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(54) **Resin impregnated coated article with improved aesthetic properties**

(57) The present invention relates to a coated article comprising a base layer, a coating layer comprising a resin composition, and an extinction layer comprising at

least one reducing agent capable of at least partially discoloring the resin composition.

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Description**FIELD OF THE INVENTION**

[0001] The present invention relates to a coated article with improved aesthetic properties, a method for preparing said coated article and an ink composition suitable for being applied in said method to produce said article.

BACKGROUND OF THE INVENTION

[0002] Resin impregnated papers/films have been used for decades as coatings in the wood working industry. For preparation of laminated boards or panels (e.g. plywood), the resin impregnated substrate (mostly paper or kraft paper) is attached to the board under heat and pressure when the resin melts thereby providing a firm bonding between the board and the impregnated paper and generating the desired board surface. Such coated boards are widely used for various purposes such as concrete shuttering, flooring, building materials and in the furniture or automotive industry.

[0003] In order to create a certain design of the surface, the paper can be printed with such design before being impregnated with the resin. The design can widely vary and can range from simple letters in brand names and company logos via text and pictograms to complex decorative patterns and photographic images (hereinafter referred to in general as "pattern"). After being applied to the board, the pattern normally is covered by the resin for impregnation. Hence the aesthetic appearance of the pattern is influenced by the transparency and color of said resin.

[0004] Particularly in cases, where a pattern is printed with a light or white pigment the color of the resin (mostly reddish brown), in particular, when a phenolic resin is used, can cause an unwanted color change of the pattern. This problem is even more severe if the resin further comprises dyes, colorants or pigments such as iron oxide, carbon black.

[0005] An additional problem arises especially when using phenolic resins. Phenolic resins result from the reaction of phenol and formaldehyde which is either performed under acidic or basic conditions. If a base catalyzed mixture of phenol and formaldehyde contains one or more moles of formaldehyde per mole of phenol it will produce a thermosetting resin ("resole"). Such resins have the disadvantage of aging, i.e. they darken when heated or are otherwise cured. The extent of darkening is known to be dependent on the curing or use temperature of the resin and the time of exposure to such temperature. After the manufacturing of panels laminated with impregnated paper the panels are stacked when still hot and they maintain a relatively high temperature for a long time (100°C and reducing gradually). Naturally cooling of panels is not homogenous, i.e. the center of the panel and the center of the stack cool down more slowly. This may result in an unwanted patchy or blotchy surface appearance of the impregnated article.

[0006] For a reduction of resol darkening the US patent US 5,110,320 teaches the use of an ammonium-based salt in the resin. Another known method for imparting color stability in phenolic resoles includes adding melamine formaldehyde resin into the formulation. While this may achieve an improvement in the aesthetic properties, it imparts brittleness, prolongs the curing time, and impacts in the mechanical properties of the article.

[0007] Hence, there is still the need for an effective method of improving or maintaining the aesthetic properties of resin impregnated papers. The objective of the present invention thus is to provide a resin impregnated coated article and methods for the manufacture thereof which overcome at least one of the above mentioned disadvantages.

SUMMARY OF THE INVENTION

[0008] This problem is solved with providing a coated article according to claim 1 and a method of manufacturing such article. Specific embodiments of the invention are subject matter of further independent or dependent claims.

[0009] According to the invention a coated article is provided, which comprises at least three layers, namely a first layer which is the base layer, a further layer which contains the resin (also called "coating layer") and a third layer comprising at least one reducing agent. The reducing agent serves to discolor at least parts of the resin. This third layer is also called "extinction layer".

[0010] Hence the coated article according to the invention comprises at least three layers, namely

- a) a base layer,
- b) a resin containing layer and
- c) a reducing agent containing layer,

said reducing agent containing layer is in contact with the resin containing layer.

[0011] The core aspect of the invention is the finding that the reducing agent eliminates at least partially the color of the resin (either the color of the resin itself and/or dyes or pigments contained therein. Therewith the reducing agent is capable of counteracting the darkening of the resin regardless of its cause (e.g. UV-light or heat). In the context of the invention this effect is either called "discoloring", "discolorization" or "elimination of color".

[0012] In one particular embodiment of the invention the reducing agent can be added to an ink used for printing a pattern onto the base layer. The inventors could show that this does not have a negative impact on the printing process and the printing quality. Hence established materials, production machines and processes can be applied in the method according to the invention.

[0013] In this embodiment of the invention the at least one reducing agent comes into contact only with parts of the resin layer, namely with those parts of the resin layer which covers the pattern. Only those parts are discolored by the reducing agent and the pattern retains its desired appearance. Hence a particular advantage of this embodiment of the invention is that it allows a spatially selective color elimination of the resin layer. The color of the resin layer can either be due to the color of the resin itself and/or dyes or pigments contained therein.

[0014] In a further embodiment of the invention the pattern can be printed onto the base layer (e.g. the paper) and then the reducing agent is applied onto the printed pattern. Although this embodiment requires a further production step it can be advantageous in certain situations, e.g., if the ink and the reducing agent are not sufficiently compatible.

[0015] The extinction layer represents a reservoir for the reducing agent. The discoloring effect according to the invention thus can be maintained over a longer period of time due to continuous diffusion of the reducing agent from the extinction layer to or into the coating layer.

[0016] According to one particular embodiment of the invention the reducing agent is capable of reducing the dye contained in the impregnating resin and thereby discolor it. In this embodiment the reducing agent thus serves as a dye discoloring agent. Agents for discoloring dyes by reduction are for a long time known to the skilled person from waste water treatment in the field of dye manufacturing. Hence the skilled person can select the appropriate reducing agent for the dye in the resin layer which is to be discolored.

