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**(54) MULTICOLOR DYNAMIC PRINTING METHOD AND APPARATUS**

DYNAMISCHES VIELFARBENDRUCKVERFAHREN UND VORRICHTUNG

PROCEDE ET APPAREIL D'IMPRESSION DYNAMIQUE POLYCHROME

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## Description

### TECHNICAL FIELD

[0001] The present invention pertains to improvements in the field of dynamic printing. More particularly, the invention relates to an improved multicolor electrocoagulation printing method and apparatus.

### BACKGROUND ART

[0002] In US Patent N° 4,895,629 of January 23, 1990, Applicant has described a high-speed electrocoagulation printing method and apparatus in which use is made of a positive electrode in the form of a revolving cylinder having a passivated surface onto which dots of colored, coagulated colloid representative of an image are produced. These dots of colored, coagulated colloid are thereafter contacted with a substrate such as paper to cause transfer of the colored, coagulated colloid onto the substrate and thereby imprint the substrate with the image. As explained in this patent, the positive electrode is coated with a dispersion containing an olefinic substance and a metal oxide prior to electrical energization of the negative electrodes in order to weaken the adherence of the dots of coagulated colloid to the positive electrode and also to prevent an uncontrolled corrosion of the positive electrode. In addition, gas generated as a result of electrolysis upon energizing the negative electrodes is consumed by reaction with the olefinic substance so that there is no gas accumulation between the negative and positive electrodes.

[0003] The dispersion containing the olefinic substance and the metal oxide is applied onto the surface of the positive electrode in a manner so as to form on the electrode surface micro-droplets of olefinic substance containing the metal oxide. As described in the aforementioned patent, this may be achieved by means of a device comprising a rotatable brush provided with a plurality of radially extending horsehair bristles having extremities contacting the electrode surface, and a distribution roller arranged in spaced-apart parallel relation to the brush such as to contact the bristles thereof at their extremities. The distribution roller has a plurality of peripheral longitudinally extending grooves and is partially immersed in a bath containing the dispersion. As the distribution roller rotates in the dispersion, the grooves are filled with the dispersion which is thus transferred to the bristles to coat the extremities thereof. Rotation of the brush, on the other hand, causes the coated bristles to transfer the dispersion onto the surface of the positive electrode and thereby form the desired micro-droplets of olefinic substance containing the metal oxide. Instead of a brush, use can be made of a roller provided with a plurality of radially extending strips of chamois leather adapted to contact the electrode surface, the strips being coated in the same manner as the bristles. Rotation of such a roller causes the

coated strips to impinge upon the surface of the positive electrode such as to transfer thereon the dispersion and thereby form the desired micro-droplets of olefinic substance containing the metal oxide.

[0004] The electrocoagulation printing ink which is injected into the gap defined between the positive and negative electrodes consists essentially of a liquid colloidal dispersion containing an electrolytically coagulable colloid, a dispersing medium, a soluble electrolyte and a coloring agent. Where a pigment is used, a dispersing agent is added for uniformly dispersing the pigment into the ink.

[0005] When a polychromic image is desired, the negative and positive electrodes, the positive electrode coating device and the ink injector are arranged to define a printing unit and several printing units each using a coloring agent of different color are disposed in tandem relation to produce several differently colored images of coagulated colloid which are transferred at respective transfer stations onto the substrate in superimposed relation to provide the desired polychromic image. Alternatively, the printing units can be arranged around a single roller adapted to bring the substrate into contact with the dots of colored, coagulated colloid produced by each printing unit, and the substrate which is in the form of a continuous web is partially wrapped around the roller and passed through the respective transfer stations for being imprinted with the differently colored images in superimposed relation.

[0006] Since each printing unit of the above multicolor printing apparatus requires a high precision cylinder which is usually in stainless steel, as a positive electrode, such an apparatus is not only cumbersome but also very costly. Moreover, as several high precision cylinders are required for forming differently coloured images of coagulated colloid, it is difficult to provide a polychromic image in which the differently coloured images are perfectly superimposed.

[0007] It is an object of the present invention to provide an improved multicolour electrocoagulation printing method and apparatus.

[0008] According to the present invention there is provided a multicolour electrocoagulation printing method comprising the steps of: a) providing a single positive electrode formed of an electrolytically inert metal and having a continuous passivated surface moving at substantially constant speed along a predetermined path, said passivated surface defining a positive electrode active surface; b) forming on said positive electrode active surface a plurality of dots of coloured, coagulated colloid by electrocoagulation of an electrolytically coagulable colloid in the presence of a colouring agent, said dots of coloured, coagulated colloid being representative of a desired image; c) bringing a substrate into contact with the dots of coloured, coagulated colloid to cause transfer of the coloured, coagulated colloid from the positive electrode active surface onto said substrate and thereby imprint said substrate with the image; and

d) repeating steps (b) and (c) several times to define a corresponding number of printing stages arranged at predetermined locations along said path and each using a colouring agent of different colour, and to thereby produce several differently coloured images of coagulated colloid which are transferred at respective transfer positions onto said substrate in superimposed relation to provide a polychromic image.

**[0009]** According to the present invention there is further provided multicolour electrocoagulation printing apparatus comprising: a single positive electrode formed of an electrolytically inert metal and having a continuous passivated surface defining a positive electrode active surface; means for moving said positive electrode active surface at a substantially constant speed along a predetermined path; and a plurality of printing units arranged at predetermined locations along said path, each printing unit comprising: means for forming on said positive electrode active surface a plurality of dots of coloured, coagulated colloid by electrocoagulation of an electrolytically coagulable colloid in the presence of a colouring agent of different colour, said dots of coloured, coagulated colloid being representative of a desired image; and means for bringing a substrate into contact with the dots of coloured, coagulated colloid at a respective transfer station to cause transfer of the coloured, coagulated colloid from the positive electrode active surface onto said substrate and thereby imprint said substrate with the image.

**[0010]** In contrast to conventional dynamic and static printing methods and apparatuses where a central impression cylinder is used to convey a web to planetary printing units for impression by respective plate cylinders, the electrocoagulation printing method and apparatus to be described utilize a single positive electrode on which dots of coloured, coagulated colloid are formed in sequence and the substrate which is generally in the form of a web travels independently of the positive electrode, from one printing unit to another, so as to contact the coloured, coagulated colloid in sequence. The invention enables one to significantly improve the registration of the differently coloured images upon their transfer onto the web or other substrate, thereby providing a polychromic image of high definition.

**[0011]** Where the desired image is reproduced by electrocoagulation of a colloid, the positive electrode used can be in the form of a moving endless belt as described in Applicant's US Patent No. 4,661,222, or in the form of a revolving cylinder as described in the aforementioned US Patent No. 4,895,629. In later case, the printing units are arranged around the positive cylindrical electrode.

**[0012]** When use is made of a positive electrode of cylindrical configuration rotating at substantially constant speed about its central longitudinal axis, step (b) of the above electrocoagulation printing method is carried out by:

i) providing a plurality of negative electrolytically inert electrodes electrically insulated from one another and arranged in rectilinear alignment to define a series of corresponding negative electrode active surfaces disposed in a plane parallel to the longitudinal axis of the positive electrode and spaced from the positive electrode active surface by a constant predetermined gap, the negative electrodes being spaced from one another by a distance at least equal to the electrode gap;

ii) coating the positive electrode active surface with an olefinic substance and a metal oxide to form on the surface micro-droplets of olefinic substance containing the metal oxide;

iii) filling the electrode gap with a substantially liquid colloidal dispersion containing the electrolytically coagulable colloid, the coloring agent, a liquid dispersing medium and a soluble electrolyte;

iv) electrically energizing selected ones of the negative electrodes to cause point-by-point selective coagulation and adherence of the colloid onto the olefin and metal oxide-coated positive electrode active surface opposite the electrode active surfaces of the energized negative electrodes while the positive electrode is rotating, thereby forming the dots of colored, coagulated colloid; and

v) removing any remaining non-coagulated colloid from the positive electrode active surface.

**[0013]** As explained in US Patent No. 4,895,629, spacing of the negative electrodes from one another by a distance which is equal to or greater than the electrode gap prevents the negative electrodes from undergoing edge corrosion. On the other hand, coating of the positive electrode with an olefinic substance and a metal oxide prior to electrical energization of the negative electrodes weakens the adherence of the dots of coagulated colloid to the positive electrode and also prevents an uncontrolled corrosion of the positive electrode. In addition, gas generated as a result of electrolysis upon energizing the negative electrodes is consumed by reaction with the olefinic substance so that there is no gas accumulation between the negative and positive electrodes.

**[0014]** Examples of suitable electrolytically inert metals from which the positive and negative electrodes can be made are stainless steel, platinum, chromium, nickel and aluminum. The positive electrode is preferably made of stainless steel or aluminum so that upon electrical energization of the negative electrodes, dissolution of the passive oxide film on such an electrode generates trivalent ions which then initiate coagulation of the colloid.

