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(54) **FORMALDEHYDE-FREE, AQUEOUS COMPOSITION FOR DISCHARGE PRINTING OF FABRIC**

(57) The present invention relates to a composition for discharge printing of fabric, a discharge printing process for printing said composition to the fabric, the use of

the composition for discharge printing and to a fabric treated with the composition in a discharge printing process according to the invention.

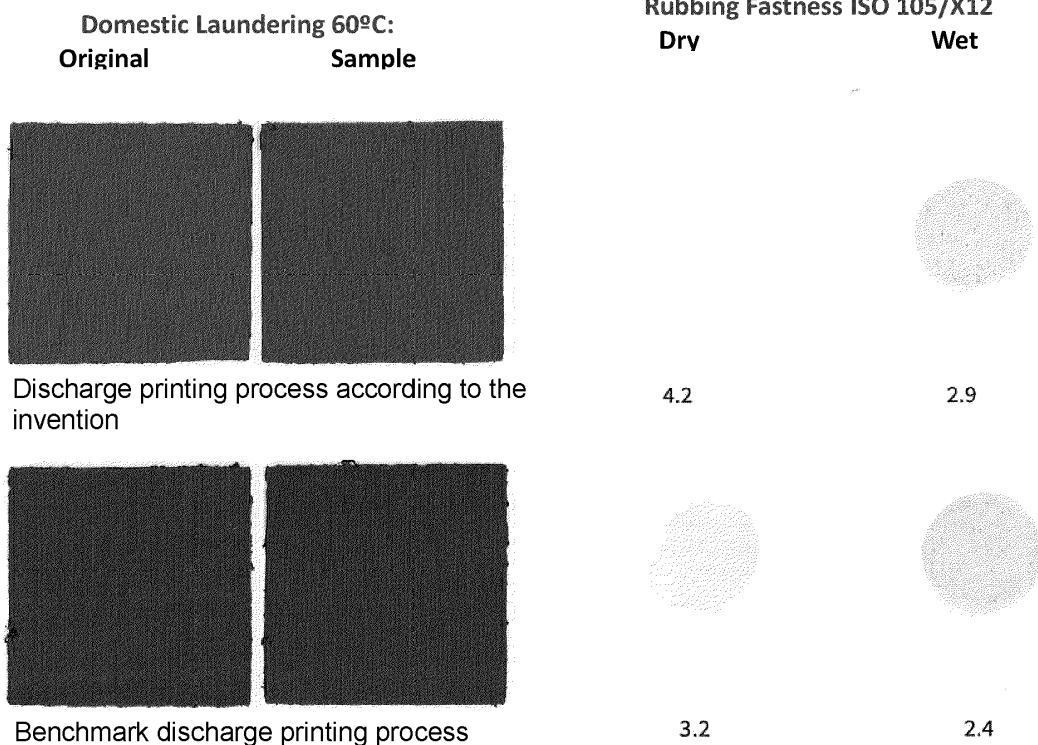


Figure 1

Description**FIELD OF THE INVENTION**

- 5 **[0001]** The present invention relates to formaldehyde-free, aqueous composition for discharge printing of dyed fabric, to the use and manufacturing method thereof, as well as to the discharge printing process.

BACKGROUND OF THE INVENTION

- 10 **[0002]** Discharge printing relates to a special printing process for whitening or coloring fabrics. The key element in discharge printing is a discharge printing composition comprising a reducing agent. Discharge printing starts from a colored fabric which is colored with a dye. The dye is sensitive to reducing agents and degrades upon treatment with discharge printing compositions comprising the reducing agent. The discharge printing composition is printed onto the fabric and the dye of the fabric is discharged in the printed pattern area. A white patterned discharge fabric can thus be
 15 produced wherein the natural color of the fabric becomes visible. In other applications the printing composition further comprises a pigment which is resistant to the reducing agent. A colored discharge fabric is thus obtained wherein the whitened print pattern is overlaid with color of the resistive pigment. Commonly known reducing agents useful for discharge printing are Rongalit ST liquid and/or Rongalit C powder (both based on sodium formaldehyde sulfoxylate derivatives). Printing compositions used for discharge printing commonly comprise further components such as thickener,
 20 binders, and auxiliaries like softeners, emulsifiers, crosslinking agents, rheology modifiers etc. and pigment preparations. **[0003]** Known discharge printing processes demand for steaming and curing process steps following the printing step to destroy residues of the discharged dye and formaldehyde containing reducing agents. Further process steps are involved in discharge printing processes, including a fixing process step for fixation of binders and a final washing step to eliminate all chemical residuals including formaldehyde.
- 25 **[0004]** The problem with existing systems and processes is that customers often complain about the odor of formaldehyde during drying, steaming, and fixing processes when using common discharge printing compositions and processes. In addition, brand manufacturers are seeking more environmental sustainable systems and processes that do not release formaldehyde. Therefore, discharge printing processes have been developed wherein the steaming step was avoided. Those processes are known as Dry Discharge Printing. Reducing agents used in these processes however
 30 still employ zinc formaldehyde sulfoxylate derivatives. These reducing agents are characterized by their high reductive effect which also effect undesired degradation of thickeners necessarily used in printing paste compositions. As a result, viscosity of the printing paste often tended to run out of the specification range which is disadvantageous in industrial discharge printing processes. In order to overcome those drawbacks, alternative used thickeners are used resisting the reductive effect of zinc formaldehyde sulfoxylate derivatives. However, those thickeners demanded for more complex
 35 printing compositions and costs.

OBJECTS OF THE INVENTION

- 40 **[0005]** It is therefore an object of the present invention to provide a composition capable for discharge printing of fabric circumventing the use of formaldehyde-containing reducing agents, reduction of complexity and process time, and maintaining printing paste stability during the printing process further improving the print quality of discharge printed fabric.

SUMMARY OF THE INVENTION

- 45 **[0006]** The object is solved by the following items:

Item 1: A formaldehyde-free, aqueous composition for discharge printing of fabric, wherein the composition comprises at least one reducing agent, at least one synthetic thickener, at least one wetting agent, at least one pH modifier, optionally at least one pigment, and optionally at least one binder.

- 50 Item 2: The composition according to item 1, wherein the at least one synthetic thickener is a polyacrylic compound, preferably selected from an acrylic acid copolymer, preferably including high density oil and auxiliaries.

Item 3: The composition according to at least one of items 1 or 2, wherein the at least one binder is based on poly(butyl acrylate), copolymer of two or more of butyl(acrylate), ethyl(acrylate) and styrene, polyvinyl acrylate, acrylonitrile, or mixtures thereof.

- 55 Item 4: The composition according to at least one of the items 1 to 3, wherein the wetting agent is selected from urea, glycerin, or mixtures thereof.

Item 5: The composition according to at least one of the items 1 to 4, wherein the reducing agent comprises or consists of a sulfinic acid derivative.

Item 6: The composition according to at least one of the items 1 to 5 further comprising one or more components selected from the group of crosslinking agents, softeners, emulsifiers, antifoaming agents, rheology modifiers and oxidation protection agents or a mixture thereof.

Item 7: The composition according to at least one of the items 1 to 6, wherein the composition is free from any natural thickener.

Item 8: The composition according to at least one of the items 1 to 7, wherein the composition comprises from 3 to 30% by weight of at least one reducing agent, from 0.05% to 6% by weight of at least one synthetic thickener, from 3 to 45% by weight of at least one wetting agent, from 0.05 to 4% by weight of at least one pH adjuster, from 0 to 30% by weight of at least one binder, from 0 to 2% by weight of at least one emulsifier, from 0 to 1% by weight of at least one anti foaming agent, from 0 to 3% by weight of at least one crosslinking agent, from 0 to 3% by weight of at least one softener, from 0 to 2% by weight of at least one rheology modifier, from 0 to 2% by weight of at least one oxidation protection agent, from 0 to 6% by weight of at least one pigment dispersion, the remainder to 100% by weight is water, wherein the % by weight is based on the total weight of the composition.

Item 9: Process for manufacturing the composition according to at least one of the items 1 to 8 comprising the following Step A and optionally Steps B and C: Step A: Mixing and homogenizing all components for the composition according to at least one of the items 1 to 8, except the at least one pigment, in case at least one pigment is present in the composition according to at least one of items 1 to 8, Step B: Adding at least one dispersion comprising the at least one pigment to the mixture obtained in Step A, Step C: Mixing and homogenizing the mixture obtained in Step B.

Item 10: Use of formaldehyde-free, aqueous composition according to at least one of the items 1 to 8 or use of the formaldehyde-free, aqueous composition manufactured according to the process as defined in item 9 for discharge printing processes, in particular for white discharge or color discharge printing processes of fabric.

Item 11: A discharge printing process for printing fabric, the process comprising the following steps: Step 1: providing a colored fabric, Step 2: printing step: printing the fabric using the formaldehyde-free, aqueous composition according to at least one of items 1 to 8 or printing the fabric using the formaldehyde-free, aqueous composition manufactured according to item 9, Step 3: first drying step: drying the fabric obtained in step 2, Step 4: washing step: washing the fabric obtained in step 3, wherein the fabric is rinsed with a rinsing fluid and/ or is soaped with a soaping fluid, Step 5: second drying step: drying the fabric obtained in step 4.

