CORE-SHELL TYPE BINDER AND A METHOD FOR PREPARATION THEREOF

The present invention proposes a core-shell type binder wherein each of core and shell comprise copolymer or terpolymer of acrylic-based monomers; at least one of the core or the shell comprises a suitable crosslinking agent; core and shell have different glass transition temperatures, and the crosslinking agent content of the binder is less than 5% (w/w) based on the total weight of said monomers.
The present invention relates to a core-shell type binder for pigment printing, a paste comprising such binder, and a method of production thereof.

Technical Field of the Invention

Background of the Invention

Printing in textile is a process for applying patterns to textile materials. It is a common printing process/method due to the simplicity of application thereof. This method has advantages such as ease of a near final print at the printing stage itself, quality of the prints, applicability onto various substrate materials and the ability to avoid any washing processes after fixation (Yaman et.al., Journal of Engineered Fibers and Fabrics, Vol. 7 Issue 2, (2012), 40-46). The coating composition for pigment printing includes an emulsion of conventional or in rare cases core-shell type polymeric binders, water, pigments and rheology modifiers, as well as other additives. The binder must provide a good bond with the fiber of the textile substrate.

In pigment printing, insoluble pigments which have basically no affinity for the fiber, are fixed thereon with binding agents applied according to a desired pattern. A good quality pigment print is characterized by its brilliance and high color value relative to the pigment concentration in the paste (printing composition), minimum stiffening in the handle of textile and generally acceptable fastness properties. Successful pigment printing systems are based upon three equally important components: pigment dispersions, binders and crosslinking agents, and auxiliary agents (e.g. thickener) giving a required rheology to the printing composition and the final product (W.C. Miles, Textile Printing, Society of Dyers and Colourist Bradford England, p. 140 (2004)).

Crosslinking increases crocking, washing and dry cleaning fastness properties, but detrimentally affects the handle of the fabric. When the binder molecule have no self crosslinking groups, an additional crosslinking agent such as urea formaldehyde or melamine formaldehyde condensate, methylolated urethane compounds etc, having at least two reactive groups per molecule are added in the binder system (V.A. Shenai, Chemistry of Textile Auxiliaries, Sevak Publisher Mumbai, p. 231 (2002)).

It is generally desirable to effect crosslinking once the binder has achieved its final location, or concurrently with the drying process, in order to enhance the properties of the treated substrate. Many of the conventional crosslinking agents such as, for example, copolymerized N-methylol acrylamide and added urea/formaldehyde resins inherently contain or liberate formaldehyde, a skin and eye irritant, a mutagen and a suspect carcinogen. The use of methylolacrylamide as a cross linker in polymer emulsions is well known in the industry. In generally, N-methylolacrylamide (NMA) has been used in aqueous formulations with many different applications, including; fabric coatings, textile finishes, binders and adhesives. These emulsions have a variety of uses including as binders and coatings. A primary use of these emulsions is for imparting adequate resistance to water and solvents depending on the performance desired in the final products, such as with nonwoven fabrics and coated papers.

In many commercial binders, 4-6% (w/w) crosslinking agent is used based on total monomer content, to have more resistant printing against water and alkali media. Crosslinking of NMA can be achieved by thermal curing or by catalysis with acids or bases. Also formaldehyde release during the crosslinking reactions of (NMA) in the binders can be caused by instability of the crosslinks, during thermal curing or catalysis with acids or bases [Bufkin, 1978].

Various attempts have been made to reduce the free-formaldehyde content in different types of products by adding substances to bind the formaldehyde. These include adding substances such as ammonia, hydrazine derivatives, urea, thiourea, ethylene urea, acrylamide polymers and others. EP 0 438 284 A1 discloses acid curing lacquers based on nonaqueous alkyl-urea resin combinations having reduced formaldehyde emissions through use of a compound having an acidic alpha-methylene group such as acetooacetamide. In addition, various formaldehyde scavengers have been developed in the textile industry including the use of urea, nitrogen containing aromatic heterocyclics and nonaromatic alcohols, e.g. as in EP 0302 289 A1.

As mentioned in Emulsion Latex Handbook (Taiseisha Co. Ltd.), emulsion polymers are prepared by reacting radically reactive monomers in an aqueous medium that contains an emulsifier and a water-soluble radical initiator. Examples of the emulsifier include surfactants such as alkylbenzenesulfonates (e.g. sodium dodecylbenzenesulfonate), dialkyl sulfosuccinates (e.g. sodium dodecysulfosuccinate) and polyoxyethylene alkylphenol ether sulfate (e.g. sodium polyoxyethylene alkylphenyl ether sulfate). Examples of the water soluble radical initiator include persulfates (e.g. ammonium persulfate, sodium persulfate, potassium persulfate) and water soluble hydroperoxide (e.g. hydrogen peroxide, t-butyl hydroperoxide).

