CONCENTRATED DYE SOLUTION

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ABSTRACT

Concentrated aqueous dye solutions comprising one or more cationizable dyes, an organic acid and water and their use for dyeing and/or printing organic substrates and for producing inkjet printing inks.
CONCENTRATED DYE SOLUTION

[0001] The present invention relates to a concentrated storage-stable aqueous dye solution and more particularly to a concentrated storage-stable aqueous dye solution without any solubilizer content. The invention further relates to the use of the present invention's concentrated dye solution, if appropriate after dilution with water, especially for dying and printing paper, including card and board.

[0002] Industrial dyeing and printing is typically carried out in an aqueous medium. Pulverulent dyes must accordingly first be dissolved in mostly warm or hot water to be usable for printing and dyeing.

[0003] Metering systems developed for this purpose utilize weighing or volumetric methods to control the metered addition of dyes and they require stable dye solutions instead of powders and granules.

[0004] Such dye solutions have the advantage that they are easily meterable, do not dust and do not require costly dissolving operations.

[0005] The solutions should possess optimum stability, so that they do not precipitate during transportation or storage. Typically, they should be stable for a prolonged period between nought and five degrees Celsius, but also at around 50°C. Similarly, frozen solutions shall be stable after pouring and should not present any stability problems during pumping. Precipitates can cause disruptions in pumping or metering systems and lead to unacceptable machine shut-downs and costly cleaning and maintenance.

[0006] One problem of known aqueous dye solutions is the large amounts of added solubilizers, which lead to a high carbon content in the dye house or paper mill effluence. This leads to effluence of high total organic carbon (TOC) and chemical oxygen demand (COD), and hence causes high water-treating costs. It is accordingly an object of the present invention to provide a concentrated aqueous dye solution for which the dye does not have to be isolated and dried (high energy costs) and which includes few or no solubilizers.

[0007] It has now been found that a concentrated aqueous dye solution without addition of solubilizers is stable when the dye is not isolated but ultrafiltered to concentrate it and free it of reaction-based solubilizers (such as 1-methyl-2-pyrididone or dimethylacetamide).

[0008] The concentrated aqueous dye solutions of the present invention comprise one or more cationizable dyes, an organic acid and water.

[0009] The present invention's concentrated aqueous dye solutions in a further preferred embodiment comprise dyes of the formula (I)

![Chemical Structure](image)

where

[0010] each A is independently —NH— or —O—,
[0011] B is a polyvalent group or atom,
[0012] n' and n'' are natural numbers and the sum total of n' and n'' is ≥2,
[0013] m is a natural number ≥0,
[0014] CC is a group having the formula (c₁) or (c₂)

![Chemical Structure](image)

where

[0015] each R₁₀ is independently H; C₁₋₅ alkyl; C₅₋₁₀ cycloalkyl; phenyl, benzyl or phenylethyl,
[0016] each R₁₀' is independently H; —OH or C₁₋₅ alkyl
[0017] each T₁ is independently H; —CN; —COOR₁₄; CONR₁₆R₁₇;
[0018] G is H; —R₁₁ NHR₁₂ or —R₁₁ NR₁₃ R₁₄ where
[0019] R₁₁ is C₁₋₅ alkylene or C₂₋₅ alkenylene,
[0020] R₁₂ and R₁₃ are independently H; unsubstituted C₁₋₅ alkyl; C₂₋₅ alkyl substituted by OH, CN or halogen; phenyl-C₁₋₅ alkyl where the phenyl radical is optionally singly, doubly or triply substituted by substituents selected from the group consisting of chlorine, C₁₋₅ alkyl or C₁₋₅ alkoxy; unsubstituted C₂₋₅ cycloalkyl or C₅₋₁₀ cycloalkyl singly, doubly or triply substituted by C₁₋₅ alkyl groups,
[0021] R₁₄ has meaning as for R₁₂ or R₁₃ or a hydrogen atom,
[0022] R₁₅ is C₁₋₅ alkyl radical or phenyl-C₁₋₅ alkyl radical,
[0023] R₁₆ and R₁₇ are independently H or a C₁₋₅ alkyl radical,
[0024] R₁₈ is in each occurrence independently H; a C₁₋₅ alkyl radical; —NR₁₉ R₁₈ —(CH₂)₂ —NR₁₀ R₁₉ or —CONR₁₁ R₁₇,
R$_{SO}$ is a C$_{1-6}$-alkyl radical or a hydroxy-C$_{1-6}$-alkyl radical,

R$_{23}$ is $-S-$ or $-O-$,

R$_{23}$ is a hydrogen atom or a C$_{1-4}$-alkyl radical, and

A$^{-}$ is a non-coloured anion, with the conditions that

(i) the sum total of $n'$, $n''$ and $m$ is less than the number of valences of B,$$
(ii)$ when the sum total of $n'$ and $n''=2$, then $m$ is $\geq 1$,

(iii) when the sum total of $n'$ and $n''=3$ and A=NH$_2$, then $m$ is $\geq 1$.

an organic acid and water.