Item 12: The process of item 11, wherein the washing step comprises a first cold and/ or hot rinsing step wherein the printed fabric is rinsed with a rinsing fluid selected from cold water or aqueous H₂O₂ solution and/ or, a hot soaping step wherein the printed fabric is washed with a soaping fluid, selected from soapy water at temperatures from 40 to 80°C and/ or, a second cold rinse step wherein the printed fabric is rinsed with a second rinsing fluid selected from cold water.

Item 13: The process according to at least one of items 11 or 12, wherein the first drying step is performed at temperatures from 140°C to 180°C, preferably for 1 to 5 minutes and/ or wherein the second drying step is performed at temperatures of from 120°C to 160 °C, preferably for 8 to 20 min.

Item 14: The process according to at least one of items 11 to 13, wherein the process does not comprise a curing step and/ or a steaming step.

Item 15: Fabric treated with a composition according to at least one of items 1 to 8 or a composition obtained according to item 9 in a discharge printing process according to at least one of item 11 to 14.

DETAILED DESCRIPTION OF THE INVENTION

[0007] In a first aspect the object of the present invention is solved by a formaldehyde-free, aqueous composition for discharge printing of fabric wherein the composition comprises at least one reducing agent, at least one synthetic thickener, at least one wetting agent, at least one pH modifier, optionally at least one pigment and optionally at least one binder.

[0008] The composition has the advantage that it is formaldehyde-free. Therefore, no formaldehyde is released in discharge printing processes employing the composition according to the invention. Bad odor and hazardous influence of formaldehyde is thus eliminated. The term "*formaldehyde-free*" within the context of the present application means that according to commonly known measuring methods no residues of formaldehyde can be detected when measured according to AATCC 112. In addition, the composition according to the invention has the advantage of improving the printing quality of the discharge printing process.

[0009] The term "*reducing agent*" as used within the context of the present application refers to an agent capable of reducing reactive dyes. The at least one reducing agent present in the composition according to the invention comprises or consists of a sulfinic acid derivative. The at least one reducing agent does not comprise any formaldehyde releasing compounds or moieties. It was observed that fabrics can be efficiently treated in a discharge printing process by means of said sulfinic acid derivative. It was additionally observed that process time and energy consumption of discharge

printing processes employing the composition of the invention can be significantly reduced since it is not necessary to treat the discharge printed fabric in an additional curing step as is done in conventional discharge printing processes.

[0010] Another benefit of the composition according to the invention is the simple preparation. Preparation of the composition according to the invention can be done at customers' facilities. Due to the reduction strength of the at least one reducing agent an additional steaming step commonly employed in known discharge printing processes can also be avoided. With employing the composition according to the invention, the discharge effect on the dyes is already achieved with hot air. In addition, another benefit is that with the composition according to the invention less detrimental impact on coloring pigments is observed. With this benefit more brilliant shades can be achieved by the printing process.

[0011] Within the context of the present application, the term "*sulfinic acid derivative*" means a reducing agent that comprises or consists of one or more compounds of sulfinic acid derivatives. For example sulfinic acid derivatives of the formula $\text{RSO}(\text{O})\text{X}$ can be used, wherein X signifies a cation balancing the anionic charge of $\text{RSO}(\text{O})^-$ and is selected

from H, alkali metal cation, R_4^1N^+ , wherein R^1 signifies H, C_1 to C_4 alkyl or a mixture thereof; wherein R signifies alkyl or aryl residues which may be further substituted. Typical sulfinic acid derivatives used in the composition according to the invention are sold under the trade name Rongalit®ECO.

[0012] In order to have a whitening discharge effect on the dye of the fabric in discharge printing processes, the reducing agent needs to have a certain redox potential. The term "*redox potential*" is well known in the art. It describes the ability of a compound to transfer/ accept electrons in a chemical reaction to/ from an electron acceptor/ donor compound. The redox potential is determined by using a standard hydrogen electrode or other standard electrodes. The redox potential of the sulfinic acid derivative used as reducing agent in the composition according to the invention is at least 800 mV, or at least 825 mV, or at least 850 mV. The redox potential should be at most 1000 mV, or at most 975 mV or at most 950 mV. In preferred embodiments the reduction potential of the sulfinic acid derivative reducing agent is from 800mV to 1000 mV, or from 825 to 975 mV or from 850 to 950 mV.

[0013] The at least one sulfinic acid derivative reducing agent is present in the composition according to the invention in an amount of at least 3% by weight, or at least 6% by weight, or at least 7% by weight or at least 8% by weight or at least 9% by weight. The amount is at most 30% by weight, or at most 25 % by weight, or at most 20 % by weight or at most 15% by weight or at most 13 % by weight. Preferably the amount of the at least one reducing agent in the composition according to the invention ranges from 3 to 30% by weight, or 6 to 25% by weight or 7 to 20% by weight, or 8 to 15% by weight, or from 5 to 15% by weight, or 9 to 13% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention.

[0014] The term "*fabric*" as used within the context of the present application refers to a general term for "fiber", "fiber blend", "yarn", "knit fabric" "non-woven -" and "woven" fabric. Preferably the fabric used according to the invention comprises or consists of cellulosic fiber. The term "*fiber blend*" as used within the context of the present application means that at least two fibers are combined to one fiber blend by commonly known spinning methods, wherein the at least two fibers are made of different materials: at least one fiber is made of or consists of cellulose wherein the second fiber is made of or consists of polyamide, silk, or wool. Thus, the term fiber blend as used within the context of the present applications refers to a combination of at least two fibers, wherein one of the fibers is made of cellulose and wherein the second fiber is made of polyamide, silk, wool.

[0015] The term "*woven*" as used within the context of the present application refers to a two dimensional or three-dimensional fabric which is made of yarn by weaving methods. The yarn used for making woven may consist of the fiber or fiber blend as defined above. The term "*yarn*" as used within the context of the present application refers to an agglomeration of fiber, according to this invention, an agglomeration of the above defined fiber blend, wherein the agglomeration is achieved by spinning methods. This means, that a yarn can contain two or more of the above defined fiber blends, depending on the desired yarn properties, like strength or thickness.

[0016] The term "*non-woven*" as used within the context of the present application refers to a two dimensional or three-dimensional fabric which is made of yarn bonded together by chemical means, mechanical means, heat or solvent treatment, i.e. by methods being different from weaving methods. The yarn used for making non-woven consists of the fiber or fiber blend as defined above.

[0017] The term "*knit fabric*" as used within the context of the present application refers to a two- or three-dimensional fabric which is made of yarn, as defined above, by knitting methods.

[0018] The material of the fabric used for discharge printing preferably comprises or consists of cellulose and is preferably cotton and/ or viscose.

[0019] Fabrics used in the discharge printing according to the invention are usually pre-dyed with a ground dye. The term "*ground dye*" used within the context of the present application means that a fabric that is completely or in part dyed with one or more dyes sensitive to the reducing effects imparted by the at least one reducing agent. Suitable dyes used as dischargeable ground dyes usually contain azo groups which are decomposed when treated with the sulfinic acid derivative reducing agent, such that a discharge effect can be observed. Such dyes are commonly known as reactive

dyes.

[0020] The term "*reactive dye*" as used within the context of the present application means "*fiber-reactive azo dyes*" or "*vinyl sulfone dyes*". Reactive dyes are well known in the art. Reactive dyes are characterized in that the chromophore of the dye contains one or more substituents capable of reacting with a fabric substrate such as fiber blends, yarn, woven, non-woven and knit fabric consisting or comprising e.g. cellulose, polyamide, silk, wool. Reactive dyes are a class of organic substances dyes that contain at least one substituent which reacts with the substrate and thus forms a covalent bond between the molecule of the dye and the substrate to be colored. For example, WO 2007/039573 A2 relates to azo reactive dyes and mixtures of fiber-reactive azo dyes, to processes for their preparation and to their use for dyeing and printing hydroxyl- and carboxamido-containing materials. Furthermore WO 2004/088031 also discloses to azo reactive dyes and mixtures of fiber reactive dyes, their preparation and their use. WO 2015/149940 relates to compounds that are obtained by coupling two aminoaryl compounds in diazotized form onto 3- aminophenyl urea. These compounds are used as azo reactive dyes in dyeing and printing processes. Examples for reactive dyes with which the fabric, which will be treated with the composition according to the invention, is dyed are Reactive Red 35, Reactive Red 106, Reactive Orange 13, Reactive Blue 250, Reactive blue 28, Reactive Yellow 15, Reactive Yellow 43 or Reactive Black 5.

[0021] The term "*discharge printing*" as used within the context of the present application refers to a method of discharging, i.e. removing, color from dyed, i.e. colored, fabric by applying a composition, e.g. the composition according to the invention, under printing conditions to the fabric. According to the present invention the composition for discharge printing can be used in form of a paste. According to the present invention, at least one composition according to the invention is used to discharge color from the fabric. Optionally, additional pigments resistive to the sulfinic acid derivative reducing agent can also be comprised in the composition according to the invention, such that coloring of the discharge printed areas on the fabric is achieved. In course of the printing process, the discharge printing composition is applied to colored fabric thereby effecting discharge of the color. The term "*discharge*" within the context of the present application means that the ground dye of the fabric is whitened. "*Whitening*" in this context means that the color of the ground dye is faded by treatment of the sulfinic acid derivative reducing agent. A preferred whitening effect is achieved in case the ground dye has faded completely such.