Preparation of core-shell polymers is generally achieved by stepwise emulsion polymerization, which basically comprises a first step of preparing core particles of latex and a second step of preparing the shell polymer. The core particles act as seed particles onto whose surface the shell polymers become preferentially deposited.
An emulsion polymer contains at least one copolymerized ethylenically unsaturated monomer. At a high temperature above 75°C, ethylenically unsaturated monomer forms reactive radicals if any initiator is present in the reaction media. Ethylenically unsaturated monomers include, for example, (meth)acrylate, ethyl acrylate, butyl acrylate, 2-ethyl acrylate, decyl acrylate, lauryl acrylate, methyl methacrylate, butyl methacrylate, isodecyl methacrylate, lauryl methacrylate, hydroxyethyl (meth)acrylate and hydroxypropyl (meth)acrylate; (meth)acrylamide; (meth)acrylonitrile; styrene and substituted styrenes, butadiene; vinyl acetate, vinyl butyrate and other vinyl esters; and other vinyl monomers such as ethylene, vinyl chloride, vinylidene chloride. The use of the term (meth) followed by another such as acrylate or acrylamide, as used throughout the disclosure, refers to both acrylates or acrylamides and methacrylates and methacrylamides, respectively.

Calculated glass transition temperature ($T_g$) of an emulsion polymer is typically from -65°C to 65°C, or alternatively, from -55°C to 20°C. $T_g$'s of the co- or terpolymers can be estimated using Fox equation. Glass transition temperatures of co- or terpolymers (here, core and shell) can be tuned by mixing and polymerizing of predetermined relative amounts of different monomers (1 to n) having different glass transition temperatures ($T_{g,1}$ to $T_{g,n}$) when they are polymerized to form their homopolymers, said relative amounts being approximately calculated using e.g. Fox equation given below:

$$\frac{1}{T_{g,f}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} + ... + \frac{w_n}{T_{g,n}}$$

where n is the number of different monomers (1, 2, ..., (n-1), n) constituting a final product (here, core or shell) with a glass transition temperature of $T_{g,f}$; $T_{g,1}$, $T_{g,2}$, and $T_{g,n}$ are glass transition temperatures (in Kelvin) of homopolymers of each monomer 1, 2 and n, respectively; and $w_1$, $w_2$ and $w_n$ are the mass fractions of each monomer 1, 2 and n, respectively. In the literature, Fox Equation is represented in various forms (e.g. as in Brostow et.al., Materials Letters 62 (2008) 3152-3155; or as in US 2011/0092118 A1).

Thus, it is necessary to provide a binder which achieves crosslinking performances comparable with the binders containing higher amounts of NMA, which are employed in pigment printing on textiles.

It is further necessary to provide a method for preparation of such binder.

Objects of the Invention

Primary object of the present invention is to overcome the abovementioned shortcomings of the prior art. Another object of the present invention is to provide a binder which reduces the amount of released formaldehyde from pigment printing binder during and after curing on a printed textile substrate, without decreasing the fastness performances; and a pigment printing paste comprising such binder.

A further object of the present invention is to provide a method for preparation of such binder.

Summary of the Invention

The present invention proposes a core-shell type binder wherein each of core and shell comprise copolymer or terpolymer of acrylic-based monomers; at least one of the core or the shell comprises a suitable crosslinking agent; core and shell have different glass transition temperatures, and the crosslinking agent content of the binder is less than 4% (w/w) based on the total weight of said monomers.

Detailed Description of the Invention

The present invention proposes a core-shell type binder for pigment printing. Said binder is a multi-layer emulsion particle having a polymeric core component and polymeric shell component which can be employed in coating compositions for pigment printing applications in textile industry.

In the binder according to the present invention, each of core and shell comprise copolymer or terpolymer of acrylic-based monomers. At least one of the core or the shell comprises a suitable crosslinking agent. The core and shell of the binder according to the present invention have different glass transition temperatures.

In the binder according to the present invention, the crosslinking agent content is less than 4% (w/w) based on the total weight of said monomers. Although low amounts of crosslinking agent in the pigment printing compositions used in experiments, surprisingly, performance of the binder according to the present invention in terms of fastness properties of printed final products was comparable with commercial binders containing 4-6% (w/w) of NMA with respect to the total mass of the monomers in said binders has been achieved, thanks to the core-shell morphology of the binder.

