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(54) Titre : SUPPORT INVIOLEABLE POUR IMPRESSION THERMIQUE
(54) Title: TAMPER-PROOF MEDIUM FOR THERMAL PRINTING

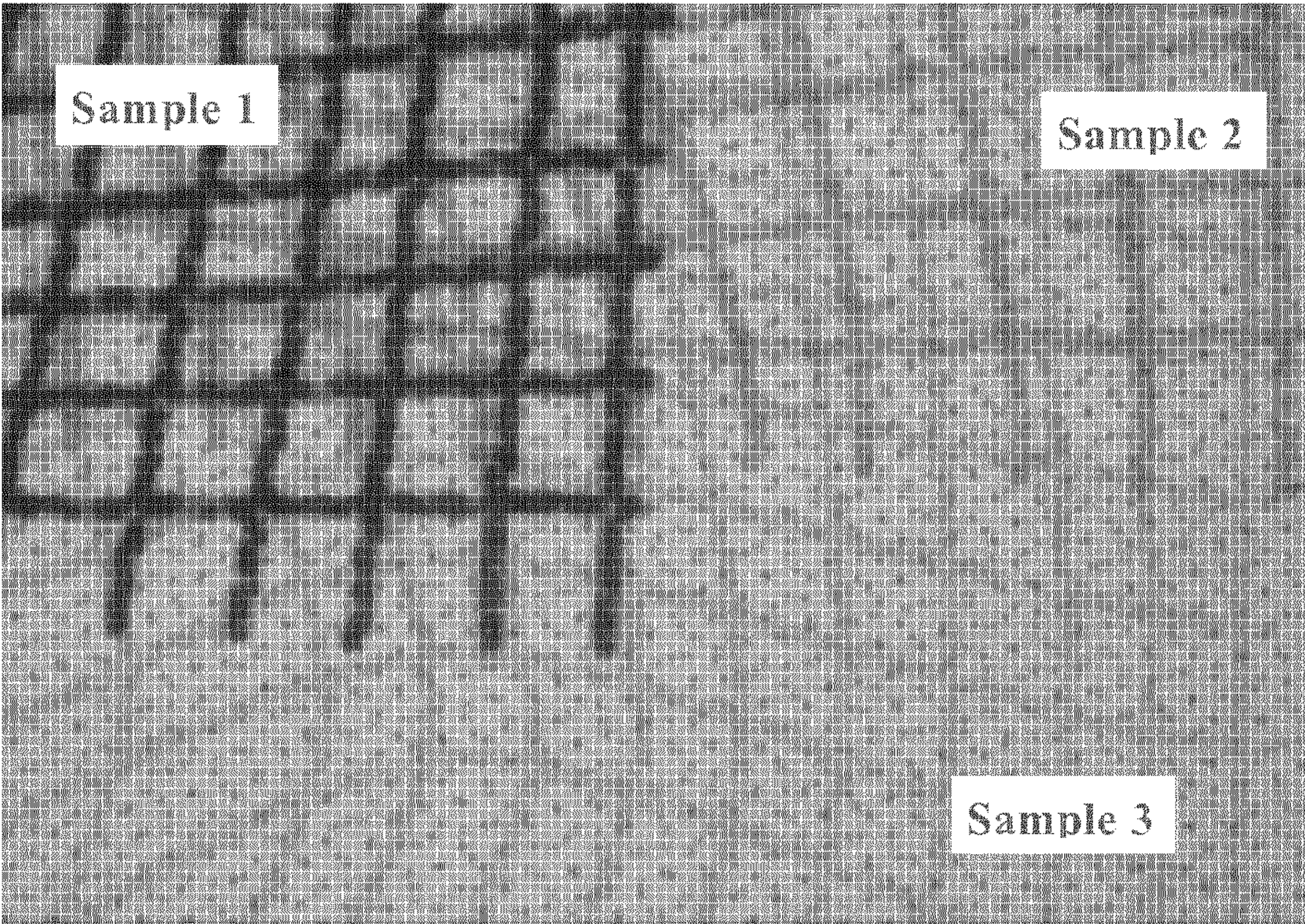


Fig. 1

(57) **Abrégé/Abstract:**
The present invention relates to method of manufacturing a tamper-proof medium for thermal printing, wherein a liquid treatment composition comprising at least one acid 5 is deposited on a substrate which comprises a thermochromic coating layer comprising at least one halochromic leuco dye.