The present invention's storage-stable high-concentration solutions of dyes of the formula (I) may also comprise a plurality of different dyes whose formulae come within the formula (I).

In preferred dyes of the formula (I), T$_1$ is a substituent of the formula

\[ \text{A} \]

In further preferred dyes, the CC group is a substituent of the formula

\[ \text{B} \]

Preferably B is a group B'CF$_3$(CH$_2$)$_{n-1}$ or B is one of the groups $[-(CH$_2$)$_{1-4}$-O-$(CH$_2$)$_{1-4}$]$_n$C or $[-(CH$_2$)$_{1-4}$-O-$(CH$_2$)$_{1-4}$]$_n$C or $[-(CH$_2$)$_{1-4}$-O-$(CH$_2$)$_{1-4}$]$_n$C or $[-(CH$_2$)$_{1-4}$-N(CH$_2$)$_{1-4}$N$[-(CH$_2$)$_{1-4}$]$_2$. It is particularly preferable for B to be a carbon atom.

Particularly preferred compounds of the formula of the formula (I) have the formula (Ia)

\[ \text{C} \]

where

CC is a substituent of the formula (c$_1$) or (c$_2$) and

n' is 1, 2, 3 or 4, with the conditions that

when n'=1, then B* is C(CH$_3$OH)$_{1-3}$,

when n'=2, then B* is C(CH$_3$OH)$_{1-3}$,

when n'=3, then B* is C(CH$_3$OH)$_{1-3}$,

when n'=4, then

B* is C; $[-(CH$_2$)$_{1-4}$-O-$(CH$_2$)$_{1-4}$]$_n$C;

$[-(CH$_2$)$_{1-4}$-O-$(CH$_2$)$_{1-4}$]$_n$C;

$[-(CH$_2$)$_{1-4}$-O-$(CH$_2$)$_{1-4}$]$_n$C or $[-(CH$_2$)$_{1-4}$]$_n$(CH$_2$)$_{1-4}$N$[-(CH$_2$)$_{1-4}$]$_2$. It is particularly preferable for B to be a carbon atom.

Compounds of the formula of the formula (la) are very special wherein CC is a substituent of the formula (c$_1$) or (c$_2$) and

n'' is 1, 2, 3 or 4, with the conditions that

when n''=1, then B* is C(CH$_3$OH)$_{1-3}$,

when n''=2, then B* is C(CH$_3$OH)$_{1-3}$,

when n''=3, then B* is C(CH$_3$OH)$_{1-3}$,

when n''=4, then B* is C.

The present invention's storage-stable high-concentration solutions of dyes of the formula (I) have a formula (I) dye content of up to 40% by weight of dye reckoned on the total weight of the solution. Preferred dye solutions have a dye content in the range from 5% to 40% by weight of dye or a dye content in the range from 10% to 35% by weight of dye and most preferably a dye content in the range from 15% to 25% by weight of dye.

The level of organic acids in the present invention's storage-stable high-concentration solutions of dyes of the formula (I) is between 0.5% by weight and 25% by weight reckoned on the total weight of the solution. Preferred dye solutions comprise from 1% to 15% by weight of added organic acids or from 2% to 10% by weight of added organic acids and most preferably from 3% to 7% by weight of added organic acids.

Preferred organic acids are acids of the formula A(-COOH) where A is C$_{1-12}$-alkanoyl or C$_{1-12}$-alkenoyl which may each be interrupted by nitrogen atoms and or oxygen atoms and which may each be additionally substituted by hydroxyl or NO$_2$ (where R and R* are independently C$_{1-6}$-alkanoyl or C$_{1-6}$-alkenoyl or C$_{1-6}$-hydroxyalkenyl, or unsubstituted phenyl or hydroxy- or sulphur- or C$_{1-6}$-alkanoyl- or unsubstituted phenyl) and with n as a natural number of 1, 2 or 3, n is preferably 1 or 2 and more preferably 1.

Particular preference is given to formic acid, acetic acid, malonic acid, propionic acid, lactic acid, tartaric acid, benzoic acid, succinic acid. Acetic acid is the most preferred organic acid. These acids will be present in a partially deprotonated (dissociated) state, as would be expected from their pK value and from the pH value of the dye solution.

Examples of preferred non-coloured anions are chlorides, bromides, sulphates, bisulphates, methysulphates, aminosulphonates, perchlorates, benzenesulphonates,
oxalates, malonates, acetates, propionates, lactates, succinates, tartrates, malates, methanesulphonates and benzoates. But also complex anions such as for example zinc chloride double salts and anions of boric acid, citric acid, glycolic acid, diglycolic acid and adipic acid or addition products of orthoboric acid with polyalcohols having at least one cis diol group. These anions may of course also be exchanged, for example by means of ion exchangers or customary precipitation reactions. The ions can also be exchanged by diafiltration or ultrafiltration. The halides chloride and bromide are particularly preferred anions and chloride is most preferred.

In principle, the salts of the added organic acids can likewise perform the anion function. In a particularly preferred embodiment, the anions are chlorides and the added organic acid is acetic acid.

