PROCESS FOR THE PRODUCTION OF A COATED AND PRESSED CELLULOSIC FIBROUS FLAT SUBSTRATE, SUITABLE COATING COMPOSITIONS, THEIR PRODUCTION, THE COATED AND PRESSED SUBSTRATES AND THEIR USE AS SUBSTRATES FOR GRAPHIC PROCESSES

Publication Classification

Abstract

The invention provides a process for the production of a coated and pressed cellulosic fibrous flat substrate of loose, optionally bonded fibers, by application of (M) an aqueous coating composition, containing a binder (B), a white pigment (W) and a dispersant (D), wherein at least a part of the white pigment (W) is (A) a particulate ammonium polyphosphate of crystalline form II of average particle size<40 μm and with a water solubility<10 g/l at 25°C, to the face of the substrate and subjecting to pressure in particular for the production of coated and pressed substrates of outstanding surface properties, particularly suitable for graphic processing, and of outstanding non-flammability properties, suitable coating compositions, their production, the coated and pressed substrates and their use as substrates for graphic processes, especially printing.
PROCESS FOR THE PRODUCTION OF A COATED AND PRESSED CELLULOSIC FIBROUS FLAT SUBSTRATE, SUITABLE COATING COMPOSITIONS, THEIR PRODUCTION, THE COATED AND PRESSED SUBSTRATES AND THEIR USE AS SUBSTRATES FOR GRAPHIC PROCESSES

[0001] In the production of coatings on webs of loose, optionally bonded fibrous material, especially on paper, a coating composition is usually applied to the web of paper or other fibrous material and is pressed e.g. with a plate or through press rolls or by other means, in order to obtain a surface with certain physical and aesthetic properties such as gloss, strength, pliability and printability.

[0002] Since many fibrous materials, especially cellulosic materials, and/or any compounds with which they have been treated, may be flammable, it is often desired to treat them with a flame retarding agent. In the case of webs of fibrous material, mainly paper, such a treatment may be carried out by adding a flame retardant to the paperstuff of which the paper is then made, or in a size composition with which the paper is impregnated. For the production of a coated paper the coating is then applied on the so pretreated paper which is then subjected to pressure e.g. plate- or roll-pressed. By this the applied coating—which may itself be flammable—may however constitute a delaying hindrance for the flame retarding effect in the substrate.

[0003] According to another way of application a flame retarding paint may be applied to the substrate after it has been finished (either uncoated or coated, as mentioned above) so that, when applied on a coated substrate, this paint may impair the aesthetic aspect and also some of the physical properties which were provided by the previously applied coating (such as gloss or printability) or, when applied on an uncoated substrate, it may not replace a coating (or “enamel”) because of its different way of application and mostly also because of its different composition.

The application of such paints is sometimes also designated as “coating”, but this term signifies in this case only that the paint is applied as a continuous film, and this is usually directly dried after its application without subjecting it to a particular pressure treatment.

[0004] In U.S. Pat. No. 5,049,187-A there are described fire retardant aqueous coating solutions for use in forming a fire retardant protective overcoat on a surface requiring such protection, which are comprised of 1) a water soluble film-forming cross-linkable copolymer of methyl vinyl ether and maleic anhydride, 2) a water-soluble polyhydric alcohol which serves to cross-link the copolymer when a coating of the composition is applied over the surface and dried, and 3) a water-soluble ammonium polyphosphate; these compositions are useful for forming a transparent overcoat in particular for photographic elements, AMGARD PI of Albright & Wilson Americas Inc. being mentioned among others as an example of an ammonium polyphosphate component 3).

[0005] EP-460516-A and GB-224846-A relate to flame retardant aqueous compositions comprising an ammonium polyphosphate, a defined heat-curable resin and some defined further components (the same AMGARD PI as above being mentioned as an example of the ammonium polyphosphate).

[0006] These compositions on standing form a gel which on shearing forms a pourable emulsion which on application to a fabric under shearing then regels rapidly. They are applied to the back of the fabric by back-coating.

[0007] U.S. Pat. No. 5,498,471-A describes an aqueous non-flowing coating or impregnating composition for a non-woven or paper substrate for flexible circuit boards, which composition includes a) a cross-linked product of an aqueous dispersion of a cross-linkable copolymerize of acrylic esters and styrene and b) an aqueous solution of a precondensate containing hydroxymethyl groups (amino-plastics and phenoplastics) and which further contains as a particulate dispersed flame retardant red phosphorus of a grain size of 45 to 100 μm (Exolit 405 being named as an example) and an ammonium polyphosphate of a grain size of 25 to 75 μm (Exolit 422 being named as an example). The coating composition is applied to the substrate and dried, then the coated substrate is laminated under pressure with the conductive metal (copper) foil, by which the surface appearance of the coating is no longer visible. If it were desired to print the paper or non-woven backing of the laminated metal any such printing treatment would thus have to be carried out on the non-coated side of the non-woven or paper so that, from the view point of any printing or other graphic use of the non-woven or paper surface after lamination, the coating has been applied to the back of the paper or non-woven. These coating compositions and the produced coatings contain the red phosphorus which provides a corresponding shade to the composition and coating; in the example this shade is hidden by the addition of a blue pigment (Lucylon Blue).

[0008] In CS-B-239173 there is described a coating of paper, cardboard or carton with a coating mix containing 10-40% of aluminium hydroxide and 60 to 90% of kaolin as pigments, 0.2 to 2% based on the pigment, of a flame retardant, e.g. of secondary ammonium phosphate, and further 0.1 to 1.5%, based on the pigment, of molecular colloids and 5 to 15%, based on the pigment, of polyvinyl acetate.

[0009] In the above documents the ammonium polyphosphates are employed in a form, a way of application and concentration that provides just a form of flame retarding effect but that is of no particular bearing in the appearance and graphic utilization of the treated substrate.

[0010] It has now been found that particularly hard and insoluble flame retarding polyphosphates of a particular particle size, as defined below and which are not combined with red phosphorus, are surprisingly well suitable in particular also as fillers or white pigments in coating compositions for the production of coated and pressed substrates, as defined below, of outstanding surface properties, particularly suitable for graphic processing, and of outstanding non-flammability properties.

[0011] The invention relates to a process for the production of coated and pressed cellulosic fibrous substrates of loose, optionally bonded fibers, to suitable coating compositions of defined particle size of the dispersed particles, to their production, to the coated and pressed substrates and to their use as substrates for graphic processes, especially printing.

[0012] The invention thus firstly provides a process for the production of a coated and pressed cellulosic fibrous flat substrate of loose, optionally bonded fibers, by application of
[0013] (M) an aqueous coating composition, containing a binder (B), a white pigment (W) and a dispersant (D), wherein at least a part of the white pigment (W) is

[0014] (A) a particulate ammonium polyphosphate of crystalline form 11 of average particle size<40 μm and with a water solubility<10 g/l at 25°C., to the face of the substrate and subjecting to pressure.