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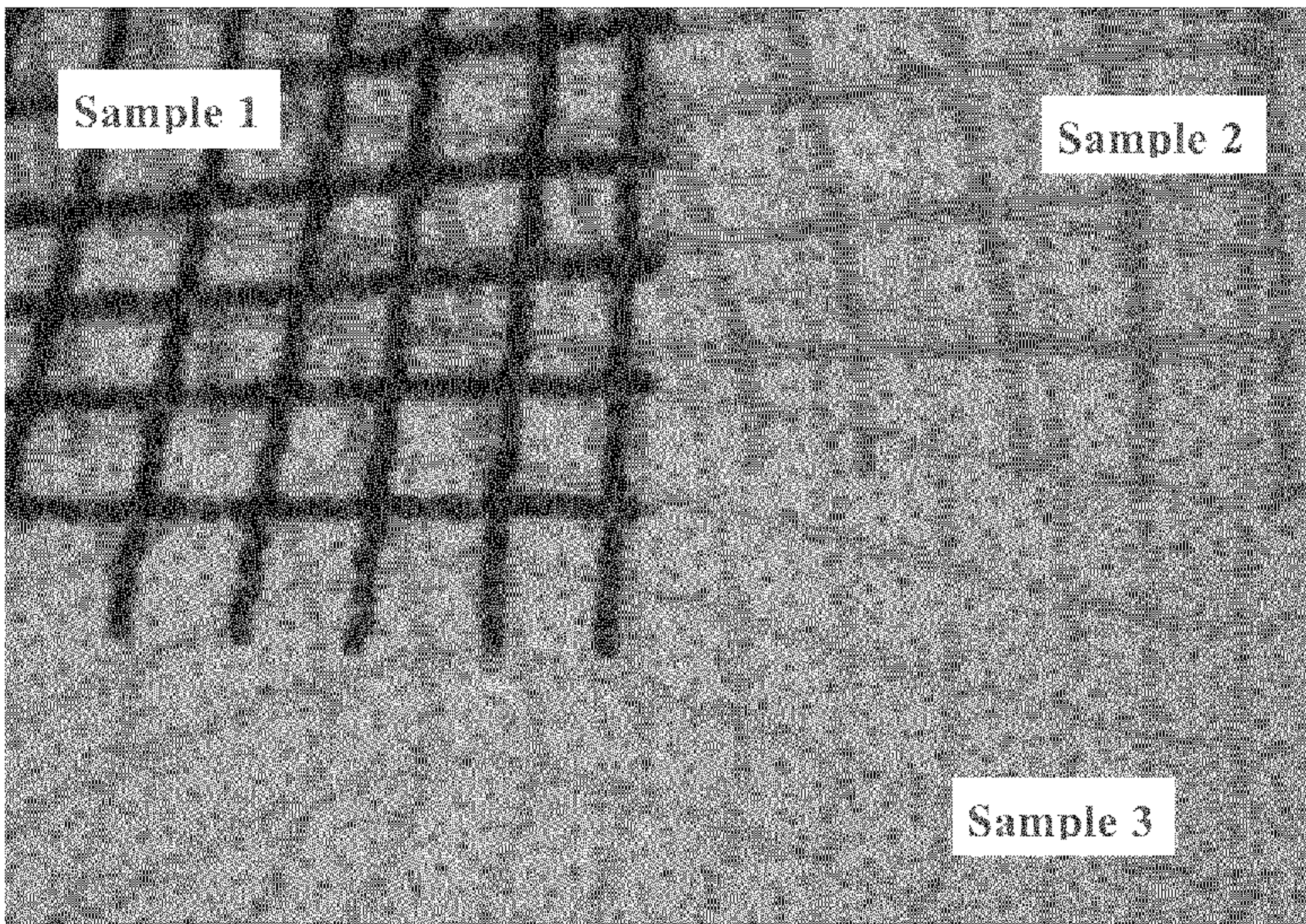


Fig. 1

(57) Abstract: The present invention relates to method of manufacturing a tamper-proof medium for thermal printing, wherein a liquid treatment composition comprising at least one acid 5 is deposited on a substrate which comprises a thermochromic coating layer comprising at least one halochromic leuco dye.

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Claims

1. A method of manufacturing a tamper-proof medium for thermal printing, the method comprising the following steps:
 - 5 a) providing a substrate, wherein the substrate comprises on at least one side a thermochromic coating layer comprising at least one halochromic leuco dye,
 - b) providing a liquid treatment composition comprising at least one acid, and
 - c) applying the liquid treatment composition onto at least one region of the thermochromic coating layer in form of a preselected pattern.
- 10 2. The method of claim 1, wherein the substrate is selected from the group comprising paper, cardboard, containerboard, plastic, cellophane, textile, wood, metal, glass, mica plate, or nitrocellulose, preferably paper, cardboard, containerboard, or plastic.
- 15 3. The method of any one of the preceding claims, wherein the at least one halochromic leuco dye is colourless.
- 20 4. The method of any one of the preceding claims, wherein the at least one halochromic leuco dye is selected from the group consisting of arylmethane phthalide dyes, quinone dyes, triarylmethane dyes, triphenylmethane dyes, fluoran dyes, phenothiazine dyes, rhodamine lactam dyes, spiropyran dyes, and mixtures thereof.
- 25 5. The method of any one of the preceding claims, wherein the thermochromic coating layer comprises the at least one halochromic leuco dye in an amount from 1 to 60 wt.-%, preferably from 5 to 55 wt.-%, more preferably from 10 to 50 wt.-%, even more preferably from 15 to 45 wt.-%, and most preferably from 20 to 40 wt.-%, based on the total weight of the thermochromic coating layer.

