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(54) Paper coatings.

(57) A method for reducing the particle size of cellulose in water and/or an organic solvent (preferably water) comprising

a) forming a slurry or paste of cellulose material in water, the cellulose material having a dry weight average particle size of 1 to 100 microns (preferably 1 to 20 microns) ; and

b) reducing the average particle size of the cellulose material to 1 to 10 microns (preferably 1 to 3 microns), preferably by milling, to form a carrier ;

an additive being optionally added to the water prior to addition of cellulose or to end of operations a) or b) above. The additive when added, is preferably an optical brightener. The method is useful in the field of paper coatings where it permits more efficient use of additives.

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The invention relates to microcrystalline cellulose for use in paper-coating applications. The invention further relates to an improved coating composition which contains a "carrier" substance for additives, particularly optical brighteners.

Conventionally, coated printing papers are prepared using paper-coating compositions which comprise a pigment (for example kaolin, calcium carbonate or titanium dioxide) which is dispersed in water, and a binder.

In the past, the binders used were exclusively high molecular weight, naturally-occurring products, such as starch or casein. Nowadays, these have largely been replaced entirely or partially by synthetic high molecular weight copolymers in the form of aqueous dispersions.

Other additives commonly found in coating compositions are dispersants, water-soluble polymers, optical brighteners and alkali for pH adjustment.

Because of the very high level of pigment solids required for a coating composition, anionic dispersants are used as deflocculants, causing particle repulsion and reduced viscosity.

The water-soluble polymers previously mentioned act as cobinders and impart water retention to the paper coating composition. They may be naturally-occurring polymers such as starch and casein or alternatively synthetic compounds such as polyvinyl alcohol (PVOH), carboxymethylcellulose (CMC) and water soluble polyacrylates.

Commercial optical brightening agents are added to increase the level of whiteness of the coated paper and the efficiency of these compounds depends very much on the coating composition. It is known that if the brightener molecule can bond to a substance by means of adsorption or hydrogen bond formation, the brightener performance is appreciably enhanced.

Some water-soluble polymers used in coating compositions, such as PVOH and CMC, do adsorb optical brighteners to some extent, but the water-insoluble binders, in aqueous dispersion, have a negative influence on brightener performance.

The invention relates to a paper coating composition containing a substance which allows the easy addition of additives to a paper, and which in particular greatly enhances the performance of commercial optical brighteners.

The substance is cellulose, preferably microcrystalline cellulose, having a particle size of 1 to 10 microns, preferably 1 to 3 microns, in aqueous suspension. It is well known that cellulose swells in water and that the "dry" particle size of a cellulose particle will be considerably smaller than the "wet" particle size.

Commercial optical brighteners are very substantive to microcrystalline cellulose and once adsorbed they appreciably improve the whiteness of the coated paper.

Microcrystalline cellulose, sold in powder form, has been commercially available for many years and is used extensively in the pharmaceutical industry. It has been used to a limited extent in the paper industry but its potential has been restricted by its large particle size and lack of surface area.

The present invention provides a method for reducing the particle size of cellulose (preferably microcrystalline cellulose) in water and/or an organic solvent (preferably water) comprising

a) forming a slurry or paste of cellulose material in water, the cellulose material having a dry weight average particle size of 1 to 100 microns (preferably 1 to 20 microns); and

b) reducing the average wet particle size of the cellulose material to 1 to 10 microns (preferably 1 to 3 microns), preferably by milling, to give a carrier;

an additive being optionally added to the water prior to addition of cellulose or at the end of operations a) or b) above.

The present invention enables the additive to be adsorbed on to the carrier substance.

Preferably the process according to the invention comprises

a) slurrying microcrystalline cellulose powder in water to give dispersion of 2 to 15%, preferably 5 to 10%, weight solids, preferably at a temperature of 5 to 60°C, preferably 20-40°C; and

b) reducing the wet particle size of the dispersion, preferably using a bead mill; and

c) adding the additive to the dispersion of reduced particle size.

