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

(57) Substrates for printing are provided by stabilizing the leucomethylene blue dye contained therein with an additive selected from the group consisting of citric acid, aspartic acid, malonic acid, oxalic acid, ascorbic acid, tartaric acid, ketomalonic acid monohydrate, glucose and methionine.

EP 0 097 220 A2

THE STABILIZATION OF LEUCOMETHYLENE BLUE DYES ON A PRINTING SUBSTRATE

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 technologies 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 U.S. patents 4,211,616 and 4,309,255, along with the art cited therein. No prior art of which we are aware, however, suggests the use of the additives which are the subject matter of the present invention.

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

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% 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%, generally about 15%. As a result of the treatment, the paper contains approximately 10 mg of leuco dye for each standard size page of 8 1/2 x 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 indicative 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 nc 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
Ascorbic 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- sulfoBLMB.

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.

A typical formulation is the following applied to Hammermill Bond paper. One coat of a solution containing o-sulfobenzoylleucomethylene blue (o-SBLMB) (1%), oxalic acid (1%), and ascorbic acid (0.1%), with the pH adjusted to 2.3 using either phosphoric acid or potassium hydroxide as needed. Three coats of a solution containing potassium bromide (20%), and potassium hydrogen phosphate (1.4%), with the pH adjusted to 11 as above.

Several identical formulations were prepared, spray coated and monitored for background formation. The time to an unacceptable background was approximately doubled when a stabilizer was present. These studies were carried out at various pHs, all with 1.4% potassium dihydrogen phosphate and oxalic acid. The following times, in months, to reach an unacceptable background level were obtained with the first number corresponding to the pH, the second to the condition with no stabilizer, then with stabilizer, and finally the percent increase: 7, 1.3, 2.9, 223%; 11, 2.25, 4.1, 182%; 13,3.8, 7.2, 189%.

CLAIMS

1. A printing substrate comprising a leucomethylene blue dye characterized in that the substrate also includes a stabilizing amount of an additive selected from the group consisting of citric acid, aspartic acid, malonic acid, oxalic acid, ascorbic acid, tartaric acid, ketomalonic acid monohydrate, glucose and methionine.

2. A printing substrate as claimed in claim 1, wherein the stabilizer is present in a molar amount approximately 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 contains bromide ions.