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6. The method of any one of the preceding claims, wherein the thermochromic coating layer further comprises a colour developing agent, preferably in an amount from 1 to 80 wt.-%, preferably from 10 to 75 wt.-%, more preferably from 20 to 70 wt.-%, even more preferably from 30 to 65 wt.-%, and most preferably from 40 to 60 wt.-%, based on the total weight of the thermochromic coating layer.

7. The method of any one of the preceding claims, wherein the at least one acid is selected from the group consisting of hydrochloric acid, sulphuric acid, sulphurous acid, phosphoric acid, citric acid, oxalic acid, acetic acid, formic acid, sulphamic acid, tartaric acid, phytic acid, boric acid, succinic acid, suberic acid, benzoic acid, adipic acid, pimelic acid, azelaic acid, sebaic acid, isocitric acid, aconitic acid, propane-1,2,3-tricarboxylic acid, trimesic acid, glycolic acid, lactic acid, mandelic acid, acidic organosulfur compounds, acidic organophosphorus compounds, HSO_4^- , H_2PO_4^- or HPO_4^{2-} , being at least partially neutralized by a corresponding cation selected from Li^+ , Na^+ , K^+ , Mg^{2+} or Ca^{2+} , and mixtures thereof, preferably the at least one acid is selected from the group consisting of hydrochloric acid, sulphuric acid, sulphurous acid, phosphoric acid, oxalic acid, boric acid, suberic acid, succinic acid, sulphamic acid, tartaric acid, and mixtures thereof, more preferably the at least one acid is selected from the group consisting of sulphuric acid, phosphoric acid, boric acid, suberic acid, sulphamic acid, tartaric acid, and mixtures thereof, and most preferably the at least one acid is phosphoric acid.

8. The method of any one of the preceding claims, wherein the liquid treatment composition further comprises a dye, a pigment, a fluorescent dye, a phosphorescent dye, an ultraviolet absorbing dye, a near infrared absorbing dye, a thermochromic dye, a halochromic dye, metal ions, transition metal ions, lanthanides, actinides, magnetic particles, quantum dots, or a mixture thereof, preferably the liquid treatment composition comprises a dye, and most preferably a solvent-soluble dye.

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9. The method of any one of the preceding claims, wherein the liquid treatment composition comprises the at least one acid in an amount from 0.1 to 100 wt.-%, based on the total weight of the liquid treatment composition, preferably in an amount from 1 to 80 wt.-%, more preferably in an amount from 3 to 60 wt.-%, and
5 most preferably in an amount from 10 to 50 wt.-%.

10. The method of any one of the preceding claims, wherein the preselected pattern is a continuous layer, a pattern, a pattern of repetitive elements and/or a repetitive combination(s) of elements, preferably the preselected pattern is a
10 guilloche, a one-dimensional bar code, a two-dimensional bar code, a three-dimensional bar code, a QR-code, a dot matrix code, a security mark, a number, a letter, an alphanumeric symbol, a logo, an image, a shape, a signature, a design, or a combination thereof.

15 11. The method of any one of the preceding claims, wherein the liquid treatment composition is applied by spray coating, inkjet printing, offset printing, flexographic printing, screen printing, plotting, contact stamping, rotogravure printing, spin coating, slot coating, curtain coating, slide bed coating, film press, metered film press, blade coating, brush coating, stamping and/or a pencil, and preferably by
20 inkjet printing.

12. A tamper-proof medium for thermal printing obtainable by a method according to any one of claims 1 to 11.

25 13. The tamper-proof medium of claim 12, wherein the tamper-proof medium is a branded product, a security document, a non-secure document, or a decorative product, preferably the product is a packaging, a container, a compact disc (CD), a digital video disc (DVD), a blue ray disc, a sticker, a label, a seal, a tag, a poster, a passport, a driving licence, a bank card, a credit card, a bond, a ticket, a postage
30 stamp, tax stamp, a banknote, a certificate, a brand authentication tag, a business

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card, a greeting card, a voucher, a tax banderol, a point-of-sale receipt, a plot, a fax, a continuous recording sheet or reel, or a wall paper.

14. Use of a tamper-proof medium for thermal printing according to claim 12 or
5 13 in security applications, in overt security elements, in covert security elements, in brand protection, in deviation prevention, in microlettering, in micro imaging, in decorative applications, in artistic applications, in visual applications, in packaging applications, in printing applications, in monitoring applications, or in track and trace applications.