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(54) Process for multi-color electrolytic printing.

(57) The invention relates to a process for multi-color electrolytic printing.

This process is achieved by applying to selected portions of a substrate a plurality of electric currents of controlled voltage and controlled pulsewidth, said substrate comprising a plurality of leuco dyes each having a different sensitivity to the threshold potential and pulse width of current required to convert the leuco dye to the colored form thereof.

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PROCESS FOR MULTI-COLOR ELECTROLYTIC PRINTING

The present invention is concerned with a process for multi-colored electrolytic printing.

Electrolytic printing per se is fairly well known in the art. The basic concept involves production of images by application of electric current to selected portions of a substrate, such as paper, which has been impregnated with a material which changes color upon the application of electric potential. The following references deal with some aspects of electrolytic printing:

(a) Fujitsu Scientific & Technical Journal, Sept. 1976, page 131, Article by T. Kitakohji;

(b) United States patent 3 713 996 to Letter (Bausch & Lomb)

(c) United States patent 3 816 838 to Higaki et al (Kanzaki Paper Mfg. Co.)

(d) United States patent 3 864 684 to Shimuzu (Mitsubishi Paper Mills)

(e) United States patent 3 772 159 to Sakata et al (Jujo Paper Co.).

None of the listed prior art references describes or suggests the critical features of the present invention.

Object of the invention is a process for multi-color printing using a mixture of dyes and a plurality of electrical stimuli.

The object of the invention is achieved by a process which is characterized in that to selected portions of a substrate which comprises a plurality of leuco dyes, each having a different sensitivity to threshold potential and pulse width of current required to convert it to its colored form, a plurality of electrical stimuli is applied, one for each leuco dye, with each of the plurality of electrical stimuli converting one leuco dye to its colored form.

According to the present invention, electrolytic printing with a plurality of colors is achieved. A substrate such as paper is impregnated with a plurality of dyes in the leuco form thereof. The dyes in their leuco forms are selected so that they differ in the electrical stimulus required to convert each dye from the leuco form to the colored form. In particular, the dyes differ in the threshold potential and pulse width of the applied current required to convert them from the leuco form to the colored form. A plurality of electrical stimuli, one for each leuco dye, is applied at an electrode to selected portions of the substrate. Each stimulus converts one leuco dye to its colored form. Thus, multi-color electrolytic printing is achieved by careful dye selection and control of the potentials and pulse widths in the electrode.

Each leuco dye has a characteristic threshold potential at which it reacts to form the parent dye. Independent of this voltage, as long as the threshold value is surpassed, the leuco dye reacts with a characteristic

electrical pulse width (i.e. kinetic rate) under a specified set of printing conditions to form the parent dye. Thus, for example, when a three-color system of leuco dyes is chosen so that the dye with the lowest threshold potential is activated by a long electrical pulse width, another dye with an intermediate threshold potential is activated by a somewhat shorter pulse width, and a third dye has a high threshold potential but needs only a short pulse width, three colors and black can be printed at one electrode and color facsimile printing is achieved.

To illustrate the above concept, the following table gives a general example, listing arbitrary solution threshold potentials and printing pulse widths.

Color	Voltage	Pulse Width
Color #1	0.5 V	1.5 msec
Color #2	1.0	0.5
Color #3	1.5	0.2
Black	1.5	1.0

Black printing can be generated by developing all three colors simultaneously, as shown in the table, using high voltage and long pulse widths. In another variation of the invention, a fourth dye can be added to the system to give black. The process of the present invention is also useful to develop intermediate variations of color between two dyes, by discharge of the higher threshold potential and careful modulation of the pulse width.

The process of the present invention is applicable to many mixtures of suitable leuco dyes. It is to be un-

derstood that when the expression "plurality of colors" is used, black is to be considered a color. That is to say, the present invention is useful for printing with black and another color simultaneously. In one particularly useful variation of the present invention, the substrate comprises three different leuco dyes, one for each of the primary colors of cyan, magenta and yellow. Selection of dyes from the three primary colors makes possible printing throughout the entire spectrum of colors.

The process of the present invention is also useful to produce intermediate shades or combinations of printed colors on a substrate by using intermediate levels of voltage and pulse width.

The following examples are given solely for the purposes of illustration and are not to be considered limitations on the invention, many variations of which are possible without departing from the spirit and scope thereof.

The following show selective generation of multiple colors in single pass electrolytic printing systems.

Example One:

A paper substrate is coated sequentially with two leucodye solutions. The first coating solution contains 0.2 % benzoylleucomethylene blue (leucodye) in acetone. The second solution is aqueous and contains 0.35 % Potassium iodide (leucodye) in addition to an electrolyte buffer mixture - 4.5 % ammonium bromide, 5 % potassium bromide, 1.4 % potassium dihydrogen phosphate, and 1 % urea. The second solution is adjusted to pH 7. The printing behavior is listed in the table below.

Applied Voltage	Print Pulse	Color
10 V	1.0 millisecond	Brown
15 V	0.75 "	Black
25 V	0.5 "	Blue

Example Two:

A paper substrate 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. The printing behavior is listed in the table below.

Applied Voltage	Print Pulse	Color
25 V	200 microseconds	Blue
20 V	900 "	Black

C L A I M S

1. Process for multi-color electrolytic printing with a plurality of colors, characterized in that to selected portions of a substrate which comprises a plurality of leuco dyes, each having a different sensitivity to threshold potential and pulse width of current required to convert it to its colored form, a plurality of electrical stimuli is applied, one for each leuco dye, with each of the plurality of electrical stimuli converting one leuco dye to its colored form.

2. Process as claimed in claim 1, characterized in that the substrate comprises the leuco form of two dyes of different colors.

3. Process as claimed in claims 1 and 2, characterized in that the substrate comprises the leuco form of a black dye and a leuco form of a dye of another color.

4. Process as claimed in claims 1 and 2, characterized in that the substrate comprises the leuco form of three dyes, one for each of the primary colors cyan, magenta and yellow.

5. Process as claimed in claim 1, characterized in that intermediate levels of voltage and pulse width are employed to produce intermediate shades or combinations of printed colors on a substrate.