In one embodiment of the invention, the additive may be a surface sizing agent and/or a dyestuff. However, the preferred additive is an optical brightener. This particular aspect of the invention will be discussed further hereinunder.

The present invention also provides an aqueous slurry or paste (a carrier), for use in a paper-coating composition, containing microcrystalline cellulose having an average particle size of 1 to 10 microns, preferably 1 to 3 microns. This greatly enhances the performance of commercial optical brighteners that are often used in paper coating compositions.

The slurry, paste or dispersion may be given several passes through the mill until the wet particle size averages 1 to 10 microns, preferably 1 to 3 microns.

Commercial optical brighteners are very substantive to microcrystalline cellulose, and once adsorbed they

improve the whiteness of the coated paper substantially. It is a particular feature of this invention that the use of optical brighteners results in an unexpectedly high increase in whiteness.

A summary of optical brighteners may be found, for example, in the article by H. Gold in Venkataraman, "The Chemistry of Synthetic Dyes", Academic Press, New York and London 1971, Vol. 5, chapter 8, pp. 536-679 (which is herewith incorporated by reference). Optical brighteners are commercially available and therefore do not require more detailed comment here. However, a more detailed characterization of this category of compounds may be found in German Laid-Open Application DOS No. 2,628,878 and German Published Application DAS No. 1,795,047 (which are incorporated herein by reference).

These publications describe optical brighteners based on stilbene derivatives which are the preferred optical brighteners for the purposes of this invention.

The viscosity of the cellulose increases during milling and, if desired, compounds may be added which reduce viscosity. For example, the cellulose may be milled in the presence of dispersing agent, suitable examples of which are mentioned hereinunder in connection with pigments, optionally in the presence of a filler such as calcium carbonate or clay. Dispersants may be used in a quantity of up to 10% by weight (on dry cellulose). An especially effective and preferred dispersant for the purposes of this invention is carboxymethyl cellulose (CMC)

To avoid colouration of the cellulose by metal contamination during milling, sequestering agents may be added. Depending on the construction of the bead mill, a grey colour resulting from metal pick-up may be observed in the milled cellulose. If sequestering agents are used, they are used in a quantity of up to 0.4% by weight, (based on the weight of dry cellulose), usually in the form of commercially-available material which has a 40% concentration.

Preferred sequestering agents are ethylene diamine tetraacetic acid (EDTA), diethylene triamine pentaacetic acid (DTPA), diethylene triamine pentamethylene phosphonic acid (DTPMA) and nitrilotriacetic acid (NTA) or their sodium salts.

By creating a carrier according to the invention, the surface area of the cellulose is greatly increased, creating much higher adsorption capacities for the additive. The additive, which may be in liquid or powder form, is then added to the carrier.

Preferably 1 to 50%, more preferably 8 to 25% additive, based on the dry weight of cellulose, is added to a slurry according to the invention.

The amount used depends on the substantivity of the additive and should be adjusted so that once the cellulose particle size is reduced, almost all the adsorption sites are taken up and very little additive is left free in the water. If required, hardness salts, such as magnesium sulfate may be used to increase the substantivity of the additive. Normally an addition of 10 to 100 ppm magnesium sulfate to the water is sufficient.

The preparation of the aqueous carrier according to the invention may also be carried out by adding the additive and any dispersant and/or hardness salts to the water, prior to the addition of the cellulose powder. The mixture is then milled as before.

The preferred dry microcrystalline cellulose powder that is added to water to form the carrier has an average particle size of 2 to 100 microns. It is relatively simple to bring the size distribution to the required level using classification techniques. Once mixed with water, however, the particles swell and their size is increased by a factor of 10 to 100. It is therefore important that the particle size be reduced after the powder has been mixed with the water.

Further according to the invention there is provided a process for coating paper comprising applying the carrier defined above, optionally containing one or more additives, to the surface of paper.