Preferred dye solutions according to the present invention consist of up to 40% by weight of dye, from 0.5% to 25% by weight of the organic acid and, made up to 100% by weight, of water, but especially of 10% to 35% by weight of dye, from 1% to 15% by weight of the organic acid and, made up to 100% by weight, of water, with especially preferred dye solutions consisting of 15% to 25% by weight of dye, from 2% to 10% by weight of the organic acid and, made up to 100% by weight, of water.

Particularly preferred dye solutions according to the present invention consist of up to 40% by weight of dye as chloride, from 0.5% to 25% by weight of the organic acid and, made up to 100% by weight, of water, but especially of 10% to 35% by weight of dye as chloride, from 1% to 15% by weight of the organic acid and, made up to 100% by weight, of water, with especially preferred dye solutions consisting of 15% to 25% by weight of dye as chloride, from 2% to 10% by weight of the organic acid and, made up to 100% by weight, of water.

Very particularly preferred dye solutions according to the present invention consist of up to 40% by weight of dye as chloride, from 0.5% to 25% by weight of acetic acid and, made up to 100% by weight, of water, but especially of 10% to 35% by weight of dye as chloride, from 1% to 15% by weight of acetic acid and, made up to 100% by weight, of water, with especially preferred dye solutions consisting of 15% to 25% by weight of dye as chloride, from 2% to 10% by weight of acetic acid and, made up to 100% by weight, of water.

The invention also provides a process for producing the invention’s dye solutions which is characterized in that an aqueous solution or suspension of at least one crude cationic dye is pressed through a semipermeable membrane by applying a pressure to remove salts and synthesis by-products having molecular weights below 500 and some water.

In a preferred embodiment, the permeate is continuously or intermittently replaced or supplemented by water or buffer solution so that the volume of the batch changes only minimally, if at all. In other words, the dye concentration remains constant or substantially constant. The dye concentration of the permeate does not change by more than 20% in a preferred embodiment, by not more than 10% in a particularly preferred processes and by not more than 5% in very particularly preferred processes.

Following this diafiltration or ultrafiltration, the dye solution is brought to the desired concentration by concentrating.

The membranes used in the process of the present invention are TFMS™ membranes, for example the G10, G20, G50 or DL5 membranes from GE Osmonics Desal (GE Osmonics Inc., 5951 Clearwater Drive, Minnetonka, Minn. 55343, United States), of which the DL5 membrane is particularly preferred.

In a further, preferred version, the counterions of the cationic dye are exchanged, or further anions added, prior to diafiltration. The newly added anions mean that the original anions are easily removable through ultrafiltration or diafiltration. The counterions of the cationic functions are exchanged by halides in a particularly preferred embodiment and by chloride in a very particularly preferred embodiment.

The present invention further provides for the production of stable liquid formulations of anionic dyes by ultrafiltration of the aqueous solution or suspension of the crude dye.

Ultrafiltration or diafiltration of the reaction solution, which is obtained as per the examples of WO 02/062902, although the dyestuff is not isolated, can be used to render the reaction solution free of further, undesirable additions. Free of undesirable additions is to be understood as meaning in particular that, post ultrafiltration or diafiltration, the solutions comprise less than one % by weight and preferably less than 0.5% by weight of further materials.

Undesirable further materials are in particular inert salts and electrolytes which, having been used to neutralize and/or salt the dye out, come from the synthesis stage and are carried along in the synthesis solution or suspension, such as alkali metal or alkaline earth metal salts, for example ammonium, magnesium chloride, magnesium sulphate, magnesium bisulphate, sodium chloride, sodium sulphate, sodium bisulphate, potassium chloride, potassium sulphate or potassium bisulphate, especially sodium chloride.

This is followed by the addition of the required amount of organic acid. In principle, the organic acid can also be added before or during the ultrafiltration or diafiltration.

As well as the water-soluble, organic acids identified, the dye solutions of the present invention may comprise biocides.

Any biocide is suitable. But preference is given to biocides having FDA approval. Any biocide capable of controlling the growth of Gram-positive or Gram-negative bacteria, yeasts or fungi can be used in the solutions of the present invention. Suitable biocides are for example 3-thiazolone derivatives, which are for example alkylated and/or chlorinated or used as mixtures. Typically, biocides are added in an amount of up to 0.15% by weight per ready-produced composition.

The concentrated solutions can also be diluted again with water before they are used for dyeing. The concentrated solutions can also be shaded with further dyes before use. But the concentrated solutions can also be used for shading other dyes.

Dyes especially useful for shading or for being shaded include all dyes which the Colour Index identifies as
C.I. Basic Red or C.I. Basic Brown or C.I. Basic Blue or C.I. Basic Violet, and especially one or more of the following dyes can be used for shading: C.I. Basic Brown 23 or C.I. Basic Red 12 or C.I. Basic Blue 1 or C.I. Basic Red 14 or C.I. Basic Violet 10 or C.I. Basic Blue 26.

[0068] Dyes of the formula (II) and/or of the formula (III) are similarly useful for shading or for being shaded.

[0069] The concentrated solutions can also be used for shading brown dyes of the formula (II), or the concentrated solutions can be shaded with dyes of the formula (II).