[0022] There are numerous printing methods for printing fabric known in the art: e.g. block printing, perrotine printing, roller, cylinder or machine printing, stencil printing, screen-printing or flat printing, digital textile printing, flexo textile printing. The composition according to the invention is suitable to be used in every known method for printing fabrics, in particular for printing woven, non-woven and knit fabric. The printing process or the printed fabric, is particularly characterized in that definite patterns or designs are applied to the fabric. The term "*printed*" as used within the context of the present application therefore refers to a fabric, which has been subjected to a printing process as defined above by discharging the ground dye from the fabric. The term "*printed*" also refer to fabric wherein the discharged ground dye is replaced by a pigment which is persistent to the at least one reducing agent of the composition according to the invention and thus re-colors the fabric. The discharge printing process without pigments is also termed "*white discharge printing*". The discharge printing process with pigments is also termed as "*colored discharge printing*".

[0023] In addition, the composition according to the invention comprises at least one synthetic thickener. The thickener is used to build up a desired end level of viscosity of the composition to be able to be printed and keep the form of the print pattern with good sharpness avoiding flushing of water with color.

[0024] A desired viscosity of the composition according to the invention is at least 3,000 mPa·s, or at least 3,500 mPa·s, or at least 3,800 mPa·s. The viscosity of the composition should be at most 5,000 mPa·s, or at most 4,500 mPa·s, or at most 4,200 mPa·s. Preferred ranges of viscosity of the composition according to the invention range of from 3,000 mPa·s to 5,000 mPa·s, or from 3,500 mPa·s to 4,500 mPa·s, or from 3,800 mPa·s to 4,200 mPa·s. Typical thickeners used in printing processes are characterized by their viscosity build up behavior. Basically, natural thickeners and synthetic thickeners are used for printing processes in printing fabrics. However, in view of the composition according to the invention, natural thickeners suffer from their poor time delayed viscosity build up behavior. Viscosity development of natural thickeners in printing compositions to a desired end level therefore may take inadequate time. Thus, related to compositions according to the invention processability of discharge printing processes using natural thickeners is severely impaired. To the contrary synthetic thickeners as used in the composition according to the invention are based on polymers obtained from acrylic acid and derivatives therefrom and are preferred for the claimed discharge printing process. Desired viscosity levels of the composition according to the invention build up within 1 hour, preferably within 40 min, more preferably within 30 min. Processability of discharge processes are therefore dramatically increased over processes using natural thickener products. Viscosity properties of liquids or amorphous solid develop primarily on inter-particle forces within the solution, including friction and attraction between molecules in the macrostructure. These Van der Waals forces are critical facets of a sample's resistance to deformation, or flow, which defines the material's viscosity. Dynamic viscosity expresses the measure of the shear stress per unit area required before a sample begins to deform. Viscosity is typically expressed in units of milli Pascal seconds, mPa·s. A Standard Test Method for determining dynamic viscosity and density of liquids are conducted by a stabinger viscometer according to ASTM D7042.

[0025] The at least one synthetic thickener is present in the composition according to the invention in an amount of at least 0.05% by weight, or at least 0.5% by weight, or at least 1% by weight, or at least 1.5% by weight, or at least 1.8% by weight. The amount of the at least one synthetic thickener in the composition according to the invention is at most 6% by weight, or at most 5% by weight, or at most 4% by weight, or at most 3% by weight, or at most 2.3% by weight. Preferably the amount of the least one synthetic thicker in the composition according to the invention ranges from 0.05 to 6% by weight, or from 0.5 to 5% by weight, or from 0.5 to 4% by weight, or from 1 to 4% by weight, or from 1.5 to 3% by weight, or from 1.8 to 2.3% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention.

[0026] Synthetic thickeners used in the composition according to the invention are further characterized in that they do not undergo adverse reactions with the at least one reducing agent. Discharge printed fabric exhibit a high color yield, brilliance and levelness and are free from speck problems, i.e. it is possible to print with very fine screens enabling sharp outline print pictures. In general, effectiveness of viscosity built up of afore-mentioned synthetic thickeners in discharge compositions according to the invention are improved over natural thickeners. It is therefore possible to use the thickeners in a lesser amount than natural thickeners while achieving the same viscosity of the discharge printing compositions. The term "*synthetic thickener*" as used within the context of the present application refers to a thickener, i.e. a compound capable of building up desired viscosity level of a liquid composition, which is of no natural origin, i.e. not derived from plants, algae or animal products. In one embodiment, the at least one thickener is a polyacrylic compound, i.e. a polymer or copolymer built from one or more derivatives of acrylic acids and acrylic esters wherein the at least one synthetic thickener is a copolymer based on acrylic acid monomers or derivatives thereof. Synthetic thickeners are preferably used as an inverse emulsion of the copolymer based on acrylic acid monomers or derivatives thereof in oil which, when combined with water swell and increase viscosity. Preferably the synthetic thickener includes high density oil and/ or auxiliaries such as non-ionic surfactants. Suitable synthetic thickeners are known under the tradename Lutexal, Lyoprint, Tubivis, Printex, Uniprint.

[0027] In one preferred embodiment of the first aspect of the invention the composition is free from any natural thickener. Natural thickeners, such as those based on sodium alginate or guar, tend to need long time to build up a final viscosity level, which is needed for applying the composition for discharge printing homogeneously onto the fabric. Thus, process time of the discharge printing process is significantly longer in case natural thickener is used in the composition according to the invention. The term "natural thickener" as used within the context of the present application refers to a thickener natural origin, e.g. derived from plants, e.g. guar beans, algae, or animal products.

[0028] The composition according to the invention further optionally comprises at least one binder. The at least one binder has the advantage of forming a film on the fabric to which the binder is applied. By the film formation the at least one pigment optionally present in the composition according to the invention is fixed on the fabric. Therefore, under the term "*binder*" as used within the context of the present application, a component is to be understood, capable of forming a film on the fabric to which it is compiled and thereby fixing pigment(s) onto the substrate. The binder as optionally present in the composition according to the invention is designed as aqueous dispersion comprising a liquid medium and therein dispersed polymer particles. The liquid medium comprises or consists of water, one or more surfactants or mixtures thereof. Preferably, the liquid medium does not contain any organic solvent. This has the advantage that the binder then has a low flammability. The polymer particles dispersed in the liquid medium have an average particles size of 120 to 300 nm. The polymer particles are responsible for forming the film. The liquid medium is the reaction medium for forming the polymer particles and functions as stabilizer for the therein dispersed polymer particles during transport and storage. The polymer particles dispersed within the liquid medium are manufactured by way of emulsion polymerization. The monomers of which the polymer particles should be made of, are dispersed within the liquid medium, and polymerization is initiated by means of free radical polymerization. Suitable monomers are unsaturated monomers selected from the group comprising vinyl chloride, dichloroethane, acrylic acid, methacrylic acid, acrylamide, acrylonitrile, acrylic acid esters, vinyl esters, styrene, diolefins, like butadiene, or mixtures thereof. The binder comprises high amounts of polymer particles, in particular at least 35 % by weight, or at least 40% by weight, or at least 45% by weight or at most 50% by weight, based on the total weight of the binder, wherein the remainder up to 100% by weight is made of the liquid medium which is water, surfactant or mixtures thereof. As mentioned, the binder as used within the composition according to the invention is designed as dispersion as defined above, and thus, is present in the composition according to the invention as dispersion comprising or consisting of polymer particles dispersed within a liquid medium. The film forming on the substrate to which the binder (or in the present case, the composition according to the invention) takes place, once the substrate (in the present case, the fabric) is subjected to a heating step, in particular a drying step. The liquid medium then is removed e.g. by evaporation and the formerly dispersed polymer particles coagulate and flow together, thereby forming a three-dimensionally network, i.e. the film, within which pigments are entrapped. Since the film is a three-dimensionally network, fixation of said film on the substrate, in particular the fabric is achieved. Consequently, it is another advantage of the binder to ensure that the entrapped pigment is fast to wear and cleaning. Suitable polymers are for example poly(butyl acrylate), copolymer of butyl(acrylate), ethyl(acrylate) and styrene, polyvinyl acrylate, acrylonitrile, or mixtures thereof. Suitable binders are known under the tradenames Helizarin (acryl vinyl copolymer

aqueous dispersion), Cresacryl, Unicryl or Tubifast. In case the at least one binder is present in the composition according to the invention, then the amount is at least 2.5% by weight, or at least 5% by weight, or at least 10 % by weight, or at least 15 % by weight. In case the binder is present in the composition according to the invention then the amount is at most 30% by weight, or at most 25 % by weight, or at most 20% by weight, or 19% by weight. Preferably, in case the binder is present in the composition according to the invention, the amount of the binder in the composition according to the invention ranges from 2.5 to 30% by weight, or from 5 to 25% by weight, or from 5 to 19% by weight, or from 10 to 20% by weight, or from 15 to 20% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention.

[0029] The composition according to the invention comprises at least one wetting agent. Within the context of the present application the term "wetting agent" means a hygroscopic compound. The wetting agent used in the composition according to the invention avoids too fast drying of the fabric treated in the discharge printing process. Although shorter overall drying times are achieved with the composition according to the invention since higher drying temperatures can be applied, the discharge of the ground dye of the fabric needs a humid environment. Too fast drying of the discharge printed areas on the fabric can therefore result in incomplete discharge effects. Preferred wetting agents are urea and glycerin. Additional wetting agents are glycol, polyglycol and salts. In one embodiment urea is used as a wetting agent. In another embodiment preferably a mixture of urea and glycerin is used as wetting agent.