**[0015]** The gap which is defined between the positive

and negative electrodes can range from about 50  $\mu$  to about 100  $\mu$ , the smaller the electrode gap the sharper are the dots of coagulated colloid produced. Where the electrode gap is of the order of 50  $\mu$ , the negative electrodes are the preferably spaced from one another by a distance of about 75  $\mu$ .

**[0016]** Examples of suitable olefinic substances which may be used to coat the surface of the positive electrode include unsaturated fatty acids such as arachidonic acid, linoleic acid, linolenic acid, oleic acid and palmitoleic acid and unsaturated vegetable oils such as corn oil, linseed oil, olive oil, peanut oil, soybean oil and sunflower oil. The olefinic substance is advantageously applied onto the positive electrode active surface in the form of an oily dispersion containing the metal oxide as dispersed phase. Examples of suitable metal oxides include aluminum oxide, ceric oxide, chromium oxide, cupric oxide, magnesium oxide, manganese oxide, titanium dioxide and zinc oxide; chromium oxide is the preferred metal oxide. Depending on the type of metal oxide used, the amount of metal oxide may range from about 20 to about 60% by weight, based on the total weight of the dispersion. Preferably, the olefinic substance and the metal oxide are present in the dispersion in substantially equal amounts. A particularly preferred dispersion contains about 50 wt.% of oleic acid or linoleic acid and about 50 wt.% of chromium oxide.

**[0017]** The oily dispersion containing the olefinic substance and the metal oxide is advantageously applied onto the positive electrode active surface by providing a distribution roller extending parallel to the positive cylindrical electrode and having a peripheral coating comprising an oxide ceramic material, applying the oily dispersion onto the ceramic coating to form on a surface thereof a film of the oily dispersion uniformly covering the surface of the ceramic coating, the film of oily dispersion breaking down into micro-droplets containing the olefinic substance in admixture with the metal oxide and having substantially uniform size and distribution, and transferring the micro-droplets from the ceramic coating onto the positive electrode active surface. As explained in Applicant's copending Canadian patent application No. 2,113,535 filed January 14, 1994, the use of a distribution roller having a ceramic coating comprising an oxide ceramic material enables one to form on a surface of such a coating a film of the oily dispersion which uniformly covers the surface of the ceramic coating and thereafter breaks down into micro-droplets containing the olefinic substance in admixture with the metal oxide and having substantially uniform size and distribution. The micro-droplets formed on the surface of the ceramic coating and transferred onto the positive electrode active surface generally have a size ranging from about 1 to about 5 $\mu$ .

**[0018]** A particularly preferred oxide ceramic material forming the aforesaid ceramic coating comprises a fused mixture alumina and titania. Such a mixture may comprise about 60 to about 90 weight % of alumina and

about 10 to about 40 weight % of titania.

**[0019]** According to a preferred embodiment of the invention, the oily dispersion is applied onto the ceramic coating by disposing an applicator roller parallel to the distribution roller and in pressure contact engagement therewith to form a first nip, and rotating the applicator roller and the distribution roller in register while feeding the oily dispersion into the first nip, whereby the oily dispersion upon passing through the first nip forms a film uniformly covering the surface of the ceramic coating. The micro-droplets are advantageously transferred from the distribution roller to the positive electrode by disposing a transfer roller parallel to the distribution roller and in contact engagement therewith to form a second nip, positioning the transfer roller in pressure contact engagement with the positive electrode to form a third nip, and rotating the transfer roller and the positive electrode in register for transferring the micro-droplets from the distribution roller to the transfer roller at the second nip and thereafter transferring the micro-droplets from the transfer roller to the positive electrode at the third nip.

**[0020]** Preferably, the applicator roller and the transfer roller are each provided with a peripheral covering of a resilient material which is resistant to attack by the olefinic substance, such as a synthetic rubber material. For example, use can be made of a polyurethane having a Shore A hardness of about 50 to about 70 in the case of the applicator roller, or a Shore A hardness of about 60 to about 80 in the case of the transfer roller.

**[0021]** In some instances, depending on the type of olefinic substance used, Applicant has noted that the film of oily dispersion only partially breaks down on the surface of the ceramic coating into the desired micro-droplets. Thus, in order to ensure that the film of oily dispersion substantially completely breaks on the ceramic coating into micro-droplets of olefinic substance containing the metal oxide and having substantially uniform size and distribution, step (b)(ii) of the electrocoagulation printing method of the invention is preferably carried out by providing first and second distribution rollers extending parallel to the positive cylindrical electrode and each having a peripheral coating comprising an oxide ceramic material, applying the oily dispersion onto the ceramic coating of the first distribution roller to form on a surface thereof a film of the oily dispersion uniformly covering the surface of the ceramic coating, the film of oily dispersion at least partially breaking down into micro-droplets containing the olefinic substance in admixture with the metal oxide and having substantially uniform size and distribution, transferring the at least partially broken film from the first distribution roller to the second distribution roller so as to cause the film to substantially completely break on the ceramic coating of the second distribution roller into the desired micro-droplets having substantially uniform size and distribution, and transferring the micro-droplets from the ceramic coating of the second distribution roller onto the positive elec-

trode active surface. Preferably, the ceramic coatings of the first distribution roller and the second distribution roller comprise the same oxide ceramic material.

[0022] According to a preferred embodiment, the oily dispersion is applied onto the ceramic coating of the first distribution roller by disposing an applicator roller parallel to the first distribution roller and in pressure contact engagement therewith to form a first nip, and rotating the applicator roller and the first distribution roller in register while feeding the oily dispersion into the first nip, whereby the oily dispersion upon passing through the first nip forms a film uniformly covering the surface of the ceramic coating.

[0023] According to another preferred embodiment, the at least partially broken film of oily dispersion is transferred from the first distribution roller to the second distribution roller and the micro-droplets are transferred from the second distribution roller to the positive electrode by disposing a first transfer roller between the first distribution roller and the second distribution roller in parallel relation thereto, positioning the first transfer roller in pressure contact engagement with the first distribution roller to form a second nip and in contact engagement with the second distribution roller to form a third nip, rotating the first distribution roller and the first transfer roller in register for transferring the at least partially broken film from the first distribution roller to the first transfer roller at the second nip, disposing a second transfer roller parallel to the second distribution roller and in pressure contact engagement therewith to form a fourth nip, positioning the second transfer roller in pressure contact engagement with the positive electrode to form a fifth nip, and rotating the second distribution roller, the second transfer roller and the positive electrode in register for transferring the at least partially broken film from the first transfer roller to the second distribution roller at the third nip, then transferring the micro-droplets from the second distribution roller to the second transfer roller at the fourth nip and thereafter transferring the micro-droplets from the second transfer roller to the positive electrode at the fifth nip.

[0024] Where the positive cylindrical electrode extends vertically, step (b)(iii) of the above electrocoagulation printing method is advantageously carried out by continuously discharging the colloidal dispersion onto the positive electrode active surface from a fluid discharge means disposed adjacent the electrode gap at a predetermined height relative to the positive electrode and allowing the colloidal dispersion to flow downwardly along the positive electrode active surface, the colloidal dispersion being thus carried by the positive electrode upon rotation thereof to the electrode gap to fill same. Preferably, excess colloidal dispersion flowing downwardly off the positive electrode active surface is collected and the collected colloidal dispersion is recirculated back to the fluid discharge means.

[0025] The colloid generally used is a linear colloid of high molecular weight, that is, one having a molecular

weight comprised between about 10,000 and about 1,000,000, preferably between 100,000 and 600,000. Examples of suitable colloids include natural polymers such as albumin, gelatin, casein and agar, and synthetic polymers such as polyacrylic acid, polyacrylamide and polyvinyl alcohol. A particularly preferred colloid is an anionic copolymer of acrylamide and acrylic acid having a molecular weight of about 250,000 and sold by Cyanamid Inc. under the trade mark ACCOSTRENGTH 86. The colloid is preferably used in an amount of about 6.5 to about 12% by weight, and more preferably in an amount of about 7% by weight, based on the total weight of the colloidal dispersion. Water is preferably used as the medium for dispersing the colloid to provide the desired colloidal dispersion.

[0026] The colloidal dispersion also contains a soluble electrolyte and a coloring agent. Preferred electrolytes include alkali metal halides and alkaline earth metal halides, such as lithium chloride, sodium chloride, potassium chloride and calcium chloride. The electrolyte is preferably used in an amount of about 6.5 to about 9% by weight, based on the total weight of the dispersion. The coloring agent can be a dye or a pigment. Examples of suitable dyes which may be used to color the colloid are the water soluble dyes available from HOECHST such as Duasyn Acid Black for coloring in black and Duasyn Acid Blue for coloring in cyan, or those available from RIEDEL-DEHAEN such as Anti-Halo Dye Blue T. Pina for coloring in cyan, Anti-Halo Dye AC Magenta Extra V01 Pina for coloring in magenta and Anti-Halo Dye Oxonol Yellow N. Pina for coloring in yellow. When using a pigment as a coloring agent, use can be made of the pigments which are available from CABOT CORP. such as Carbon Black Monarch<sup>®</sup> 120 for coloring in black, or those available from HOECHST such as Hostaperm Blue B2G or B3G for coloring in cyan, Permanent Rubine F6B or L6B for coloring in magenta and Permanent Yellow DGR or DHG for coloring in yellow. A dispersing agent is added for uniformly dispersing the pigment into the dispersion. Examples of suitable dispersing agents include the non-ionic dispersing agent sold by ICI Canada Inc. under the trade mark SOLSPERSE 27000. The pigment is preferably used in an amount of about 6.5 to about 12% by weight, and the dispersing agent in an amount of about 0.4 to about 6% by weight, based on the total weight of the dispersion.