[0017] In a particular embodiment of the invention the coated article consists of the three layers, with the support layer being paper impregnated with a phenolic resin. The paper was printed (for example with a company's logo) with an ink containing a dye discoloring agent before impregnation; therewith forming the extinction layer. This coated article can favourably be laminated onto boards or panels.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The base layer according to the invention can be flexible or rigid. Most preferred the base layer is a paper, in particular a kraft paper. The base layer can be applied onto a support layer. The support layer can be selected from the group consisting of cardboard, plywood, chipboard, fibre board, oriented strand board (OSB), glue wood, laminated veneer lumber (LVL), parallel strand lumber (PSL) and oriented strand lumber (OSL). A particularly preferred support is plywood.

[0019] The reducing agent preferably has a standard electrode potential E^0 between - 150 mV and -1500 mV. In order to be capable of reducing a dye, the standard electrode potential of the reducing agent (the dye discoloring agent) has to be more negative than the standard electrode potential of the respective dye. In a preferred embodiment of the invention the difference between the standard electrode potentials of the reducing agent and the dye is more than 0.5 Volt, preferably more than 0.75 Volt and more preferably more than 1.0 Volt.

[0020] The reducing agent preferably is selected from the group consisting of reducing sugars, hydrides, organic acids and inorganic salts or a mixture thereof.

[0021] According to a preferred embodiment of the invention, the reducing agent is selected from the group consisting of dihydroxyacetone, glycolaldehyde, glyceraldehyde, erythrose, threose, ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, talose, fructose, lactose, maltose, cellobiose, diborane, lithium aluminium hydride, sodium borohydride, lithium borohydride, SnCl_2 , SnF_2 , Sn(OH)_2 , sodium dithionite (Color Index reducing agent 1), thiourea dioxide (Color Index reducing agent 11), sodium hydroxymethanesulfinate (Color Index reducing agent 2), Color Index reducing agent 3, Color Index reducing agent 4, Color Index reducing agent 5, Color Index reducing agent 7, Color Index reducing agent 8, zinc formaldehyde sulfoxylate (Color Index reducing agent 6), Color Index reducing agent 9, Color index reducing agent 10, calcium formaldehyde carboxylate (Color Index reducing agent 12), sodium sulphite, sodium bisulphite, diisobutylaluminium hydride, oxalic acid, formic acid, ascorbic acid, $(\text{NH}_4)_2\text{HPO}_3$, CuHPO_3 , SnHPO_3 and $\text{Al}_2(\text{HPO}_3)_3$, alkali hypophosphite, FeCl_2 , FeCO_3 , FeSO_4 , amides such as urea, organic amines such as hexamethylenetetramine or a mixture thereof. Reduction agents for discoloring of specific dyes are disclosed in part 1 of the Colour Index (2004, fourth edition, www.colour-index.com), the disclosure of which is expressively incorporated herein by reference.

[0022] Particularly preferred reducing agents are fructose, sodium dithionite, tin chloride, iron(II)sulfate, and boronhydride. Fructose is the most preferred reducing agent.

[0023] In one embodiment of the invention the dye in the resin is an organic polycyclic dye, organic monoazo dye, organic diazo dye, organometal complex(e) or an inorganic pigment such as metal oxide or complex. Dyes can be perinone, anthraquinone, azo dye complexes and thioindigoid.

[0024] In a preferred embodiment of the invention the dye in the resin of the coating layer is selected from the group

consisting of Acid Yellow 23, Acid Red 18, Acid Yellow 36, Acid Black 194, Direct Red 239, Reactive Red 120, Acid Blue 9, Acid Red 27, Acid Red 51, Direct Blue 199, Direct Red 254, Reactive Red 195, Acid Red 14, Acid Yellow 17, Acid Black 1, Direct Yellow 86, Direct Black 168, Food Black 2.

[0025] In a most preferred embodiment the dye in the coating layer is Acid Black 2 and Direct Red 254.

[0026] In a preferred embodiment of the invention the coated article comprises a coating layer with a dye and a reducing agent in the extinction layer as outlined in the table below. Such "pairs" of dye and reducing agent are particularly advantageous in order to obtain an effective decolorization in those areas where the coating layer is in direct contact with the extinction layer:

Dye in the coating layer	Reducing agent of the extinction layer
Direct Red 254	SnCl ₂ , FeSO ₄ , sodium dithionite, fructose
Acid black	FeSO ₄ , fructose
Indigo	Sodium dithionite, sodium hypochlorite, potassium permanganate
C.I. Direct Red 80	Sodium borohydride
C.I. Disperse Red 60	Sodium borohydride, sodium dithionite
C.I. Disperse Blue 79	Sodium borohydride, sodium dithionite
C.I. Disperse Orange 62	Sodium borohydride, sodium dithionite
Non azo-dye such as: Disperse Blue 250, 354, 364 or 366; Solvent Violet 8; Solvent blue 43, Solvent blue 57; Lumogen F Blau 650; Lumogen F Violet 570	Sodium hydroxymethansulfinate

[0027] According to a preferred embodiment of the invention the reducing agent is part of the ink used for applying a pattern onto the base layer. In this embodiment the ink layer thus serves as the extinction layer. Hence the invention also relates to an ink (also called ink composition) comprising at least one coloring agent (dye or a pigment, both here referred to as dye if not otherwise specified) and at least one reducing agent. The dye in the ink preferably is not discolored by the reducing agent, or at least to a lower extent than the dye in the resin.

[0028] In one embodiment of the invention the ink contains 0.5 to 20 % (w/v), preferably 2 to 15 % (w/v), more preferred 7.5 to 12.5 % (w/v) and even more preferred 10 % (w/v) of at least one reducing agent.

[0029] The composition preferably has a solid content of between 50 wt% and 60 wt%, preferably 55 wt%. In this embodiment especially approximately 10% (w/v) of reducing agent is preferred (e.g. fructose). The binder preferably is casein.

[0030] The pigment of the ink can be of any color, e.g. a black, yellow, orange, red, violet, blue, brown or white pigment, whereby a white pigment is preferred.