Preferably, said copolymer or terpolymer is one or more substance selected from the list consisting of acrylic
copolymers such as styrene acrylic copolymer, vinyl acrylic copolymer, copolymer of vinyl acetate with vinyl ester of a branched organic acid having 9 to 11 Carbon atoms (vinyl acetate/VeoVa™ copolymer), terpolymer of vinyl acetate and acrylate with vinyl ester of a branched organic acid having 9 to 11 Carbon atoms (vinyl acetate/acrylic/VeoVa™ terpolymer), vinyl acetate/ethylene copolymer (VAE), vinyl acetate/ethylene/acrylic terpolymer (VAEA), and a styrene/acrylic acid ester copolymer. Main reasons to prefer these substances are their availability, affordability (low prices thereof), their performance through laboratory experiments.

In a preferred embodiment according to the present invention, the styrene/acrylic acid ester copolymer is selected from the list consisting of styrene ethyl acrylate copolymer, styrene butyl acrylate copolymer, styrene 2-ethylhexyl acrylate copolymer and styrene cyclohexyl acrylate copolymer. These substances are also highly available and affordable, and they showed suitable performance in laboratory tests.

In a preferable aspect according to the present invention, the core has a glass transition temperature within the range between -30 and 0°C, preferably within the range between -20°C and -5°C; and the shell has a glass transition temperature within the range between 0°C and 50°C, preferably within the range between 10°C and 30°C. In this case, mechanical resistance of the binder is enhanced by providing that the shell is rather hard. It is further preferable that the glass transition temperature of the shell allows film formation under room temperature (20°C) or standard temperature (25°C), in which case the film formation can be achieved without additional heating costs. This is easily achieved when the glass transition temperature of the shell is within the range between 10°C and 20°C.

In an alternative preferable aspect according to the present invention, the core has a glass transition temperature within the range between 0°C and 50°C, preferably within the range between 10°C and 30°C; and the shell has a glass transition temperature within the range between -30°C and 0°C, preferably within the range between -20°C and -5°C. In this case, film formation is easily achieved at ambient temperatures even in cold places, for instance at an unheated factory in winter, e.g. under normal temperature (0°C).

In a preferred embodiment according to the present invention, the crosslinking agent content of the core is less than 1% (w/w) based on the total weight of the polymeric material (i.e. based on the total weight of the co- or terpolymerization products of respective monomers) comprised by the core; and the crosslinking agent content of the shell is within the range between 1% and 3% (w/w), preferably within the range between 1.5% and 2.5% (w/w), more preferably within the range between 1.8% and 2.2% (w/w), based on the total weight of the polymeric material (i.e. based on the total weight of the co- or terpolymerization product of respective monomers) comprised by the shell. Even by employing such low values of crosslinking agent in the binder according to the present invention, final products (i.e. pigment printed textiles) obtained using the pigment paste comprising said binder showed highly acceptable performance especially in terms of relevant fastness measurement results when compared with those obtained using conventional binders comprising 4-6% (w/w) of crosslinking agent (NMA) based on the total weight of the polymeric material (i.e. based on the total weight of the co-or terpolymerization product of the monomers) comprised by the binder. Thus the amount of crosslinking agent used in binders and accordingly in pigment pastes is reduced, and release of any toxic or unwanted substance (e.g. formaldehyde caused by NMA) in final products (here, pigment printed fabrics) is minimized without sacrificing expected performance therefrom.

Preferably the binder has a core:shell weight ratio within the range between 20:80 and 80:20, more preferably within the range between 20:80 and 60:40, even more preferably within the range between 20:80 and 40:60. These core:shell weight ratios secure that both core and shell are substantially present without being basically omittable, and the above mentioned advantages of core-shell morphology is significantly observed with these ratios.

In a preferred embodiment according to the present invention, the crosslinking agent is selected from a list consisting of N-methylolacrylamide, diacetone acrylamide, adipic acid dihydrazide, and acetoacetoxy ethylmethacrylate, polyamine.

Accordingly, a method is for obtainment of the binder according to the present invention. The method comprises a first emulsion polymerization step for formation of a core from a first pre-emulsion comprising a copolymerizable or terpolymerizable (shortened as co- or terpolymerizable) first mixture of monomers, followed by a second emulsion polymerization step for formation of a shell coated on said core, from a second pre-emulsion different from the first pre-emulsion comprising a copolymerizable or terpolymerizable second mixture of monomers different than said first mixture of monomers; such that the first pre-emulsion and the second pre-emulsion in total comprise less than 4% (w/w) of crosslinking agent based on the total weight of respective monomers; and such that the glass transition temperatures of the copolymerization or terpolymerization products of the first mixture of monomers and the second mixture of monomers are different.