[0027] After coagulation of the colloid, any remaining non-coagulated colloid is removed from the positive electrode active surface, for example, by scraping the surface with a soft rubber squeegee, so as to fully uncover the colored, coagulated colloid. Preferably, the non-coagulated colloid thus removed is collected and mixed with the collected colloidal dispersion, and the collected colloidal dispersion in admixture with the collected non-coagulated colloid is recirculated back to the aforesaid fluid discharge means.

## BRIEF DESCRIPTION OF DRAWINGS

**[0028]** Further features and advantages of the invention will become more readily apparent from the following description of preferred embodiments as illustrated by way of examples in the accompanying drawings, in which:

Figure 1 is a schematic top plan view of a multicolor electrocoagulation printing apparatus according to a preferred embodiment of the invention, comprising four printing units each using a coloring agent of different color;

Figure 2 is a fragmentary sectional view thereof, showing one of the printing units;

Figure 3 is a view similar to Fig. 2, but showing a different embodiment;

Figure 4 is a fragmentary perspective view of the apparatus illustrated in Fig. 1, showing one of the printing heads used for electrocoagulation of the colloid; and

Figure 5 which is on the same sheet of drawings as Fig. 2 is a fragmentary longitudinal view of the printing head illustrated in Fig. 4.

## MODES FOR CARRYING OUT THE INVENTION

**[0029]** Referring first to Fig. 1, there is illustrated a multicolor electrocoagulation printing apparatus comprising a central positive electrode 20 in the form of a revolving cylinder and four identical printing units 22 arranged around the cylindrical electrode 20. In the embodiment shown, the first printing unit 22A at the left of the figure is adapted to print in yellow color, the second printing unit 22B in magenta color, the third printing unit 22C in cyan color and the fourth printing unit 22D in black color. The cylindrical electrode 20 extends vertically and has a shaft 24 which is driven by a motor (not shown) for rotating the electrode about a vertical axis coincident with the shaft 24. A substrate in the form of a continuous web 26 is fed to the printing units for being imprinted with differently colored images which are transferred at respective transfer stations onto the web in superimposed relation to provide a polychromic image, the web 26 being guided to the respective transfer stations by guide rollers 28.

**[0030]** As best shown in Fig. 2, the printing units 22 each comprise a cleaning device 30 for cleaning the surface 32 of the positive electrode 20, a positive electrode coating device 34 for coating the surface 32 with an olefinic substance and a metal oxide, a polishing brush 36 for polishing the olefin and metal oxide-coated surface 32, a device 38 for discharging a colloid onto the surface 32, a printing head 40 provided with negative

electrodes 42 for electrocoagulating the colloid to form on the positive electrode surface 32 dots of colored, coagulated colloid representative of a desired image and a soft rubber squeegee 44 for removing any remaining non-coagulated colloid from the surface 32. Each printing unit 22 further includes a pressure roller 46 for bringing the web 26 into contact with the dots of colored, coagulated colloid to cause transfer of the colored, coagulated colloid onto the web 26 and thereby imprint the web with the image. As shown in Fig. 1, the provision of two pairs of diametrically opposed pressure rollers 46 arranged about the cylindrical electrode 20 prevents the electrode 20 from flexing since the forces exerted by the rollers 46 of each pair cancel each other out.

**[0031]** The positive electrode cleaning devices 30 each comprise a rotating brush 48 and two high pressure water injectors 50 arranged in a housing 52. Each brush 48 is provided with a plurality of radially extending bristles 54 made of horsehair and having extremities contacting the surface 32. Any coagulated colloid remaining on the surface 32 after transfer of the dots of colored, coagulated colloid at the transfer station of a preceding printing unit is thus removed by the brush 48 and washed away by the powerful jets of water produced by the injectors 50.

**[0032]** The positive electrode coating devices 34 each comprise a vertically extending distribution roller 56, an applicator roller 58 extending parallel to the distribution roller 56 and in pressure contact engagement therewith to form a nip 60, and a transfer roller 62 extending parallel to the roller 56 and in contact engagement therewith to form a nip 64. The transfer roller 62 is in pressure contact engagement with the positive electrode 20 upon rotation thereof. Each coating device 34 further includes a feeding device 68 for supplying to the applicator roller 58 the olefinic substance in the form of an oily dispersion containing the metal oxide as dispersed phase.

**[0033]** The distribution roller 56 has a solid core 70 of metal provided with a peripheral coating 72 of oxide ceramic material. A pair of stub shafts 74 (only one shown) integral with the core 70 extends outwardly from the extremities of the roller 56. The applicator roller 58 and transfer roller 62 also have a solid core 76 of metal, but are provided with a peripheral covering 78 of polyurethane. The rollers 56 and 58 are rotated in register by means of a motor (not shown) driving the shaft 74 of the distribution roller 56. The drive from the motor rotates the distribution roller 56 in a counterclockwise manner, which in turn transmits a clockwise rotation to the applicator roller 58.

**[0034]** The feeding device 68 is adapted to discharge the oily dispersion onto the applicator roller 58 at an upper portion thereof. The dispersion then flows downwardly under gravity along the roller 58 and is carried to the nip 60 by the roller 58 during rotation thereof. The

dispersion upon passing through the nip 60 forms a film uniformly covering the surface of the ceramic coating 70 of the distribution roller 56, the film breaking down into micro-droplets containing the olefinic substance in admixture with the metal oxide and having substantially uniform size and distribution. The micro-droplets formed on the roller 56 are carried by the latter to the nip 64 where they are transferred onto the transfer roller 62. The micro-droplets are then carried by the roller 62 to the nip 66 where they are transferred onto the positive electrode 20.

[0035] The positive electrode coating device 34' illustrated in Fig. 3 is similar to the device 34 shown in Fig. 2, except there are two distribution rollers 56 and 56' with an additional transfer roller 62' arranged therebetween. Such an arrangement ensures that the film of oily dispersion formed on the distribution roller 56 substantially completely breaks down into the desired micro-droplets prior to transfer onto the positive electrode 20, should the film only partially break down on the surface of the ceramic coating 72 of the distribution roller 56. As shown, the transfer roller 62' extends parallel to the distribution rollers 56 and 56' and in pressure contact engagement with the roller 56 to form a nip 80 and permit the roller 62' to be driven by the distribution roller 56 upon rotation thereof, the transfer roller 62' being in contact engagement with the distribution roller 56' to form a nip 64'. The distribution roller 56, applicator roller 58 and transfer roller 62' thus rotate in register. The second distribution roller 56', on the other hand, is in pressure contact engagement with the transfer roller 62 to form a nip 82 and permit the roller 56' to be driven by the transfer roller 62 upon rotation thereof. The distribution roller 56', transfer roller 62 and positive electrode 20 thus rotate in register. Any partially broken film of oily dispersion formed on the surface of the ceramic coating 72 of the distribution roller 56 is transferred from the roller 56 to the transfer roller 62' at the nip 80 and thereafter transferred from the roller 62' to the distribution roller 56' at the nip 64', the film substantially completely breaking down on the surface of the ceramic coating 72 of the roller 56' into the desired micro-droplets having substantially uniform size and distribution. The micro-droplets of olefinic substance containing the metal oxide are then transferred from the roller 56' to the transfer roller 62 at the nip 82 and thereafter transferred from the roller 62 to the positive electrode 20 at the nip 66.

[0036] The polishing brushes 36 used for polishing the olefin and metal oxide-coated surface 32 of the positive electrode 20 are similar to the brushes 48, each brush 36 being provided with a plurality of radially extending bristles 54 made of horsehair and having extremities contacting the surface 32. The friction caused by the bristles 54 contacting the surface 32 upon rotation of the brush 36 has been found to increase the adherence of the micro-droplets onto the positive electrode surface 32.

[0037] As shown in Fig. 4, each printing head 40 com-

prises a cylindrical body 84 mounted between a pair of upper and lower arms 86,86' which are pivotally connected to a column 88 with bushings 90, for pivotal movement of the printing head 40 between an operative position (shown in Figs. 1, 2 and 3) whereat the negative electrodes 42 are spaced from the positive electrode 20 by a constant predetermined gap 92 and a cleaning position (shown in Fig. 4) whereat the negative electrodes 42 are exposed to permit cleaning thereof. The column 88 is mounted on a horizontal beam 94 provided with a metal reinforcing member 96, the beam 94 being supported at a predetermined height by a plurality of vertical beams 98 (only one shown). The column 88 is fixed at its upper end to an attachment arm 100 which is connected to the shaft 24 of the electrode 20. A pair of collars 102,102' fixed to the column 88 support the upper and lower arms 86 and 86', respectively. The printing head 40 includes a pair of stub shafts 104,104' extending through the arms 86 and 86', respectively, bushings 106 being provided to enable the body 84 to be rotated about a vertical axis coincident with the shafts 104,104' and thereby permitting a greater access to the negative electrodes 42 for cleaning same. A releasable locking mechanism (not shown) is provided to secure the body 84 in the desired position.

