Patented Aug. 21, 1934 1,970,539

UNITED STATES PATENT OFFICE

1,970,539

PROCESS FOR ELECTROCHEMICALLY PRODUCING STABLE IMAGES AND CHARACTERS

Viktor Bausch, Jr., Berlin, Germany

No Drawing. Application February 16, 1932, Serial No. 593,428. In Germany February 21, 1931

24 Claims. (Cl. 204—1)

It is known to produce characters electrochemically by bringing a paper saturated with the solution of an electrolyte between electrodes, a coloured material being produced at the points at which the electric current passes.

The coloured substance which forms the characters may be produced firstly from the decomposition products of the electrolyte, e. g. from potassium iodide, secondly by the action of the ions activated by the electrolysis on a reagent present in the paper, e. g. production of the blue colour by kathodic treatment of thymolphthalein, thirdly by anodic oxidation of leuco bases to their corresponding dyestuffs, e. g. anodic oxidation (tetramethyl-p-diamino triphenylmethane to malachite green), fourthly by producing organic metal compounds by means of a soluble metal electrode from which metal ions are discharged during the passage of current, said ions forming a coloured compound or a lake with a suitable organic substance, fifthly by kathodic reduction of salts which form hydrogen sulphide and secondary production of coloured metal sulphides.

All these known process have substantial disadvantages. The iodine marks, very precise and produced by means of very low current strengths, are not absolutely stable owing to the high vapour pressure of iodine. In addition, the high price of iodine compounds imposes narrow limits upon the economical use of these substances.

When soluble electrodes are used, which, it is true, produce stable marks or images, there is the substantial disadvantage that the electrode, more particularly the anode, is so much attacked in a very short time that it must be replaced, so that continuous working, more particularly on the so-called tape writing machines is impossible. The secondary production of coloured metal sulphides by the primary kathodic reduction of salts which form hydrogen sulphide cannot come into consideration when only small current strengths are available or a very high speed of writing is required, such as for example, in picture telegraphy, since this reaction requires a very high electrical output on account of its sluggishness.

Those processes which depend on the production of coloured reaction products by anodic oxidation of more particularly organic bodies or by the secondary reaction of organic agents with the cations or anions activated from a conducting electrolyte by electrolysis certainly have the advantage of the insoluble electrodes, but on the other hand they also have the substantial disadvantage that the organic agents which come into question either all tend to autoxidize or else the coloured reaction products produced are unstable. As a result, either the paper which has not yet been passed through the writing apparatus is not stable in the prepared condition or else the characters produced disappear again after a time, or again those places of the image which ought to remain white colour over after a time.

In particular the organic bodies which react in a secondary reaction with cations or anions activated from the conducting electrolyte by the electrolysis either alone or in presence of a further reagent which promotes the production of dyestuff, with formation of a sufficiently stable colouring material, all have the disadvantageous property of colouring in the atmosphere, so that the white places of the image become so dark after a short time that the picture or the writing can no longer be recognized. In the converse case the electrochemically produced colouring material of the characters or images, is unstable so that after a short time the said characters or images bleach out, particularly in the light, the white places of the image naturally being retained. Practically only those agents come into consideration, therefore, the primary or secondary electrolytically produced decomposition products of which comprise stable dyestuffs or colouring materials.

The practical use of such agents, however, necessitates the elimination of spontaneous subsequent colouring of the white places of the image by the action of the atmosphere of the light.

According to the present invention this is produced by changing, eliminating or removing from the image support one or several colour-forming agents, directly or only a short time after the passage through the electrodes or directly or a short time after the image has been made, in such a way that the possibility of further formation of colour or dyestuff, either by interior or exterior influences, is excluded.

This action, which corresponds somewhat to the fixing of a photographic plate, could be brought about by means of a chemical after-treatment. Such an after-treatment, however, is very difficult to carry out practically and in the case of many telegraphic apparatus cannot be carried out at all.

Preferably the removal of one or several of the colour-farming agents or else the rendering of the same innocuous as regards further formation of colour, is effected by using for the

colour-forming agent such a body or such bodies which volatilize during the drying of the image support which is always to be written on whilst moist.