[0030] The wetting agent is present in the composition according to the invention in an amount of at least 3% by weight, or at least 5% by weight, or at least 10 % by weight, or at least 15 % by weight, or at least 20% by weight. The amount of the wetting agent in the composition according to the invention is at most 45% by weight, or at most 40% by weight, or at most 35% by weight, or at most 30% by weight. Preferably the amount of the wetting agent in the composition according to the invention ranges from 3 to 45% by weight, or from 5 to 40% by weight, or from 10 to 35% by weight, or from 15 to 30% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention.

[0031] In a preferred embodiment wherein the composition according to the invention comprises urea and glycerin as wetting agents, the amount of urea present in the composition according to the invention is at least 0.5% by weight, or at least 2% by weight, or at least 5% by weight, or at least 10% by weight. The amount of the urea in that case is at most 30% by weight, or at most 25% by weight, or at most 20% by weight. Preferably the amount of urea is in that case from 0.5% to 30% by weight, or from 2% to 25% by weight, or from 10% to 20% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention. The amount of glycerin present in the composition according to the invention is then at least 0.1% by weight, or at least 1% by weight, or at least 3% by weight. The amount of the glycerin in that case is at most 15% by weight, or at most 10% by weight, or at most 5% by weight. Preferably the amount of glycerin is in that case from 0.1% to 15% by weight, or from 2% to 10% by weight, or from 3% to 5% by weight or from 1 to 5% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention. In any case, however, the total combined amount of glycerin and urea is not less than 3% by weight and at most 45% by weight.

[0032] The composition according to the invention comprises at least one pH modifier. The pH modifier assists to maintain the pH value of the composition within a specified range. Within the specified pH value range, the thickener is stabilized, and the homogeneous character of the composition is maintained. Preferable pH values of the composition according to the invention range from pH 8 to pH 9. Preferred pH modifiers are selected from tertiary amines, ammonia or ammonium salts and derivatives thereof which are preferably volatile upon drying of the fabric. A preferred pH modifier is triethanolamine. The at least one pH modifier is present in the composition according to the invention in an amount of at least 0.05% by weight, or at least 0.1% by weight, or at least 0.5% by weight or at least 0.75% by weight. The pH modifier is present in the composition according to the invention in an amount of at most 4% by weight, or at most 2% by weight, or at most 1% by weight, or at most 1.25% by weight. Preferably, the amount of the pH modifier in the composition according to the invention ranges of from 0.05% to 4% by weight, or from 0.1 to 2% by weight, or from 0.5 to 1% by weight, or from 0.75 to 1.25% by weight, or from 0.1 to 0.4% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention.

[0033] Since the composition according to the invention is an aqueous composition, the remainder up to 100% by weight is water. The composition according to the invention is preferably applied to the fabric as a printing paste. Thus, some certain amounts of a fluid carrier are necessary in order to be able to provide a homogenous printing paste in which all required compounds are homogeneously dispersed. The term "*fluid carrier*" as used within the context of the present application refers to a liquid capable of imparting a fluid character to the composition according to the invention, such that the components of the printing paste can be homogeneously printed onto the fabric. According to the present invention water is used as one fluid carrier.

[0034] The composition according to the invention optionally comprises at least one pigment. The at least one pigment may be added to the composition according to the invention in form of a pigment dispersion. Thus, the composition according to the invention may comprise at least one dispersion comprising at least one pigment. In case the at least one pigment is used in the composition, the color discharged areas on the fabric become instantaneously colored with

the pigment during the printing process. In case a pigment is present in the composition according to the invention also at least one binder as defined herein is present, since then the pigment(s) are fixed to the fabric by the binder and thus the fabric is (re)colored. Pigments employed in the colored discharge process according to the invention need to be resistant to the at least one reducing agent. Typical pigments useful within the scope of the invention are of the anthraquinoid, phthalocyanin, triphenylmethane type, carbon black, inorganic pigments, quinacridone, monoazo and diazo pigments. In a composition desired for colored discharge printing according to the invention the at least one pigment dispersion is present in the composition in an amount of at least 0.01% by weight, or at least 0.02 % by weight, or at least 0.5% by weight or at least 1% by weight. In one embodiment, the amount of the least one pigment dispersion in the composition according to the invention is at most 6% by weight, or at most 5% by weight or at most 4% by weight or at most 3% by weight. Preferably the amount of the least one pigment dispersion in the composition according to the invention ranges of from 0.01% to 6% by weight, or from 0.02% by weight to 5% by weight, or from 0.5% by weight to 4% by weight, or from 1% by weight to 3% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention.

[0035] According to the first aspect of the invention the composition can further comprise one or more additives selected from the group comprising crosslinking agents, softeners, emulsifiers, antifoaming agents, rheology modifiers and oxidation protection agents or mixtures thereof.

[0036] A crosslinking agent enables fixation of the pigment to the fabric in colored discharge printing process. Fastness of the dyed fabric is therefore improved. The crosslinking agent can be present in the composition according to the invention in an amount of at least 0.1% by weight, or at least 0.2% by weight, or at least 0.5 % by weight or at least 0.75% by weight. The crosslinking agent can be present in the composition according to the invention in an amount of at most 3% by weight, or at most 2.5% by weight, or at most 2% by weight, or at most 1.5% by weight. Preferably the amount of the crosslinking agent in the composition according to the composition ranges of from 0 to 3% by weight, or from 0.1% to 3% by weight or from 0.2% to 2.5% by weight, or from 0.5% to 2% by weight or from 0.75% to 1.5% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention.

A suitable crosslinking agent is known under the tradename Luprintol® Fixing Agent SE.01 liq.

[0037] A softener imparts a smooth hand feeling to the fabric treated in a discharge printing process. Softeners used in the composition according to the invention are silicon based. The softener can be present in the composition according to the invention in an amount of at least 0.1% by weight, or at least 0.2% by weight, or at least 0.5 % by weight or at least 0.75% by weight. The softener agent can be present in the composition according to the invention in an amount of at most 3% by weight, or at most 2.5% by weight or at most 2% by weight or at most 1.5% by weight. Preferably the amount of the softener in the composition according to the composition ranges of from 0 to 3% by weight, or from 0.1% to 3% by weight or 0.2% to 2.5% by weight, or 0.2% to 2.0% by weight or from 0.5% to 2% by weight or from 0.75% to 1.5% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention. A suitable softener is known under the tradename Luprintol® Soft VSN liq.

[0038] An emulsifier enables the composition according to the invention to be provided as an emulsion, in particular a stable emulsion. Several of the components of the composition according to the invention are themselves provided in emulsified forms by the manufacturers. The emulsifier combines components provided in emulsified form to form a combined main emulsion. Accordingly, it is possible to homogeneously disperse each of the components into the main emulsion, which enables manufacturing of homogeneous and precise print patterns. The at least one emulsifier can be present in the composition according to the invention in an amount of at least 0.05% by weight, or at least 0.1% by weight, or at least 0.3% by weight, or at least 0.5% by weight. The emulsifier can be present in the composition according to the invention in an amount of at most 2% by weight, or at most 1.5% by weight, or at most 1%, or at most 0.8% by weight. Preferably the amount of the at least one emulsifier in the composition according to the invention ranges of from 0 to 2% by weight, or from 0.05% to 2% by weight or from 0.1% to 1.5% by weight, or from 0.3% to 1% by weight, or from 0.5% to 0.8% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention. A suitable emulsifier is known under the tradename Luprintol® Emulsifier PE New liq c.

[0039] An antifoaming agent prevents adverse effects of foam formation during manufacturing of the composition according to the invention and/ or during discharge printing employing said composition. Foaming tends to make the composition for discharge printing inhomogeneous, such that an inhomogeneous print pattern may result on the fabric. The antifoaming agent can be present in the composition according to the invention in an amount of at least 0.05% by weight, or at least 0.1% by weight, or at least 0.15% by weight. The antifoaming agent can be present in the composition according to the invention in an amount of at most 1% by weight, or at most 0.8% by weight, or at most 0.4% by weight, or at most 0.3% by weight. Preferably the amount of the antifoaming agent in the composition according to the invention ranges of from 0 to 1% by weight, or from 0.05% to 1% by weight, or from 0.1% to 0.8% by weight, or from 0.1% to 0.4% by weight or from 0.15% to 0.3 % by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention. A suitable antifoaming agent is known under the tradename Antimussol® UDF (1:10).

[0040] A rheology modifier improves the surface tension of the composition according to the invention. Further the

rheology modifier improves stability of the thickener. Effectively the stability of the print face on the fabric is therefore improved. Preferred rheology modifiers used in the composition according to the invention are polyacrylate copolymer emulsions or polyurethane dispersions, or mixtures thereof. The at least one rheology modifier can be present in the composition according to the invention in an amount of at least 0.05% by weight, or at least 0.1% by weight, or at least 0.15% by weight or at least 0.3% by weight. The at least one rheology modifier can be present in the composition according to the invention in an amount of at most 2% by weight, or at most 1.5% by weight, or at most 1% by weight, or at most 0.8% by weight. Preferably the amount of the rheology modifier in the composition according to the invention ranges of from 0 to 2% by weight, or from 0.05% to 2% by weight, or from 0.1% to 1.5% by weight, or from 0.15% to 1% by weight, or from 0.2% to 1% by weight, or from 0.3% to 0.8% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention. A suitable rheology modifier is known under the tradename Luprintol Additive RM 01 liq.