[0038] The negative electrodes 42 of each printing head 40 are electrically insulated from one another and arranged in rectilinear alignment along the length of the body 84 to define a series of corresponding negative electrode active surfaces 108, as best shown in Fig. 5. In the operative position, the printing head 40 is positioned relative to the positive electrode 20 such that the surfaces 108 of the negative electrodes 42 are disposed in a plane parallel to the central longitudinal axis of the electrode 20 and are spaced from the positive electrode surface 32 by the gap 92. The electrodes 42 are also spaced from one another by a distance at least equal to the electrode gap 92 to prevent edge corrosion of the negative electrodes.

[0039] The device 38 which is used to fill the electrode gap 92 with a colloidal dispersion containing an electrolytically coagulable colloid, a dispersing medium, a soluble electrolyte and a coloring agent comprises an elongated hollow body 110 defining a container for receiving the colloidal dispersion and a fluid discharge nozzle 112 at the lower end of the body 110 for continuously discharging the dispersion onto the positive electrode surface 32. The body 110 is fixed to the upper arm 86 such that when the printing head 40 is in the working position, the nozzle 112 is disposed adjacent the electrode gap 92 at a predetermined height relative to the positive electrode 20. As the colloidal dispersion is being discharged from the nozzle 112 onto the positive electrode surface 32, it flows downwardly along the surface 32 and is carried by the positive electrode 30 upon rotation thereof to the electrode gap 92 to fill same. Excess colloidal dispersion flowing downwardly off the surface 32 is collected in a trough 114 which is con-

ected by conduit 116 to a reservoir 118. A recirculation pump 120 is connected to the reservoir 118 for recirculating the collected dispersion back to the device 38 through conduit 122. The trough 114 has an arcuate outer wall 124 adapted to be contacted by a stop member 126 fixed to the lower arm 86' when the printing head is moved to the operative position, for providing the desired electrode gap 92. A similar stop member 126 is fixed to the upper arm 86 for contact engagement with an abutment member (not shown) disposed above the electrode 20.

**[0040]** Electrical energizing of selected ones of the negative electrodes 42 causes point-by-point selective coagulation and adherence of the colloid onto the olefin and metal oxide-coated surface 32 of the positive electrode 20 opposite the electrode active surfaces 108 of the energized negative electrodes 42 while the electrode 20 is rotating, thereby forming a series of corresponding dots of colored, coagulated colloid representative of a desired image. After electrocoagulation of the colloid, any remaining non-coagulated colloid is removed from the positive electrode surface 32 by the squeegee 44 so as to fully uncover the dots of colored, coagulated colloid adhered on the surface 32. Any non-coagulated colloid removed by the squeegee 44 is collected in the trough 114, mixed with excess colloidal dispersion in the reservoir 118 and the collected non-coagulated colloid in admixture with the excess colloidal dispersion is recirculated back to the device 38 by the pump 120, for discharge onto the positive electrode surface 32.

**[0041]** The optical density of the dots of colored, coagulated colloid may be varied by varying the voltage and/or pulse duration of the pulse-modulated signals applied to the negative electrodes 42. Synchronisation of the data furnished to the printing heads 40 is ensured by proper electronic circuitry (not shown).

**[0042]** The pressure rollers 46 which serve to bring the web 26 into contact with the dots of colored, coagulated colloid at the respective transfer stations are each in pressure contact engagement with the positive electrode 20 to form a nip 128 through which the web 26 is passed and permit the rollers 46 to be driven by the positive electrode 20 upon rotation thereof. As the web 26 is contacted with the dots of colored, coagulated colloid, the colored, coagulated colloid is transferred onto the web 26 to thereby imprint same with the image. The differently colored images produced by the printing units 22A, 22B, 22C and 22D are thus transferred onto the web 26 in superimposed relation to provide a polychromic image. Since a single positive electrode 20 is used and the web 26 contacts only the positive electrode surface 32 upon passing through the respective nip 128 of each transfer station, a polychromic image of high definition is obtained.

## Claims

1. A multicolour electrocoagulation printing method comprising the steps of:
  - a) providing a single positive electrode (20) formed of an electrolytically inert metal and having a continuous passivated surface (32) moving at substantially constant speed along a predetermined path, said passivated surface (32) defining a positive electrode active surface;
  - b) forming on said positive electrode active surface (32) a plurality of dots of coloured, coagulated colloid by electrocoagulation of an electrolytically coagulable colloid in the presence of a colouring agent, said dots of coloured, coagulated colloid being representative of a desired image;
  - c) bringing a substrate (26) into contact with the dots of coloured, coagulated colloid to cause transfer of the coloured, coagulated colloid from the positive electrode active surface (32) onto said substrate (26) and thereby imprint said substrate (26) with the image; and
  - d) repeating steps (b) and (c) several times to define a corresponding number of printing stages arranged at predetermined locations along said path and each using a colouring agent of different colour, and to thereby produce several differently coloured images of coagulated colloid which are transferred at respective transfer positions onto said substrate (26) in superimposed relation to provide a polychromic image.
2. A method according to Claim 1, characterised in that said positive electrode (20) is a cylindrical electrode having a central longitudinal axis and rotating at substantially constant speed about said longitudinal axis, and characterised in that said printing stages are arranged around said positive cylindrical electrode (20).
3. A method according to Claim 1 or to Claim 2, characterised in that step (b) is carried out by:
  - i) providing a plurality of negative electrolytically inert electrodes (42) electrically insulated from one another and arranged in rectilinear alignment to define a series of corresponding negative electrode active surfaces (108) disposed in a plane parallel to the longitudinal axis of said positive electrode (20) and spaced from the positive electrode active surface by a constant predetermined gap (92), said negative electrodes being spaced from one another by a distance at least equal to said electrode gap

(92);

ii) coating the positive electrode active surface (32) with an olefinic substance and a metal oxide to form on said surface micro-droplets of olefinic substance containing the metal oxide;

iii) filling said electrode gap (92) with a substantially liquid colloidal dispersion containing said electrolytically coagulable colloid, said colouring agent, a liquid dispersing medium and a soluble electrolyte;

iv) electrically energizing selected ones of said negative electrodes (42) to cause point-by-point selective coagulation and adherence of the colloid onto the olefin and metal oxide-coated positive electrode active surface (32) opposite the electrode active surfaces (108) of said energized negative electrodes (42) while said positive electrode (20) is rotating, thereby forming said dots of coloured, coagulated colloid; and

v) removing any remaining non-coagulated colloid from said positive electrode active surface.

4. A method according to Claim 3, characterised in that step (b) (ii) is carried out by providing a distribution roller (56) extending parallel to said positive electrode (20) and having a peripheral coating (72) comprising an oxide ceramic material, applying said olefinic substance in the form of an oily dispersion containing said metal oxide as dispersed phase onto the ceramic coating (72) to form on a surface thereof a film of said oily dispersion uniformly covering the surface of said ceramic coating (72), said film of oily dispersion breaking down into micro-droplets containing said olefinic substance in admixture with said metal oxide and having substantially uniform size and distribution, and transferring said micro-droplets from said ceramic coating (72) onto said positive electrode active surface.

5. A method according to any one of Claims 1 to 3, characterised in that it further includes the step of removing after step (c) of each printing stage any remaining coagulated colloid from said positive electrode active surface (32).

6. Multicolour electrocoagulation printing apparatus comprising:

a single positive electrode (20) formed of an electrolytically inert metal and having a continuous passivated surface (32) defining a positive electrode active surface;

means for moving said positive electrode active surface at a substantially constant speed along a predetermined path; and

a plurality of printing units (22) arranged at predetermined locations along said path, each

printing unit (22) comprising:

means (34, 34', 33, 42, 44) for forming on said positive electrode active surface a plurality of dots of coloured, coagulated colloid by electrocoagulation of an electrolytically coagulable colloid in the presence of a colouring agent of different colour, said dots of coloured, coagulated colloid being representative of a desired image; and

means (46) for bringing a substrate (26) into contact with the dots of coloured, coagulated colloid at a respective transfer station to cause transfer of the coloured, coagulated colloid from the positive electrode active surface (32) onto said substrate (26) and thereby imprint said substrate (26) with the image.

7. Apparatus according to Claim 6, characterised in that said positive electrode (20) is a cylindrical electrode having a central longitudinal axis and characterised in that said means for moving said positive electrode active surface includes means for rotating said positive cylindrical electrode about said longitudinal axis, said printing units (22) being arranged around said positive cylindrical electrode (32).