[0070] The dyes of the formula (II) have the following structure:

where B₁ and B₂ are independently —OH and NH₂ and D₂=H or a residue of the formula

and

R₂ₐ, R₂ₜ, R₄ or R₅ are independently H or —SO₂H and M₉ or M₁₀ independently have the meanings of M₁ to M₁₀ with

M₁ being H,
M₂ being (CH₃)₂N(CH₃)₂,
M₃ being (CH₂)₂N(CH₂CH₃)₂,
M₄ being CH₂CH₂—NH,
M₅ being —CHCH—N—CH₃,
M₆ being —CHCH—NH—CH₃,
M₇ being —CHCH—NH—CH₃,
M₈ being —CH₂CH₂—NH—CH₃,
M₉ being (CH₂)₂NH₂
M₁₀ being (CH₂)₂NH₂

[0071] and

[0072] R₉ or R₁₀ independently have the meanings of R₁ to R₅.

[0073] The dyes of the formula (II) are known per se and can be prepared as described in DE3715066.

[0074] The concentrated solutions can also be used for shading brown dyes of the formula (III), or the concentrated solutions can be shaded with dyes of the formula (III).
The dyes of the formula (III) have the following structure:

![Structure of dye (III)](image)

where

- \( R^1, R^2 \) or \( R^3 \) are independently \( H, CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, sec-C_4H_9 \),
- \( R^4 \) is \(-C_6H_{4}-, -C_6H_{5}-, -CH(CH_3)CH_2-\) or \(-CH_2H_{4}-\),
- \( Y \) is hydrogen or nitro,
- \( q \) is 1 or 2.

The concentrated dye solutions of the present invention are used in particular, if appropriate after dilution with water, for dyeing and printing paper, including board and card, these materials being dyeable for example in the pulp, by coat or by dipping. In addition, such a liquid formulation can also be used for a continuous or batch dyeing process for textile materials, especially cellulose. The concentrated dye solutions of the present invention can be used as a base for producing inkjet inks or other inks and combinations for the contactless printing of substrates such as paper or textiles. The formulations of the present invention can also be used without further modification for the contactless printing of substrates such as paper or textiles.

The present invention further provides for the use of the present invention’s dye preparations of anionic dyes for producing wood stains for staining solid wood or wood chippings or chipboards or wood fibre boards. Staining wood in form of beams, boards or finished objects like furniture, parts of buildings is a preferred use of the wood stains according to the invention. The application of the liquid formulations according to the invention may be carried out over the whole or part of the wood’s surface (to compensate for color defects in the wood or veneer). The liquid formulations according to the invention may be used in water stains (main solvent water), solvent stains (ca. 30-95% organic solvent), or chemical stains (which are generally water thinnable).

The examples which follow illustrate the invention. Parts in the examples as well as in the application as a whole are by weight and % ages always weight % ages unless otherwise stated.

**PREPARATION EXAMPLE 1**

425 parts of isatoic anhydride are added gradually at 50°C. to a mixture of 118 parts of pentaerythritol and 8.7 parts of sodium carbonate in 434 parts of N,N-dimethylacetamide. The suspension is stirred for 2 hours and diluted with 4340 parts of water. This is followed by filtration, washing with water and drying at 60°C. under reduced pressure to obtain a white powder which is a mixture consisting of 4 components having the formulae (1a, 1b, 1c, 1d):

![Component 1a](image)

![Component 1b](image)

![Component 1c](image)

![Component 1d](image)
PREPARATION EXAMPLE 2

[0086] 434 parts of the amino components of Example 1 are added to a mixture of 1736 parts of ice, 781 parts of 30% HCl, 694 parts of acetic acid and 260 parts of N,N-dimethylacetamide and are diazotized with 182 parts of 4 N sodium nitrite solution. The temperature is maintained at 0-5°C by addition of 870 parts of ice. To the diazo solution obtained are added 3281 parts of an approximately 20% aqueous solution of 6-hydroxy-4-methyl-3-pyridonil-3'-methylypyridinium chloride. The pH is adjusted to 3 at a temperature of 10-20°C by addition of 130 parts of 30% sodium hydroxide solution. After subsequent stirring for 1 hour, 50 parts of Hyflo-Supercel filter earth are added before filtration through a porcelain suction filter with absorbent pad. The clear dye solution obtained (9700 g; 8900 ml) is diafiltered in a laboratory ultrafiltration system having a DL,5 membrane at 40-45°C and a pressure of 15 bar until the conductivity in the permeate stays constant. In the process, the volume is kept substantially constant. This required about 33000 parts (ml) of demineralized water. The pH is maintained at 4.0-4.5 during the ultrafiltration by addition of acetic acid. The retentate is concentrated at a pressure of 12-15 bar to 5180 parts (g) and then admixed with 140 parts of acetic acid to obtain a solution having a total dye content of about 20% by weight, consisting of the components having the formulae (2a, 2b, 2c, 2d):
This solution (20.7% dye as chloride, 5.5% of acetic acid, 73.8% of water) dyes paper in a brilliant yellow hue ($\lambda_{max} = 423$ nm in dimethylformamide/water), the concentrated solution being dilutable if necessary. The dyeings obtained have excellent wet fastnesses (to plain water, alcohol, milk, soapy water, acetic acid, urine, etc.)