[0031] A non-limiting example of a suitable inorganic black pigment includes carbon black. Examples of carbon black pigments include those manufactured by Mitsubishi Chemical Corporation, Japan (such as, e.g., carbon black No. 2300, No. 900, MCF88, No. 33, No. 40, No. 45, No. 52, MA7, MA8, MA100 or No. 2200B) various carbon black pigments of the RAVEN® series manufactured by Columbian Chemicals Company, Marietta, Ga., (such as, e.g., RAVEN® 5750, RAVEN® 5250, RAVEN® 5000, RAVEN® 3500, RAVEN® 1255 or RAVEN® 700); various carbon black pigments of the REGAL® series, the MOGUL® series or the MONARCH® series manufactured by Cabot Corporation, Boston, Mass., (such as, e.g., REGAL® 400R, REGAL® 330R, REGAL® 660R, MOGUL® L, MONARCH® 700, MONARCH® 800, MONARCH® 880, MONARCH® 900, MONARCH® 1000, MONARCH® 1100, MONARCH® 1300 or MONARCH® 1400); or various black pigments manufactured by Evonik Degussa Corporation, Parsippany, N.J., (such as, e.g., Color Black FW1, Color Black FW2, Color Black FW2V, Color Black FW18, Color Black FW200, Color Black S150, Color Black S160, Color Black S170, PRINTEX® 35, PRINTEX® U, PRINTEX® V, PRINTEX® 140U, Special Black 5, Special Black 4A or Special Black 4). A non-limiting example of an organic black pigment includes aniline black, such as C.I. Pigment Black 1.

[0032] Other examples of inorganic pigments include metal oxides and ceramics, such as the oxides of iron, zinc, cobalt, manganese or nickel. Non-limiting examples of suitable inorganic pigments include those from the Shepherd Color Company (Cincinnati, Ohio) such as Black 10C909A, Black 10P922, Black 1G, Black 20F944, Black 30C933, Black 30C940, Black 30C965, Black 376A, Black 40P925, Black 411 A, Black 430, Black 444, Blue 10F545, Blue 10G511,

Blue 10G551, Blue 10K525, Blue 10K579, Blue 211, Blue 212, Blue 214, Blue 30C527, Blue 30C588, Blue 30C591, Blue 385, Blue 40P585, Blue 424, Brown 10C873, Brown 10P835, Brown 10P850, Brown 10P857, Brown 157, Brown 20C819, Green 10K637, Green 187 B, Green 223, Green 260, Green 30C612, Green 30C654, Green 30C678, Green 40P601, Green 410, Orange 10P320, StarLight FL 37, StarLight FL105, StarLight FL500, Violet 11, Violet 11C, Violet 92, Yellow 10P112, Yellow 10C242, Yellow 10C272, Yellow 10P110, Yellow 10P225, Yellow 10P270, Yellow 196, Yellow 20P296, Yellow 30C119, Yellow 30C236, Yellow 40P140 or Yellow 40P280.

[0033] In addition to the foregoing inorganic pigments that may have their surfaces fluorinated as taught herein, the same teachings may be employed with organic pigments. The following is a list of organic pigments that may be treated accordance with the teachings herein. Non-limiting examples of suitable yellow pigments include C.I. Pigment Yellow 1, C.I. Pigment Yellow 2, C.I. Pigment Yellow 3, C.I. Pigment Yellow 4, C.I. Pigment Yellow 5, C.I. Pigment Yellow 6, C.I. Pigment Yellow 7, C.I. Pigment Yellow 10, C.I. Pigment Yellow 11, C.I. Pigment Yellow 12, C.I. Pigment Yellow 13, C.I. Pigment Yellow 14, C.I. Pigment Yellow 16, C.I. Pigment Yellow 17, C.I. Pigment Yellow 24, C.I. Pigment Yellow 34, C.I. Pigment Yellow 35, C.I. Pigment Yellow 37, C.I. Pigment Yellow 53, C.I. Pigment Yellow 55, C.I. Pigment Yellow 65, C.I. Pigment Yellow 73, C.I. Pigment Yellow 74, C.I. Pigment Yellow 75, C.I. Pigment Yellow 81, C.I. Pigment Yellow 83, C.I. Pigment Yellow 93, C.I. Pigment Yellow 94, C.I. Pigment Yellow 95, C.I. Pigment Yellow 97, C.I. Pigment Yellow 98, C.I. Pigment Yellow 99, C.I. Pigment Yellow 108, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 113, C.I. Pigment Yellow 114, C.I. Pigment Yellow 117, C.I. Pigment Yellow 120, C.I. Pigment Yellow 124, C.I. Pigment Yellow 128, C.I. Pigment Yellow 129, C.I. Pigment Yellow 133, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 147, C.I. Pigment Yellow 151, C.I. Pigment Yellow 153, C.I. Pigment Yellow 154, Pigment Yellow 155, C.I. Pigment Yellow 167, C.I. Pigment Yellow 172 or C.I. Pigment Yellow 180.