8. Apparatus according to Claim 6 or to Claim 7, characterised in that said means for forming said dots of coloured, coagulated colloid comprises:

a plurality of negative electrolytically inert electrodes (42) electrically insulated from one another and arranged in rectilinear alignment to define a series of corresponding negative electrode active surfaces (108) disposed in a plane parallel to the longitudinal axis of said positive electrode (20) and spaced from the positive electrode active surface (32) by a constant predetermined gap (92), said negative electrodes (42) being spaced from one another by a distance at least equal to said electrode gap (92);

means (34,34') for coating the positive electrode active surface with an olefinic substance and a metal oxide to form on said surface (32) micro-droplets of olefinic substance containing the metal oxide;

means (38) for filling said electrode gap (92) with a substantially liquid colloidal dispersion containing said electrolytically coagulable colloid, said colouring agent, a liquid dispersing medium and a soluble electrolyte;

means for electrically energizing selected ones of said negative electrodes (42) to cause point-by-point selective coagulation and adherence of the colloid onto the olefin and metal oxide-coated positive electrode active surface (32) opposite the electrode active surfaces of said

energized negative electrodes (108) while said positive electrode (20) is rotating, thereby forming said dots of coloured, coagulated colloid; and

means (44) for removing any remaining non-coagulated colloid from said positive electrode active surface.

9. Apparatus according to Claim 3, characterised in that said negative electrodes (42) are arranged in an elongated head (40) along the length thereof, said head (40) having a longitudinal axis and being pivotally movable about a pivot axis extending parallel to the longitudinal axis of said head (40) for moving said negative electrodes (42) between a first position whereat said negative electrode active surfaces (108) are spaced from said positive electrode active surface (32) by said constant predetermined gap (92) and a second position whereat said negative electrode active surfaces (108) are exposed to permit cleaning thereof.

10. Apparatus according to Claim 8, characterised in that said means (34) for coating said positive electrode active surface (32) comprises a distribution roller (56) extending in spaced-apart parallel relation to said positive electrode, said distribution roller having a peripheral coating (72) comprising an oxide ceramic material, applicator means (58,68) for applying said olefinic substance in the form of an oily dispersion containing said metal oxide as dispersed phase onto the ceramic coating (72) to form on a surface thereof a film of said oily dispersion uniformly covering the surface of said ceramic coating (72), said film of oily dispersion breaking down into micro-droplets containing said olefinic substance in admixture with said metal oxide and having substantially uniform size and distribution, and transfer means (62) arranged between said distribution roller (56) and said positive electrode (20) for transferring said micro-droplets from said ceramic coating (72) onto said positive electrode active surface (32).

11. Apparatus according to Claim 8, characterised in that said means (34) for coating said positive electrode surface (32) comprises first and second distribution rollers (56,56') arranged in spaced-apart parallel relation to one another and to said positive electrode (20), said first and second distribution rollers (56,56') each having a peripheral coating (72) comprising an oxide ceramic material, applicator means (58,68) for applying said olefinic substance in the form of an oily dispersion containing said metal oxide as dispersed phase onto the ceramic coating (72) of said first distribution roller (56) to form on a surface thereof a film of said oily dispersion uniformly covering the surface of said

ceramic coating (72), said film of oily dispersion at least partially breaking down into micro-droplets containing said olefinic substance in admixture with said metal oxide and having substantially uniform size and distribution, first transfer means (62') arranged between said first distribution roller (56) and said second distribution roller (56') for transferring the at least partially broken film from said first distribution roller (56) to said second distribution roller (56') so as to cause said film to substantially completely break on the ceramic coating (72) of said second distribution roller (56') into said micro-droplets having a substantially uniform size and distribution, and second transfer means (62) arranged between said second distribution roller (56') and said positive electrode (20) for transferring said micro-droplets from the ceramic coating (72) of said second distribution roller (56') onto said positive electrode active surface (32).

12. Apparatus according to Claim 8, characterised in that each said printing unit (22) further includes means (36) for polishing the olefin and metal oxide-coated positive electrode active surface (32) to increase adherence of said micro-droplets onto said positive electrode active surface (32), prior to filling said electrode gap (92) with said colloidal dispersion.

13. Apparatus according to Claim 8, characterised in that said positive electrode (20) extends vertically and characterised in that said means (38) for filling said electrode gap (92) with said colloidal dispersion comprises fluid discharge means (38) disposed adjacent said electrode gap (92) and at a predetermined height relative to said positive electrode (20) for continuously discharging said colloidal dispersion onto said positive electrode active surface (32), whereby said colloidal dispersion flows downwardly along said positive electrode active surface (32) and is carried by said positive electrode (20) upon rotation thereof to said electrode gap (92) to fill same.

14. Apparatus according to Claim 6 or to Claim 7, characterised in that there are at least two printing units (22) each including one said pressure roller (46) and characterised in that said pressure rollers (46) are arranged in pairs with the pressure rollers (46) of each pair being diametrically opposed to one another.

15. Apparatus according to any one of Claims 6 to 8, characterised in that each said printing unit (22) further includes means (30) for removing any remaining coagulated colloid from said positive electrode active surface (32) after transfer of said dots of coloured, coagulated colloid onto said substrate (26).

16. Apparatus according to Claim 6, characterised in that said electrolytically inert metal is stainless steel or aluminum.
17. Apparatus according to Claim 8, characterised in that said olefinic substance is selected from the group consisting of arachidonic acid, oleic acid, linoleic acid, linolenic acid, palmitoleic acid, corn oil, linseed oil, olive oil, peanut oil, soybean oil and sunflower oil, and characterised in that said metal oxide is selected from the group consisting of aluminum oxide, ceric oxide, chromium oxide, cupric oxide, magnesium oxide, manganese oxide, titanium dioxide and zinc oxide.

### Patentansprüche

1. Mehrfarben-Elektrokoagulationsdruckverfahren mit den folgenden Verfahrensschritten:
- a) Bereitstellen einer einzelnen, positiven Elektrode (20), die aus einem elektrolytisch inaktiven Metall gebildet ist und eine kontinuierlich passivierte Oberfläche (32) aufweist, die sich mit einer im wesentlichen konstanten Geschwindigkeit entlang eines vorbestimmten Weges bewegt, wobei die passivierte Oberfläche (32) eine positive, aktive Elektrodenoberfläche definiert;
- b) Bilden mehrerer gefärbter, koagulierter Kolloidpunkte auf der positiven, aktiven Elektrodenoberfläche (32) mit Hilfe der Elektrokoagulation eines elektrolytisch koagulierbaren Kolloids in Anwesenheit eines Farbagenses, wobei die gefärbten, koagulierten Kolloidpunkte für ein gewünschtes Bild repräsentativ sind;
- c) Herstellen des Kontakts zwischen einem Substrat (26) und den gefärbten, koagulierten Kolloidpunkten, um einen Übertragung des gefärbten, koagulierten Kolloids von der positiven, aktiven Elektrodenoberfläche (32) auf das Substrat (26) zu veranlassen, wodurch das Substrat (26) mit dem Bild bedruckt wird; und
- d) mehrfaches Wiederholen der Schritte b) und c), um eine entsprechende Anzahl von Druckstufen zu definieren, die in vorbestimmten Orten entlang des Weges angeordnet sind und die jeweils ein Farbagens verschiedener Farbe nutzen, wodurch mehrere verschiedenfarbiger Bilder koagulierter Kolloide erzeugt werden, die in einer überlagernden Beziehung in jeweiligen Übertragungsstellungen auf das Substrat (26) übertragen werden, so daß ein mehrfarbiges Bild entsteht.
2. Verfahren nach Anspruch 1, dadurch **gekennzeichnet**, daß die positive Elektrode (20) als eine

zylindrische Elektrode ausgebildet ist, die eine zentrale Längsachse aufweist, und die sich um die Längsachse mit im wesentlichen konstanter Geschwindigkeit dreht, und daß die Druckstufen um die positive, zylindrische Elektrode (20) herum angeordnet sind.

3. Verfahren nach Anspruch 1 oder 2, wobei der Verfahrensschritt b) wie folgt ausgeführt wird:

- i) Bereitstellen mehrerer negativer, elektrolytisch inaktiver Elektroden (42), die von einander elektrisch isoliert sind und in einer geradlinigen Ausrichtung angeordnet sind, um eine Folge entsprechender negativer, aktiver Elektrodenoberflächen (108) zu definieren, die in einer Ebene parallel zur Längsachse der positiven Elektrode (20) angeordnet sind und von der positiven, aktiven Elektrodenoberfläche mit Hilfe eines konstanten, vorbestimmten Spaltes (92) beabstandet sind, wobei die negativen Elektroden in einem Abstand voneinander angeordnet sind, der wenigstens gleich dem Elektrodenspalt (92) ist;
- ii) Beschichten der positiven, aktiven Elektrodenoberfläche (32) mit einer olefinischen Substanz und einem Metalloxid, um auf der Oberfläche Mikrotröpfchen der olefinischen Substanz auszubilden, die das Metalloxid enthalten;
- iii) Füllen des Elektrodenspalt (42) mit einer im wesentlichen flüssigen, kolloidalen Dispersion, die das elektrolytisch koagulierbare Kolloid, das Farbagens, ein flüssiges Dispergierungsmedium und einen löslichen Elektrolyt enthält;
- iv) elektrisches Beaufschlagen von ausgewählten, negativen Elektroden der negativen Elektroden (42), um Punkt für Punkt eine selektive Koagulation und Haftung des Kolloids an der mit Olefin und Metalloxid beschichteten, positiven, aktiven Elektrodenoberfläche (32) zu veranlassen, die den aktiven Elektrodenoberflächen (108) der beaufschlagten negativen Elektroden (42) gegenüberliegt, wobei sich die positive Elektrode (20) hierbei dreht, wodurch die gefärbten, koagulierten Kolloidpunkte ausgebildet werden; und
- v) Entfernen jeglichen verbleibenden nicht koagulierten Kolloids von der positiven, aktiven Elektrodenoberfläche.