[0015] As a flat substrate of loose, optionally bonded fibers there is meant any such substrate in which the fibers are processed in loose form to a web, which may be bonded with suitable binders. These substrates are in particular those in which the loose fibers in the form of webs serve for the production of paper, paperboard, board or non-wovens, or are in the form of non-coated sheets of paper, paperboard or board or of pre-formed non-coated wovens or tissues.

[0016] As a flat substrate made of loose optionally bonded fibers there is more particularly meant any such substrate, in which loose fibres have been directly processed to a flat substrate from an aqueous suspension or by forming a fiber mat from dry loose fibers mechanically or also with the aid of air; i.e. by processes in which the fibers are not in the form of yarns or strands or any woven or knitted fabric. As a substrate there may thus be employed any fibrous cellulose flat substrate made of loose optionally bonded fibers, as suitable for the application of a particulate-pigment-containing coating and subjecting to pressure (e.g. with plates, air knives or press rolls), in particular webs of cellulosic fibers, mainly webs or sheets of paper, paperboard or board or non-woven tissue webs or mats. Preferably the process of the invention is employed for the production of coated paperboard or, most preferably, coated paper. The said mat, web or sheet (preferably paper or paperboard) may be formed of any conventional cellulosic fibrous material, e.g. from annual plants or wood, e.g. chemical, semichemical and mechanical or groundwood pulp, or also reclaimed or recycled paper (which may e.g. be broke, gray paper, deinked paper, etc. and may optionally be bleached) and/or made from processed rags.

[0017] The webs, mats or sheets to be employed as a substrate, may have been produced by any conventional methods. In a web of paper or paperboard the loose fibers may be bonded only mechanically and with the own fibre substance (e.g. starch, pectine etc.) or preferably also by means of suitable additives, e.g. a size. The coating may be applied in one sequence during papermaking, or analogously in making the board or paperboard. Alternatively the production of paper, paperboard or board may be carried out only until a non-coated sheet of paper, paperboard or board is formed and coating and pressing may be carried out separately. Also for non-wovens it is possible to apply the coating to the optionally bonded web in one sequence in the production of the non-woven tissue or in a separate treatment.

[0018] The aqueous coating composition (M) to be employed in the process of the invention contains as an essential component a white pigment (W) which is in particulate solid form, suitably dispersed in the coating formulation.

[0019] In the coating of the invention the particulate white pigment (W) may consist substantially only of (A) or maybe a mixture of (A) with a one or more components, in particular with one or more white mineral pigments (P) and/or with one or more melamine (poly)phosphates (L).

[0020] (W) may thus consist of one particulate component or of a mixture of particulate components, at least a part of which is the particulate ammonium polyphosphate (A) of crystalline form II which is of the stated very small particle size and very low solubility. Preferably its water solubility is <0 g/l at 25°C.

[0021] The ammonium polyphosphates (A) are preferably of high molecular weight and are preferably substantially linear. They may be represented by the average formula (NH₄PO₄)ₓ, wherein n represents the degree of polymerisation and is preferably>800, more preferably>1000, e.g. even>4000.

[0022] The acid number of (A) is preferably <1, more preferably <0.8, and the viscosity of an aqueous 20% suspension of (A) is preferably below 200 mPas, more preferably below 120 mPas, most preferably in the range of 50 to 100 mPas.

[0023] The particulate ammonium polyphosphate (A) is of crystalline form II, which may have been produced by any known or conventional methods as are suitable for the production of such an ammonium polyphosphate of low water solubility, e.g. by reaction of phosphoric acid anhydride with ammonia and/or diammoniumphosphate, optionally in the presence of urea or melamine, at elevated temperature, at least a part of the reaction being carried out preferably at a temperature in the range of 170 to 375°C, or by tempering of a corresponding ammonium polyphosphate of crystalline form I, IV or V at a suitable temperature between 200 and 375°C.

[0024] Processes of this kind are known in the art and are described e.g. in EP-A-49763, 88265, 411381, 480183 and 537475 and in DE-A-2330174.

[0025] The ammonium polyphosphates II known in the art usually have a varying average particle size, e.g. in the range of 500 to 5 μm. According to the invention there are employed (A) of average particle size below 40 μm. Preferably the average particle size is low, preferably in the range of 0.1 to 35 μm, more preferably 1 to 25 μm, most preferably 2 to 15 μm, the lower average particle sizes, in particular below 25 μm, especially below 15 μm or even≤10 μm (e.g. in the range of 2 to 15 μm) being particularly preferred. Further it is also preferred that the particles of (A) be all of a size below 40 μm. If desired, the particles of (A) may even be all below 30 μm or even below 25 μm. The small particle size of (A) may e.g. be produced by comminuting a conventional ammonium polyphosphate II, suitably by grinding or milling to the desired particle size, and if necessary screening, or e.g. by selecting the inferior size particles in production lots of a broad range of particle sizes e.g. by suitable screening and/or sieving. For the purpose of the invention it is in particular preferred to comminute crystalline ammonium polyphosphate II produced by tempering at the high temperatures mentioned above, although it is very hard and milling will require suitable ball mills or bead mills and a corresponding milling time, or to separate correspondingly small particle size proportion from a so produced ammonium polyphosphate II. The harder qualities of ammonium polyphosphate II are preferred for the process
of the invention. It is in particular surprising that these small particle size ammonium polyphosphates are suitable as white pigments or white fillers in coatings, especially paper coatings, and more particularly that they are of similar or even superior properties as compared to conventional mineral white pigments or fillers.

[0026] As (P), i.e. as a white mineral pigment or filler, there is intended any such inorganic white pigment or filler as conventionally employed in coating compositions and which may comprise true minerals and also inorganic compounds analogous to mineral products, i.e. modified minerals or also synthetically produced inorganic compounds of analogous or related properties to mineral white pigments or fillers. As mineral products there may be mentioned e.g. kaolin, calcium carbonate, barites, bentonite, mica, montmorillonite, slate, talc and titanium dioxide. As products obtained by processing minerals there may be mentioned e.g. calcium carbonate or sulphate, barium sulphate, satin white and argillaceous minerals. As products obtained by a synthetic reaction to produce a compound of properties similar to those of mineral forms there may be mentioned e.g. titanium dioxide, silica, calcium carbonate or sulphate, barium sulphate (blanc fixe), alums and cementitious powders. Their particle size may range in a scope as per se conventionally employed in coating compositions; in particular their average particle size may be well below 40 µm and also well below 25 µm. White mineral pigments used in coating compositions for paper are mostly of a particle size in the range of 0.1 to 10 µm, best pigment properties and light scattering being achieved mostly at a particle size in the range of 0.2 to 2 µm, particle sizes in the higher ranges of e.g. 2.1 to 10 µm being usually more suitable for fillers.

[0027] The term “white pigment” as used herein is intended to include as well particulate white components with typical white pigment properties (such as crystallinity, size and light refraction) as also particulate white components which may be used as fillers (e.g. where the light scattering properties may be somewhat inferior to those of the typical pigments, but which still contribute to the whiteness and opacity of the coating).