[0034] Non-limiting examples of suitable magenta or red or violet organic pigments include C.I. Pigment Red 1, C.I. Pigment Red 2, C.I. Pigment Red 3, C.I. Pigment Red 4, C.I. Pigment Red 5, C.I. Pigment Red 6, C.I. Pigment Red 7, C.I. Pigment Red 8, C.I. Pigment Red 9, C.I. Pigment Red 10, C.I. Pigment Red 11, C.I. Pigment Red 12, C.I. Pigment Red 14, C.I. Pigment Red 15, C.I. Pigment Red 16, C.I. Pigment Red 17, C.I. Pigment Red 18, C.I. Pigment Red 19, C.I. Pigment Red 21, C.I. Pigment Red 22, C.I. Pigment Red 23, C.I. Pigment Red 30, C.I. Pigment Red 31, C.I. Pigment Red 32, C.I. Pigment Red 37, C.I. Pigment Red 38, C.I. Pigment Red 40, C.I. Pigment Red 41, C.I. Pigment Red 42, C.I. Pigment Red 48(Ca), C.I. Pigment Red 48(Mn), C.I. Pigment Red 57(Ca), C.I. Pigment Red 57:1, C.I. Pigment Red 88, C.I. Pigment Red 112, C.I. Pigment Red 114, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 144, C.I. Pigment Red 146, C.I. Pigment Red 149, C.I. Pigment Red 150, C.I. Pigment Red 166, C.I. Pigment Red 168, C.I. Pigment Red 170, C.I. Pigment Red 171, C.I. Pigment Red 175, C.I. Pigment Red 176, C.I. Pigment Red 177, C.I. Pigment Red 178, C.I. Pigment Red 179, C.I. Pigment Red 184, C.I. Pigment Red 185, C.I. Pigment Red 187, C.I. Pigment Red 202, C.I. Pigment Red 209, C.I. Pigment Red 219, C.I. Pigment Red 224, C.I. Pigment Red 245, C.I. Pigment Violet 19, C.I. Pigment Violet 23, C.I. Pigment Violet 32, C.I. Pigment Violet 33, C.I. Pigment Violet 36, C.I. Pigment Violet 38, C.I. Pigment Violet 43 or C.I. Pigment Violet 50.

[0035] Non-limiting examples of blue or can organic pigments include C.I. Pigment Blue 1, C.I. Pigment Blue 2, C.I. Pigment Blue 3, C.I. Pigment Blue 15, C.I. Pigment Blue 15:3, C.I. Pigment Blue 15:34, C.I. Pigment Blue 15:4, C.I. Pigment Blue 16, C.I. Pigment Blue 18, C.I. Pigment Blue 22, C.I. Pigment Blue 25, C.I. Pigment Blue 60, C.I. Pigment Blue 65, C.I. Pigment Blue 66, C.I. Vat Blue 4 or C.I. Vat Blue 60.

[0036] Non-limiting examples of green organic pigments include C.I. Pigment Green 1, C.I. Pigment Green 2, C.I. Pigment Green 4, C.I. Pigment Green 7, C.I. Pigment Green 8, C.I. Pigment Green 10, C.I. Pigment Green 36 or C.I. Pigment Green 45.

[0037] Non-limiting examples of brown organic pigments include C.I. Pigment Brown 1, C.I. Pigment Brown 5, C.I. Pigment Brown 22, C.I. Pigment Brown 23, C.I. Pigment Brown 25, and C.I. Pigment Brown, C.I. Pigment Brown 41 or C.I. Pigment Brown 42.

[0038] Non-limiting examples of orange organic pigments include C.I. Pigment Orange 1, C.I. Pigment Orange 2, C.I. Pigment Orange 5, C.I. Pigment Orange 7, C.I. Pigment Orange 13, C.I. Pigment Orange 15, C.I. Pigment Orange 16, C.I. Pigment Orange 17, C.I. Pigment Orange 19, C.I. Pigment Orange 24, C.I. Pigment Orange 34, C.I. Pigment Orange 36, C.I. Pigment Orange 38, C.I. Pigment Orange 40, C.I. Pigment Orange 43 or C.I. Pigment Orange 66.

[0039] The white pigment of the ink composition can be selected from the group consisting of calcium carbonate, kaolin, talc, calcium sulfate, barium sulfate, titanium dioxide, zinc oxide, zinc sulfide, zinc carbonate, satin White, aluminium silicate, diatomaceous earth, calcium silicate, magnesium silicate, synthetic amorphous silica, colloidal silica, colloidal alumina, pseudo-boehmite, aluminum hydroxide, alumina, modified alumina, lithopone, zeolite, hydrated halloysite, magnesium carbonate, magnesium hydroxide, and mixtures thereof. In a preferred embodiment, the white pigment is zinc sulfide, titanium dioxide (including rutile titanium dioxide), or a mixture thereof. In a preferred embodiment, the white pigment is titanium dioxide.

[0040] The choice of dye depends on the application and the ink used, whether it is aqueous, solvent based, or hot melt, and on the printer type: flexography, continuous ink jet or drop-on-demand, piezo or thermal ink jet.

[0041] In a preferred embodiment the dye is suitable for flexography.

[0042] In the ink composition according to the present invention, the solvent can be a water-based solvent.

[0043] In another embodiment a water-soluble organic solvent can be used having an ability to dissolve a solute and is preferably selected from water-soluble solvents having a smaller vapor pressure than water. Examples thereof include: polyhydric alcohols, such as ethylene glycol, propylene glycol, butanediol, pentanediol, 2-butene-1,4-diol, 2-methyl-2,4-pentanediol, glycerin, 1,2,6-hexanetriol, diethylene glycol, and dipropylene glycol; ketones, such as acetonylacetone; esters, such as γ -butyrolactone, diacetin, and triethyl phosphate; lower alkoxy lower alcohols, such as 2-methoxyethanol and 2-ethoxyethanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; and thiodiglycol. Further, solvents usable herein include not only those that are liquid at room temperature but also those that are solid at room temperature and, when heat melted, can function as a solvent, and those that, when used in combination with an aqueous solution or other solvent(s), can function as a solvent. Although the amount of the water-soluble organic solvent used may be suitably determined, it is preferably, for example, 5 to 50% by weight based on the total weight of the ink.

[0044] According to a preferred embodiment of the present invention, the ink composition may further comprise an additional organic solvent. Examples of additional solvents usable herein include imidazole, methylimidazole, hydroxyimidazole, triazole, nicotinamide, dimethylaminopyridine, ϵ -caprolactam, 1,3-dimethyl-2-imidazolidinone, lactamide, sulfolane, dimethylsulfoxide, 1,3-propanesultone, methyl carbamate, ethyl carbamate, 1-methylol-5,5-dimethylhydantoin, hydroxyethylpiperazine, piperazine, ethyleneurea, propyleneurea, ethylene carbonate, propylene carbonate, dimethyl sulfoxide, N-methyl-2-pyrrolidinone, 2-pyrrolidinone, acetamide, formamide, dimethylformamide, N-methylformamide, and dimethylacetamide. The addition of the organic solvent can prevent the creation of a precipitate, for example, at a low temperature and permits printing to be stably performed under such an environment.