4. Verfahren nach Anspruch 3, dadurch **gekennzeichnet**, daß der Verfahrensschritt b) ii) dadurch ausgeführt wird:

- daß eine Verteilenwalze (56) vorgesehen ist, die sich parallel zur positiven Elektrode (20)

erstreckt und eine äußere Beschichtung (72) aufweist, die ein Oxid-Keramik-Material enthält,

- daß die olefinische Substanz in Form einer öligen Dispersion, die das Metalloxid in der dispergierten Phase enthält, auf die Keramikbeschichtung (72) angewendet wird, um auf einer Oberfläche der Keramikbeschichtung (72) einen Film der öligen Dispersion zu bilden, der die Oberfläche der Keramikbeschichtung (72) gleichmäßig bedeckt, wobei der Film der öligen Dispersion in Mikrotropfchen zerfällt, die die olefinische Substanz mit einer Beimischung des Metalloxids enthalten, und die eine im wesentlichen gleichmäßige Größe und Verteilung aufweisen, und
  - daß die Mikrotropfchen von der Keramikbeschichtung (72) auf die positive, aktive Elektrodenoberfläche übertragen werden.
5. Verfahren nach einem der Ansprüche 1 bis 3, **gekennzeichnet** durch den weiteren Verfahrensschritt: Entfernen jeglichen verbleibenden koagulierten Kolloids von der positiven, aktiven Elektrodenoberfläche (32) nach Verfahrensschritt c) jeder Druckstufe.
6. Mehrfarben-Elektrokoagulationsdruckvorrichtung, die Vorrichtung aufweisend:
- eine positive Elektrode (20), die aus einem elektrolytisch inaktiven Metall gebildet ist und eine kontinuierlich passivierte Oberfläche (32) aufweist, welche eine positive, aktive Elektrodenoberfläche definiert;
  - Mittel zum Bewegen der positiven, aktiven Elektrodenoberfläche mit einer im wesentlichen konstanten Geschwindigkeit entlang eines vorbestimmten Weges; und
  - mehrere Druckeinheiten (22), die in vorbestimmten Stellungen entlang des Weges angeordnet sind, jede Druckeinheit (22) aufweisend:
  - Mittel (34, 34', 38, 42, 44) zum Ausbilden mehrerer gefärbter, koagulierter Kolloidpunkte auf der positiven, aktiven Elektrodenoberfläche mit Hilfe der Elektrokoagulation eines elektrolytisch koagulierbaren Kolloids in der Anwesenheit eines verschiedenfarbigen, gefärbten Agens, wobei die gefärbten, koagulierten Kolloidpunkte für ein gewünschtes Bild repräsentativ sind; und
  - Mittel (46), um ein Substrat (26) in einer jeweiligen Übertragungsstation mit den gefärbten, koagulierten Kolloidpunkten in Kontakt zu bringen, so daß eine Übertragung des gefärbten, koagulierten Kolloids von der positiven, aktiven Elektrodenoberfläche (32) auf das Substrat (26) veranlaßt wird, wodurch das Substrat (26)

mit dem Bild bedruckt wird.

7. Vorrichtung nach Anspruch 6, dadurch **gekennzeichnet**, daß die positive Elektrode (26) als eine zylindrische Elektrode ausgebildet ist, die eine zentrale Längsachse aufweist, und daß die Mittel zum Bewegen der positiven, aktiven Elektrodenoberfläche Mittel zum Drehen der positiven, zylindrischen Elektrode um die Längsachse umfassen, wobei die Druckeinheiten (22) um die positive, zylindrische Elektrode (32) herum angeordnet sind.
8. Vorrichtung nach Anspruch 6 oder 7, die Mittel zum Ausbilden der gefärbten, koagulierten Kolloidpunkte aufweisend:
- mehrere negative, elektrolytisch inaktiven Elektroden (42), die voneinander elektrische isoliert sind und in einer geradlinigen Ausrichtung angeordnet sind, um eine Folge entsprechender negativer, aktiver Elektrodenoberflächen (108) zu definieren, die in einer Ebene parallel zu der Längsachse der positiven Elektrode (20) angeordnet sind und durch einen konstanten, vorbestimmten Spalt (92) von der positiven, aktiven Elektrodenoberfläche (32) beabstandet sind, wobei die negativen Elektroden (42) in einem Abstand voneinander beabstandet sind, der wenigstens gleich dem Elektrodenspalt (92) ist;
  - Mittel (34, 34') zur Beschichtung der positiven, aktiven Elektrodenoberfläche mit einer olefinischen Substanz und einem Metalloxid, um auf der Oberfläche (32) Mikrotropfchen der olefinischen Substanz zu bilden, die das Metalloxid enthalten;
  - Mittel (38) zum Füllen des Elektrodenspalt (32) mit einer im wesentlichen flüssigen, kolloidalen Dispersion die das elektrolytisch koagulierbare Kolloid, das Farbagens, ein flüssiges Dispergierungsmedium und einen löslichen Elektrolyt enthält;
  - Mittel für elektrische Beaufschlagung ausgewählter negativer Elektroden (42), um Punkt für Punkt eine getrennte Koagulation und Haftung des Kolloids auf der mit Olefin und Metalloxid beschichteten, positiven, aktiven Elektrodenoberfläche (32) zu veranlassen, die der aktiven Elektrodenoberfläche der beaufschlagten negativen Elektroden (108) gegenüberliegt, wobei sich die positive Elektrode (20) hierbei dreht, wodurch die gefärbten, koagulierten Kolloidpunkte gebildet werden; und
  - Mittel (44) zum Entfernen jeglichen verbleibenden nicht-koagulierten Kolloids von der positiven, aktiven Elektrodenoberfläche.
9. Vorrichtung nach Anspruch 8, dadurch **gekenn-**

zeichnet, daß die negativen Elektroden (42) entlang der Länge eines gestreckten Kopfes (40) angeordnet sind, wobei der Kopf (40) eine Längsachse aufweist und um eine Schwenkachse geschwenkt werden kann, die sich parallel zur Längsachse des Kopfes (40) erstreckt, um die negativen Elektroden (42) zwischen einer ersten Stellung und einer zweiten Stellung zu bewegen, wobei die negativen, aktiven Elektrodenoberflächen (108) in der ersten Stellung durch den konstanten, vorbestimmten Spalt (42) von den positiven, aktiven Elektrodenoberflächen beabstandet sind, und wobei die negativen, aktiven Elektrodenoberflächen (108) in der zweiten Stellung freiliegend sind, um eine Reinigung zu ermöglichen.

10. Vorrichtung nach Anspruch 8, die Mittel (34) zum Beschichten der positiven, aktiven Elektrodenoberfläche (32) aufweisend:

- eine Verteilerwalze (56), die sich beabstandet und parallel zu der positiven Elektrode erstreckt, wobei die Verteilerwalze eine äußere Beschichtung (72) aufweist, die ein Oxid-Keramik-Material umfaßt,
- Anwendungsmittel (58, 68) zum Anwenden der olefinischen Substanz in Form einer öligen Dispersion, die das Metalloxid in der dispergierten Phase enthält, auf die Keramikbeschichtung (72), um auf einer Oberfläche der Keramikbeschichtung (72) einen Film der öligen Dispersion zu bilden, der die Oberfläche der Keramikbeschichtung (72) gleichmäßig bedeckt, wobei der Film der öligen Dispersion in Mikrotröpfchen zerfällt, die die olefinische Substanz mit einer Beimischung des Metalloxids enthalten und eine im wesentlichen gleiche Größe und Verteilung aufweisen, und
- Übertragungsmittel (62), die zwischen der Verteilerwalze (56) und der positiven Elektrode (20) zur Übertragung der Mikrotröpfchen von der Keramikbeschichtung (72) auf die positive, aktive Elektrodenoberfläche (32) angeordnet sind.