[0028] According to a particular feature of the invention, (W) contains also a particulate melamine (poly)phosphate (L). Melamine (poly)phosphates are known substances and may be represented by the general formula \( (C_{n}H_{2n}N_{m})_{p}(NH)_{3-p}(HPO)_{n} \), in which \( n \) is as defined above, \( m \) is a number corresponding to the proportion of melamine employed and \( p \) is a number in the range from 0 to \( m \). They can be produced by known methods or analogously to known methods, in particular analogously to ammonium polyphosphates, by reaction of melamine with phosphorus pentoxide and optionally ammonia and/or urea under elevated temperature conditions. Where desired or required, their particle size may be reduced by comminuting analogously as described above for (A). The particle size of (L) is in particular compatible with the one of the other components, in particular it is similar to the one of (A), i.e. the average particle size is below 40 µm, preferably below 25 µm, with preferably no particles exceeding 40 µm, those with an average particle size below 15 µm or even ≤10 µm (e.g. in the range of 0.5 to 15 or 1 to 10 µm) being particularly preferred. Their solubility in water is also very low, in particular lower than the one of (A) and they are preferably practically insoluble; their solubility in water at 20° C. is e.g. below 6 g/l, especially below 1 g/l. Commercially available grades are e.g. of a water solubility of ≤0.1 µl.

[0029] If another particulate white pigment component, i.e. (P) or (L) or both, is present together with (A) in (W), this may be e.g. (P) alone or (L) alone or a mixture of (P) and (L). Where (W) is a mixture of (A) with other components, in particular with mineral pigments (P) and/or with (L), (A) is expediently present in an efficient proportion. Preferably (A) constitutes at least 4% by weight of (W), advantageously 5 to 100% of (W), more preferably 20 to 100%, the remaining up to 96, 95 or respectively 80% being (P) or (L) or (P)+(L).

[0030] If only (P) is present together with (A) in (W) the weight ratio of (P) to (A) in (W) is e.g. in the range of from 0.1/10 to 10/0.5 advantageously 0.1/10 to 1/0.1, preferably 0.1/10 to 5/1, more preferably 0.1/10 to 4/1. When (L) is present in (W) it may replace a part or even all of (P). If (L) is present, the weight ratio of [(L)+(P)]/(A) is e.g. in the range of from 0.1/10 to 10/0.5, advantageously 0.1/10 to 1/0.1, preferably 0.1/10 to 5/1, more preferably 0.1/10 to 4/10.

[0031] If both (P) and (L) are present together with (A), the weight ratio of (P) to (L) may be in any desired range as suitable for the envisaged purpose, e.g. in the range of from 0.1/10 to 10/0.1 advantageously 0.1/10 to 4/10, preferably 0.1/10 to 2/10, more preferably 0.1/10 to 1/10.

[0032] According to a preferred feature no (P) is present in (W), especially when (L) is present.

[0033] A further essential component of the aqueous coating compositions (M) is the binder (B). As a binder (B) there may be employed any conventional binder or mixture of binders as is usually employed in coating compositions, especially in paper coatings. Representative binders are conventional polymers, e.g.

[0034] (B₁) styrene-butadiene polymers,
[0035] (B₂) acrylic co- or ter-polymers,
[0036] (B₃) polyvinyl acetates
[0037] and (B₄) polyurethanes.

[0038] The binder (B) may be present in (M) in concentrations conventional per se, as suitable for binding the pigment particles to the substrate. The ratio of (B) to (W) on a dry basis is e.g. in the range of 1.0 to 1/20, preferably 1/1 to 1/2, more preferably 1/3 to 1/8.

[0039] The dispersants (D) may be any dispersants or mixtures of dispersants as conventionally employed in paper coating compositions and are preferably anionic or non-ionic dispersants. They may be simple non-polymeric compounds or polymers, e.g. also of protective colloid character. As examples of non-polymeric non-ionic dispersants there may be mentioned adducts of ethylene oxide and optionally propylene oxide to an aliphatic alcohol such as C₁₂₋₁₄ fatty alcohols (natural or synthetic alcohols) to a mono- or dialkylphenol with 6 to 18 carbons atoms in the total of alkyl radicals present, with an HLB e.g. in the range of 8 to 16. As examples of non-polymeric anionic dispersants there may be mentioned aliphatic sulphonic acids in salt form such as sodium C₁₂₋₁₄-alkane sulphonates, or araliphatic sulphonylic acids in salt form such as sodium mono- or dialkylbenzeno-
nesulphonates with 6 to 18 carbon atoms in the total of alkyl radicals present, and aliphatic carboxylic acid salts (soaps) such as C₁₂₂₄-fatty acid salts, e.g. alkali metal salts (preferably sodium salts) or ammonium salts (including also amine salts of low molecular amines, such as mono-, di- or tri-ethanol- or -isopropanol-amine), or also natural products or derivatives, in particular from pulping processes, such as talloil soaps and lignine sulphonates. Preferably the dispersants (D) are polymers, more preferably water soluble polymers, in particular polyacrylic acid salts (e.g. alkali metal or ammonium salt, usually of an average molecular weight in the range of 2000 to 10000) or polyphosphates (e.g. a water soluble ammonium polyphosphates, e.g. of a degree of polymerisation of 3 to 30, e.g. tetra or hexametaphosphate), and may be present in very low concentrations as suitable for maintaining a uniform distribution of the undisolved particles in the aqueous composition. Preferably the concentration of (D) is in the range of 0.01 to 1%, more preferably 0.1 to 0.5% referred to the weight of the dry content of the coating composition (M).

[0040] The coating compositions (M) may optionally contain further components, as may be desired or suitable depending on the desired effect, on the employed method and employed apparatus for application and on the nature and composition of the substrate, e.g. dyestuffs and/or optical brighteners and any optional assistants such as surface active agent, thickeners, resins and/or formulation additives. Thus (M) may further contain one or more further additives selected from

[0041] (C) which is

[0042] (C₁) at least one optical brightener

[0043] and/or (C₂) at least one dyestuff,

[0044] (E) a thickening agent,

[0045] (F) at least one resin other than (B)

[0046] and (G) at least one formulation additive, suitable for modifying or maintaining the physical form of the composition and which is suitably employed in minor amounts.

[0047] (C₁) may be any optical brightener suitable for the optical brightening of cellululosic substrates, especially paper, and/or for use in coating compositions, and is preferably anionic. Among the anionic optical brighteners are preferred those of the 4,4'-bistriazinylaminostilbene-2,2'-di-sulphonic acid series, especially those in which each triazinyl ring is substituted with two amino groups, one of which is an optionally sulphonated anilic radical and the other is aliphatic. There may be employed known optical brighteners as are commercially available and as are conventionally employed also in coatings.

[0048] (C₂) may be any dye suitable for the dyeing of cellululosic substrates, especially paper, for which it is preferably a water soluble preferably anionic dye, and/or for use in coating compositions, for which it may be a water soluble preferably anionic dye, or may also be a dye insoluble in water.

[0049] Among the anionic dyes are preferred

[0050] (C₃) direct dyes.