[0045] If necessary, additives may be added to the ink composition. Examples of additives are penetration accelerators, viscosity modifiers, binders, surface tension modifiers, hydrotrophy agents, humectants, pH adjusters, antimolds, chelating agents, preservatives, and rust preventives.

[0046] When the ink is used in a printing method wherein the ink is charged, it is possible to add a specific resistance modifier selected from inorganic salts, such as lithium chloride, sodium chloride, and ammonium chloride.

[0047] Examples of suitable binders include aqueous dispersions of aromatic or aliphatic polyurethanes, proteins, such as casein or casein derivatives, polyvinyl alcohols or polyvinyl alcohol derivatives, polymers and copolymers of acrylic acid or acrylic acid derivatives, such as, for example, acrylates, poly(vinyl chloride)/poly(vinyl acetate)-copolymer, styrene acrylate polymer, maleic resin, rubber resin, phenolic resin, silicone resin, heat-bodied linseed oil, oligomeric carbohydrates such as dextrin, natural rubber, gum arabic, shellac and cellulose derivatives. Particularly preferred is casein or casein derivatives. However, the skilled person makes a suitable choice from the binders possible in principle.

[0048] Penetration accelerators usable herein include: lower alcohols, such as ethanol, isopropanol, butanol, and pentanol; cellosolves, such as ethylene glycol monobutyl ether; carbitols, such as diethylene glycol monobutyl ether, triethylene glycol monobutyl ether glycol ether; and surfactants.

[0049] Surface tension modifiers usable herein include diethanolamine, triethanolamine, alcohols, such as glycerin and diethylene glycol, and nonionic, cationic, anionic, or amphoteric surfactants.

[0050] Preferred hydrotrophy agents usable herein include urea, alkylureas, ethyleneurea, propyleneurea, thiourea, guanidine acid salts, and tetraalkylammonium halides.

[0051] Humectants can also affect other properties of the ink composition and the printed images made therefrom, such as viscosity, pH, surface tension, optical density, and print quality. Such humectants typically include ethylene glycol, propylene glycol, diethylene glycols, glycerine, dipropylene glycols, polyethylene glycols, polypropylene glycols, alkane diols, amides, ethers, carboxylic acids, esters, alcohols, organosulfides, organosulfoxides, sulfones, alcohol derivatives, 3-pyrrolidone, ether derivatives, amino alcohols, and ketones. The amount of a particular additive will vary depending on a variety of factors including the molecular weight of the pigment or dye, the viscosity, the amount of any salt added, as well as the nature of the pigment or dye.

[0052] The ink composition of the invention comprises this not exclusive number of embodiments:

Embodiment 1

[0053] In one embodiment the ink composition according to the invention comprises or consists of:

5 to 20 % (w/w)	binder
5 to 25 % (w/w)	dye/pigment
1 to 15 % (w/w)	one or more additives (optionally)
0.5 to 20 % (w/w)	reducing agent

[0054] The solvent can be e.g. water or alcohol or a mixture thereof.

[0055] In one embodiment of the invention the ink composition as above contains 5 to 15 % (w/w), more preferred

approximately 10 % (w/w). The binder preferably is casein and the reducing agent is a reducing sugar, most preferred fructose.

Emodiment 2

[0056] In yet another embodiment of the invention the ink composition comprises or consists of:

30 - 70 % (w/w)	dye/pigments
2 - 30 % (w/w)	more particularly 5 - 20 wt % binder
1 - 3 % (w/w)	one or more additives (optionally)
0.5 to 20 % (w/w)	reducing agent

[0057] The solvent can be e.g. water or alcohol or a mixture thereof.

[0058] The ink composition as above can contain e.g. 5 to 15 % (w/w), more preferred approximately 10 % (w/w). The binder preferably is casein and the reducing agent is a reducing sugar, most preferred fructose.

Embodiment 3

[0059] In yet another embodiment of the invention the ink composition comprises or consists of:

2 - 6 % (w/w)	dye, preferably an acid or direct dye
5 - 15 % (w/w)	humectant
0.2 - 0.8 % (w/w)	a first additive, e.g. surface tension modifier, such as triethanolamine
0.05 - 0.2 % (w/w)	one or more further additives, e.g. a preservative or biocide.
0.5 to 20 % (w/w)	reducing agent

[0060] The solvent can be water or an organic solvent, such as N-methyl-2-pyrrolidone or a mixture thereof.

[0061] The ink composition as above can contain e.g. 5 to 15 % (w/w), more preferred approximately 10 % (w/w). The binder preferably is casein and the reducing agent is a reducing sugar, most preferred fructose.

Embodiment 4

[0062] In yet another embodiment of the invention the ink composition comprises or consists of:

2 - 6 % (w/w)	dye/pigment
5 - 15 % (w/w)	one or more additives
2.5 - 7.5 % (w/w)	binder, e.g. an poly(vinyl chloride)/poly(vinyl acetate)-copolymer
0.5 to 20 % (w/w)	reducing agent

[0063] The solvent can be non-aqueous, e.g. methyl ethyl ketone

[0064] The ink composition as above can contain e.g. 5 to 15 % (w/w), more preferred approximately 10 % (w/w). The binder preferably is casein and the reducing agent is a reducing sugar, most preferred fructose.

[0065] Ink compositions are generally known to the person skilled in the art, e.g. from "Industrial Dyes" 2003, K. Hunger (editor), Wiley-VCH, chapter 5.6 "Ink dyes", the disclosure of which is expressively incorporated herein by reference, or WO 2006/005513 A1. In order to obtain an ink composition as of the invention, the reducing agent can be admixed and/or dispersed with/in the commonly known ink compositions.