The method preferably comprises the following steps of:

a) loading a temperature-controlled stirred reactor vessel with a pre-mixture comprising water, pH buffer and a minor amount of an emulsifier, wherein said minor amount is 5%-20%, preferably 8%-12% of a total amount of an emulsifier;

b) preparation of a first pre-emulsion and a second pre-emulsion for use in preparation of the core and the shell,
said first and second pre-emulsions comprising remaining amount of emulsifier distributed to the first and second pre-emulsions; said remaining amount being equal to the difference between respective predetermined total amounts and said minor amounts; the amounts of emulsifier in the first and second pre-emulsions being determined in accordance with a core:shell weight ratio pre-determined for the binder,

c) under inert atmosphere, heating the reactor to a reaction temperature ranging between 70°C and 90°C, preferably between 75°C and 85°C; then loading a minor first amount of a pre-initiator solution and a minor first part of the first pre-emulsion into the reactor; followed by introducing the remaining first pre-emulsion slowly, preferably throughout 45 minutes to 90 minutes; then after a further duration within the range between 10 minutes and 20 minutes, preferably 13 minutes and 17 minutes, introducing the second pre-emulsion slowly, preferably throughout 90 minutes to 150 minutes; slowly introducing remaining amount of the pre-initiator solution, preferably continuously from beginning of the introduction of said remaining first pre-emulsion up to the end of the introduction of the second pre-emulsion; then after following 20 to 40 minutes, preferably after 25 to 35 minutes, addition of a radical initiator and an activator under a temperature ranging between 50°C and 78°C, preferably ranging between 60°C and 70°C; and then cooling down the reactor to a temperature below 50°C;

d) filtering the reaction product and thus obtainment of a binder,
weight ratios can be calculated using e.g. Fox Equation or an equivalent or alternative thereof, which correlates
glass transition temperatures of homopolymers of monomers used in a co- or terpolymer and the weight or molar
ratios of said monomers in a reaction mixture, with the glass transition temperature of a co- or terpolymer obtained
from said monomers with said weight or molar ratios; the co- or terpolymer being the core or shell of the core-shell
type binder according to the present invention.

[0037] The first and/or the second pre-emulsions each comprise a different mixture of monomers with pre-calculated
weight ratios of said monomers differing between the first and second pre-emulsions for each monomer; wherein the
glass transition temperature of co- or terpolymers to be prepared by co- or terpolymerization of said monomers are pre-
determined by such pre-calculation using a suitable correlation known in the art e.g. Fox Equation.

[0038] Since the preferred co- or terpolymers to be used in core and/or shell are selected from the list consisting of
acrylic copolymers such as styrene acrylic copolymer, vinyl acrylic copolymer, copolymer of vinyl acetate with vinyl ester
of a branched organic acid having 9 to 11 Carbon atoms, terpolymer of vinyl acetate and acrylate with vinyl ester of a
branched organic acid having 9 to 11 Carbon atoms, vinyl acetate/ethylene copolymer, vinyl acetate/ethylene/acrylic
terpolymer, and a styrene/acyric acid ester copolymer; suitable monomers to obtain said materials are to be used in
preparation of the first and/or second pre-emulsions. Suitable monomers for this purpose can be selected by a person
skilled in the art of polymerization. Examples of such monomers suitable for employing in the first and/or second pre-
emulsions include vinyl acetate (VAc), butyl acrylate (BA), styrene (St), methyl methacrylate (MMA), 2-ethylhexyl acrylate
(2-EHA), but are not limited thereto and other suitable crosslinkable monomers can also be employed for obtainment of
the core and/or shell of the binder according to the present invention. Both first and second emulsion polymerization
steps are performed in a stirred reactor, and under a reaction temperature ranging between 70°C and 90°C, and more
preferably 75°C and 85°C.

[0039] As a preparation to emulsion polymerization, a pre-mixture comprising (preferably de-ionized) water, a pH
buffer and a minor amount of emulsifier which is 5-20%, preferably 8%-12% of a total amount of an emulsifier are loaded
into the reactor, and heated to the reaction temperature under inert atmosphere.

[0040] The first and second pre-emulsions for use in the method comprising the remaining amount of the emulsifier,
which is 80-95%, preferably 88%-92% of the total amount of the emulsifier (e.g. the remaining 90% of the total amount
of the emulsifier), and (preferably deionized) water is to be prepared along with a solution of a pre-initiator such as
ammonium persulfate (APS).

[0041] Accordingly, a first pre-emulsion and a second pre-emulsion are to be prepared for use in preparation of the
core and the shell, with pre-determined total amounts of emulsifier for the first and second pre-emulsions, respectively.

[0042] The amounts of emulsifier for the first and second pre-emulsions are preferably determined in accordance with
the above mentioned core:shell weight ratios pre-determined for the binder. For instance, if the pre-mixture comprises
10% of the total amount of the emulsifier as said minor amount, and if the core:shell weight ratio is pre-determined as
40:60, the remaining 90% of the emulsifier is distributed between the first and second pre-emulsions such that
0.40-90%=36% of the total amount of the emulsifier is comprised by the first pre-emulsion and 0.60-90%=54% of the
total amount of the emulsifier is comprised by the second pre-emulsion.