[0051] The insoluble dyes are in particular

[0052] (C₄⁻) colour pigments.

[0053] There may be employed any direct dyes and pigments e.g. as defined under these name in the “Colour Index” (published by The Society of Dyers and Colourists) and known in the art, in particular as are commercially available and as are conventionally employed also in coatings.

[0054] As (E) there may be employed known thickening agents, in particular as are conventionally employed in coating compositions for paper coatings; preferably (E) an acrylic polymer or a poly-urethane.

[0055] As (F) there may be employed any resins as conventionally employed in coating pastes, in particular a resin containing hydroxymethyl groups or oxirane rings and which is curable, in particular with a suitable binder (B). Preferably (F) is a curable resin selected from:

[0056] (F₃) melamine/formaldehyde resins,

[0057] (F₄) urea/formaldehyde resins,

[0058] (F₅) glyoxal resins,

[0059] (F₆) epoxy resins

[0060] and (F₇) polyurethanes.

[0061] Among the mentioned resins (F) are preferred (F₃), (F₄) and (F₅), especially (F₅).

[0062] Components (E) and (F) serve for adjusting the consistency of (M) and the mechanical properties of the final coating, such as strength, pliability, elasticity and touch of the coated and pressed dry product, and their amount and kind will also depend on the chosen application method and apparatus.

[0063] In the formulation of the coating composition a binder, such as (B), depending on its particular constitution may also contribute to a minor degree to the thickness of the composition and/or to the mechanical properties of the final coated product, and vice versa (E) or (F) may also contribute to a minor degree to the binding of the components in (M). The choice and concentration of any components (E) and/or (F) will mainly depend on the desired properties of (M) and the mechanical properties of the coated product in the presence of a certain chosen binder (B), and it is in the skill of the coating specialist to choose the components and to adjust their concentrations depending on the desired mechanical properties of the coating mass (M) and of the coated product and also on the employed apparatus and method.

[0064] Component (G) is at least one formulation additive, i.e. a product for providing and maintaining a certain constitution of the composition (M), in particular—for example—in order to protect it against the damaging action of micro-organisms or to avoid a disturbing foam formation or further, if desired, in order to provide or modify the flowability properties of the composition and/or also in order to select a preferred pH which may be suitable for the particular composition and favour its storage and application properties.
As (G) there may in particular be employed:

- (Gₐ) an anti-microbial agent,
- (Gₖ) a defoamer,
- (Gₜ) a flow agent
- (Gₐ) an acid, base and/or buffer for pH-adjustment.

As (G₉) there may be employed any antimicrobial agent as commercially available and conventionally employed for protecting an aqueous coating composition from the damaging action of micro-organisms; it may e.g. be microbial growth inhibitor or a microbicide (e.g. a fungicide), as commercially available, e.g. of the 1,2-benzisothiazolin-3-one series, and may be employed in an efficient concentration, e.g. <3% by weight referred to (M), suitably in the commercially indicated concentrations, e.g. in a concentration of 0.01 to 3%, preferably 0.05 to 1%, more preferably 0.1 to 0.2% by weight referred to (M).

As (G₉) there may be employed any defoamer as commercially available and conventionally employed in coating compositions, e.g. a defoamer of the polydimethylsiloxane or alkoxane series. It may be employed in a suitable efficient concentration, e.g. in the commercially indicated concentrations, e.g. in a concentration of 0.01 to 1%, preferably 0.05 to 0.2%, more preferably 0.05 to 0.1% by weight referred to (M).

As (Gₜ) there may be employed any flow agents as commercially available and conventionally employed for modifying the flow properties of coating compositions. (Gₜ) may e.g. be a preferably saturated fatty acid salt (e.g. of 16-24 carbon atoms in the fatty acid) preferably a stearic acid salt, e.g. an alkali metal salt, alkaline earth metal salt or ammonium salt, and is present in a suitable efficient concentration, e.g. in the range of 0.01 to 5%, preferably 0.05 to 2%, more preferably 0.1 to 1.5% by weight referred to (M). A flow agent (Gₜ) is preferably employed, in particular to adjust the viscosity of the coating dispersion to such values as suitable for the employed coating apparatus and speed and depending also on the kind of substrate, the particular composition of (M) and the desired effect, preferably so that the viscosity is kept at values below 3000 mPa·s, preferably below 1500 mPa·s.

The pH of (M) may vary broadly, in particular from distinctly acidic to strongly basic, especially from 5.5 to 13, preferably 7 to 10, more preferably 8 to 9; if required or desired, it may be adjusted by the addition of one or more additives (Gₐ), which may e.g. be a base such as ammonium hydroxide, alkali metal hydroxide or carbonate or magnesium oxide, a strong mineral acid such as phosphoric acid or sulphuric acid, or a strong aliphatic carboxylic acid e.g. with 1 to 6 carbon atoms (such as formic, acetic, oxalic, lactic or citric acid) and/or optionally a buffer salt such as ammonium or sodium hydrogen phosphates.

The consistency of the flame-proofing coating composition (M), in particular its dry substance content, density and viscosity may vary broadly, depending e.g. on the method of application and the employed apparatus, on the substrate and on the desired effect. The dry substance content of (M) may in particular be in the range of 1 to 90%, advantageously 5 to 85%, preferably 20 to 80%, more preferably 25 to 75%. The proportion of (W) and of (A) in (M) may thus also vary accordingly. Preferably (W) represents the main component—i.e. >50%, more preferably 60 to 95% by weight—of the dry substance content of (M) and more preferably (A) or even a mixture of (A) with (L) as described above represents a substantial proportion, e.g. >8%, or even the main component—i.e. ≥50%, more preferably 60 to 95% by weight—of the dry substance content of (M), and thus (A) may outweigh each or even all other components of the dry substance content of (M). The viscosity of (M) may thus also vary broadly so long as (M) may still be spread on the substrate, the rotational viscosity measured in a Brookfield viscosimeter at 50 rpm and 20°C may e.g. be in the range of 1 to 15000 mPa·s, advantageously 10 to 8000 mPa·s, preferably 100 to 3000 mPa·s, more preferably 400 to 1500 mPa·s.

The coating compositions of the invention is a dispersion of the above described very fine particle size of the dispersed particulate solid components, i.e. white pigment (W) [(A) and, if present, also (P) and/or (L), being in particular of an average particle size below 25 μm and any other optionally present pigment (C₉⁺)] which is also a particle size in the stated range (in particular in the microcrystalline to cryptocrystalline grain size range), which are present together with the binder (B), the dispersant (D) and any other component of (M). The binders (B) present, which may be more or less hydrophilic and more or less dissolved or swollen in the aqueous phase, are not considered within the above definition of dispersed particulate solid components of very fine particle size. More particularly the particulate dispersed pigment components present in (M) essentially consist only of (W) and optionally (C₉⁺). More preferably no pigments (C₉⁺) are present and the particulate dispersed solid components consist essentially only of (W).

