	145	140	165	112

- 1) Binder, styrene butadiene latex (Dow Chemical Co. US)
 2) Dispersant, sodium polyacrylate (Lamberti SpA, IT)
 3) Defoaming agent, (Lamberti SpA, IT)
 4) Optical brightener (CIBA, CH)
 5) ASE Thickener from Lamberti SpA
 6) comparative

Table 2

PAPER COATING COMPOSITION :	°Brightness ¹⁾	Gloss @ 75° ²⁾
1	100.8	72.5
2	100.6	72.1
3	101.1	72.8
4	100.5	72.0
5	100.3	72.4
6	100.4	72.7
7	100.9	72.6
8	100.6	75.2
9 ³⁾	99.2	65.8

- 10 1) Brightness, Tappi Method T452
 2) Specular Gloss at 75°, Tappi Method T480
 3) comparative

CLAIMS

1. Paper coating compositions comprising a) from 30 to 80% by weight of inorganic pigment; b) from 0.05 to 3.0 parts by weight each 100 parts by weight of pigment of at least one water soluble nonionic comb polyurethane containing polyoxyethylene side-chains having each molecular weight higher than 500 and ethylene oxide content from 80 to 99.9% by weight; c) at least 15% by weight of water, and having Brookfield® viscosity at 25°C and 100 rpm of less than 3,000 mPa*s.
2. Paper coating compositions according to claim 1 wherein the comb polyurethane has total ethylene oxide content higher than 50% by weight.
3. Paper coating compositions according to claim 2 wherein the comb polyurethane has total ethylene oxide content higher than 70% by weight.
4. Paper coating compositions according to claim 2 or 3 wherein the comb polyurethane has molecular weight higher than 100,000 and polyoxyethylene side-chains having molecular weight from 2,000 to 20,000 and ethylene oxide content from 90 to 99.9% by weight.
5. Paper coating compositions according to claim 1 wherein the comb polyurethane is obtained by reacting a bifunctional isocyanate containing polyoxyethylene side-chains having each molecular weight higher than 500 and ethylene oxide content from 80 to 99.9% by weight with one or more compounds having molecular weight from 34 to 300 and two groups which react with isocyanates.
6. Paper coating compositions according to any of the preceding claims containing 0.01 to 3% by weight of a dispersing agent and from 1 to 15% by weight of a binder.

7. Paper coating compositions according to claim 6. wherein the dispersing agent is anionic un-crosslinked polyacrylate derivatives having molecular weight from 5,000 to 40,000.
8. Paper coating compositions according to claim 1 wherein the inorganic pigment has from 40 to 90% by weight of the particles finer than 2 microns and is chosen among kaolins, calcium carbonate, talc, titanium dioxide, barium sulfate, gypsum and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/053301

A. CLASSIFICATION OF SUBJECT MATTER
INV. D21H19/62 D21H21/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 03/046038 A1 (AVECIA LTD [GB]; RICHARDS STUART NICHOLAS [GB]) 5 June 2003 (2003-06-05) page 1, lines 1-9 pages 1-2, lines 35-10 page 3, lines 5-11 page 12, lines 3-40 page 13, lines 3,4 page 15, lines 31-36	1-5,8
Y	US 2003/195293 A1 (LUBNIN ALEXANDER V [US] ET AL) 16 October 2003 (2003-10-16) page 1, paragraphs 2,8 page 7, paragraph 77-79 page 8, paragraph 94	1-5,8
	----- -/-- -----	

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

3 May 2010

Date of mailing of the international search report

20/05/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Beins, Ulrika

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/053301

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 897 281 B2 (LUBNIN ALEXANDER V [US] ET AL) 24 May 2005 (2005-05-24) cited in the application page 1, lines 11-17	1-8
A	EP 0 060 430 A2 (GOLDSCHMIDT AG TH [DE]) 22 September 1982 (1982-09-22) cited in the application page 1, lines 11-17	1-8
A	WO 99/67310 A1 (AKZO NOBEL NV [NL]; EKA CHEMICALS AB [SE]; BIERMANN CHRISTIAN [DE]; MA) 29 December 1999 (1999-12-29) pages 1,2,9	1-8
A	US 5 716 676 A (SCHUETZE DETLEF-INGO [DE] ET AL) 10 February 1998 (1998-02-10) column 1, lines 13-37 column 2, lines 6-14	1-8
A	DE 195 26 278 A1 (BAYER AG [DE]) 23 January 1997 (1997-01-23) page 1, lines 3,4 page 1, line 38 - page 2, line 2	1-8

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/053301

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 03046038	A1	05-06-2003	AT 458765 T 15-03-2010
		AU 2002339083 A1 10-06-2003	
		CN 1615322 A 11-05-2005	
		EP 1458778 A1 22-09-2004	
		JP 4194946 B2 10-12-2008	
		JP 2005510600 T 21-04-2005	
		TW 277630 B 01-04-2007	
		US 2004260013 A1 23-12-2004	
US 2003195293	A1	16-10-2003	AU 2003213741 A1 27-10-2003
			BR 0309010 A 01-02-2005
			CA 2481327 A1 23-10-2003
			CN 1656135 A 17-08-2005
			EP 1492831 A1 05-01-2005
			JP 2005522543 T 28-07-2005
			MX PA04009729 A 13-12-2004
			WO 03087183 A1 23-10-2003
			US 2004214937 A1 28-10-2004
US 6897281	B2	24-05-2005	AU 2003213741 A1 27-10-2003
			BR 0309010 A 01-02-2005
			CA 2481327 A1 23-10-2003
			CN 1656135 A 17-08-2005
			EP 1492831 A1 05-01-2005
			JP 2005522543 T 28-07-2005
			MX PA04009729 A 13-12-2004
			WO 03087183 A1 23-10-2003
			US 2003195293 A1 16-10-2003
			US 2004214937 A1 28-10-2004
EP 0060430	A2	22-09-1982	DD 202170 A5 31-08-1983
WO 9967310	A1	29-12-1999	AT 222268 T 15-08-2002
			AU 750834 B2 01-08-2002
			AU 5073799 A 10-01-2000
			BR 9911453 A 20-03-2001
			CA 2336180 A1 29-12-1999
			CN 1306547 A 01-08-2001
			CZ 20004804 A3 15-08-2001
			DE 69902538 D1 19-09-2002
			DE 69902538 T2 10-04-2003
			DK 1090054 T3 11-11-2002
			ES 2181458 T3 16-02-2003
			ID 27891 A 03-05-2001
			JP 2002518563 T 25-06-2002
			NO 20006199 A 22-02-2001
WO 9967310	A1		NZ 508425 A 25-10-2002
			PT 1090054 E 31-12-2002
			RU 2214423 C2 20-10-2003
US 5716676	A	10-02-1998	NONE
DE 19526278	A1	23-01-1997	CA 2227145 A1 06-02-1997
			WO 9704169 A1 06-02-1997
			EP 0839228 A1 06-05-1998
			JP 11509587 T 24-08-1999
			US 6008289 A 28-12-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/053301

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