[0043] As a beginning of the emulsion polymerization, a minor first amount of a pre-initiator solution (e.g. 5% of a total
pre-initiator amount to be used throughout the method) and a minor first part of the first pre-emulsion (e.g. 5% of a total
amount of the first pre-emulsion to be used throughout the method) is introduced into the reactor. Then, remaining
second part of the first pre-emulsion is slowly (e.g. in about 1 hour) introduced into the reactor, preferably throughout
45 minutes to 90 minutes. Thus core particles start to grow in the reactor. Mean particle size of the core particles depends
on the duration before the second pre-emulsion is introduced into the reactor. Preferably, said duration is within the
range between 10 and 20 minutes, more preferably within the range between 13 and 17 minutes.

[0044] Upon achieving a desired mean particle size of core particles, duration of which can be experimentally deter-
mined and/or modeled beforehand, the second pre-emulsion is slowly (e.g. in about 2 hours) introduced into the reactor,
preferably throughout 90 minutes to 150 minutes. A second amount of the pre-initiator solution which is greater than the
minor first amount of the pre-initiator solution (e.g. the remaining 95% of the total amount used throughout the method)
is slowly introduced into the reactor, preferably from the beginning of the emulsion polymerization up to the end of
the introduction of the second pre-emulsion.

[0045] Then, after 20 to 40 minutes, preferably after 25-35 minutes, under a temperature preferably ranging between
80°C and 90°C, preferably at a temperature ranging between 83°C and 87°C, pre-initiator (e.g. APS) is added into the
reactor in an amount ranging between 0.05% and 0.15% (w/w), preferably between 0.075% and 0.125% (w/w) based
on the total weight of the monomers.

[0046] After following 20 to 40 minutes, preferably after 25 to 35 minutes, under a temperature preferably ranging
between 50°C and 78°C, preferably ranging between 60°C and 70°C, a radical initiator e.g. tert-butyly hydroperoxide and
an activator e.g. sodium metabisulfite, tartaric acid, ascorbic acid are added into the reactor for scavenging and consuming
any unreacted monomers; and the reactor is cooled down to a temperature below 50°C. Preferably, additives such as
antifoaming agent, biocide, pH control additives (acidic or basic additives or buffers) can be added into the reactor according to any further requirements of the binder. The reaction product is then filtered and thus, a core-shell type binder according to the present invention is obtained.

A pigment printing paste comprising the binder according to the present invention and a method for preparation thereof are also hereby provided. Preferably the paste has a viscosity within the range between 20 and 25 Pa·s, a pH value between 8 and 9. The paste preferably comprises 10% to 25% (w/w) of the binder according to the present invention; 1.5% to 2.5%, preferably 1.75% to 2% (w/w) of thickener (preferably a synthetic thickener), 0.05% to 0.15% (w/w) of a pH control additive (e.g. ammonia as a cost effective example), and a complementary amount of water, based on the total weight of the paste.

Accordingly, the method for preparation of a pigment printing paste comprises mixing a binder according to the present invention with a mixture comprising water, a pH control additive and a thickener; wherein the paste preferably comprises 10% to 25% (w/w) of said binder; 1.5% to 2.5% (w/w), more preferably 1.75% to 2% (w/w) of a synthetic thickener, 0.05% to 0.15% (w/w) of a pH control additive which is preferably ammonia, and a complementary amount of water, based on the total weight of the paste.

An exemplary experiment for obtaining the binder and the use of the obtained binder in pigment printing is provided below. The following example is intended only to further illustrate the invention and not to limit the scope of the invention that is defined by the claims.

**Example**

Styrene/butyl acrylate copolymer binder according to the present invention, comprising a polymeric core and shell with glass transition temperatures of 30°C (≈303K) and -20°C (≈253K), respectively, was prepared. Relevant $T_g$ calculations performed using Fox Equation are given below. The effect of additives (here, acrylic acid, methacrylic acid, N-methylol Acrylamide etc. with total ratio in pre-emulsions lower than 4% (w/w) based on the total monomer content) on final $T_g$ values is omitted. Upon obtainment of individual copolymer samples for both core and shell, their $T_g$ values are compared with relevant target $T_g$ values, and accepted if obtained values are within a ±1K interval from said target values.