The aqueous compositions (M) can be produced by mixing the components in a suitable way, analogous to conventional methods. In particular the coating compositions (M) may be produced by first mixing (W), more particularly the pigment components (A) and optionally any (L) and/or (P), with water and optionally (Gₜ), adding (D) and then (B) followed by the addition of any further of the components (C), (E), (F) and/or (G) as required or desired. The mixing is expediently carried out with stirring and at a concentration of the components in water at which the composition is readily stirrable.

The produced composition (M)—which in particular is a flowable aqueous dispersion—is ready for use and can be handled and applied analogously to any other coating composition for paper, paperboard, board or non-woven tissue, by means of conventional coating techniques in which pressure is applied either during the coating or after application of the coating composition or both.

As a fibrous flat substrate of loose, optionally bonded fibers there may be employed any suitable support web or sheet, especially paper, parchment (A) or board made from any desired conventional primary and/or secondary substances which are suitable for the production of paper, paperboard or board, in particular made from conventional
fibre material, principally cellulosic fibre material, for example from hardwood (for example maple, birch, beech, poplar), from softwood (for example pine, spruce, larch, fir), from annual plants (for example straw, jute, ramie, bagasse, flax, hemp, reed, sisal, coconut, cotton) or from textile fibres (for example rags, cotton, linen, flax, ramie, jute) or also from recycled paper production waste or from used paper, where the non-digested fibres, namely textile fibres, wood fibres and fibres from annual plants, can be processed in a manner which is conventional per se to give pulp, for example by mechanical and/or chemical and/or thermal methods (in particular wood pulp, mechanical wood pulp, brown wood pulp, yellow straw pulp, chemical pulp, semichemical pulp, chemical wood pulp, mechanical wood pulp), and the recycled printed paper or used paper, can, if necessary, be deinked. If desired or if necessary, the material can be bleached with conventional bleaching agents, for example reductively and/or oxidatively (for example with sodium hydrosulphite, thiourea dioxide or hydrogen peroxide). The substrates may be lignin-free or lignin-containing, e.g. containing ≤5%, preferably ≤10%, of lignin, based on dry fibres, such as paper containing wood pulp or semichemical pulp or board containing wood pulp or semichemical pulp. The pulp or the corresponding fibres can, if desired after blending, various types of fibre and/or types of pulp with one another, for example from mechanically digested pulp and/or chemically (sulphite or sulphate method) and/or thermally digested pulp and/or combination-digested pulp (semichemical pulp), be processed further, optionally with at least 10% of recycled paper or used paper. It is possible to use any desired conventional additives which are suitable for papermaking, such as, for example drainage and/or retention agents, and if desired optical brighteners, dyes, sizing agents and/or fillers (for example kaolin, talc or other silicates or calcium carbonate), as can usually be admixed with the aqueous pulp composition before sheet formation, and fixatives.

The aqueous pulp suspension intended and formulated for the production of the web can be applied in any conventional manner to the wire end, where the dewatering to the desired water content takes place. From the wire end, the web is then transported to the press section, where the water content is reduced further, for example usually in the range from 70 to 30%, so that the moist sheet reaches the dry end with a water content of ≤30%. After the dry end, the support sheet produced is usually fed through the calender (intermediate or dry calender) or otherwise through drying rolls and can if desired by given a surface sizing. The coating with (M) can be carried out subsequently during papermaking, or the not yet coated paper or board may be dried and rolled up and the coating with (M) is then carried out afterwards, more particularly at the final user’s factory, more particularly immediately before printing. (M) may be applied to the face of the substrate or also to both sides.

The coating of the invention may be carried out by any suitable method conventional per se in which pressure is applied either during coating or after application of the coating composition (M) to the substrate or both. The substrate coated with (M) may thus be dried at elevated temperature, preferably at a temperature in the range of 60 to 150°C, preferably through drier rolls, and may then optionally be calendared or embossed, or the coated and not yet dried web may be subjected to pressure by conventional means, e.g. by means of an air knife, a rod or bar, a blade or brushes (for improving penetration and distribution of the coating) or to roll pressure, and is then dried, or and the coated substrate may be subjected to plate or cylinder pressure optionally after drying e.g. through drier rolls.

Conventional application coating techniques which may be mentioned and are suitable for the application of (M) according to the invention are e.g.: air knife coating, rod or bar coating, blade coating, transfer roll coating, size press coating, kiss roll coating, spray coating, brush coating, dip coating, reverse roll coating and cast coating. In some of these processes is already applied during application of the coating composition, such as in air knife coating, rod or bar coating, blade coating, transfer roll coating, size press coating, reverse roll coating and cast coating, in the other pressure is applied after application of the coating composition, such as in kiss roll coating, spray coating, brush coating and dip coating. The applied pressure may vary broadly and is e.g. 0.086 bar, preferably is 1 bar supramatmospheric pressure, and may range e.g. up to the maximum pressure allowed by the employed machine and system.

Depending on the envisaged use and quality of the product, the pressure applied in coating or immediately afterwards, for softening and equalizing the surface may already suffice; according to a particularly preferred feature of the invention, the coated paper or board after having been coated is subjected to pressure, e.g. through drier rolls, or according to a still further preferred feature, it is subjected to pressure after having been immediately dried, preferably this latter variant comprises subjecting the coated and immediately dried substrate to pressure by means of cylinders or plates, in particular by calendaring or embossing, or and when applying a water mark to the paper or and when printing. If multilayered board is being produced, the respective lower, middle and upper layers are couched to one another in the press section before drying; for each of the layers there may be employed a composition (M).

The quantity of (A) applied to the substrate may be in any desired range; suitably it is present in such a proportion as to provide—in the (M)-coated substrate—a perceivable effect in the coating, in particular in the physical properties of the coated material (mainly brilliance, whiteness, opacity and printability) and especially in flame retardant properties. The invention thus further provides a process for coating and flame-proofing the stated substrates by coating with (M) as described above, wherein (A) is present in a concentration efficient for providing a flame-proofing action. (M) may be applied to the substrate in a coating weight (dry substance) e.g. in the range of 0.1 to 100 g/m² (for paper preferably 0.1 to 60 g/m² more preferably—depending on the way of application—to 30 or even 5 to 25 g/m², for paperboard preferably 0.2 to 100 g/m more preferably 2 to 50 g/m², for non-woven tissue web preferably 0.1 to 100 g/m² more preferably 5 to 50 g/m²).

The suitable and preferred concentrations and viscosities may vary not only depending on the particular substrate, composition and desired effect but also on the chosen particular application method and apparatus. Thus for some representative application methods of those mentioned above the preferred way of working is as follows:

Air Knife Coating

An excess of coating mix (M) is applied to the base paper and the mobile portion is metered off by means of air.
The air is delivered through a carefully controlled slot having an air pressure between 5 and 45 kilo Pascals, that cuts into the fluids portion of the coating layer like a knife. The solids content of (M) is preferably in the range 55-55% and and the viscosity is preferably in the range of 10000 mPa-s, with which defect free and print mottle free coatings may be achieved. Typical coat weights using air knife configurations preferably range from 4-30 g/m². The preferred metering will in particular be selected depending on the particular employed apparatus, nature of the substrate and composition of (M), mainly by:

1. The energy of the air jet.
2. The angle of the airjet in conjunction with the coated surface and the backing roll.
3. The distance between the application and metering points.
5. Solids content and viscosity of the coating composition (M).