It is known electrochemically to produce images by anodic oxidation, for example, of aromatic amines. If, instead of the solid aromatic amines hitherto used, an amine is chosen which volatilizes during the drying of the image support, which, however, can be oxidized very readily to a very stable dyestuff or colouring material, then no further colouring can occur in the white places of the image by subsequent autoxidation of the amine since this is no longer present, and the image is to a certain extent fixed.

In place of the anodic oxidation of a suitable volatile amine other volatile bodies may also be used as the colour-forming agent whch show this characteristic. Preferably only such bodies are used which volatilize more slowly than water. For example, volatile hydroxy-benzenes or hydroxy-napthalenes, or derivatives thereof, inasmuch as they are sufficiently volatile, come into consideration, either alone or together with another organic or inorganic agent with which they further react to form a colour or dye, preferably in an alkaline medium, which is formed by the electrolytically activated cations from the neutral or slightly acid conducting electrolyte. This process also has the advantage that when writing kathodically the electrode which does the writing need not consist of noble metal. The employment of volatile substances as colour-forming bodies comes more particularly into consideration for the continuously operating so-called tape writers which are fed with moist rolls of electro-chemically sensitive paper. The volatile agent is very well excluded from air and light in the moist rolls. Since the moist rolls must be stored in such a way that the moisture necessary for the electrolytic process cannot be lost, a premature volatilization of the volatile agent is impossible. After the paper strip has passed from the roll through the electrodes, the image support soon dries, the unreacted colour-forming agent volatilizing at the same time.

According to the foregoing description the action of the atmosphere is to be used as the means for fixing the marks produced, i. e. the heat of the room, the sensitive colour-forming agent being expelled from the image support by volatilization. Light can also be used in a similar manner as the fixing agent. According to the invention in this case those bodies are to be used as colour-forming agent which have the property of reacting by ordinary electrochemical attack, directly or indirectly, e. g. by way of a conducting electrolyte, alone or in combination with another body, with formation of colour, and which lose this property as soon as they have been exposed to the light.

These properties are shown, for example, by the light sensitive diazo-compounds (Liesegangs photographisches Archiv 1891, page 143; Eders Jahrbuch 1892, page 458; Photographische Korrespondenz 1895; Ber. 1902, Teil 34, p. 1668; Plotnikow, Lehrbuch der allgemeinen Photochemie, 1920, p. 540 ff).

Such diazo-compounds are extraordinarily stable in neutral or weakly acid media provided they are kept away from the influence of light; on the other hand they are so sensitive as well that by a small displacement of the hydrogen ion concentration of the surrounding medium towards the alkali side they instantly enter into combination with themselves or with a phenol present or one of the known azo components with the formation of extremely stable azo dyestuff. If now such diazo-compounds which are sensitive to light, i. e. are decomposed by light, are used as colour-forming bodies in the image support, then the sensitivity in all the white places of the image is completely removed as soon as the completed image has been exposed for a short time to a natural or artificial source of light. Light sensitive diazo-compounds come into consideration which unite with an azo component in alkaline medium which is applied from the first or incorporated with the image support together with the diazo compound and the conducting electrolyte, or else is added only immediately before the passage through the electrodes, or which combines with itself to form a dyestuff without any such components.

The process is not limited to the employment of diazo compounds. Other organic or inorganic bodies may be used which may be capable of forming dyestuff inasmuch as they lose this capability of responding to the light or other action.

Examples

1. Absorbent paper is thoroughly saturated with an aqueous solution of 10 parts by weight of potassium chlorate and 10 parts by weight of potassium chloride in which 3 parts by weight of o-toluidine are dispersed. The paper is then "anodically" written. Dark characters are obtained on a bright background. During the drying of the moist paper the colour-forming o-toluidine volatilizes so that even after the passage of time the white places of the image remain white.

