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(54) **The stabilization of leucomethylene blue dyes on a printing substrate.**

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Description

This invention relates to substrates for printing on which leucomethylene blue dyes have been stabilized against background formation by the addition of an additive material.

Leucomethylene blue dyes find widespread application in color printing technologies such as thermal printing, pressure printing and electrolytic printing. One common problem with the different leuco dyes used in these technlogies is their spontaneous conversion to the dye form by ambient conditions. In order to circumvent this problem, many methods involving protection of the leuco dyes have been used, such as encapsulation and the use of stilt layers. Such methods have given some success in various printing technologies, but they are not applicable to electrochromic printing, where the mechanism requires an aqueous electrolyte layer to be in intimate contact with the colour-forming agent. It is in electrochromic printing that the present invention finds its most particularly useful application.

Electrochromic printing is well known in the art. The present state of electrochromic printing is referenced by US—A—4,211,616 and EP—A—47367, along with the art cited therein.

EP—A—47367 discloses a substrate for electrochromic recording characterised in that the substrate comprises paper containing a water soluble leuco methylene blue compound containing a sulphonated aromatic or sulphonated aliphatic moiety.

EP—A—0056096, which forms part of the prior art according to Artcle 54(3) and (4) EPC for all designated contracting states, discloses in Example 2 a paper substrate which is coated sequentially with an aqueous solution containing two leuco dyes followed by three coatings of aqueous electrolyte solution. The first solution contains 1% potassium iodide (leuco dye), 1% o-sulfobenzoylleucomethylene blue (leuco dye), 0.1% ascorbic acid, 1% oxalic acid, and adjusted to pH 2.3. The electrolyte solution contains 9% ammonium bromide, 10% potassium bromide 1.4% potassium dihydrogen phosphate, and adjusted to pH 7.

EP—A—0058855 which also forms part of the prior art according to Article 54(3) and (4) EPC for all contracting states, discloses a printing substrate manufactured from *inter alia* a coating formulation comprising a leuco dye/electrolyte dispersion in water which consists of 1.0% benzoyl leuco-methylene blue, 4.5% NH_4Br and 5% Kbr. A dye stabiliser is used in the coating formulation; this stabiliser is 0.1% ascorbic acid.

According to the invention there is provided an electrochromic printing substrate comprising a leucomethylene blue dye characterised in that the substrate also includes a stabilising amount of an additive selected from the group, consisting of citric acid, aspartic acid, malonic acid, oxalic acid, tartaric acid, ketomalonic acid monohydrate, glucose and methionine, as sole stabilising agent.

In typical use for electrochromic printing, according to the present invention, paper is treated with an aqueous solution containing from about .5 to 5% by weight of a leuco dye. Generally about 1% by weight is the most preferred level. The solution also contains a stabilizer in an amount which is, at minimum equal to the molar amount of the dye. The stabilizer may be present up to about 5% by weight concentration. In most instances the solution will also contain bromide ions in an amount of from 1% to 30% by weight, generally about 15% by weight. As a result of the treatment, the paper contains approximately 10 mg of leuco dye for each standard size page of 215×280 mm (8-1/2×11 inch) dimensions.

It has been observed that the use of one of the above-named additives render leucomethylene blue dyes less prone to background formation by oxidation. The mechanisms by which this result is obtained is not at all understood. The ease of electron removal of a compound is indicated by its oxidation potential. A shift to higher potential is indicatve of greater resistance towards oxidation. Some of the substances which stabilize against background formation raise the oxidation potential of the leuco dyes, but some of them do not. Furthermore, although most of the useful additives are poly-functional carboxylic acids, not all such materials work. Specifically, succinic acid is of no help. Galactose shows decreased effectiveness while maltose, lactose, d-fructose, dl-asparagine, glycine, l-cystine and dl-methionine are ineffective.

The operative additives do, however, have a community of physical and mechanical properties. They are all solids which are soluble in water and they all contain an oxygen atom doubly bonded to a carbon atom. The experimental results obtained using the additives of the present invention are summarized in the following table I, showing results obtained with *o*-sulfobenzoylleucomethylene blue (o-SBLMB) as the substrate leucodye.

TABLE I

Additive	Shift to higher potential	Stabilization against background formation
Citric acid	yes	yes
Aspartic acid	yes	yes
Malonic acid	yes	yes
Oxalic acid	yes	yes
Tartaric acid	yes	yes
Ketomalonic acid monohydrate	yes	yes
Glucose	no	yes
Methionine	no	yes
Acetic acid	no	no
Toluenesulfonic acid	no	no
Succinic acid	no	no
Mercaptoacetic acid	no	no
3,3'-Thiodipropionic acid	no	no

As may be seen from inspection of the above table, whatever the mechanism involved in stabilization against background formation, it obviously does not, of necessity, involve shifting the oxidation potential of the leuco dye. It should also be noted that reducing sugars other than glucose did not give satisfactory results. Galactose has minimal effect while lactose and d-fructose have no effect. The following leucomethylene blue dyes show a shift to higher potential in the presence of oxalic acid equal in magnitude to that shown by o-SBLMB: 2-chloro-5-sulfo-BLMB and 2,4-dichloro-5-sulfo-BLMB.

Most importantly, it should be emphasized that the addition of these additives does not significantly hinder the printing process, nor does it impair the quality of the print obtained. Rather, the archival nature of the print is greatly increased.

The most preferred additive is malonic acid.

Claims

1. An electrochromic printing substrate comprising a leucomethylene blue dye characterised in that the substrate also includes a stabilising amount of an additive, selected from the group consisting of citric acid, aspartic acid, malonic acid, oxalic acid, tartaric acid, ketomalonic acid monohydrate, glucose and methionine, as sole stabilising agent.

2. A printing substrate as claimed in claim 1, wherein the stabiliser is present in a molar amount at minimum equal to the molar amount of the leuco dye.

3. A printing substrate as claimed in claim 1 or 2, wherein the substrate material is paper.

4. A printing substrate as claimed in any one of claims 1 to 3, which also contain bromide ions.

Patentansprüche

1. Elektrochromes Drucksubstrat mit einer leukomethylenblauen Farbe, dadurch gekennzeichnet, daß das Substrat ebenfalls eine stablisierende Menge an Zitronensäure, Asparaginsäure, Malonsäure, Oxalsäure, Weinsäure, Ketomalonsäuremonohydrat, Glukose und/oder Menthionin als einziges Stabilisierungsmittel enthält.

2. Drucksubstrat nach Anspruch 1, wobei der Stabilisator in mindestens molarer Menge, bezogen auf die Leukofarbenmenge, enthält.

3. Drucksubstrat nach Anspruch 1 oder 2, wobei das Substrat Papier ist.

4. Drucksubstrat nach einem der Ansprüche 1 bis 3, das ebenfalls Bromidionen enthält.

Revendications

1. Substrat d'impression électrochrome comprenant un leucodérivé de bleu de méthylène, caractérisé en ce que le substrat contient aussi une quantité stabilisante d'un additif, choisi dans le groupe constitué par l'acide citrique, l'acide aspartique, l'acide malonique, l'acide oxalique l'acide tartrique, le monohydrate d'acide cétomalonique, le glucose et la méthionine, comme seul agent stabilisant.

2. Substrat d'impression selon la revendication 1, dans lequel le stabilisant est présent en une quantité molaire au minimum égal à la quantité molaire du leucodérivé.

3. Substrat d'impression selon la revendication 1 ou 2, dans lequel la matière du substrat est du papier.

4. Substrat d'impression selon l'une quelconque des revendications 1 à 3, qui contient aussi des ions bromure.