[0066] According to the invention all known or unknown curable resins can be used in order to generate the coating layer. In particular, the resin can be selected from the group consisting of phenol-formaldehyde resins, amino resins such as urea-formaldehyde and melamine formaldehyde resins, epoxy resins, vinylester resins and polyester resins or mixtures thereof. In a particular preferred embodiment the resin contains phenolic resins. In a most preferred embodiment the resin in the coating layer consists of phenolic resin only.

[0067] The resins may be modified or unmodified resins. The amino resins may be modified e.g. by glycol, caprolactam, acetoguanamine, benzoguanamine or p-toluene-sulphonamide, by alkylation or etherification. The phenol-formaldehyde resins may be modified e.g. by urea, melamine, lignin, resorcinol, modified phenols, cresols, bisphenols or other equivalent compounds. Any amino and phenolic resins known to the skilled person may be used as the amino and phenolic resins.

By combining different types of resins, e.g. phenolic and amino resins, together in a suitable ratio, it is possible to improve and optimize the properties of the coating. In the resin mixture, any solvent in which the resin is soluble may be used as the solvent for the resin.

[0068] The resin containing coating composition (also called "resin composition") forming the coating layer can comprise between about 0.01 and about 5 wt%, more preferably between about 0.02 and about 3 wt%, and most preferably, about 1 wt% of dye A preferred dosage for direct red 254 is 0.2 wt% and acid black 2 is 1.5 wt%. Possible and preferred dyes have been mentioned *supra*.

[0069] The coating composition can further comprise additives, e.g. waxes, surfactants, softeners, hardeners, wetting agents, anti-foam agents, diluents and/or alkalis. Preferred hardeners are sulfamic acid, ethanol amine hydrochloride, triethanol ammonium sulfate or hardener combinations such as morpholine / p-toluene sulfonic acid, N-methyl ethanol amine / SO₂ or N-methyl ethanol amine / ethanol amine / SO₂. The hardeners may be added to the impregnating procedure in amounts of 0.1 to 3 % by weight. Surface-active agents can, for example, be ethoxylated fatty acids or alkyl phenol ethoxylates, which may be used in amounts between 0.2 and 1.0% by weight. Typical separating agents can be wax emulsions in amounts between 0.2 and 2.0% by weight. Possible anti-foaming agents may be weakly foaming special surfactant combinations in amounts between 0.1 and 1.0 % by weight.

[0070] The flow values of the resin compositions can range from 2 to 20% and preferably from 4 to 8% which can be achieved by employing modifiers. Such modifiers can be, but are not restricted to, di- and polyols, polyether diols and alkoxyated alcohols. The alkoxyated alcohols comprise methoxylated, ethoxylated and propoxylated alcohols, diols and polyols. Preferred compounds belong to the group of C₂ to C₁₂ diols, such as 1,4-butane diol, 1,5-pentane diol and 1,6-hexane diol. These diols preferably can be added in an amount of 8 to 20 weight parts per 100 parts resin.

[0071] To the resin composition, in particular containing a phenolic resin, an ammonium salt can be added. Preferred ammonium salts include ammonium aluminium hexafluoride, ammonium borane hexafluoride, ammonium chloride, ammonium phosphate and ammonium citrate. Suitable ammonium-containing stabilisers are disclosed in US 5,110,320 the disclosure of which is hereby incorporated in its entirety. Particularly preferred stabilizers are ammonium aluminum hexafluorid, ammonium boron hexafluorid, ammonium chloride, ammonium phosphate and ammonium citrate.

[0072] Preferably a formaldehyde-phenol resin is used for preparing the coating layer. By varying the catalyst type and the formaldehyde (F) and phenol (P) molar ratio, two classes of PF resin can be synthesized: resoles (resols) and novolaks (novolacs). Resoles are synthesized under basic conditions with excess formaldehyde (i.e. F/P>1); novolaks are synthesized under acidic conditions with excess phenol (i.e. F/P<1).

[0073] In a first embodiment of the invention, this resin is a novolak. A novolak is a phenolic resin which is not inherently reactive. It is prepared by reacting phenol with formaldehyde under acidic conditions at a formaldehyde/phenol molar ratio of below 1:1, in particular at a molar ratio from 0.75 to 0.85:1. This can result in a linear polymer of molecular weight of 1000 to 1500. Further cross-linking can take place by the addition of more formaldehyde, usually in the form of hexamine.

[0074] In yet another preferred embodiment of the invention the resin is a resol which is formed from the base catalysed reaction of phenol and formaldehyde and requires an excess of formaldehyde. For solution resin, they are reacted to a low molecular weight of 300 to 700, so that the polymer is still soluble. Further heating will cause condensation reactions and result in a high molecular weight cross-linked polymer.

[0075] In preferred embodiment the resol resin used for the coating layer has a molar ratio of formaldehyde to phenol from 1.6 to 2.5 and/or an alkalinity between 1.5 and 3%. The resol can contain commonly known additives such as e.g. urea or glycols.

[0076] As outlined *supra* the base layer favourably is paper, most preferred a kraft paper. The paper can have a weight of 20 to 150 g/m², preferably of 30 to 80 g/m².

[0077] The impregnated paper can then be attached under pressure and heat to a panel or board in order to provide a coated board or coated panel. In this embodiment the board or panel serves as a support layer. Possible support layers to be coated with an impregnated paper according to the invention are plywood, chipboard, fibre board, oriented strand board (OSB), glue wood, laminated veneer lumber (LVL), parallel strand lumber (PSL) and oriented strand lumber (OSL). The most preferred embodiment is plywood panel. The coated board or panel can be applied in the wood working industry, in particular in construction industry for concrete shuttering.

[0078] In a specifically preferred embodiment of the invention the coated article comprises the following structures; preferably it consists of such structures:

- a) a support layer, most preferred plywood
- b) a paper printed with an ink composition comprising one or more reducing agents
- c) a resin containing coating layer covering at least partially the base layer.