Still further according to the invention there is provided paper to which a carrier according to the invention has been applied.

It is found that the fine particle size cellulose carrier, after application to the paper, dries to form a film. As a result, the surface properties of the paper are enhanced in such a way that if the coated paper is to be printed, the printing properties are far superior to those of paper which has not received this surface treatment.

The cellulose particles shrink on drying to give a smooth, tough film. The interstices in the paper surface are filled with the carrier, and when dry the paper surface has a smooth feel and appearance. The large hydrogen bonding capacity of the micronised cellulose ensures a high surface strength for the coated paper. This surface modification is particularly noticeable if the cellulose carrier is applied on its own or together with the additive, using any commercial coating technique or a size press.

Any commercial optical brightener, dyestuff or other art-recognised additive, having affinity for cellulose can then be added to the modified microcrystalline cellulose carrier. The amounts of additive are adjusted so that almost total adsorption is achieved. The carrier with additive is then added to the coating composition, thereby imparting to the coated paper whatever property the additive confers, for example, high whiteness, high colour yield or surface wet/dry strength.

Yet still further according to the invention there is provided a pigment-containing composition for use in paper coating comprising per 100 parts by weight of pigment,

a) from 5 to 25 parts by weight of binder (in the form of an aqueous dispersion),

b) from 0.1 to 10 parts by weight of water soluble cobinder and/or water retention aid; and

c) 0.1 to 5 parts by weight of the carrier to which 0.1 to 50%, preferably 0.1 to 20% by weight of additive may optionally be adsorbed according to the invention.

Suitable pigments for use in the coating composition include, china clay (kaolin), calcium carbonate, sulfate or silicate, titanium dioxide, talc, barium sulfate, zirconium oxide and alumina. These pigments may be used independently or in admixture.

Appropriate copolymers for use in the binder mixture are all commercial synthetic binders which are available in the form of an aqueous dispersion. These polymers have a glass transition temperature of from -40° to +50°C. Examples of typical monomers from which these copolymers may be prepared are esters of acrylic acid and of methacrylic acid, acrylonitrile, methacrylonitrile, acrylamide, methacrylamide, vinyl chloride, vinylidene chloride, ethylenically monounsaturated or polyunsaturated hydrocarbons, e.g. ethylene, propylene, butylene, styrene, butadiene, isoprene and chloroprene, vinyl esters, vinylsulphonic acid and esters of ethylenically unsaturated carboxylic acids, e.g. hydroxypropyl acrylate and hydroxypropyl methacrylate.

Where appropriate, other assistants may also be added to the paper coating composition, for example alkalis, e.g. sodium hydroxide, potassium hydroxide or ammonia. These compounds are used primarily to adjust the pH of the mixture to around 8.5 but they also act as viscosity modifiers, keeping the coating mix fluid.

To achieve good dispersion of the ingredients, from 0.2 to 5% by weight of a dispersant, e.g. a low molecular weight polymer of acrylic acid and preferably an ammonium salt or an alkali metal (e.g. sodium) salt of a polyacrylic acid having a K value of from 10 to 35, may be employed. The K values of the polymers are measured by the method of H. Fikentscher, Cellulose-Chemie 13 (1932), 58-64 and 71-74, in 0.5% strength aqueous solution at 25°C.

The water-soluble polymers may be regarded as co-binders because they themselves possess pigment binding properties. The synthetic products, and also the natural cobinders, act as thickeners, i.e. they increase the viscosity of the aqueous paper-coating compositions. In addition they increase the water retention of the coating composition and some such polymers activate additives to some extent. Their use in the latter respect has always been limited because even small amounts affect the rheology of the mix and these low levels are not sufficient for efficient brightener development.

To prepare, for example, a paper-coating composition according to the invention which comprises an optical brightener, the carrier (as herein defined) is mixed with the other coating composition ingredients, preferably once the pigment/binder mixture has been prepared, in a manner as described below.