Bar (or Rod) Coating

An excess of coating mix (M) is applied to the base paper with the surplus being metered off using a rod or bar (normally termed metering bar or rod). The metering bar may be stationary or rotating with or against the direction of the web. Smooth bars normally meter the coating by an applied pressure, whilst wire wound bars (sometimes called Meyer bars), have a secondary metering effect. The coating mix is contained in the valleys between the windings, thus depending on the size of the wire used, the valleys will contain a corresponding amount of coating mix. Depending on the coat weight required, a particular bar may be chosen. The solids content of (M) is preferably in the range 30-63% and and the viscosity is preferably in the range of 100-1500 mPa-s, with which defect free and print mottle free coatings may be achieved. Typical coat weights using bar or rod configurations preferably range from 2-15 g/m². The preferred metering will in particular be selected depending on the particular employed apparatus, nature of the substrate and composition of (M), mainly by:

1. The type of bar or rod chosen
2. The pressure applied to the bar and its position relative to the backing roll.
3. Base paper properties, e.g. roughness, porosity.
4. The distance between the application and metering points.
5. Solids content and viscosity of the coating composition (M).

Blade Coating

An excess of coating mix (M) is applied to the base paper with the surplus being metered off (scraped off) using a blade. There are many types and configurations of blade; i.e. stiff, bent, flexible, but all have generic requirements for coating quality. The viscosity of the coating mix (M) will change depending on the shear rate applied to it during the coating process. This will depend upon the coater speed, pressure applied to the blade, blade geometry (i.e. angle, thickness, etc.) and the degree of compressibility of the web. The solids content of (M) is preferably in the range 45-75% and the viscosity is preferably in the range of 700-3500 mPa-s, with which defect free and print mottle free coatings may be achieved. Typical coat weights using blade configurations preferably range from 2-25 g/m². The preferred metering will in particular be selected depending on the particular employed apparatus, nature of the substrate and composition of (M), mainly by:

1. The type of blade and configuration
2. The pressure applied to the blade and its position relative to the backing roll.
3. Base paper properties, e.g. roughness, porosity.
4. The distance between the application and metering points.
5. Solids content and viscosity of the coating composition (M).
6. Hydrodynamic effects (rheology).

Transfer Roll Coating

The coating mix (M) is progressively transferred from one roll to other, being evened out as it travels before being transferred to the web. Any conventional number of transfer rolls can be employed, but preferably 2 to 15 are used. The rolls can be made of various materials and can operate in different directions and speeds. The solids content of (M) is preferably in the range of 30-60% and the viscosity is preferably in the range of 100-800 mPa-s, with which defect free and print mottle free coatings may be achieved. Typical coat weights using transfer roll configurations preferably range from 0.5-15 g/m². The preferred metering will in particular be selected depending on the particular employed apparatus, nature of the substrate and composition of (M), mainly by:

1. The number of transfer rolls and type of covering.
2. The pressure applied between the transfer rolls, and to the base sheet.
3. Base paper properties, i.e., roughness, and porosity.
4. Solids content and viscosity of the coating composition (M).

The application of (M) can be carried out on one or both sides, depending on the type and purpose of the paper or board. One-sided application is suitable, for example, for a cardboard top layer, for label, poster or packing paper. Two-sided application is suitable, for example, for graphic papers, book printing, magazine, newspaper, letter, drawing or office paper, or also for special single-layer types of cardboard, such as, for example Bristol board.

The invention provides the possibility of producing a most broad choice of coatings in various kinds and of optimum properties and in particular of high flame retardant properties. In particular, by the possibility of using various ways of application and of processing (also in the drier section and/or in calendering), by employing various kinds, consistencies and quantities of coating composition on vari-
ous kinds of substrates, a correspondingly very broad choice of coated product of high flame retarding efficiency and fine appearance, in particular optimum whiteness and graphic properties, becomes available.

[0015] According to the coating process of the invention it is possible to obtain, even with coating compositions (M) that do not contain any (P), coatings of excellent, surprisingly high whiteness, brilliancy, opacity and surface properties and simultaneously with high flame retarding efficiency. By combining an optical brightener in (M) the whiteness may even be increased. They are suitable for producing coated substrates, especially paper, paperboard and board, of outstanding graphic properties, especially printability properties, for which any kind of printing method is suitable, e.g. offset printing, ink jet, laser or screen printing or any other kind of printing methods, including typography and photocopying. Also the further physical properties of the coated material are not impaired, such as strength, pliability and compressibility, and the flame retarding properties are optimal. The coating process of the invention is suitable for producing any kind of coated paper, paperboard, board or non-woven tissue, especially coated paper for printing purposes, preferably of 50 to 400 g/m², such as letter, magazine, newspaper, drawing or office paper, book printing paper, label paper, poster paper, wall paper, packing paper and building paper. The fastness properties are also optimal and the paper and board sheets surface-coated with (W) in accordance with the invention are even very resistant to yellowing caused by the action of light and/or heat. The (M)-coated products may be recycled analogously to any other coated paper, where in the recycling process the insoluble components (W) settle out and can be separated, and any traces of suspended or (colloiddially) dissolved component of (M) may be precipitated or flocculated with suitable flocculating agents as conventionally employed in backwater purification and sludge dewatering.

[0016] A further subject-matter of the invention is the process for the production of a substrate which has been graphically processed, in particular written on, printed and/or graphically processed in any other manner by application of at least one graphic ink pattern to said substrate, and drying, which is characterized in that the substrate used for this purpose is a flat substrate as described above, especially paper, paperboard, board or non-woven tissue, which has been coated with (M) and subjected to pressure as described above.

[0017] By the coating process of the invention, in particular as described above, there may be produced coated paper or paperboard with a smooth, level, regular surface, which is particularly suitable as a substrate for printing. Especially printing processes as mentioned above can be used, principally intaglio printing, newspaper printing, letterpress printing and offset printing in general. In particular, a same level paper or paperboard can be used as substrate both for intaglio printing and for offset printing.

[0018] Printing can be carried out using any desired conventional printing inks which contain constituents which are conventional per se, essentially at least one dye and a suitable carrier or a suitable binder and optionally additives. As dyes, principally pigments (for example those as defined and also listed under “Pigments” in the Colour Index), optionally combined with mineral fillers, come into consider-

eration, as usually employed in printing inks; as binders, principally resins, which are advantageously mixed with oils, come into consideration. The resins are mostly alkyd resins and/or pheryl-modified colophony resins and can, if desired, be blended with further carrier substances, such as suitable types of asphalt; as oils, oxidatively drying oils (principally vegetable oils, in particular linseed oil or wood oil) and physically drying mineral oils can be employed. As additives, drying agents are advantageously employed, such as, for example, tin, cobalt or manganese salts, for example manganese octanoate, or and optionally further additives, such as waxes. Such components and additives or corresponding printing inks are known in general terms and are described in large number in the specialized literature, for example in EP-A-42515, 228372 and 666293. If desired, however, water-borne printing inks can also be used, for example those as described in EP-A-633143. The composition of such printing inks is, for example,

[0019] 10-35% of colorant (consisting of 10-25% of pigment and 0-15% of mineral filler)

[0020] 20-73% of resins (if desired blended up to half with blend substances, such as asphalt or oxidatively drying oils)

[0021] 15-60% of mineral oil

[0022] 2-12% of additives (for example drying agents and, if desired, waxes).