11. Vorrichtung nach Anspruch 8, die Mittel (34') zur Beschichtung der positiven Elektrodenoberfläche (32) aufweisend:

- erste und zweite Verteilerwalzen (56, 56'), die beabstandet und parallel zueinander und zu der positiven Elektrode (20) angeordnet sind, wobei die ersten und die zweiten Verteilerwalzen (56, 56') jeweils eine äußere Beschichtung (72) aufweisen, die ein Oxid-Keramik-Material enthält,
- Anwendungsmittel (58, 68) zum Anwenden der

olefinischen Substanz in Form einer öligen Dispersion, die das Metalloxid in der dispergierten Phase enthält, auf die Keramikbeschichtung (72) der ersten Verteilerwalze (56), um auf einer Oberfläche der ersten Verteilerwalze (56) einen Film der öligen Dispersion zu bilden, der die Oberfläche der Keramikbeschichtung (72) gleichmäßig bedeckt, wobei der Film der öligen Dispersion wenigstens teilweise in Mikrotröpfchen zerfällt, die die olefinische Substanz mit einer Beimischung des Metalloxids enthalten, und die im wesentlichen eine gleichmäßige Größe und Verteilung aufweisen,

- erste Übertragungsmittel (62'), die zwischen der ersten Verteilerwalze (65) und der zweiten Verteilerwalze (56') zur Übertragung des wenigstens teilweise zerfallenen Films von der ersten Verteilerwalze (56) auf die zweite Verteilerwalze (56') so angeordnet sind, daß der Film im wesentlichen vollständig auf der Keramikbeschichtung (72) der zweiten Verteilerwalze (56') in die Mikrotröpfchen zerfällt, die eine im wesentlichen gleichmäßige Größe und Verteilung aufweisen, und
- zweite Übertragungsmittel (62), die zwischen der zweiten Verteilerwalze (56) und der positiven Elektrode (20) zur Übertragung der Mikrotröpfchen von der Keramikbeschichtung (72) der zweiten Verteilerwalze (56') auf die positive, aktive Elektrodenoberfläche (32) angeordnet sind.

12. Vorrichtung nach Anspruch 8, wobei jede der Druckeinheiten (22) weiterhin Mittel (36) zum Polieren der mit Olefin und Metalloxid beschichteten, positiven, aktiven Elektrodenoberfläche (32) vor dem Füllen des Elektrodenspalt (92) mit der kolloidalen Dispersion umfaßt, um die Haftung der Mikrotröpfchen auf der positiven, aktiven Elektrodenoberfläche (32) zu verbessern.

13. Vorrichtung nach Anspruch 8, dadurch gekennzeichnet, daß sich die positive Elektrode (20) quer erstreckt, und daß die Mittel (38) zum Füllen des Elektrodenspalt (92) mit der kolloidalen Dispersion Fluidausstoßmittel (38) umfassen, die ihr das kontinuierliche Ausstoßen der kolloidalen Dispersion auf die positive, aktive Elektrodenoberfläche (32) benachbart zu dem Elektrodenspalt (92) und in einer vorbestimmten Höhe relativ zu der positiven Elektrode (20) angeordnet sind, wobei die kolloidale Dispersion entlang der positiven, aktiven Elektrodenoberfläche 32 abwärts fließt und mittels der positiven Elektrode (20) bei deren Drehung zu dem Elektrodenspalt (92) getragen wird, um diesen zu füllen.

14. Vorrichtung nach Anspruch 6 oder 7, dadurch **gekennzeichnet**, daß wenigstens zwei Druckeinheiten (22) vorgesehen sind, die jeweils eine der Druckwalzen (46) umfassen, und daß die Druckwalzen (46) paarweise angeordnet sind, wobei Paare der Druckwalzen (46) diametral zueinander angeordnet sind. 5
15. Vorrichtung nach einem der Ansprüche 6 bis 8, dadurch **gekennzeichnet**, daß jede der Druckeinheiten (22) Mittel (30) zum Entfernen jeglichen verbleibenden koagulierten Kolloids von der positiven, aktiven Elektrodenoberfläche (32) nach der Übertragung der gefärbten, koagulierten Kolloidpunkte auf das Substrat (26) umfaßt. 10
16. Vorrichtung nach Anspruch 6, dadurch **gekennzeichnet**, daß das elektrolytische Edelmetall ein rostfreier Stahl oder Aluminium ist. 20
17. Vorrichtung nach Anspruch 8, dadurch **gekennzeichnet**, daß die olefinische Substanz aus einer Gruppe ausgewählt ist, die Arachidonsäure, Ölsäure, Linolsäure, Linolensäure, Palmitoleinsäure, Maisöl, Leinsamenöl, Olivenöl, Erdnußöl, Sojabohnenöl und Sonnenblumenöl umfaßt, und daß das Metalloxid aus einer Gruppe ausgewählt ist, die Aluminiumoxid, Cerdioxid, Chromoxid, Kupferoxid, Magnesiumoxid, Maganoxid, Titandioxid und Zinkoxid umfaßt. 25  
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## Revendications

1. Procédé d'impression en couleurs par électrocoagulation, comprenant les étapes suivantes : 35
- a) la disposition d'une électrode positive unique (20) formée d'un métal électrolytiquement inerte et ayant une surface passivée continue (32) qui se déplace à une vitesse pratiquement constante le long d'un trajet prédéterminé, la surface passivée (32) délimitant une surface active d'électrode positive, 40
- b) la formation, à la surface active (32) d'électrode positive, de plusieurs points d'un colloïde coloré coagulé par électrocoagulation d'un colloïde électrolytiquement coagulable en présence d'un agent de coloration, les points du colloïde coloré coagulé étant représentatifs d'une image voulue, 50
- c) la mise d'un substrat (26) au contact des points du colloïde coloré coagulé pour provoquer le report du colloïde coloré coagulé de la surface active (32) d'électrode positive au substrat (26) et pour l'impression de cette manière du substrat (26) par l'image, et 55
- d) la répétition des étapes (b) et (c) plusieurs fois pour la délimitation d'un nombre corres-
- pondants d'étages d'impression occupant des emplacements prédéterminés le long dudit trajet et utilisant chacun un agent de coloration d'une couleur différente, avec production de cette manière de plusieurs images de couleurs différentes du colloïde coagulé qui sont reportées à des positions respectives de report sur le substrat (26) sous forme superposée pour la formation d'une image polychrome.
2. Procédé selon la revendication 1, caractérisé en ce que l'électrode positive (20) est une électrode cylindrique ayant un axe longitudinal central et tournant à une vitesse pratiquement constante autour de l'axe longitudinal, caractérisé en ce que les étages d'impression sont placés autour de l'électrode cylindrique positive (20).
3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'étape (b) est exécutée par les opérations suivantes :
- (i) la disposition de plusieurs électrodes électrolytiquement inertes négatives (42) isolées électriquement les unes des autres et formant un alignement rectiligne pour la délimitation d'une série de surfaces actives correspondantes (108) d'électrodes négatives disposées dans un plan parallèle à l'axe longitudinal de l'électrode positive (20) et séparées de la surface active de l'électrode positive par un espace prédéterminé constant (92), les électrodes négatives étant séparées les unes des autres par une distance au moins égale à l'espace (92) des électrodes,
- (ii) le revêtement de la surface active (32) de l'électrode positive d'une substance oléfinique et d'un oxyde métallique pour la formation sur la surface de microgouttelettes d'une substance oléfinique contenant l'oxyde métallique,
- (iii) le remplissage de l'espace (92) des électrodes par une dispersion colloïdale pratiquement liquide contenant le colloïde électrolytiquement coagulable, l'agent de coloration, un fluide de dispersion liquide et un électrolyte soluble,
- (iv) l'excitation électrique de certaines électrodes choisies parmi les électrodes négatives (42) pour provoquer une coagulation et une adhérence sélectives point par point du colloïde sur la surface active (32) d'électrode positive revêtue de l'oléfine et de l'oxyde métallique, opposée aux surfaces actives (108) des électrodes négatives excitées (42), pendant que l'électrode positive (20) tourne, avec formation de cette manière des points du colloïde coloré coagulé, et
- (v) l'extraction de tout colloïde non coagulé restant de la surface active d'électrode positive.