PREPARATION EXAMPLE A1

A mixture consisting of 7.7 g of 4-aminoacetanilide and 22.9 g of 3-aminoacetanilide is diazotized with sodium nitrite by known methods and to the mixture of the obtained diazonium salts 58.5 g of 6-hydroxy-4-methyl-1-(3'-dimethylamino)propyl-3-pyridinio-2-pyridone betaine base are added as coupling component and these are coupled by known methods at a pH of 1.8-2.2.

The acetylamino group is then hydrolyzed with 57.5 g of 30% hydrochloric acid by known methods and thereupon the two aminoazo compounds are diazotized with 13.8 g of sodium nitrite by known methods and the diazonium salts obtained are coupled with 11 g of resorcinol at 0-5°C.

This provides a brown solution comprising 11.2 g of the dye of the formula
which dyes wood-containing paper in brown shades.

PREPARATION EXAMPLE A2

[0091] 22.1 parts (½ mol) of the compound of formula

[0092] Coupling 26.1 parts (½ mol) of the diazonium salt of the compound of the formula (A2b)

are diazotized at 0-5°C. with 3.45 parts of sodium nitrite (½ mol) in a hydrochloric acid medium and coupled at a pH of 1-3 onto 5.4 parts of 1,3-diaminobenzene (½ mol) to obtain the dye of the formula (A2a)

prepared by known methods by diazotization and coupling of 1-amino-3-acetylaminobenzene-6-sulfonic acid onto pyridone and subsequent saponification onto the dye of the formula (A2a) provides an isomer mixture of the dye of the formula:
(The possible coupling sites are marked by arrows).

This isomer mixture dyes wood-containing paper in brown shades.

Table 1 below indicates the construction of further dyes preparable according to Preparation Example A2. They conform to the formula

[0096] where B₁ and B₂ are independently —OH and NH₂ and D₃=H or a residue of the formula

<table>
<thead>
<tr>
<th>M₁</th>
<th>M₂</th>
<th>M₃</th>
<th>M₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>———H</td>
<td>———(CH₂)₂N(CH₃)₂</td>
<td>———(CH₂)₃N(CH₂CH₃)₂</td>
<td>———CH₃CH=——N ———NH</td>
</tr>
<tr>
<td>———CH₃CH=——N ———NH</td>
<td>———CH₃CH=——N ———NH</td>
<td>———CH₃CH=——N ———NH</td>
<td>———CH₃CH=——N ———NH</td>
</tr>
</tbody>
</table>
Table for \( M_4 \) and \( M_5 \)

\[
\begin{align*}
M_4 & \quad \text{Table for } R_4 \text{ and } R_5 \\
M_5 & \quad \text{Table for } R_4 \text{ and } R_5
\end{align*}
\]

---

**TABLE 1**

| Dye No. | \( R_3 \) | \( M_3 \) | \( SO_2H \) | \( H \) | \( R_1 \) | \( R_2 \) | \( R_3 \) | \( R_4 \) | \( R_5 \) | \( R_6 \) | \( R_7 \) | \( R_8 \) | \( R_9 \) | \( R_{10} \) | \( B_1 \) | \( B_2 \) |
|---------|---------|---------|--------|------|------|------|------|------|------|------|------|------|------|------|------|
| A3      | R_2    | M_2    | SO_2H  | H    | 3    | H    | H    | H    | H    | 3    | M_3  | M_4  | H    | H    | OH   | OH   |
| A4      | R_2    | M_2    | SO_2H  | H    | 4    | H    | H    | H    | H    | 3    | M_3  | M_4  | H    | H    | OH   | NH_2 |
| A5      | R_3    | M_3    | SO_2H  | H    | 4    | H    | H    | H    | H    | 3    | M_3  | M_4  | H    | H    | OH   | NH_2 |
| A6      | R_3    | M_2    | SO_2H  | H    | 4    | H    | H    | H    | H    | 3    | M_3  | M_4  | H    | H    | OH   | NH_2 |
| A7      | R_3    | M_1    | SO_2H  | H    | 3    | D_2  | R_3  | M_2  | SO_2H | H    | 3    | M_3  | M_4  | H    | H    | OH   | NH_2 |
| A8      | R_3    | M_2    | SO_2H  | H    | 3    | D_2  | R_3  | M_2  | H    | 4    | M_3  | M_4  | H    | H    | OH   | NH_2 |
| A9      | R_3    | M_2    | SO_2H  | H    | 3    | D_2  | R_3  | M_2  | H    | 4    | M_3  | M_4  | H    | H    | OH   | NH_2 |
| A10     | R_3    | M_2    | SO_2H  | H    | 3    | D_2  | R_3  | M_2  | H    | 4    | M_3  | M_4  | H    | H    | OH   | NH_2 |
| A11     | R_3    | M_2    | SO_2H  | H    | 4    | D_2  | R_3  | M_2  | H    | 3    | M_3  | M_4  | H    | OH   | NH_2 |
| A12     | R_3    | M_1    | H      | H    | 3    | D_2  | R_3  | M_2  | SO_2H | H    | 3    | M_3  | M_4  | H    | OH   | NH_2 |
| A13     | R_4    | M_4    | H      | H    | 3    | D_2  | R_3  | M_2  | SO_2H | H    | 3    | M_3  | M_4  | H    | OH   | NH_2 |
| A14     | R_4    | M_4    | H      | H    | 3    | D_2  | R_3  | M_2  | SO_2H | H    | 3    | M_3  | M_4  | H    | OH   | NH_2 |
| A15     | R_4    | M_4    | H      | H    | 3    | D_2  | R_3  | M_2  | SO_2H | H    | 3    | M_3  | M_4  | H    | OH   | NH_2 |
| A16     | R_4    | M_4    | H      | H    | 3    | D_2  | R_3  | M_2  | SO_2H | H    | 3    | M_3  | M_4  | H    | OH   | NH_2 |
| A17     | R_4    | M_4    | H      | H    | 3    | D_2  | R_3  | M_2  | SO_2H | H    | 3    | M_3  | M_4  | H    | OH   | NH_2 |
| A18     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A19     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A20     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A21     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A22     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A23     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A24     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A25     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A26     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A27     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A28     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A29     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A30     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A31     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
| A32     | R_4    | M_4    | H      | H    | 4    | D_2  | R_3  | M_2  | SO_2H | H    | 4    | M_3  | M_4  | H    | OH   | NH_2 |
TABLE I-continued