**Glass transition temperature of styrene homopolymer:** $T_{g,1}=105°C$ (≈378K)

**Glass transition temperature of butyl acrylate homopolymers:** $T_{g,2}=-45°C$ (≈228K)

For determination of a suitable theoretical styrene/butyl acrylate composition for obtainment of a core with a $T_{g,c}$ (glass transition temperature of the core) of 30°C (303K), the Fox Equation is used as follows; where $w_1$ and $w_2$ represent weight ratios of styrene and butyl acrylate in the core, respectively, with respect to the total weight of the core after omission of other ingredients such as additives:

$$\frac{1}{T_{g,c}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

$$\frac{1}{303(K)} = \frac{w_1}{378(K)} + \frac{1 - w_1}{228(K)}$$

$$\frac{1}{303(K)} = \frac{228 \cdot w_1 + 378 \cdot (1 - w_1)}{86184} (K^{-1})$$

Thus a first pre-emulsion for preparation of the core will have a composition mainly comprising $w_1= 0.624 (=62.4\%)$ (w/w) of styrene and $w_2=1-0.624=0.376 (=37.6\%)$ (w/w) of butyl acrylate based on the total weight of the monomers (i.e. here, styrene and butyl acrylate).

Similarly, for determination of a suitable theoretical styrene/butyl acrylate composition for obtainment of a shell with a $T_{g,c}$ (glass transition temperature of the core) of -20°C (253K), the Fox Equation is used as follows; where $w_1$ and $w_2$ represent weight ratios of styrene and butyl acrylate in the shell, respectively, with respect to the total weight of the shell after omission of other ingredients such as additives:

$$\frac{1}{T_{g,c}} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$
Thus a second pre-emulsion for preparation of the shell will have a composition mainly comprising $w_1 = 0.249$ (24.9%) (w/w) of styrene and $w_2 = 1 - 0.249 = 0.751$ (75.1%) (w/w) of butyl acrylate based on the total weight of the monomers (i.e., here, styrene and butyl acrylate).

For the synthesis of the binder, deionized water was charged to a 2 Liter flask reactor and heated under inert atmosphere (i.e., reactor headspace was continuously purged with nitrogen) to 80-82°C, where 70-90°C has been basically considered to be highly suitable. Then ammonium persulfate (APS) solution was added as a pre-initiator into the reactor. Then, as a step of formation of the core, an aqueous first pre-emulsion of monomers distributed homogeneously stabilized by emulgators, was charged into the reactor and stirred for 20 minutes. After 3 hours, as a step of formation of the shell, an aqueous second pre-emulsion along with an initiator was charged into the reactor, at 80-82 °C. Afterwards, post additives mainly used in the relevant technical field were added, and then the reaction mixture (i.e., final emulsion) was cooled down to ambient temperature (around room temperature).

This final emulsion was filtered and total amount of binder, mean particle size ($\mu$m), MFFT (minimum film forming temperature, in °C), $T_g$ (°C), pH, Brookfield viscosity (Pa·s), solid content (%) and density (g/cm³) thereof were determined.

Pigment printing pastes were prepared from thus synthesized binder according the formulation (w/w) given in the below Table 1.

Red and blue pigments were added to provide color to the pigment printing pastes prepared for the experiments. Each pigment printing paste comprised 30 grams of pigment per 1000 g of pigment printing paste. The pastes were applied onto cotton and polyester fabrics according to Zimmer pigment printing table. A 75 mesh template of artificial silk was used in transferring the paste onto fabric in a certain pattern. Two different fabrics of 100% cotton and 65% cotton/35% polyester blend were used.

Printed fabrics were pre-dried at 120°C for 2 minutes and then cured at 150°C for 5 minutes. Then performance of the binder in terms of wet and dry abrasion fastness’s, washing resistances, color measurements (ΔE, L, a, b measurements) before and after washing, contour sharpness measurements, paste penetration (%P) and K/S values (color intensity comparisons of average values of spectrophotometric measurement results each obtained from several printed points on the fabric, and from several points on the non-printed back side of the printed fabric), etc., of the binder according to the present invention on the printed fabric was compared with a conventional binder containing 6% (w/w) crosslinking agent (NMA) by weight of the total monomer content in said conventional binder.

Paste penetration (%P) was calculated according to the following formula, wherein $(K/S)_{\text{back}}$ and $(K/S)_{\text{front}}$ represent the K/S values obtained from the non-printed back side and from the printed side of the fabric, respectively; wherein a %P value of zero means that there is no penetration on the non-printed back side of the fabric, and a %P value of 100 means that the non-printed and printed sides are spectrophotometrically identical:

$$\%P = \left[ \frac{(K/S)_{\text{back}}}{(K/S)_{\text{front}}} \right] \times 100$$

Contour sharpness which serves as a comparative measure for comparing the lateral spread of printing pastes
OEKO-TEX-100 standard tests for determination of free formaldehyde content were performed on the printed fabrics. The results confirmed that the formaldehyde emission of the final product (i.e., the printed fabric) was considerably reduced by using the binder according to the present invention, without sacrificing expected performance in comparison with pigment printing paste comprising conventional binder.