[0041] An oxidation protection agent protects the pigments used in the composition according to the invention from oxidation during printing and drying. Effectively, lesser yellowing is achieved in discharge printing processes and printing pictures are improved in quality when using oxidation protection agents in the composition. Preferred oxidation protection agents used in the composition according to the invention are m-nitro-benzene sulphonate or derivatives thereof. The at least one oxidation protection agent is present in the composition according to the invention in an amount of at least 0.05% by weight, or at least 0.1% by weight, or at least 0.2% by weight, or at least 0.3% by weight, or at least 0.5% by weight. The at least one oxidation protection agent can be present in the composition according to the invention in an amount of at most 2% by weight, or at most 1.5% by weight, or at most 1%, or at most 0.8% by weight. Preferably the amount of the at least one oxidation protection agent in the composition according to the invention ranges of from 0 to 2% by weight, or from 0.05% to 2% by weight, or from 0.1% to 1.5% by weight, or from 0.2% to 1.5% by weight, or from 0.3% to 1% by weight, or from 0.3% to 0.8%, or from 0.5% to 1.5% by weight. Amounts in % by weight are in each case based on the total weight of the composition according to the invention. A suitable oxidation agent is known under the tradename Revatol NS liq.

[0042] According to the first aspect of the invention the composition comprises or consists of
 from 3 to 30% by weight of at least one reducing agent,
 from 0.05% to 6% by weight of at least one synthetic thickener,
 from 3 to 45% by weight of at least one wetting agent,
 from 0.05 to 4% by weight of at least one pH adjuster,
 from 0 to 30% by weight of at least one binder,
 from 0 to 2% by weight of at least one emulsifier,
 from 0 to 1% by weight of at least one antifoaming agent,
 from 0 to 3% by weight of at least one crosslinking agent,
 from 0 to 3% by weight of at least one softener,
 from 0 to 2% by weight of at least one rheology modifier,
 from 0 to 2% by weight of at least one oxidation protection agent,
 from 0 to 6% by weight of at least one pigment dispersion,
 the remainder to 100% by weight is water,
 wherein the % by weight are based on the total weight of the composition according to the invention.

[0043] Further, the composition according to the invention can comprise or consist of
 from 3 to 30% by weight of at least one reducing agent,
 from 0.05% to 6% by weight of at least one synthetic thickener,
 from 3 to 45% by weight of at least one wetting agent,
 from 0.05% to 4% by weight of at least one pH modifier,
 from 0.05 to 2% by weight of at least one emulsifier,
 from 0.05 to 1% by weight of at least one antifoaming agent,
 from 0.1 to 3% by weight of at least one crosslinking agent,
 from 0.1 to 3% by weight of at least one softener,
 from 0.05 to 2% by weight of at least one rheology modifier,
 from 0.05 to 2% by weight of at least one oxidation protection agent, and optionally
 from 0.01 to 6% by weight of at least one pigment dispersion,
 from 2.5 to 30% by weight of at least one binder,
 the remainder to 100% by weight is water,
 wherein the % by weight are based on the total weight of the composition.

[0044] Further, the composition according to the invention can comprise or consist of
 from 5 to 15% by weight of at least one reducing agent,
 from 1% to 4% by weight of at least one synthetic thickener,
 from 10 to 30 % by weight of at least one wetting agent,

from 0.2% to 2% by weight of at least one pH modifier,
 from 0.05 to 2% by weight of at least one emulsifier,
 from 0.1 to 0.4% by weight of at least one antifoaming agent,
 from 0.5 to 2% by weight of at least one crosslinking agent,
 from 0.2 to 2% by weight of at least one softener,
 from 0.2 to 1% by weight of at least one rheology modifier,
 from 0.2 to 1.5% by weight of at least one oxidation protection agent, and optionally
 from 0.5 to 4% by weight of at least one pigment dispersion,
 from 5 to 19% by weight of at least one binder,
 the remainder to 100% by weight is water,
 wherein the % by weight are based on the total weight of the composition according to the invention.

[0045] In a second aspect the present invention relates to a process for manufacturing the discharge printing composition according to the first aspect of the invention. Thus, the above-described details, definitions and limitations with reference to the composition according to the first aspect of the invention apply in the process according to the second aspect of the invention as well. The process according to the invention comprises or consists of the following step A and optionally steps B and C:

Step A: Mixing and homogenizing all components for the composition according to at least one of the embodiments of the first aspect of the invention, except the at least one pigment, in case at least one pigment is present in the composition according to the invention,

Step B: Adding at least one dispersion comprising the at least one pigment to the mixture obtained in Step A,

Step C: Mixing and homogenizing the mixture obtained in Step B.

[0046] In step A, all components for the composition according to the invention are mixed and homogenized, except the optional at least one pigment. The composition obtained in step A results in a composition according to the invention suitable for white discharge printing. The composition may be in the form of a paste. Mixing and homogenizing can be conducted in conventionally used equipment for mixing and homogenizing the components, in particular for mixing and homogenizing components for pastes, in particular pastes for discharge printing. Preferred equipment for step A is an ultra-shear mixing blade. The mixing and homogenizing of the components can be conducted for any suitable time at any suitable stirring rate, for example for 5 to 30 minutes at a stirring speed of 200 rpm to 4000 rpm.

[0047] Optional Step B comprises: Addition of the at least one pigment which can be added as a dispersion comprising the pigment to the mixture obtained in step A. It is possible to conduct step B immediately after step A. It is also possible that the mixture obtained in step A is stored for a certain time period, before being subjected to step B. In addition, it is possible to add further components to the composition obtained in step A. It is also possible that the further components are pre-mixed with the at least one pigment added to the mixture obtained in step A.

[0048] Optional Step C comprises: Mixing and homogenizing the mixture obtained in Step B. The composition obtained in step C results in a composition according to the invention suitable for color discharge printing. Mixing and homogenizing can be conducted in conventionally used equipment for mixing and homogenizing the components, in particular for mixing and homogenizing components for pastes, in particular pastes for discharge printing. Preferred equipment for step C is a high-speed mixer. Step C can be conducted immediately after Step B. It is also possible that the mixture obtained in Step B is stored for a certain time period, before being subjected to Step C. Once Step C is finalized, the composition according to the invention is ready for use, i.e., ready for being applied to the fabric. Preferably, the composition according to the invention is designed as a paste for discharge printing after step C is finalized.

[0049] Optional Steps B and C are conducted in case of a color discharge printing process. Optional Step B can be conducted prior to Step A or at the same time.

[0050] Further, it is possible that additional steps are conducted prior to step A, after step C or in between steps A, B and/or C. Possible steps are for example heating steps, cooling steps, sieving steps.

[0051] In a third aspect the invention relates to the use of the composition according to the first aspect of the invention or the use of the formaldehyde-free, aqueous composition manufactured according to the process according to the second aspect of the invention, for discharge printing processes, in particular for white discharge or color discharge printing processes of fabric. Thus, the above-described details, definitions and limitations with reference to the first aspect of the invention and the second aspect of the invention apply in the use according to the third aspect of the invention as well. Preferably the fabric used comprises or consists of cellulosic fiber such as cotton.

[0052] The term "white discharge printing process" within the context of the present application refers to a printing process wherein a printing composition without any pigment is used for discharge printing. Accordingly printed fabric is characterized by the color discharge in the printed areas wherein the natural color of the fabric fiber becomes visible.

[0053] The term "color discharge printing process" within the context of the present application refers to a printing process wherein a printing composition including at least one pigment is used for the discharge printing. The printed

fabric is characterized in that the color discharged areas are overlaid, i.e. colored or dyed with the pigment color.

[0054] In a fourth aspect the present invention relates to a discharge printing process for printing fabric. The above-described details, definitions and limitations with reference to the first aspect of the invention, the second aspect of the invention and the third aspect of the invention apply in the discharge printing process according to the fourth aspect of the invention as well. The discharge printing process according to the invention comprises or consists of the following steps:

Step 1: providing a colored fabric,

Step 2: printing step: printing the fabric using the formaldehyde-free, aqueous composition according to the first aspect of the invention or printing the fabric using the formaldehyde-free, aqueous composition manufactured according to second aspect of the invention,

Step 3: first drying step: drying the fabric obtained in step 2,

Step 4: washing step: washing the fabric obtained in step 3, wherein the fabric is rinsed with a rinsing fluid and/ or is soaped with a soaping fluid,

Step 5: second drying step: drying the fabric obtained in step 4.

[0055] The discharge printing process according to the invention does not need an extra steaming process step like in discharge printing processes known in the art. Thus, process time and energy consumption are significantly reduced over known discharge printing processes. The discharge printing process according to the invention does not make use of any formaldehyde releasing agents. In particular the composition according to the first aspect of the invention, rinsing fluids, washing fluids and optional finishing agents are free from formaldehyde releasing agents. Thus, bad odor or harmful burden to the environment does not occur during the discharge printing process according to the invention. It was further observed that long and intensive washing steps that are employed in discharge printing processes known in the art for eliminating formaldehyde residues can be reduced.