2. Absorbent paper is thoroughly moistened with an aqueous solution of 20 parts by weight of sodium chloride and 3 parts by weight of potassium ferricyanide in which 2 parts by weight of acetyl resorcin are dispersed. The paper is written on by means of the "kathode" and owing to the free alkali formed electrolytically as a result of the passage of current the resorcin combines with the ferricyanide with the formation of a dark brown colouring matter. When the paper is dried the acetyl resorcin which is the colour-forming body proper volatilizes with the water. The residue of ferricyanide, which merely imparts to the image a slightly yellowish ground colour, may remain in the image support without any danger to the stability of the written image.

3. Absorbent paper is thoroughly saturated with an aqueous solution of 10 parts by weight of ammonium chloride and 2 parts by weight of diazotized p-amidodiphenyl-amine, to which 10 parts by weight of a 1% alcoholic solution of resorcin have been added. The paper is written on "kathodically." The ammonia electrolytically liberated at the kathode during the passage of current instantly brings about the combination of the diazo-compound with the phenol, with production of a brown insoluble dyestuff. The still moist image is exposed to a powerful source of light as a result of which the diazo-compound is so changed with accompanying loss of its yellow colour that it loses the capability of combining with the phenol. In this way sharp dark brown marks are obtained on a white background. The danger of subsequent colouring over of the white parts of the image is excluded.

What I claim is:

1. A process for the electrochemical production

of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a support provided with a substance selected from the group: volatile hydroxybenzenes and derivatives thereof, volatile hydroxynaphthalenes and derivatives thereof, volatile aromatic amines, and light-sensitive diazo-compounds of the p-amino-diphenylamine type, together with a compound which reacts with the selected substance to produce a coloured product under the influence of the current, and the recorded characters are fixed by stabilizing the uninfluenced portion of the support.

2. A process for the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a support provided with a substance selected from the group: volatile hydroxybenzenes and derivatives thereof, volatile hydroxynaphthalenes and derivatives thereof, volatile aromatic amines, and light-sensitive diazo-compounds of the p-amino-diphenylamine type, together with a compound which reacts with the selected substance to produce a coloured product under the influence of the current and an electrolyte for promoting conduction of the current through the support, and the characters are fixed by stabilizing the uninfluenced portion of the support.

3. A process for the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a support provided with a substance selected from the group: volatile hydroxybenzenes and derivatives thereof, volatile hydroxynaphthalenes and derivatives thereof, and volatile aromatic amines, together with a compound which reacts with the selected substance to produce a coloured product under the influence of the passage of the current, and the characters are fixed by removing from the support the unchanged substance selected from the aforesaid group by evaporation thereof.

4. A process for the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a support provided with a light-sensitive diazo-compound of the p-amino-diphenylamine type together with a compound which reacts therewith under the influence of the current to form a coloured product, and the recorded characters are fixed by exposing the support to light, whereby the unreacted diazo-compound is decomposed.

5. A process for the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a support provided with a light sensitive diazo-compound of the p-amino-diphenylamine type of an azo-component, the former compound reacting with the latter under the influence of the current to form a coloured product, and the recorded characters are fixed by exposing the support to light, whereby the unreacted diazo-compound is decomposed.

6. A process as claimed in claim 5 in which the support is also provided with alkali halide to promote conduction of the current.

7. A process for the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a moist support provided with o-toluidine and an oxidizing agent, the former compound being oxidized by the latter to a dark product under the action of the electric current, and the image is fixed by drying the moist support, during which operation the unchanged o-toluidine volatilizes.

8. A process for the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a moist support provided with o-toluidine and potassium chlorate, the former compound being oxidized by the latter to a dark product under the action of the electric current, and the image is fixed by drying the moist support, during which operation the unchange o-toluidine volatilizes.

9. A process as claimed in claim 8 in which the support is also provided with alkali halide to promote conduction of the current.

10. A process for the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, in which the characters are formed by an electric current on a moist support provided with acetyl resorcin and potassium ferricyanide, which interact under the influence of the electric current with formation of a dark product, and the image is fixed by drying the moist support, during which operation the unchanged acetyl resorcin volatilizes.