<table>
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<tr>
<th>Dye No.</th>
<th>R₁</th>
<th>M₁</th>
<th>R₂</th>
<th>Position of azo bridge 1</th>
<th>H or R₃</th>
<th>D₄</th>
<th>M₄</th>
<th>R₅</th>
<th>Position of azo bridge 2</th>
<th>H or R₆</th>
<th>D₇</th>
<th>M₇</th>
<th>R₈</th>
</tr>
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<td>M₂</td>
<td>SO₂H</td>
<td>H</td>
<td>4</td>
<td>D₄</td>
<td>R₃</td>
<td>M₃</td>
<td>SO₂H</td>
<td>H</td>
<td>4'</td>
<td>NH₃</td>
<td>NH₃</td>
</tr>
<tr>
<td>A34</td>
<td>R₂</td>
<td>M₂</td>
<td>SO₂H</td>
<td>H</td>
<td>3</td>
<td>D₄</td>
<td>R₃</td>
<td>M₃</td>
<td>H</td>
<td>3'</td>
<td>NH₃</td>
<td>NH₃</td>
<td></td>
</tr>
<tr>
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<td>R₂</td>
<td>M₈</td>
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<td>H</td>
<td>3</td>
<td>D₄</td>
<td>R₃</td>
<td>M₃</td>
<td>H</td>
<td>3'</td>
<td>OH</td>
<td>OH</td>
<td></td>
</tr>
</tbody>
</table>

PREPARATION EXAMPLE A36

Preparation of the diazo component: to 326 parts of isatoic anhydride in 1000 parts of dioxane are added dropwise 187 parts of dimethylaminoethanol at 60°C. Subsequent stirring for 1 hour is followed by concentrating in a water jet vacuum and distilling in a fine vacuum. 402 parts of 2'-dimethylaminoethyl anthranilate pass over at 160°C/0.1 Torr.

PREPARATION EXAMPLE A37

Preparation of the diazo component: to 326 parts of isatoic anhydride in 1000 parts of dioxane are added dropwise 187 parts of dimethylaminoethanol at 60°C. Subsequent stirring for 1 hour was followed by solvent removal in a vacuum and distilling 402 parts of 2'-dimethylaminoethyl anthranilate passed over at 160°C/0.1 Torr.
PREPARATION EXAMPLE 3

[0103] 1.25 kg of the dye solution of Preparation Example 2 are mixed with 7.75 kg of an approximately 10% liquid formulation of the dye of Preparation Example A1 at RT (=room temperature). This gives a stable dye solution which dyes paper in a yellowish brown hue (λ_{max} = 433 nm in water/acetate).

PREPARATION EXAMPLE 4

[0104] 4.2 kg of the dye solution of Preparation Example 2 are mixed with 2.5 kg of the dye solution of Preparation Example A36 at RT. The stable dye solution obtained dyes paper in a reddish yellow hue (λ_{max} = 450 nm in water/acetate).

[0105] Drying Prescriptions

[0106] Dyeing Prescription A

[0107] Dyeing Prescription B

[0108] Dyeing Prescription C

[0109] An absorbent web of unsized paper is pulled at 40-50° C. through an aqueous dye solution consisting of 95 parts of water and 5 parts of the inventive dye solution of Preparation Example 2.

[0110] Excess dye solution is squeezed by two rolls. The dried web of paper has a yellow colour in each case.