[0056] The composition according to the first aspect of the invention or manufactured according to the process of the second aspect of the invention used in the discharge printing process according to the fourth aspect of the invention is preferably designed as a paste. Printing can be performed by conventional printing methods known in the art for printing fabrics, for example by rotative or flat printing machine.

[0057] After drying the printed fabric is subjected in step 4 to a washing step for washing the fabric. The fabric is rinsed with a rinsing fluid and/ or is soaped with a soaping fluid to remove the components of the printing paste. The term "*rinsing fluid*" means within the context of the present application a fluid capable for flushing solid and/ or soluble residues from the fabric remaining after the first drying according to step 3 on the fabric. Preferably the rinsing fluid is water or is based on an aqueous solution of H_2O_2 . In one embodiment the fabric is rinsed with water and/ or is soaped with a soaping fluid to remove the components of the printing paste. The term "*soaping fluid*" refers to an aqueous fluid for removing lipophilic residues from the fabric remaining after the first drying step according to step 3 on the fabric. Typically, a soaping fluid is based on an aqueous fluid comprising detergents. The washing step can comprise one or more of the following procedures: cold rinse, warm rinse, and/ or hot soaping. The washing step can be immediately conducted after the first drying step. It is also possible that the printed fabric is stored after the first drying step for a certain time, before being subjected to the washing step.

[0058] After washing the printed fabric is subjected to a second drying step. The cleaned fabric is thus provided in dry form and can be subjected to possible further processing steps like a finishing step. Other possible steps like heating, cooling, pressing can be conducted to bring the printed fabric in shape ready for use.

[0059] The discharge printing process according to the invention comprises as step 4 a washing process which comprises or consists of

a first cold and/ or hot rinsing step wherein the printed fabric is rinsed with a rinsing fluid selected from cold water or aqueous H_2O_2 solution and/ or,

a hot soaping step wherein the printed fabric is washed with a soaping fluid, selected from soapy water at temperatures from 40 to 80°C and/ or,

a second cold rinse step wherein the printed fabric is rinsed with a second rinsing fluid selected from cold water.

[0060] The printed fabric can be rinsed with a rinsing fluid comprising water or an aqueous H_2O_2 solution. The printed fabric is thus released from water soluble components which remained on the printed fabric after the first drying step. In a preferred embodiment the fluid in the first rinsing step comprises H_2O_2 . The H_2O_2 deteriorates residuals from the at least one reducing agent remaining on the printed fabric after the first drying step.

[0061] In the soaping step the printed fabric is soaped with a hot soaping fluid. The printed fabric is thereby freed from lipophilic residuals remained after the first drying step on the printed fabric. Hot soaping of the printed fabric is preferably done at 40 to 80°C. More preferably soaping is done at 50 to 75 °C or 60 to 75°C. Preferably the soaping fluid contains a non-ionic soaping agent, such as commercially known Imerol Jet-B liq c.

[0062] A second rinsing step is performed subsequent to the hot soaping step. The second rinsing step is conducted

with cold water which removes any residuals from the soaping step. After the second rinsing step the printed fabric is cleaned and is further subjected to the afore-mentioned second drying step.

[0063] Further, the discharge printing process according to the invention comprises step 3, i.e. the first drying step which is performed at temperatures from at least 140°C, or at least 145°C, or at least 150 °C, or at least 155°C or at least 155°C. The temperatures should be at most 180°C, or at most 175°C or at most 165°C. In preferred embodiments the temperatures are from 140°C to 180°C, or from 145°C to 175°C, or from 150°C to 170°C or from 155°C to 165°C. The drying conditions enable rapidly effects of white discharge on the fabric. In case a composition is used including a pigment, high fastness of the pigment is achieved. The drying time of the first drying step is set to at least 1 min, or at least 2 min and to at most 5 min or at most 4 min. Preferably the drying time is from 1 to 5 min, or from 2 to 4 min.

[0064] The discharge printing process according to the invention comprises step 5, i.e. the second drying step, which is performed at temperatures of at least from 120°C, or at least 125°C, or at least 130°C, or at least 135°C. The temperatures of the second drying step should be at most 160°C, or at most 155°C or at most 150°C. In preferred embodiments the temperatures in the second drying step are chosen from 120°C to 160°C, or 125°C to 155°C, or from 130°C to 150°C, or from 135°C to 145°C. The drying time in the second drying step is set to at least 8 min or at least 10 min or at least 12 min and at most to 20 min, or at most 18 min. Preferably the drying time is from 8 to 20 min or from 10 to 20 min, or from 12 to 18 min.

[0065] For an industrial implementation of the process the fabric can be provided as a fabric web. The fabric web can be stored on fabric rolls. According to the fourth aspect of the invention the fabric web is unwound from the fabric roll, is conveyed to one or more steps of the discharge printing process and is then rewound to a fabric roll.

[0066] According to the fourth aspect of the invention, the discharge printing process can be conducted in that printing (step 2) and first drying (step 3) of the fabric web is performed as an inline process, wherein the fabric web is passed through a printing unit wherein the printing step (step 2) of the fabric web is performed and is passed through a first drying unit wherein the first drying (step 3) of the fabric web is performed, preferably the fabric web is run at a conveyor speed of from 10 to 30 m/min through the printing unit and the first drying unit.

[0067] Within the context of the present application the term "*printing unit*" means a printing machine which is constructed to convey the fabric web through the printing unit, and which is further constructed such to apply the printing composition according to the invention onto the fabric to conduct the printing step (step 2) in the discharge printing process. Within the context of the present application the term "*drying unit*" refers to a drying oven capable to apply drying and heating conditions to the fabric web, which is further constructed such that the fabric web can be conveyed through the drying unit.

[0068] According to the fourth aspect of the invention the discharge printing process is conducted in that it does not comprise a curing process. It turned out that according to the invention such curing processes are not necessary to yield excellent printed fabrics. In consequence process time and energy consumption of the discharge printing process according to the invention are significantly lowered. CO₂ emission, energy consumption and process time can be reduced by 10%, or 20%, or 25%, or 30%, or 35%, or 40% or even 45% compared to commonly known and conducted discharge printing processes using commonly known discharge printing compositions. The process step of curing as employed in the prior art comprises treatment of the fabric with hot air. Further, the process according to the invention does not make use of any steaming processes which are commonly performed with saturated water steam at high temperatures.

[0069] In a fifth aspect the present invention relates to a fabric treated with a composition according to at least one embodiment of the first aspect of the invention or with a composition obtained according to the second aspect of the invention in a discharge printing process according to at least one embodiment of the fourth aspect of the invention. Effects observed with fabrics worked according to the invention are to be seen in an improved brilliance of white discharge printed and color discharge printed fabric. Brilliance of fabrics worked according to the invention is improved over comparative fabrics worked according to discharge processes used in the art.

[0070] In addition, fabrics worked according to a color discharged process according to the invention exhibit a higher color fastness level than comparative examples worked according to known discharge printing processes.

[0071] Reference is made in this respect to Figures 1 and 2

Fig. 1 shows fabric samples treated in a color discharge process according to the invention using a composition according to the invention and comparatively fabric samples treated in a benchmark process using a benchmark composition. Fig. 1 demonstrates the higher color fastness of fabric samples worked according to the invention.

Fig. 2a shows a white discharge fabric sample and a color discharge fabric sample respectively worked in discharge processes according to the invention using respectively a composition for white discharge printing and color discharge printing according to the invention.

Fig. 2b shows a white discharge fabric sample and a color discharge fabric sample respectively worked according to a benchmark discharge processes known in the art using respectively benchmark compositions for white discharge printing and color discharge printing as also known in the art.

EXAMPLES

Example 1: Preparation of a composition according to the invention for discharge printing

[0072] In a first step A, a mixing vessel equipped with a blade stirrer was charged under stirring according to the specifications shown in table 1:

Table 1					
Component	Function	Mixing Order	white discharge [g/kg]	color discharge [g/kg]	
Luprintol® Emulsifier PE liq c	emulsifier	1	6	6	
Antimussol® UDF (1:10)	defoamer	2	1	1	
Triethanolamine	pH modifier	3	10	10	
Glycerine	wetting agent	4	50	50	
Urea	wetting agent	5	200	200	
Helizarine® LTC liq	binder	6	-	180	
Luprintol® fixing agent SE.01 liq	crosslinking agent	7	10	10	
Luprintol® Soft VSN liq	softener	8	5	5	
Luprintol® Additive RM liq	rheology modifier	9	5	5	
Revatol NS liq	ox. protection agent	10	5	5	
Rongalit® ECO p	reducing agent	11	100	100	
Lutexal® GP ECO p	thickener	12	20	20	
Printofix® T-B	pigment	13	-	20	
Water	fluid carrier	14	408	388	
			Σ 1000	Σ 1000	

1.1 Composition for white discharge printing

[0073] After subsequent mixing of components 1 to 12 and 14, stirring was continued for another 20 min at 2000 r/min until a final viscosity of 3,500 mPa·s was reached. The pH value of the composition was pH= 8.5.

1.2 Composition for color discharge printing

[0074] After subsequent mixing of components 1 to 12 and 14, stirring was continued for another 20 min until a final viscosity of 3,500 mPa·s was reached. The pH value of the composition was pH= 8.6.