With the aid of a powerful dispersing blender, 100 parts of selected pigments are dispersed in water containing 0.1 to 0.5 parts sodium hydroxide and 0.1 to 0.5 parts of a commercial dispersant based on a low molecular weight polyacrylic acid, so that the solids of the mix are 50-70%.

To this are added 5 to 20 parts of a commercial synthetic copolymer binder and optionally 0.2 to 2.0 parts of a water-soluble polymer as cobinder. Finally, 0.2 to 5 parts of a brightened cellulose carrier are added. The pH of the coating composition is adjusted to 8.0 to 9.0 with sodium hydroxide or ammonia.

The final solids of the coating composition is 50 to 70%.

Once applied to paper, using for example an air-knife coater, a blade coater, a metering bar coater or a size press, the whiteness of the sheet is far superior to that where cellulose is not used. Traditional water-soluble polymers, used as "carriers" for additives, are not able to generate the increased levels of whiteness seen with the present invention.

This method may be used with any other suitable additive replacing the optical brightener.

The traditional method of preparation for coating compositions is to slurry the pigments in water containing dispersant and then add copolymer binder, water soluble cobinder and, say, optical brightener After pH adjustment to 8.0 to 9.0, the mix is ready for use.

With this traditional method, the additive is added as a liquid and, since very little of the additve is actually adsorbed on to a composition component, most of it migrates with the water phase into the base sheet or is left in the coating after drying. In the particular case of optical brighteners, high levels of brightener are used to produce low levels of whiteness, showing that the traditional use of additives in coating compositions is far from efficient.

In a conventional coating process, the amount of optical brightener-containing coating mix applied to the paper surface has a direct influence on the level of whiteness, measured on the finished paper. For example, a coat weight i.e., the amount of dry weight added to the original base paper and measured in grams per square meter (gsm) of say 5 gsm almost always develops a higher measured whiteness than one with an 18 gsm coat weight. This is due to the "free" optical brightener migrating into and adsorbing on the base sheet. If the coat

weight is low, e.g. 5 gsm, the whiteness of the base sheet shows through the coating and contributes to the measured value. On the other hand, a coat weight of 18gsm tends to mask the base sheet, resulting in a lower measured whiteness.

The present invention using the novel carrier substance allows a high whiteness to be achieved, even with high coat weights.

Although the advantages of the present invention are particularly apparent when the additive is a commercial optical brightening agent, many more additives may be used in conjunction with micronised microcrystalline cellulose.

For example, direct dyestuffs, both anionic and cationic in nature, adsorb quite readily on to the carrier paste. Colour can therefore be introduced into coatings and the surface treatment of paper.

Much work has been carried out in recent years on the application of dyestuffs to the surface of paper, using the size press. This particular application has difficulties, mainly due to the uneven absorption of liquid dye on the paper surface, leading to a mottling or "orange peel" effect.

With this invention, the carrier paste is dyed to the required colour and then applied to the paper surface. This proposal has the same effect as coating using coloured pigments. The colouration media is particulate, albeit in a very fine form. With dyestuff however, recycling of paper is much easier due to the ease with which decolourization can be carried out using oxidative bleach. This is not the case where coloured pigments have been used; many are resistant to oxidative bleaches.

Other additives which can also be successfully applied to the cellulose carrier include cationic sizes, cationic water repellent agents, dry and wet strength resins and other surface modification chemicals, which, even if not substantive to cellulose, can be "fixed" using a cationic chemical.

The invention will now be illustrated by the following examples.

EXAMPLE 1

The preparation of a carrier for additives.