Following objects are thus achieved with the present invention:

- overcoming the abovementioned shortcomings of the prior art;
- provision of a binder which reduces the amount of released formaldehyde from pigment printing binder during and after curing on a printed textile substrate, without decreasing the fastness performances; and a pigment printing paste comprising such binder;
- provision of a method for preparation of such binder
- provision of a pigment printing paste comprising such binder, and its preparation method.

Claims

1. A core-shell type binder wherein each of core and shell comprise copolymer or terpolymer of acrylic-based monomers, at least one of the core or the shell comprises a suitable crosslinking agent, and core and shell have different glass transition temperatures, characterized in that the crosslinking agent content of the binder is less than 4% (w/w) based on the total weight of said monomers.

2. Binder according to the Claim 1, wherein said copolymer or terpolymer is one or more substance selected from the list consisting of acrylic copolymers such as styrene acrylic copolymer, vinyl acrylic copolymer, copolymer of vinyl acetate with vinyl ester of a branched organic acid having 9 to 11 Carbon atoms, terpolymer of vinyl acetate and acrylate with vinyl ester of a branched organic acid having 9 to 11 Carbon atoms, vinyl acetate/ethylene copolymer, vinyl acetate/ethylene/acrylic terpolymer, and a styrene/acrylic acid ester copolymer.

3. Binder according to the Claim 2, wherein the styrene/acrylic acid ester copolymer is selected from the list consisting of styrene ethyl acrylate copolymer, styrene butyl acrylate copolymer, styrene 2-ethylhexyl acrylate copolymer and styrene cyclohexyl acrylate copolymer.

4. Binder according to the Claim 1, wherein the core has a glass transition temperature within the range between -30 and 0°C, preferably within the range between -20°C and -5°C; and the shell has a glass transition temperature within the range between 0°C and 50°C, preferably within the range between 10°C and 30°C.

5. Binder according to the Claim 1, wherein the core has a glass transition temperature within the range between 0°C and 50°C, preferably within the range between 10°C and 30°C; and the shell has a glass transition temperature within the range between -30°C and 0°C, preferably within the range between -20°C and -5°C.

6. Binder according to the Claim 1, wherein the crosslinking agent content of the core is less than 1% (w/w) based on the total weight of the polymeric material comprised by the core; and the crosslinking agent content of the shell is within the range between 1% and 3%(w/w), preferably within the range between 1.5% and 2.5%(w/w), more preferably within the range between 1.8% and 2.2% (w/w), based on the total weight of the polymeric material comprised by the shell.

7. Binder according to the Claim 1, wherein the binder has a core:shell weight ratio within the range between 20:80 and 80:20, preferably within the range between 20:80 and 60:40, more preferably within the range between 20:80 and 40:60.

8. Pigment printing paste comprising the binder according to any one of the Claims 1 to 7, wherein the paste preferably comprises 10% to 25% (w/w) of said binder; 1.5% to 2.5% (w/w), more preferably 1.75% to 2% (w/w) of a synthetic thickener, 0.05% to 0.15% (w/w) of a pH control additive which is preferably ammonia, and a complementary amount of water, based on the total weight of the paste.

9. A method for preparation of a core-shell type binder, said method comprising a first emulsion polymerization step for formation of a core from a first pre-emulsion comprising a copolymerizable or terpolymerizable first mixture of monomers, followed by a second emulsion polymerization step for formation of a shell coated on said core, from a...
second pre-emulsion different from the first pre-emulsion comprising a copolymerizable or terpolymerizable second mixture of monomers different than said first mixture of monomers; such that the first pre-emulsion and the second pre-emulsion in total comprise less than 5% (w/w) of crosslinking agent based on the total weight of respective monomers; and such that the glass transition temperatures of the copolymerization or terpolymerization products of the first mixture of monomers and the second mixture of monomers are different.

10. Method according to the Claim 9 comprising the steps of:

10. Method according to the Claim 9 comprising the steps of:

e) loading a temperature-controlled stirred reactor vessel with a pre-mixture comprising water, pH buffer and a minor amount of an emulsifier, wherein said minor amount is 5%-20%, preferably 8%-12% of a total amount of an emulsifier;

f) preparation of a first pre-emulsion and a second pre-emulsion for use in preparation of the core and the shell, said first and second pre-emulsions comprising remaining amount of emulsifier distributed to the first and second pre-emulsions; said remaining amount being equal to the difference between respective predetermined total amounts and said minor amounts; the amounts of emulsifier in the first and second pre-emulsions being determined in accordance with a core:shell weight ratio predetermined for the binder,

g) under inert atmosphere, heating the reactor to a reaction temperature ranging between 70°C and 90°C, preferably between 75°C and 85°C;