[0075] In a second step B a dispersion comprising the pigment Printofix T-B was added under stirring to the composition obtained in the first step A.

[0076] In a third step C the mixture of step B was mixed and homogenized under stirring.

Comparative Example 1: Benchmark composition

[0077] A benchmark composition was prepared comprising a Zinc formaldehyde sulfoxylate and a natural thickener instead of the reducing agent and thickener of Example 1 as commonly used in the art for discharge printing processes.

[0078] In a first step A, a mixing vessel was charged under stirring according to the specifications shown in table 2:

Table 2					
Component	Function	Mixing Order	white discharge [g/kg]	color discharge [g/kg]	
glycerin	wetting agent	1	50	50	
Ammonium sulphate (1:2)	-	2	50	50	
Natural guar gum thickener 8%	thickener	3	500	500	

(continued)

	Component	Function	Mixing Order	white discharge [g/kg]	color discharge [g/kg]
5	Zinc formaldehyde sulfoxylate	reducing agent	4	100	100
	Acrylate binder	binder	5	-	180
	Printofix® T-B	pigment	6	-	20
	Water	fluid carrier	7	408	388
10				Σ 1000	Σ 1000

1.1 Composition for white discharge printing

15 **[0079]** After subsequent mixing of components 1 to 5 and 7, stirring was continued for another 10 hours at 2000 r/min until a final viscosity of 3,500 mPa·s was reached.

1.2 Composition for color discharge printing

20 **[0080]** After subsequent mixing of components 1 to 5 and 7, stirring was continued for another 10 hours min until a final viscosity of 3,500 mPa·s was achieved.

[0081] In a second step B a dispersion comprising the pigment Printofix T-B was added under stirring to the composition obtained in the first step A.

[0082] In a third step C the mixture of step B was mixed and homogenized under stirring.

25 **Example 2: Discharge printing process according to the invention**

[0083] A ground dyed satin cotton fabric, 100 gr/ m² fabric was provided

30 2.1 White discharged fabric

[0084] The fabric was provided as a fabric web wound on a fabric roll. The fabric was unwound and was guided through a printing unit at a conveyor speed of 20 m/min. In the printing unit the under Example 1.1 obtained printing composition was applied to the fabric by conventional flat screen-printing method (J. Zimmer, GmbH; Austria - Mini MDF/796). After running through the printing unit, the fabric was conveyed to a drying unit. Drying and fixation of the prints were made by drying at 160°C for 2 min. The fabric web was conveyed out of the drying unit and was rewound to a fabric roll. Subsequently, the printed fabric web was subjected to washing. The fabric web roll was unwound, and the fabric web was conveyed through a washing unit at a conveyor speed of 40 m/min. In the washing unit the fabric was cold rinsed with water and subsequently rinsed with an 1g/l aqueous H₂O₂ solution (w:v) at 40°C and 60°C for 10 minutes respectively. After that the fabric web was washed for 10 minutes in soapy water at 70°C comprising 1 g/l (w:v) of an anionic soaping agent (Kieralon Jet B conc. liq.). Subsequently the fabric web was rinsed with cold water for 10 minutes, was air dried and was rewound to a fabric roll.

2.2 Color discharged fabric

45 **[0085]** The process of Example 2.1 was repeated except that a composition obtained according to Example 1.2 was used in the discharge printing process instead of the composition obtained in Preparation Example 1.1.

Comparative Example 2: Benchmark printing process

50 **[0086]** A benchmark printing process was performed as commonly applied in the art.

2.1 White discharge fabric

55 **[0087]** The ground dyed fabric of Example 2 was provided as a fabric web wound on a fabric roll. The fabric was unwound and was guided through a printing unit at a conveyor speed of 20m/ min. In the printing unit the printing composition obtained under Comparative Example 1.1 obtained was applied to the fabric by conventional flat screen-printing method (J. Zimmer, GmbH; Austria - Mini MDF/796). After running through the printing unit, the fabric was

conveyed to a drying unit. Drying and fixation of the prints were made by drying at 135°C for 1 min, steamed at 102°C for 10 min and cured at 150°C for 5 min. The fabric web was conveyed out of the drying unit and was rewound to a fabric roll. Subsequently, the printed fabric web was subjected to washing. The fabric web roll was unwound, and the fabric web was conveyed through a washing unit at a conveyor speed of 20m/min. In the washing unit the fabric was cold rinsed with water and subsequently rinsed with an 1g/l aqueous H₂O₂ solution (w:v) at 40°C and 60°C for 10 minutes, respectively. After that the fabric web was washed in soapy water at 70°C comprising 1 g/l (w:v) of an anionic soaping agent (Kieralon Jet B conc. liq.) for 20 minutes. Subsequently the fabric web was rinsed with cold water for 30 minutes, was air dried and was rewound to a fabric roll. The washing time needed is at least twice as long as in Example 2.1.

2.2 Color discharge fabric

[0088] The process of Comparative Example 2.1 was repeated except that a composition obtained according to Comparative Example 1.2 was used in the printing process instead of the composition obtained in Comparative Example 1.1.

[0089] Examples 2.1 and 2.2 and Comparative Example 2.1 and 2.2 were compared with regard to the desired end points of the printing process according to the invention, i.e. contamination of zinc derivatives, release of formaldehyde, energy consumption and process time.

Table 3

End point	Printing process according to the invention	Benchmark printing process
Zinc derivatives	n.d.	897 ppm
Formaldehyde, before washing	n.d.	2682 ppm
Formaldehyde, after washing	n.d.	189 ppm
Energy consumption	- 45%	reference
Process time	- 47%	reference

[0090] Zinc occurrence was determined according to EN 16711-2:2016. Occurrence of formaldehyde was determined according to AATCC 112. Data of table 3 show that any zinc or formaldehyde contaminations were not detectable for the printing process according to the invention. Further, energy consumption and process time can be almost reduced to the half according to the printing process according to the invention.

Example 3: Color fastness and color strength of fabric samples worked according to the invention

[0091] 3.1 Fabric samples printed according to the color discharge process of Example 2.2 were prepared and were investigated due to their rubbing fastness.

Fabric samples prepared according to Example 2.2 were subjected to domestic laundering at 60°C. Subsequently those samples were subjected to dry and wet rub fastness measuring according to ISO 105/X12.

The fabric samples exhibited a dry rub fastness of grade 4.2 and a wet rub fastness of grade 2.9.

[0092] 3.2 The relative colour strength (K/S) of printed fabrics was measured by the light reflectance technique using the Kubelka-Munk equation. The reflectance (R) of printed fabrics was measured on a Konica Minolta MF-3700d (Japan). The color strength of the samples were determined to be increased of at least 27% compared to the following Comparative Example 3.

Comparative Example 3: color fastness and color strength of fabric samples worked according to benchmark process

[0093] 3.1 Fabric samples printed according to the color discharge process of Comparative Example 2.2 were prepared and were investigated due to their rubbing Fastness. Fabric samples prepared according to Comparative Example 2.2 were subjected to domestic laundering at 60°C. Subsequently those samples were subjected to dry and wet rub fastness measuring according to ISO 105/X12. The fabric samples exhibited a dry rub fastness of grade 3.2 and a wet rub fastness of grade 2.4.

[0094] 3.2 The relative colour strength (K/S) of printed fabrics was measured by the light reflectance technique using the Kubelka-Munk equation. The reflectance (R) of printed fabrics was measured on a Konica Minolta MF-3700d (Japan).

[0095] Test results of Example 3 and Comparative Example 3 are shown in Fig. 1. As can be seen from Figure 1, dry and wet rub fastness of fabric samples worked according to the invention are visibly improved over the fastness levels achieved by the benchmark discharge process. Further, as visible from Fig. 1, the color strength of samples worked

according to Example 3 is more pronounced than those worked according to Comparative Example 3.

Example 4: Discharge quality, sharpness and brilliance

[0096] Fabric samples worked according to Examples 2.1, Example 2.2 and Comparative fabric samples worked according to Comparative Examples 2.1 and 2.2 were compared with regard to discharge quality, sharpness and brilliance. Visibly inspections of samples worked according to the invention as shown in Fig. 2a and samples worked according to known benchmark processes and compositions as shown in Fig. 2b were made. The following observations were made:

- The white discharge sample worked according to Example 2.1 shows significant less yellowing over the white discharge sample worked according to Comparative Example 2.1. The discharge printing quality, i.e. the whitening, achieved with the composition and the process according to the present invention is therefore improved over known benchmark systems.
- Color discharge samples worked according to Example 2.2. were identified to have brighter color appearance over color discharge samples worked according to Comparative Example 2.2. Brilliance of colors of samples worked according to Example 2.2. is improved over the benchmark sample. Without being bound to theory it is believed that composition and printing process according to the invention produces less dye/ pigment degradation compared to known benchmark systems.
- A sharpened print pattern for white discharge and color discharge samples worked according to Examples 2.1 and 2.2 was observed over samples worked according to Comparative examples 2.1 and 2.2. Sharpness quality of samples worked according to the invention is therefore improved over the comparative samples.