4. Procédé selon la revendication 3, caractérisé en ce que l'étape (b)(ii) est exécutée par disposition d'un rouleau (56) de distribution qui est parallèle à l'électrode positive (20) et ayant un revêtement périphérique (72) qui comprend un matériau céramique d'oxyde, par application de la substance oléfinique sous forme d'une dispersion huileuse contenant l'oxyde métallique en phase dispersée sur le revêtement céramique (72) pour la formation, sur une surface de celui-ci, d'un film de la dispersion huileuse recouvrant uniformément la surface du revêtement céramique (72), le film de la dispersion huileuse se divisant en microgouttelettes contenant la substance oléfinique mélangée à l'oxyde métallique et ayant une dimension et une distribution pratiquement uniformes, et par transfert des microgouttelettes du revêtement céramique (72) à la surface active d'électrode positive.
5. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce qu'il comprend en outre une étape d'extraction, après l'étape (c) de chaque étage d'impression, du colloïde coagulé qui peut rester à la surface active (32) de l'électrode positive.
6. Appareil d'impression en couleurs par électrocoagulation, comprenant :
- une électrode positive unique (20) formée d'un métal électrolytiquement inerte et ayant une surface passivée continue (32) délimitant une surface active d'électrode positive,
  - un dispositif de déplacement de la surface active d'électrode positive à une vitesse pratiquement constante le long d'un trajet prédéterminé, et
  - plusieurs unités d'impression (22) occupant des emplacements prédéterminés le long dudit trajet, chaque unité d'impression (22) comprenant :
    - un dispositif (34, 34', 38, 42, 44) destiné à former, sur la surface active de l'électrode positive, plusieurs points d'un colloïde coloré coagulé par électrocoagulation d'un colloïde électrolytiquement coagulable en présence d'un agent de coloration d'une couleur différente, les points du colloïde coloré coagulé étant représentatifs d'une image voulue, et
    - un dispositif (46) destiné à mettre un substrat (26) au contact des points du colloïde coloré coagulé à un poste respectif de report pour provoquer le report du colloïde coloré coagulé de la surface active (32) d'électrode positive sur le substrat (26) et ainsi pour imprimer le substrat (26) avec l'image.
7. Appareil selon la revendication 6, caractérisé en ce que l'électrode positive (20) est une électrode cylindrique ayant un axe longitudinal central, et caractérisé en ce que le dispositif de déplacement de la surface active d'électrode positive comprend un dispositif destiné à faire tourner l'électrode cylindrique positive autour de l'axe longitudinal, les unités d'impression (22) étant placées autour de l'électrode cylindrique positive (32).
8. Appareil selon la revendication 6 ou 7, caractérisé en ce que le dispositif destiné à former les points du colloïde coloré coagulé comprend :
- plusieurs électrodes négatives électrolytiquement inertes (42) isolées électriquement les unes des autres et placées suivant un alignement rectiligne pour la délimitation d'une série de surfaces actives (108) d'électrodes négatives correspondantes disposées dans un plan parallèle à l'axe longitudinal de l'électrode positive (20) et séparées de la surface active (32) de l'électrode positive par un espace prédéterminé constant (92), les électrodes négatives (42) étant séparées les unes des autres par une distance au moins égale à l'espace (92) des électrodes,
  - un dispositif (34, 34') de revêtement de la surface active d'électrode positive d'une substance oléfinique et d'un oxyde métallique pour la formation, sur cette surface (32), de microgouttelettes d'une substance oléfinique contenant l'oxyde métallique,
  - un dispositif (38) destiné à remplir l'espace (92) entre les électrodes d'une dispersion colloïdale pratiquement liquide contenant le colloïde électrolytiquement coagulable, l'agent de coloration, un fluide de dispersion liquide et un électrolyte soluble,
  - un dispositif d'excitation électrique d'électrodes choisies parmi les électrodes négatives (42) pour provoquer la coagulation et l'adhérence sélective point à point du colloïde sur la surface active (32) d'électrode positive revêtue de l'oléfine et de l'oxyde métallique, opposée aux surfaces actives des électrodes négatives excitées (108) pendant que l'électrode positive (20) tourne, avec formation de cette manière des points du colloïde coloré coagulé, et
  - un dispositif (44) d'extraction du colloïde non coagulé pouvant rester de la surface active d'électrode positive.
9. Appareil selon la revendication 8, caractérisé en ce que les électrodes négatives (42) sont disposées dans une tête allongée (40) suivant leur longueur, la tête (40) ayant un axe longitudinal et étant mobile par pivotement autour d'un axe de pivot qui est parallèle à l'axe longitudinal de la tête (40) afin que

les électrodes négatives (42) puissent être déplacées entre une première position dans laquelle les surfaces actives (108) d'électrodes négatives sont séparées de la surface active (32) de l'électrode positive par l'espace prédéterminé contant (92), et une seconde position dans laquelle les surfaces actives (108) d'électrodes négatives sont exposées pour permettre leur nettoyage.

10. Appareil selon la revendication 8, caractérisé en ce que le dispositif (34) de revêtement de la surface active (32) d'électrode positive comprend un rouleau de distribution (56) qui est parallèle à l'électrode active et distante de celle-ci, le rouleau de distribution ayant un revêtement périphérique (72) comprenant un matériau céramique d'oxyde, un dispositif applicateur (58, 68) destiné à appliquer la substance oléfinique sous forme d'une dispersion huileuse contenant l'oxyde métallique sous forme d'une phase dispersée sur le revêtement céramique (72) pour la formation, sur une surface de celui-ci, d'un film de la dispersion huileuse recouvrant uniformément la surface du revêtement céramique (72), le film de la dispersion huileuse se divisant en microgouttelettes contenant la substance oléfinique mélangée à l'oxyde métallique et ayant une dimension et une distribution pratiquement uniformes, et un dispositif de transfert (62) placé entre le rouleau de distribution (56) et l'électrode active (20) pour le transfert des microgouttelettes du revêtement céramique (72) à la surface active (32) de l'électrode positive.
11. Appareil selon la revendication 8, caractérisé en ce que le dispositif (34) de revêtement de la surface active (32) de l'électrode positive comporte un premier et un second rouleau de distribution (56, 56') placés parallèlement l'un à l'autre et à l'électrode positive (20) à une certaine distance l'un de l'autre, le premier et le second rouleau de distribution (56, 56') ayant chacun un revêtement périphérique (72) comprenant un matériau céramique d'oxyde, un dispositif applicateur (58, 68) destiné à appliquer la substance oléfinique sous forme d'une dispersion huileuse contenant l'oxyde métallique en phase dispersée sur le revêtement céramique (72) du premier rouleau de distribution (56) pour la formation, sur une surface de celui-ci, d'un film de la dispersion huileuse qui recouvre uniformément la surface du revêtement céramique (72), le film de la dispersion huileuse se divisant au moins partiellement en microgouttelettes contenant la substance oléfinique mélangée à l'oxyde métallique et ayant une dimension et une distribution pratiquement uniformes, un premier dispositif de transfert (62') placé entre le premier rouleau de distribution (56) et le second rouleau de distribution (56') pour le transfert du film au moins partiellement divisé du premier rouleau

de distribution (56) au second rouleau de distribution (56') afin que le film se divise pratiquement totalement sur le revêtement céramique (72) du second rouleau de distribution (56') en microgouttelettes ayant une dimension et une distribution pratiquement uniformes, et un second dispositif de transfert (62) placé entre le second rouleau de distribution (56') et l'électrode positive (20) pour le transfert des microgouttelettes du revêtement céramique (72) du second rouleau de distribution (56') à la surface active (32) de l'électrode positive.

12. Appareil selon la revendication 8, caractérisé en ce que chaque unité d'impression (22) comporte en outre un dispositif (36) de polissage de la surface active (32) de l'électrode positive revêtue de l'oléfine et de l'oxyde métallique afin que l'adhérence des microgouttelettes à la surface active (32) de l'électrode positive soit accrue avant le remplissage de l'espace (92) des électrodes par la dispersion colloïdale.
13. Appareil selon la revendication 8, caractérisé en ce que l'électrode positive (20) est disposée verticalement, caractérisé en ce que le dispositif (38) de remplissage de l'espace (92) des électrodes par la dispersion colloïdale comporte un dispositif (38) d'évacuation de fluide placé afin qu'il soit adjacent à l'espace (92) des électrodes et à une hauteur prédéterminée par rapport à l'électrode positive (20) afin qu'il évacue de façon continue la dispersion colloïdale sur la surface active (32) de l'électrode positive, si bien que la dispersion colloïdale s'écoule le long de la surface active (32) de l'électrode positive et est entraînée par l'électrode positive (20) lors de la rotation de celle-ci vers l'espace (92) entre les électrodes afin que cet espace soit rempli.
14. Appareil selon la revendication 6 ou 7, caractérisé en ce que deux unités d'impression au moins (22) sont incorporées, chacune comprenant un rouleau de pression (46), caractérisé en ce que les rouleaux de pression (46) sont placés sous forme appariée, les rouleaux de pression (46) de chaque paire étant diamétralement opposés.
15. Appareil selon l'une quelconque des revendications 6 à 8, caractérisé en ce que chaque unité d'impression (22) comprend en outre un dispositif (30) d'extraction du colloïde coagulé pouvant rester à la surface active (32) de l'électrode positive après le report des points du colloïde coloré coagulé sur le substrat (26).
16. Appareil selon la revendication 6, caractérisé en ce que le métal électrolytiquement inerte est l'acier inoxydable ou l'aluminium.

17. Appareil selon la revendication 8, caractérisé en ce que la substance oléfinique est choisie dans le groupe constitué par l'acide arachidonique, l'acide oléique, l'acide linoléique, l'acide linoléique, l'acide palmitoléique, l'huile de maïs, l'huile de lin, l'huile d'olive, l'huile d'arachide, l'huile de soja et l'huile de tournesol, caractérisé en ce que l'oxyde métallique est choisi dans le groupe formé par l'oxyde d'aluminium, l'oxyde cérique, l'oxyde de chrome, l'oxyde cuivrique, l'oxyde de magnésium, l'oxyde de manganèse, le bioxyde de titane et l'oxyde de zinc.

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