[0079] Hence in this embodiment the coated article comprises at least or consists of four layers: the support layer, the paper, the extinction layer formed by the printed ink and the coating layer. The extinction layer is in contact with the coating layer.

[0080] In yet another aspect of the invention the use of an ink composition containing a first dye or pigment and one or more reducing agents is suggested for discoloring a second dye in a resin composition, whereas the first dye or pigment is not or less affected by said reducing agent.

[0081] In a preferred embodiment of the invention the colorant of the ink does not substantially interfere with the reducing agent(s) in the ink. However, the reducing agent is still capable of reducing the colorant which is present in the coating layer.

[0082] In yet a further aspect of the invention a method for preparing a coated article according to the invention is provided comprising the following steps:

- i. providing a base layer, in particular a paper
- ii. printing a pattern onto the base layer there with applying an ink composition with one or more reducing agents onto said base layer
- iii. impregnating said base layer with a resin containing coating composition and
- iv. optionally laminating said impregnated base layer onto a support layer.

[0083] The impregnation of the base layer can be performed with conventional techniques known to the skilled person, e.g. using baths, rollers, doctor blades, air knife, metering roll, doctor bars, or others. The resin compositions can be applied in one or more steps with drying and/or partial curing between the application stages.

[0084] The coated articles according to the invention are described with the following illustrative figures and examples, which should not be interpreted in order to limit the scope of protection.

Figure legends

[0085]

Fig. 1: Schematic structure of a coated article comprising a support layer (1), a base layer (2), an extinction layer (4) and a coating layer (3).

Fig. 2: Diagram showing the mechanistic principle. The starting point of the reaction is shown at the top: A coated article with a homogenously distributed dye or pigment. Due to the reduction agent contained within the underlying extinction layer, the coating layer is specifically discolored at regions of neighboring extinction layer.

EXAMPLES

Example 1

1. Printing of the kraft paper

[0086] The kraft paper is printed using the ink WM1A-002H (Woodline, Flint Group, Finland) having a viscosity of 14 s (measured according DIN 4) which equals a viscosity of approx. 28 mPas. The application rate of the liquid ink is approx. 11 g/m². A commonly known printing ink (such as e.g. known from WO2006/005513 A1, see above) was modified in order to arrive at the present invention by addition of 5, 10 and 15%, respectively, of fructose as reduction agent. The fructose was dissolved into the ink by mixing. The modified ink was used to print a pattern (company logo) on 80 g/m² natural kraft paper.

2. Impregnation

[0087] In the second step the printed kraft paper was saturated with water-based phenolic resol resin containing a molar ratio of formaldehyde to phenol from 1.6 to 2.5 having an alkalinity of 1.5 to 3% and dried to have a volatile matter content of 8% (5 min at 160°C). Resin contained red and black dyes to give resin and impregnated paper a deep reddish brown colour.

3. Lamination process

[0088] The prepared film was pressed in a hot press on 9 mm birch plywood using pressing parameters of 5 min, 135°C and 18 kg/cm² pressure. Visual evaluation of pressed samples gave the following results:

- inks containing fructose had a lighter colour than reference inks

- the best result was obtained with 10% of fructose

4. Aging analysis

[0089] The pressed samples were exposed to heat treatment (70°C/24h). All samples showed darkening of the colour of the logo. Inks containing fructose did not darken as much as the reference. Visually, the ink containing 10% of fructose had the best appearance.

Claims

1. A coated article comprising:

- a) a base layer, preferably paper;
- b) a coating layer comprising a resin composition, in particular phenolic resin;
- and
- c) an extinction layer comprising one or more reducing agents capable of at least partially discoloring the resin composition.

2. The coated article according to claim 1, whereas the extinction layer comprises a printing ink applied onto the base layer.

3. The coated article according to claims 1 or 2, wherein said reducing agent has a standard electrode potential E^0 between - 150 mV and -1500 mV.

4. The coated article according to any of the above claims wherein said reducing agent is selected from the group consisting of reducing sugars, hydrides, organic acids and inorganic salts.

5. The coated article according to any of the above claims, wherein the reducing agent is selected from the group consisting of dihydroxyacetone, glycolaldehyde, glyceraldehyde, erythrose, threose, ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, talose, fructose, lactose, maltose, cellobiose, diborane, lithium aluminium hydride, sodium borohydride, lithium borohydride, SnCl_2 , SnF_2 , $\text{Sn}(\text{OH})_2$, sodium dithionite (Color Index Reducing agent 1), thiourea dioxide (Color Index Reducing agent 11), sodium hydroxymethanesulfonate (Color Index Reducing agent 2), zinc formaldehyde sulfoxylate (Color Index Reducing agent 6), calcium formaldehyde carboxylate (Color Index Reducing agent 12), sodium sulphite, sodium bisulphite, diisobutylaluminium hydride, oxalic acid, formic acid, ascorbic acid, $(\text{NH}_4)_2\text{HPO}_3$, CuHPO_3 , SnHPO_3 and $\text{Al}_2(\text{HPO}_3)_3$, alkali hypophosphite, FeCl_2 , FeCO_3 , FeSO_4 .

6. The coated article according to any of the above claims, wherein the resin is selected from the group consisting of phenolic resins such as phenol-formaldehyde resins, urea-formaldehyde resins, melamine formaldehyde resins, epoxy resins, vinyl ester resins and polyester resins or a mixture thereof, preferably phenolic resin.

7. The coated article according to any of the above claims, wherein the resin composition comprises a dye.

8. The coated article according to claim 7, wherein said dye is selected from the group consisting of Acid Yellow 23, Acid Red 18, Acid Yellow 36, Acid Black 194, Direct Red 239, Reactive Red 120, Acid Blue 9, Acid Red 27, Acid Red 51, Direct Blue 199, Direct Red 254, Reactive Red 195, Acid Red 14, Acid Yellow 17, Acid Black 1, Direct Yellow 86, Direct Black 168 and Food Black 2.