[0111] Dyeing Prescription D

[0112] The dye preparations of Preparation Examples 3, 4 and A1-A37 can be used for dyeing similarly to Prescriptions A to C.

[0113] Dyeing Prescription E

[0114] 100 parts of freshly tanned and neutralized chrome grain leather are drummed for 30 minutes in a float of 250 parts of water at 55° C. and 0.5 part of the dye preparation made according to Preparation Example 2 and are treated for a further 30 minutes in the same bath with 2 parts of anionic fatliquor based on sulphonated fish oil. The leathers are conventionally dried and finished. The leather obtained has a level yellow hue.

[0115] Further low-affinity, vegetable-retanned leathers can likewise be dyed according to known methods.

[0116] Dyeing can be done in a similar manner with dyes of Preparation Examples 3, 4 and A1-A37.

[0117] Use Example F

[0118] 15 kg of wastepaper (woody), 25 kg of bleached groundwood and 10 kg of unbleached sulphate pulp were beaten in a pulper to form a 3% aqueous pulp suspension. The pulp suspension was diluted to 2% in a dyeing vat. This suspension was then admixed in succession with 5% of kaolin and 1.25 kg of a 5% acetic acid solution of the dye of Preparation Example 2, reckoned on dry total fibre, by stirring. After 20 minutes the pulp in the mixing vat is admixed with 1% (based on absolutely dry fibre) of a resin size dispersion. The homogeneous pulp suspension was adjusted with alum to pH 5 on the paper machine just upstream of the headbox.

[0119] The paper machine was used to produce 80 g/m² of yellow bag paper with a machine finish.

[0120] Dyeing can be done in a similar manner with dyes of Preparation Examples 3, 4 and A1-A37.

[0121] Use Example G

[0122] A dry stock containing 60% groundwood and 40% unbleached sulphate pulp is beaten with sufficient water and ground to 40 SR freeness in a hollander for the dry content to be just above 2.5% and then adjusted with water to a dry content of exactly 2.5% for the high-density pulp.

[0123] 200 parts of this high-density pulp are admixed with 5 parts of a 0.25% aqueous solution of the dye of Preparation Example 2, stirred for about 5 min., admixed with 2% of resin size and 4% of alum, based on dry stock, and again stirred for some minutes until homogeneous. The material is diluted with about 500 parts of water to 700 parts by volume and used in a known manner to prepare sheets of paper by drainage on a sheet-former. These sheets of paper have a deep yellow colour.

[0124] Dyeing can be done in a similar manner with dyes of Preparation Examples 3, 4 and A1-A37.

[0125] Use Example H

[0126] An ink composition for inkjet printing consists of

[0127] 6 parts of the dye of Preparation Example 2,

[0128] 20 parts of glycerol and

[0129] 74 parts of water.

[0130] This ink composition was then used for printing paper, papery substrates, textile fibre materials and plastic film/sheet by transferring the ink into the ink receptacle of
a commercially available inkjet printer and using it to produce a single-coloured test print on the identified sheet-like materials.

[0136] Dyeing can be done in a similar manner with dyes of Preparation Examples 3, 4 and A1-A37.

[0137] Use Example 1

[0138] A batten of coniferous wood (European spruce) and a batten of leafy wood (beech) were each cut into pieces of about 5 cm and immersed for some minutes in a diluted (10 parts water and 1 part of the dye solution according to example 2) dyestuff solution according to example 2 and after drying for ten hours light brownish batten pieces were obtained.

[0139] Dyeing can be done in a similar manner with dyes of Preparation Examples 3, 4 and A1-A37.

1. A concentrated aqueous dye solution comprising at least one cationizable dye, an organic acid and water, wherein the at least one cationizable dye is of the formula (I)

\[
\text{(I)}
\]

wherein

- each A is independently —NH— or —O—,
- B is a polyvalent group or atom,
- n' and n'' are natural numbers and the sum total of n' and n'' is ≥2,
- m is a natural number ≥0,
- CC is a group having the formula (c₁) or (c₂)

\[
\text{(c₁)}; \text{(c₂)}
\]

wherein

- each R₁₀ is independently H; C₁₋₅ alkyl; C₅₋₁₅ cycloalkyl; phenyl, benzyl or phenylethyl,
- each R₁₀' is independently H; —OH or C₁₋₅ alkyl
- each T is independently H; —CN; —COOR₁₅; CONR₁₆R₁₇; SO₂NR₁₆R₁₇;

G is H; —R₁₁NHR₁₂ or —R¹¹NR₁₃R₁₄ where
- R₁₁ is C₁₋₅ alkylene or C₂₋₅ alkenylene,
- R₁₁, R₁₃ and R₁₄ are independently H; unsubstituted C₁₋₅ alkyl; C₂₋₅ alkyl substituted by OH, CN or halogen; phenyl-C₁₋₅ alkyl where the phenyl radical is optionally singly, doubly or triply substituted by substituents selected from the group consisting of chlorine, C₁₋₅ alkyl and C₁₋₅ alkoxy; unsubstituted C₂₋₅ cycloalkyl or C₅₋₁₅ cycloalkyl singly, doubly or triply substituted by C₁₋₅ alkyl groups,
- R₁₅ is C₁₋₅ alkyl radical or phenyl-C₁₋₅ alkyl radical, R₁₆ and R₁₇ are independently H or a C₁₋₅ alkyl radical, R₁₈ is independently H or a C₁₋₅ alkyl radical; —NR₁₃R₁₄—(CH₂)₂—NR₁₅R₁₆ or —CONR₁₃R₁₇,
- R₁₀ is a C₁₋₅ alkyl radical or a hydroxy-C₁₋₅ alkyl radical, R₂₀ is —S— or —O—,
- R₂₁ is a hydrogen atom or a C₁₋₅ alkyl radical, and An⁺ is a non-coloured anion, with the proviso that