h) then loading a minor first amount of a pre-initiator solution and a minor first part of the first pre-emulsion into the reactor; followed by introducing the remaining first pre-emulsion slowly, preferably throughout 45 minutes to 90 minutes; then after a further duration within the range between 10 minutes and 20 minutes, preferably 13 minutes and 17 minutes, introducing the second pre-emulsion slowly, preferably throughout 90 minutes to 150 minutes;

i) slowly introducing remaining amount of the pre-initiator solution, preferably continuously from beginning of the introduction of said remaining first pre-emulsion up to the end of the introduction of the second pre-emulsion; then after following 20 to 40 minutes, preferably after 25 to 35 minutes, addition of a radical initiator and an activator under a temperature ranging between 50°C and 78°C, preferably ranging between 60°C and 70°C;

j) and then cooling down the reactor to a temperature below 50°C;

k) h) filtering the reaction product and thus obtainment of a binder,

wherein said first and/or the second pre-emulsion comprise two or more copolymerizable monomers with definite weight ratios to each other such that core and shell have different predetermined glass transition temperatures.

11. Method according to any of the Claims 9 or 10, wherein the monomers in the first and/or second pre-emulsions are suitable for obtainment of one or more copolymer or terpolymer according to any of the Claims 2 or 3.

12. Method according to the Claim 11, wherein the monomers in the first and/or second pre-emulsions are selected from the list consisting of vinyl acetate (VAc), butyl acrylate (BA), styrene (St), methyl methacrylate (MMA), 2-ethylhexyl acrylate (2-EHA).

13. Method according to the Claim 10, wherein the radical initiator is tert-butyl hydroperoxide and/or the activator comprises one or more substance selected from the list consisting of sodium metabisulfite, tartaric acid, and ascorbic acid.

14. Method according to any one of the Claims 9 to 13, wherein the glass transition temperature of the copolymerization or terpolymerization products of the first mixture of monomers is within the range between -30 and 0°C, preferably within the range between -20°C and -5°C and the glass transition temperature of the copolymerization or terpolymerization products of the second mixture of monomers is within the range between 0°C and 50°C, preferably within the range between 10°C and 30°C; or

the glass transition temperature of the copolymerization or terpolymerization products of the first mixture of monomers is within the range between 0°C and 50°C, preferably within the range between 10°C and 30°C, and the glass transition temperature of the copolymerization or terpolymerization products of the second mixture of monomers is within the range between -30°C and 0°C, preferably within the range between -20°C and -5°C.

15. Method according to any one of the Claims 9 to 14, wherein the crosslinking agent content of the first pre-emulsion is less than 1% (w/w) based on the total weight of the monomers comprised by the first mixture of monomers; and the crosslinking agent content of the second pre-emulsion is within the range between 1% and 3%(w/w), preferably within the range between 1.5% and 2.5%(w/w), more preferably within the range between 1.8% and 2.2% (w/w), based on the total weight of the monomers comprised by the second mixture of monomers.
16. Method according to any one of the Claims 9 to 15, wherein the first and second mixtures of monomers have a weight ratio within the range between 20:80 and 80:20, preferably within the range between 20:80 and 60:40, more preferably within the range between 20:80 and 40:60.

17. A method for preparation of a pigment printing paste, comprising mixing a binder according to any one of the Claims 1 to 7 with a mixture comprising water, a pH control additive and a thickener; wherein the paste preferably comprises 10% to 25% (w/w) of said binder; 1.5% to 2.5% (w/w), more preferably 1.75% to 2% (w/w) of a synthetic thickener, 0.05% to 0.15% (w/w) of a pH control additive which is preferably ammonia, and a complementary amount of water, based on the total weight of the paste.
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document with indication, where appropriate, of relevant passages</th>
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<tbody>
<tr>
<td>X</td>
<td>EP 0 195 661 A2 (COURTALDS PLC [GB]) 24 September 1986 (1986-09-24) * page 1, lines 4-8, 23-28 * * page 2, lines 3-5, 10-21 * * page 3, lines 1-17, 21 - page 11, line 21 * * page 6, line 15 - page 7, line 23 * * claims 1-4, 6, 9; examples *</td>
<td>1-4, 6, 7, 9-16</td>
<td>INV. 039/093 D06P1/44 D06P1/52 D06P1/54</td>
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<td>GB 2 330 586 A (SCOTT BADER CO [GB]) 28 April 1999 (1999-04-28) * the whole document *</td>
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**TECHNICAL FIELDS SEARCHED (IPC)**

- D06P
- G03G

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The present search report has been drawn up for all claims.

Place of search: The Hague

Date of completion of the search: 10 December 2015

Examiner: Duval, Monica

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Patent documents cited in the description


Non-patent literature cited in the description

- V.A. SHENAI. Chemistry of Textile Auxiliaries. Sevak Publisher Mumbai, 2002, 231 [0004]