[0023] For experimental purposes, it is also possible to use standard printing inks, as also commercially available (for example the test inks 40 8001 Inko® 11,2; 40 8002 Inko® 14,8; 40 8003 Inko® 19,5 and 40 8004 Inko® 25,0 from Farbenfabriken Michael Huber, Munich, Germany), or inks conforming to BS 4666.

[0024] Clear prints with optimum colour body, fastness and contours can be produced on the said substrates, and the printing properties not being impaired (in particular with regard e.g. to any interfering flashing phenomena, ink deposits or missing dots or ink penetration), by the presence of the above described high proportions of (A) in (M).

[0025] In the following Examples, the parts denote parts by weight and percentages denote percent by weight; the temperatures are indicated in degrees Celsius. The employed ammonium polyphosphate II is of average particle size 10 μm with no particles exceeding 40 μm obtained by comminuting the commercially available ammonium polyphosphate II Exolit® AP 422 in a ball mill, the other components employed in the compositions and examples are commercially available products. The papers employed in the following examples are those produced in the paper mill and how they are employed in the respective paper production step which corresponds to the following examples. DIN stands for Deutsche Industrie-Norm, NF stands for Norme Francaise and BS stands for British Standard.

[0026] The following coating compositions (M) are employed, which are produced by mixing at 22° C. the ammonium polyphosphate and any further pigment with water and with calcium stearate with stirring, and then adding the binder and then the other components:
Coating Composition M1

An aqueous coating composition of 60% dry substance content consisting per 100.2 parts of dry substance of

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium polyphosphate II</td>
<td>66.2</td>
</tr>
<tr>
<td>Styrene/butadiene polymer</td>
<td>12.9</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.9</td>
</tr>
<tr>
<td>Melamine/formaldehyde resin</td>
<td>0.9</td>
</tr>
<tr>
<td>Sodium polyacrylate</td>
<td>0.2</td>
</tr>
<tr>
<td>1,2-Benzo-isothiazolin-3-one</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Coating Composition M2

particularly suitable for blade, rod, cast or reverse roll coating.

Coating Composition M3

An aqueous coating composition of 50% dry substance content consisting per 100.5 parts of dry substance of

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium polyphosphate II</td>
<td>10.0</td>
</tr>
<tr>
<td>Talc</td>
<td>14.9</td>
</tr>
<tr>
<td>Titanium dioxide</td>
<td>14.9</td>
</tr>
<tr>
<td>Acrylic copolymer</td>
<td>99.7</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.5</td>
</tr>
<tr>
<td>Polydimethylsiloxane</td>
<td>0.2</td>
</tr>
<tr>
<td>Sodium polyacrylate</td>
<td>0.2</td>
</tr>
<tr>
<td>1,2-Benzo-isothiazolin-3-one</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Coating Composition M4

particularly suitable for air knife, blade, brush, rod, screen, cast or reverse roll coating.

Coating Composition M5

An aqueous coating composition of 40% dry substance content consisting per 100.9 parts of dry substance of

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melamine/formaldehyde resin</td>
<td>0.8</td>
</tr>
<tr>
<td>Sodium polyacrylate</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Coating Composition M6

particularly suitable for air knife, brush, rod, screen or reverse roll coating.

Coating Composition M7

An aqueous coating composition of 62% dry substance content consisting per 101.51 parts of dry substance of

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium polyacrylate</td>
<td>0.29</td>
</tr>
<tr>
<td>Ammonium polyphosphate II</td>
<td>28.18</td>
</tr>
<tr>
<td>Styrene/butadiene polymer</td>
<td>36.44</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>1.1</td>
</tr>
<tr>
<td>Melamine/formaldehyde resin</td>
<td>1.1</td>
</tr>
<tr>
<td>Optical brightener</td>
<td>0.83</td>
</tr>
<tr>
<td>1,2-Benzo-isothiazolin-3-one</td>
<td>0.07</td>
</tr>
</tbody>
</table>

Coating Composition M8

particularly suitable for blade and rod coating.

Coating Composition M9

An aqueous coating composition of 64% dry substance content consisting per 101 parts of dry substance of

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonium polyacrylate</td>
<td>0.2</td>
</tr>
<tr>
<td>Ammonium polyphosphate II</td>
<td>64.5</td>
</tr>
<tr>
<td>Melamine polyphosphate</td>
<td>21.5</td>
</tr>
<tr>
<td>Styrene/butadiene polymer</td>
<td>12.9</td>
</tr>
<tr>
<td>Calcium stearate</td>
<td>0.9</td>
</tr>
<tr>
<td>Melamine/formaldehyde resin</td>
<td>0.9</td>
</tr>
<tr>
<td>1,2-Benzisothiazolin-3-one</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Coating Composition M10

particularly suitable for blade coating.

As sodium polyacrylate dispersant in Coating Compositions M1 to M5 there may be employed e.g. DISP-PEX N40 (Ciba).
As ammonium polyacrylate dispersant in Coating Compositions M6 and M7 there may be employed e.g. Mowiplus XW330 (Clariant).

[0150] As acrylic copolymer binder in Coating Compositions M2 and M5 there may be employed e.g. ACRONAL S320D (BASF).

[0151] As styrene-butadiene polymer binder in Coating Compositions M1, M3, M4, M6 and M7 there may be employed e.g. INTEX 5584 (Enichem).

[0152] As melamine/formaldehyde resin in Coating Compositions M1 and M3 to M7 there may be employed e.g. Beetle Resin PT-3745 (BIP).

[0153] The melamine polyphosphate of coating composition M7 is of water solubility<0.1 g/l at 20°C, particle size distribution: 98%<25 µm and 50%-<10 µm, nitrogen content 42-44% and phosphorus content 12-14%, e.g. MELAPUR® 200 (DSM).

[0154] As calcium stearate there may be employed e.g. NOPCOTE C104 (Henkel).

[0155] The 1,2-benz-isothiazolin-3-one fungicide may be employed e.g. in the form of the commercial product PROXEL BD20 (Avecia).

[0156] The optical brightener in Coating Composition M6 is of formula

![Optical Brightener](image)

in the form of its sodium salt.

EXAMPLE 1

Blade

[0157] A wood free, surface sized and uncoated paper (100 g/m²) of 50% hardwood, 50% softwood) is coated with Coating Composition M1 by means of a trailing blade (set 30° to backing roll), at a pressure of 6 bar/mm, at a speed of 600 m/min to a coating weight of 15 g/m² (dry substance), and is then pre-dried using short wave infrared drier and completed using conventional high velocity hot air driers.