11. A process as claimed in claim 10 in which the support is also provided with alkali halide to promote conduction of the current.

12. For use in the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, a support consisting of a material selected from the group consisting of paper, fabric and cellulose hydrate film, provided with a substance selected from the group: volatile hydroxybenzenes and derivatives thereof, volatile hydroxynaphthalenes and derivatives thereof, volatile aromatic amines, and light-sensitive diazo-compounds of the p-amino-diphenylamine type, together with a compound which reacts with the selected substance to produce a coloured product under the influence of the current.

13. For use in the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, a support consisting of a material selected from the group consisting of paper, fabric and cellulose hydrate film provided with o-toluidine and potassium chlorate.

14. For use in the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, a support consisting of a material selected from the group consisting of paper, fabric and cellulose hydrate film provided with o-toluidine and potassium chlorate, and an alkali halide to promote conduction of the current.

15. For use in the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, a support consisting of a material selected from the group consisting of paper, fabric and cellulose hydrate film provided with a light-sensitive diazo-compound of the p-amino-diphenylamine type and an azo-component.

16. For use in the electrochemical production

of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, a support consisting of a material selected from the group consisting of paper, fabric and cellulose hydrate film provided with a light-sensitive diazo-compound of the p-amino diphenylamine type and an azo-component, and an alkali halide to promote conduction of the current.

17. For use in the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, a support consisting of a material selected from the group consisting of paper fabric and cellulose hydrate film provided with acetyl resorcin and potassium ferricyanide.

18. For use in the electrochemical production of stable images or characters, more particularly for the recording of telegraphically transmitted pictures, a support consisting of a material selected from the group consisting of paper fabric and cellulose hydrate film provided with acetyl resorcin and potassium ferricyanide and an alkali halide to promote conduction of the current.

19. A process for the electrochemical production of stable images or characters, more particularly for the purpose of telegraphic transmission of pictures, which consists in producing images or characters by an electric current on a background carrying bodies capable of forming stable coloured substances under the influence of the electric current and thereupon stabilizing the influenced part of the background, thereby preventing further formation of coloured substances.

20. A process for the electrochemical production of stable images or characters, more particularly for the purpose of telegraphic transmission of pictures, which consists in producing images or characters by an electric current on a background carrying, in addition to a conducting electrolyte, bodies capable of forming stable coloured substances under the influence of the electric current and thereupon stabilizing the uninfluenced part of the background, thereby preventing further formation of coloured substances.

21. A process for the electrochemical production of stable images or characters, more particularly for the purpose of telegraphic transmission of pictures, which consists in producing images or characters by an electric current on a background carrying volatile bodies capable of forming stable coloured substances under the influence of the electric current and thereupon stabilizing the uninfluenced part of the background by evaporation of the uninfluenced volatile bodies contained in the background, thereby preventing further formation of coloured substances.

22. A process for the electrochemical production of stable images or characters, more particularly for the purpose of telegraphic transmission of pictures, which consists in producing images or characters by an electric current on a background carrying water volatile bodies capable of forming stable coloured substances under the influence of the electric current and thereupon stabilizing the images or characters by evaporation of the uninfluenced water volatile bodies contained in the background, thereby preventing further formation of coloured substances.

23. A process for the electrochemical production of stable images or characters, more particularly for the purpose of telegraphic transmission of pictures, which consists in producing images or characters by an electric current on a background carrying bodies capable of forming stable coloured substances under the influence of the electric current and adapted to lose in the light their capability of forming coloured substances, and thereupon stabilizing the uninfluenced part of the background by exposure to light, thereby preventing further formation of coloured substances.

24. A process for the electrochemical production of stable images or characters, more particularly for the purpose of telegraphic transmission of pictures, which consists in producing images or characters by an electric current on a background carrying, in addition to a conducting electrolyte, bodies capable of forming stable coloured substances under the influence of the electric current and adapted to lose in the light their capability of forming coloured substances, and thereupon stabilizing the uninfluenced part of the background by exposure to light, thereby preventing further formation of coloured substances.

VIKTOR BAUSCH, JUN.