9. The coated article according to any of the preceding claims further comprising a support layer, preferably selected from the group consisting of cardboard, plywood, chipboard, fibre board, oriented strand board (OSB), glue wood, laminated veneer lumber (LVL), parallel strand lumber (PSL) and oriented strand lumber (OSL), preferably plywood.

10. An ink composition for printing a substrate, preferably a paper, comprising a binder, a reducing agent and a dye or pigment, wherein the reducing agent has a standard electrode potential E^0 between - 150 mV and -1500 mV.

11. The ink according to claim 10, wherein said reducing agent is selected from the group consisting of reducing sugars, hydrides, organic acids and inorganic salts.

12. The ink composition according to claim 11, wherein the reducing agent is selected from the group consisting of dihydroxyacetone, glycolaldehyde, glyceraldehyde, erythrose, threose, ribose, arabinose, xylose, lyxose, allose, altrose, glucose, mannose, gulose, idose, galactose, talose, fructose, lactose, maltose, cellobiose, diborane, lithium aluminium hydride, sodium borohydride, lithium borohydride, SnCl_2 , SnF_2 , $\text{Sn}(\text{OH})_2$, sodium dithionite (Color Index Reducing agent 1), thiourea dioxide (Color Index Reducing agent 11), sodium hydroxymethanesulfinate (Color Index Reducing agent 2), zinc formaldehyde sulfoxylate (Color Index Reducing agent 6), calcium formaldehyde carboxylate (Color Index Reducing agent 12), sodium sulphite, sodium bisulphite,, diisobutylaluminium hydride, oxalic acid, formic acid, ascorbic acid, $(\text{NH}_4)_2\text{HPO}_3$, CuHPO_3 , SnHPO_3 and $\text{Al}_2(\text{HPO}_3)_3$, alkali hypophosphite, FeCl_2 , FeCO_3 , FeSO_4 .
13. The ink composition according to one of the claims 10 to 12, wherein the binder is casein and the reducing agent preferably is fructose.
14. The ink composition according to any of the claims 11 to 13 comprising 0.5 to 20 %wt of the reducing agent as calculated on the sum of all components of the composition.
15. Use of an ink composition comprising a reducing agent for discoloring at least partially a resin composition being applied on a base layer.
16. Method for preparing a coated article comprising the following steps:
 - a) providing a base layer, preferably paper
 - b) applying an ink composition onto the base layer, said ink composition comprising one or more reducing agents,
 - c) impregnating the base layer of b) with a resin composition and
 - d) optionally laminating the base layer of c) on a support layer.

Fig. 1

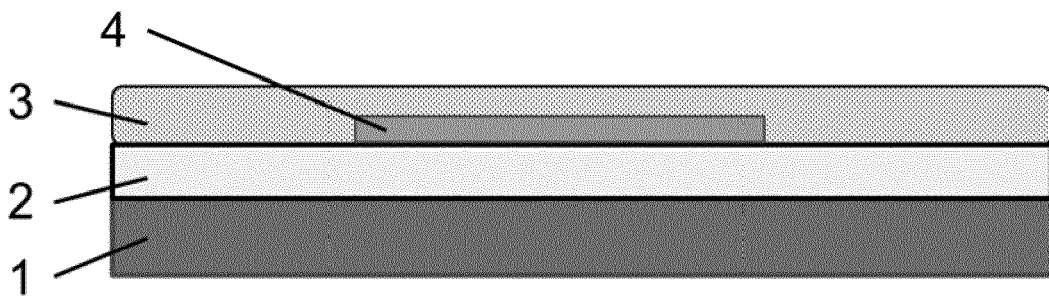
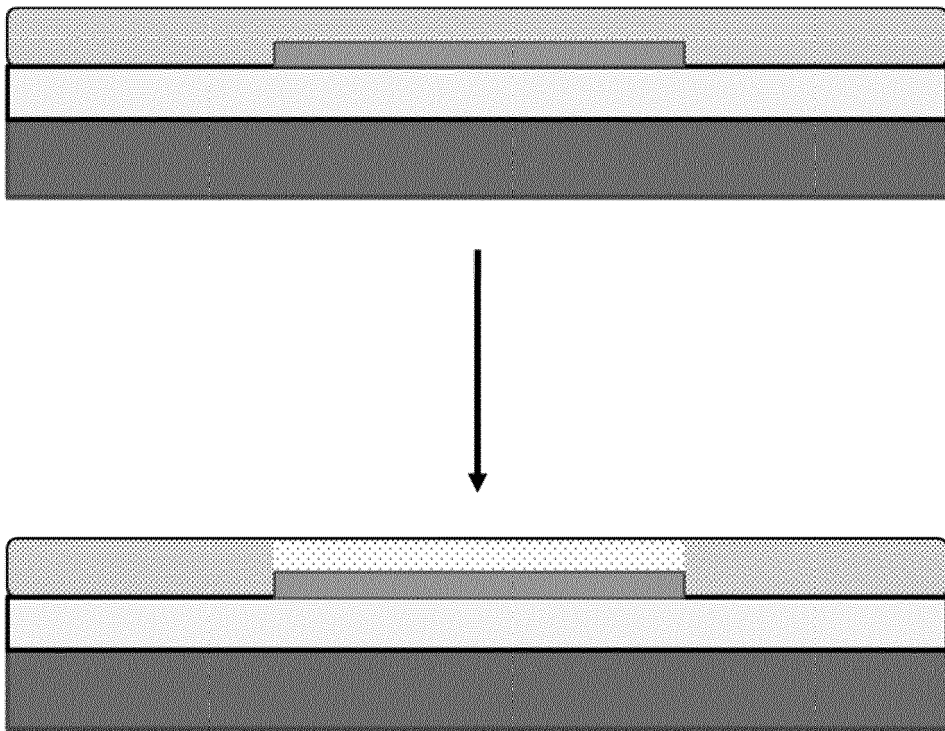


Fig. 2





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