EXAMPLE 2

Screen

[0159] Analogously as the Coating Composition M1, Coating Compositions M2, M3, M6 and M7 are employable in Example 1.

[0160] A wood free, unsized and uncoated paper (150 g/m²) made of 20% hardwood, 80% softwood) is coated with M2 by means of a screen coater (1 mm mesh), at a pressure of 1 bar, at a speed of 100 m/min to a coating weight of 50 g/m² (dry substance), and is then dried using conventional high velocity hot air driers, before being embossed at 5 bar.

[0161] There is obtained a decoratively finished paper of high whiteness and with good flame resistance determined by means of BS 476 (part 7:1987).

EXAMPLE 3

Rod

[0162] Analogously as the Coating Composition M2, Coating Compositions M3 and M5 are employable in Example 2.

[0163] A wood free, unsized and uncoated paper (85 g/m²) made of 45% hardwood, 55% softwood) is coated

with M3 by means of a smooth metering rod, at a pressure of 3 bar, at a speed of 600 m/min to a coating weight of 15 g/m² (dry substance), and is then pre-dried using short wave infrared drier and completed using conventional high velocity hot air driers, before being super-calendered at 350 KN/m.

[0164] There is obtained a gloss finished paper of high whiteness and with good flame resistance determined by means of DIN 9102 (part 1).

[0165] Analogously as the Coating Composition M3, Coating Compositions M1, M2, M4, M5 and M6 are employable in Example 3.
EXAMPLE 4

Air knife

[0167] A wood free, unsized and uncoated paper (85 g/m²) made of 45% hardwood, 55% softwood) is coated with M4 by means of a airknife, at a air pressure of 30 Kpa (0.4 mm gap), at a speed of 300 m/min to a coating weight of 15 g/m² (dry substance), and is then pre-dried using short wave infrared drier and completed using conventional high velocity hot air driers, before being super-calendered at 350 kN/m.

[0168] There is obtained a gloss finished paper of high whiteness and with good flame resistance determined by means of DIN 9102 (part 1).

[0169] Analogously as the Coating Composition M4, Coating Compositions M2, M3 and M5 are employable in Example 4.

EXAMPLE 5

Air knife

[0170] A wood free, unsized and uncoated paper (90 g/m²) made of 45% hardwood, 55% softwood) is coated with M5 by means of a airknife, at a air pressure of 30 Kpa (0.4 mm gap), at a speed of 400 m/min to a coating weight of 15 g/m² (dry substance), and is then pre-dried using short wave infrared drier and completed using conventional high velocity hot air driers, before being calendered at 100 kN/m.

[0171] There is obtained a matt finished paper of high whiteness and with good flame resistance determined by means of DIN 9102 (part 1).

[0172] Analogously as the Coating Composition M5, Coating Compositions M₆, M₇, and M₈ are employable in Example 5.

EXAMPLE 6

Blade

[0173] A wood free, surface sized and uncoated paper (100 g/m²) made of 50% hardwood, 50% softwood) is coated with Coating Composition M1 by means of a trailing blade (set 30° to backing roll), at a pressure of 6 bar/mm, at a speed of 600 m/min to a coating weight of 20 g/m² (dry substance), and is then pre-dried using short wave infrared and passed through a soft nip calender located after the last drying section, using a combination of hard-chilled iron rolls and elastomer-covered rolls.


[0175] Analogously as the Coating Composition M1, Coating Compositions M₂, M₃, M₆ and M₇ are employable in Example 6.

EXAMPLE 7

Printing

[0176] A wood free, coated paper produced according to Example 1 (120 g/m²) cut to the dimensions 360 mm x 520 mm (B3) is printed with inks conforming to BS 4666 by means of a sheet fed four colour off-set litho printing press, at a speed of 4000 impressions an hour. There is obtained a high quality print.

[0177] In the same way as the coated paper produced according to Example 1 there may be printed the papers coated according to each of Examples 2, 3, 4, 5 and 6.

1. Process for the production of a coated and pressed cellulosic fibrous flat substrate of loose, optionally bonded fibers, by application of

   (M) an aqueous coating composition, containing a binder (13), a white pigment (W) and a dispersant (D), wherein at least a part of the white pigment (W) is

   (A) a particulate ammonium polyphosphate of crystalline form II of average particle size<40 µm and with a water solubility<10 µl at 25° C.,

   to the face of the substrate and subjecting to pressure.

2. A process according to claim 1, wherein the average particle size of (A) is <25 µm, with no particles exceeding the size of 40 µm.

3. A process according to claim 1 or 2, wherein the cellulosic fibrous substrate is a non-woven substrate selected from a web of paper, paperboard, board or non-woven tissue.

4. A process according to any one of claims 1 to 3 for coating and flame-proofing, wherein (A) is present in a concentration efficient for providing a flame-proofing action.

5. A process according to any one of claims 1 to 4, wherein (A) is present in a concentration ≤±4% by weight of (W).

6. A process according to any one of claims 1 to 5, wherein (W) comprises (A) and a white mineral pigment (P) and/or a melamine polyphosphate (L).

7. A process according to any one of claims 1 to 6, wherein (M) further contains one or more further additives selected from

   (C) which is

   (C₁) at least one optical brightener

   and/or (C₂) at least one dyestuff,

   (E) a thickening agent,

   (F) at least one resin other than (B)

   and (G) at least one formulation additive suitable modifying or maintaining the physical form of the composition.

8. A process according to any one of claims 1 to 7 wherein (G) is selected from

   (G₁) an anti-microbial agent,

   (G₂) a defoamer,

   (G₃) a flow agent

   and/or (G₄) an acid, base and/or buffer for pH-adjustment.

9. A coating composition (M) as defined in claim 2.

10. A coating composition (M) according to claim 9, further defined as in any one of claims 4 to 8.

11. A process for the production of a coating composition (M) according to claim 9 or 10, wherein (W) is mixed at a temperature ≤±35° C. with water and optionally (G₄), then with (D) and then with (B) and optionally with any further of the components (C), (E), (F) and (G).
12. A cellulosic fibrous flat substrate of loose, optionally bonded fibers coated with (M) by a process according to any one of claims 1 to 8.

13. A cellulosic fibrous substrate according to claim 12, which is a coated paper, paperboard, board or non-woven tissue.

14. Use of a cellulosic fibrous flat substrate of loose, optionally bonded fibers, coated with (M) by a process according to any one of claims 1 to 8, as a substrate for a graphic process.

15. A process for the production of a cellulosic fibrous flat substrate of loose, optionally bonded fibers, which has been graphically processed, in particular written on, printed and/or graphically processed in any other manner by application of at least one graphic ink pattern to said substrate, and drying, which is characterized in that the substrate used for this purpose is a cellulosic fibrous flat substrate of loose, optionally bonded fibers, coated with (M) according to claim 12 or 13.

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