In a suitable container, 20 g microcrystalline cellulose ("Avicel" PH-105) having an average dry particle size of 20 μm, is mixed with 380 g water and 0.8g carboxymethylcellulose (CMC)using a high shear laboratory blender. The resulting dispersion is then passed through a laboratory bead mill having a chamber size of 250 ml and a glass grinding bead size of 1 mm and with a shaft rotation speed of 4000 rpm, until the average wet particle size of the carrier is 1 to 5 μm. (measured with a Horiba LA 500 particle analyzer using laser diffraction) : Yield is 400g.

The resulting white viscous paste, hereinafter referred to as the carrier paste, is now ready for mixing with an additive.

EXAMPLE 2

20 g of carrier paste, at 5% solids, and 0.1 g "Leucophor" AP Liquid, a commercial optical brightening agent based on stilbene, are mixed in a 50 ml beaker at 20°C and left for 10 minutes.

In a separate laboratory high shear blended, 75 g of SPS coating clay and 25 g of calcium carbonate are added slowly to 42.8 g water containing 0.5g "Dispex" N 40 (40% active). Once homogeneous, 20 g "Acronal" S360, a 50% active styrene/acrylate copolymer binder, is added followed by the 20.1 g brightened Carrier paste made earlier. The pH of the coating mix is adjusted to 8.5 with sodium hydroxide (30% solution). The solids content of the coating composition is approximately 60%. After mixing for 10 minutes, the coating composition is applied to paper, using a metering bar coater.

The results of this application are shown in the Table below.

EXAMPLE 3

In a laboratory high shear blender, 75 g of SPS coating clay and 25 g calcium carbonate are added slowly to 42.8 g water containing 0.5 g "Dispex" N 40 (40% active). Once homogeneous, 20 g "Acronal" S 360, a 50% active styrene/acrylate copolymer binder, is added followed by 20 g of a 2.5% CMC solution ("Finnfix" 5) and 1.0 g "Leucophor" AP Liquid. The pH of the coating mix is adjusted to 8.5 with sodium hydroxide (30% solution).

The solid content of the coating composition is approximately 60%. After mixing for 10 minutes, the coating composition is applied to paper, using a metering bar coater.

The results of this application are shown in the Table.

EXAMPLE 4

30g of carrier paste, at 5 % solids, and 0.3 g "Leucophor" U Liquid, a commercial optical brightening agent based on stilbene, are mixed in a 50 ml beaker at 30°C and left for 30 minutes.

In a separate laboratory high shear blender, 70 g of SPS coating clay and 30 g calcium carbonate are added slowly to 51.8 g water containing 0.5g "Dispex" N 40 (40% active). Once homogeneous, 20 g "Acronal" S 360, a 50% active styrene/acrylate copolymer binder, is added followed by the 30.3 g brightened carrier paste made earlier. The pH of the coating mix is adjusted to 8.5 with sodium hydroxide (30% solution). The solids content of the coating composition is approximately 55%. After mixing for 10 minutes, the coating composition is applied to paper,using a metering bar coater.

The results of this application are shown in the Table below.

EXAMPLE 5

In a laboratory high shear blender, 70 g of SPS coating clay and 30 g calcium carbonate are added slowly to 61.8 g water containing 0.5 g "Dispex" N 40 (40% active). Once homogeneous, 20 g "Acronal" S 360, a 50 % active styrene/acrylate copolymer binder, is added followed by 20 g of a 2.5% PVOH solution ("Poval" PVA 205) and 1.5 g "Leucophor" U Liquid. The pH of the coating mix is adjusted to 8.5 with sodium hydroxide (30% solution).

The solids content of the coating composition is approximately 55%. After mixing for 10 minutes, the coating composition is applied to paper, using a metering bar coater.

The results of this application are shown in the Table below.

TABLE

EXAMPLE NO	VISCOSITY (mPas)	COATING WEIGHT (g.s.m.)	WHITENESS (R457)	DELTA REFLECTANCE
2	820	5	89.4	5.2
2	820	22	94.0	9.7
3	1900	5	86.7	2.6
3	1900	22	84.9	0.9
4	670	5	90.6	6.1
4	670	22	95.3	11.0
5	1480	5	87.2	3.3
5	1480	22	85.3	1.4

The viscosity is measured using a Brookfield viscometer, spindle No 4 speed 100 rpm.