Claims

1. A formaldehyde-free, aqueous composition for discharge printing of fabric, wherein the composition comprises at least one reducing agent, at least one synthetic thickener, at least one wetting agent, at least one pH modifier, optionally at least one pigment, and optionally at least one binder.
2. The composition according to claim 1, wherein the at least one synthetic thickener is a polyacrylic compound, preferably selected from an acrylic acid copolymer, preferably including high density oil and auxiliaries.
3. The composition according to at least one of claims 1 or 2, wherein the at least one binder is based on poly(butyl acrylate), copolymer of two or more of butyl(acrylate), ethyl(acrylate) and styrene, polyvinyl acrylate, acrylonitrile, or mixtures thereof.
4. The composition according to at least one of the claims 1 to 3, wherein the wetting agent is selected from urea, glycerin, or mixtures thereof.
5. The composition according to at least one of the claims 1 to 4, wherein the reducing agent comprises or consists of a sulfinic acid derivative.
6. The composition according to at least one of the claims 1 to 5, further comprising one or more components selected from the group of crosslinking agents, softeners, emulsifiers, antifoaming agents, rheology modifiers and oxidation protection agents or a mixture thereof.
7. The composition according to at least one of the claims 1 to 6, wherein the composition is free from any natural thickener.
8. The composition according to at least one of the claims 1 to 7, wherein the composition comprises from 3 to 30% by weight of at least one reducing agent, from 0.05% to 6% by weight of at least one synthetic thickener, from 3 to 45% by weight of at least one wetting agent, from 0.05 to 4% by weight of at least one pH adjuster,

from 0 to 30% by weight of at least one binder,
 from 0 to 2% by weight of at least one emulsifier,
 from 0 to 1% by weight of at least one anti foaming agent,
 from 0 to 3% by weight of at least one crosslinking agent,
 from 0 to 3% by weight of at least one softener,
 from 0 to 2% by weight of at least one rheology modifier,
 from 0 to 2% by weight of at least one oxidation protection agent,
 from 0 to 6% by weight of at least one pigment dispersion,
 the remainder to 100% by weight is water,
 wherein the % by weight is based on the total weight of the composition.

9. Process for manufacturing the composition according to at least one of the claims 1 to 8 comprising the following Step A and optionally Steps B and C:

Step A: Mixing and homogenizing all components for the composition according to at least one the claims 1 to 8, except the at least one pigment, in case at least one pigment is present in the composition according to at least one of the claims 1 to 8,
 Step B: Adding at least one dispersion comprising the at least one pigment to the mixture obtained in Step A,
 Step C: Mixing and homogenizing the mixture obtained in Step B.

10. Use of formaldehyde-free, aqueous composition according to at least one of the claims 1 to 8 or use of the formaldehyde-free, aqueous composition manufactured according to the process as claimed in claim 9 for discharge printing processes, in particular for white discharge or color discharge printing processes of fabric.

11. A discharge printing process for printing fabric, the process comprising the following steps:

Step 1: providing a colored fabric,
 Step 2: printing step: printing the fabric using the formaldehyde-free, aqueous composition according to at least one of claims 1 to 8 or printing the fabric using the formaldehyde-free, aqueous composition manufactured according to claim 9,
 Step 3: first drying step: drying the fabric obtained in step 2,
 Step 4: washing step: washing the fabric obtained in step 3, wherein the fabric is rinsed with a rinsing fluid and/or is soaped with a soaping fluid,
 Step 5: second drying step: drying the fabric obtained in step 4.

12. The process of claim 11, wherein the washing step comprises

a first cold and/ or hot rinsing step wherein the printed fabric is rinsed with a rinsing fluid selected from cold water or aqueous H_2O_2 solution and/ or,
 a hot soaping step wherein the printed fabric is washed with a soaping fluid, selected from soapy water at temperatures from 40 to 80°C and/ or,
 a second cold rinse step wherein the printed fabric is rinsed with a second rinsing fluid selected from cold water.

13. The process according to at least one of claims 11 or 12, wherein

the first drying step is performed at temperatures from 140°C to 180°C, preferably for 1 to 5 minutes, and/or wherein
 the second drying step is performed at temperatures of from 120°C to 160 °C, preferably for 8 to 20 min.

14. The process according to at least one of claims 11 to 13, wherein the process does not comprise a curing step and or a steaming step.

15. Fabric treated with a composition according to at least one of claims 1 to 8 or a composition obtained according to claim 9 in a discharge printing process according to at least one of claims 11 to 14.

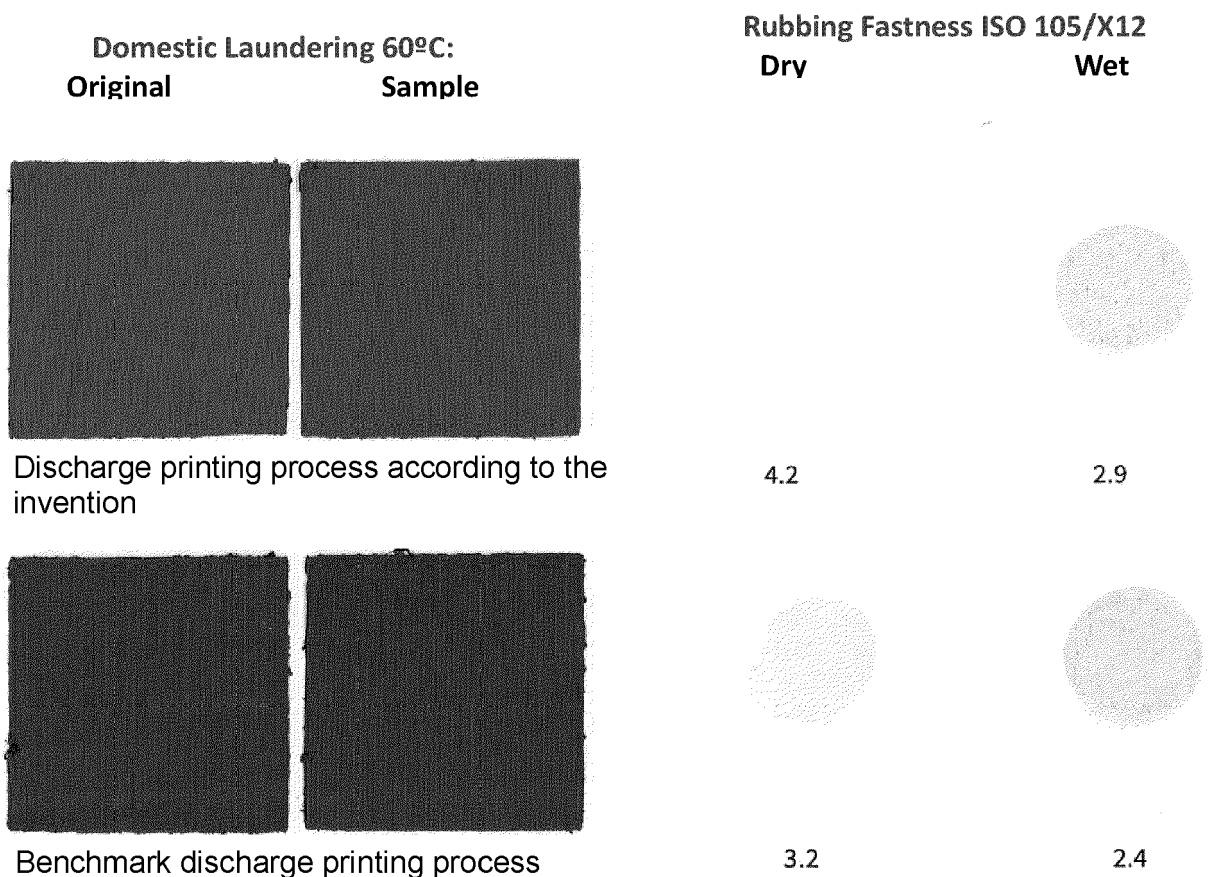


Figure 1

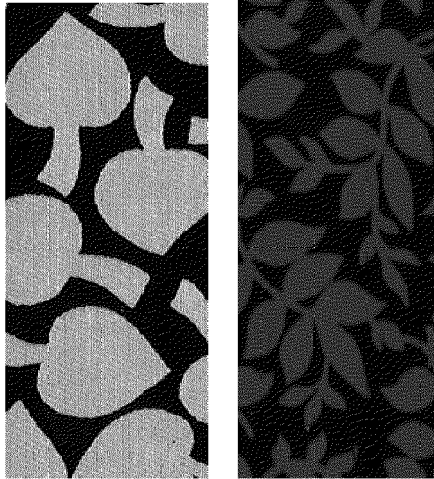


Figure 2a

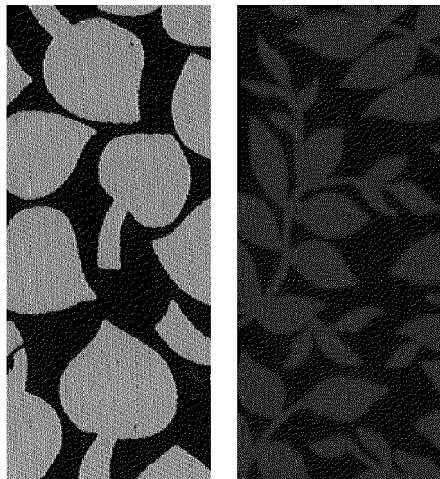


Figure 2b



EUROPEAN SEARCH REPORT

Application Number
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Place of search The Hague		Date of completion of the search 16 September 2021	Examiner Blas, Valérie
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