(i) the sum total of n', n'' and m is less than the number of valences of B,
(ii) when the sum total of n' and n''=2, then m is ≥1,
(iii) when the sum total of n' and n''=3 and A=NH, then m is ≥1.

2. A concentrated aqueous dye solution according to claim 1 wherein the at least one cationizable dye is at least one dye of the formula (II)

\[
\text{(II)}
\]
where $B_1$ and $B_2$ are independently $-\text{OH}$ or $\text{NH}_2$ and $D_3=\text{H}$
or a residue of the formula

$M_4$ is

and

$R_5$, $R_7$, $R_8$ and $R_9$ are independently $\text{H}$ or $-\text{SO}_2\text{H}$ and

$M_5$ and $M_6$ are independently $M_1$ to $M_{10}$, wherein

$M_1$ is $\text{H}$.

$M_2$ is $-\text{(CH}_2\text{)}_3\text{N(CH}_2\text{)}_2$,  

$M_3$ is $-\text{(CH}_2\text{)}_2\text{N(CH}_2\text{CH}_3\text{)}_2$,  

$M_4$ is

$M_5$ is

$M_6$ is

$M_7$ is

$M_{10}$ is $-\text{(CH}_2\text{)}_2\text{NH}_2$,  

and

$R_1$ or $R_1$ are independently $R_4$ to $R_5$, wherein

$R_1$ is $\text{H}$,

$R_2$ is

$R_3$ is

$R_4$ is $\text{CN}$,

$R_5$ is

$R_7$ is

$R_8$ is

$R_9$ is

$R_{10}$ is
$R_4$ is

or at least one dye of the formula (III)

Wherein

$R_1$, $R_2$ or $R_3$ are independently H, CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$, n-C$_4$H$_9$, i-C$_4$H$_9$, sec-C$_4$H$_9$.

$R^*$ is $-C_2H_4$, $-C_3H_7$, $-CH(CH_3)CH_2$ or $-C_4H_9$.

$Y$ is hydrogen or nitro,

$q$ is 1 or 2

and $A_n^-$ is a non-coloured anion.

3. A concentrated aqueous dye solution according to claim 1 wherein the organic acid is an organic acid of the formula $A'(-COO)_{n_1}$, where $A'$ is C$_{1-12}$-alkanoyl or C$_{1-12}$-alkenyl optionally interrupted by nitrogen atoms and/or oxygen atoms and optionally substituted by hydroxyl or NR$^aR^*$ (wherein R' and R* are independently C$_{1-12}$-alkanoyl or C$_{1-12}$-alkenyl or C$_{1-12}$-hydroxyalkanoyl or C$_{1-12}$-hydroxyalkenyl, or unsubstituted phenyl or hydroxyl- or sulphur- or C$_{1-18}$-alkanoyl- or C$_{1-18}$-alkenyl-substituted phenyl and $n$ is a natural number of 1, 2 or 3.

4. A concentrated aqueous dye solution according to claim 1 wherein the concentrated aqueous dye solution comprises up to 40% by weight of the at least one cationizable dye, from 0.5% to 25% by weight of the organic acid and is made up to 100% by weight with water.

5. A process for producing a concentrated aqueous dye solution according to claim 1, comprising the step of pressing an aqueous solution or suspension of at least one crude cationic dye of the formula (I) through a semipermeable membrane by applying a pressure to remove salts, synthesis by-products having molecular weights below 500, and a portion of the water.

6. A process for producing a concentrated aqueous dye solution according to claim 5, further comprising the step of continuously or intermittently replacing or supplementing the permeate with water or buffer solution so that the concentration of the at least one crude cationic dye in the permeate does not change by more than 20%.

7. A process for dyeing and/or printing cellulosic material, comprising the step of contacting the at least one concentrated aqueous dye solution according to claim 1 with the cellulosic material.

8. A process for producing inks and formulations for contactless printing, comprising the step of combining at least one concentrated aqueous dye solution according to claim 1, with at least one additional chemical and/or water.

9. A substrate that has been dyed or printed with a concentrated aqueous dye solution according to claim 1.

10. A process according to claim 7 wherein the cellulosic material is paper, board or card.

11. A process according to claim 8 wherein the contactless printing is inkjet printing.

12. A substrate dyed and/or printed by a process in accordance with claim 7.

13. An inkjet ink comprising the concentrated aqueous dye solution according to claim 1.

* * * * *