Whiteness is measured using a Elrepho 2000 spectrophotometer, with the UV filter out, at 457 nm.

Delta reflectance is a measure of the difference in whiteness with the UV filter in and the UV filter out. With the UV filter in, the effect of additive is not observed and therefore the measurement can be taken to be that of the base coating.

EXAMPLE 6

To 100 g of carrier paste as prepared in Example 1 but from which the CMC has been omitted, 0.75 g "Cartasol" Red K-2BN (a cationic direct dye) is then added and stirred for 10 minutes. Paper is then coated with

this coloured paste using a metering bar coater. Once dried, the sheet of paper is assessed for colour uniformity and shade.

No mottle is evident, due to the even distribution of dyed cellulose and a medium to deep red shade is observed.

As a comparison, a solution of dye was applied, mixed with an 8% aqueous solution of "Amylox" P 45 oxidized starch at 40°C. In contrast, a severe mottle was noted due to uneven dyestuff penetration into the paper sheet.

EXAMPLE 7

To 100 g of carrier paste, as prepared in Example 1, 0.95 g of "Cartasol" Red 3BF (an anioninc direct dye) is added and stirred in for 10 minutes. This mixture is then added to 200 g of a 12% aqueous solution of "Amylox" P 45 oxidized starch. 100ml of this composition is added to the nip of a laboratory size press. The nip pressure is adjusted so as to obtain a dry pick-up weight on the paper of 7.5% at a speed of 60 m/min.

A medium even shade of red is produced on the paper, compared to a severe mottle if the liquid dye is mixed with 8% Amylox P 45 and applied to the paper using the size press.

Claims

1. A method for reducing the particle size of cellulose in water and/or an organic solvent comprising
   a) forming a slurry or paste of cellulose material in water, the cellulose material having a dry weight average particle size of 1 to 100 microns; and
   b) reducing the wet average particle size of the cellulose material to 1 to 10 microns to give a carrier; additive being optionally added to the water prior to addition of cellulose or at the end of operations a) or b) above.

2. A method according to Claim 1 which comprises
   a) slurrying microcrystalline cellulose powder in water to give a dispersion of 2 to 15%, at a temperature of 5 to 60°C; and
   b) reducing the wet particle size of the dispersion; and
   c) adding the additive to the dispersion of reduced particle size.

3. A method according to claim 1 or claim 2, wherein the wet particle size is reduced by milling.

4. A method according to any one of claims 1-3, wherein the additive is an optical brightener.

5. A method according to any one of claims 1-3, wherein the additive is a surface sizing agent and/or a dyestuff.

6. An aqueous slurry or paste for use in a paper-coating composition, containing microcrystalline cellulose having an average wet particle size of 1 to 10 microns.

7. A process for coating paper, comprising applying the carrier or dispersion of reduced particle size defined in any one of claims 1 to 6, optionally containing one or more additives, to the surface of paper.

8. Paper having improved surface properties, to which the carrier or dispersion defined in any one of the preceding claims has been applied.

9. A pigment-containing composition for use in paper coating comprising per 100 parts by weight of pigment,
   a) from 5 to 25 parts by weight of binder (in the form of an aqueous dispersion),
   b) from 0.1 to 10 parts by weight of water soluble cobinder and/or water retention aid; and
   c) 0.1 to 5 parts by weight of a carrier of the type described in claim 1 to which 0.1 to 20% by weight of additive may optionally be adsorbed.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 81 0035

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	EP-A-0 201 895 (AQUALON) * claims 1-8 * ---	1-9	D21H19/52 D21H19/34
A	FR-A-1 239 314 (GEVAERT) *Résumé* -----	1-9	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D21H
C08B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 MAY 1992	FOUQUIER J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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