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(54) Method for covering the surface of technical-fabric fibers, in particular for screen-printing processes

(57) The present invention relates to a method for surface-covering technical-fabric fibers, in particular for screen-printing processes, which comprises a starting step of preparing a base solution comprising at least a molecular precursor of Si, Al, Ti, Zr oxides, a polar organic solvent, either of a protic or an aprotic type, and water to promote hydrolysis and condensing of said precursors in the presence of an acid-pH reaction acid and in the presence of a surface active agent; a step of surface

actuating fabrics with an opening larger than 50 μm and a fiber diameter larger than 10 μm , by a reaction with a concentrated mineral acid and a following treatment in concentrated H_2O_2 ; a covering step for covering the processed fabric by dipping it into the base solution, upon ageing the latter for such a time period as to induce rheologic properties for providing a homogeneous covering of fibers with a thickness less than 2 μm ; and an end thermal processing step for evaporating the solvent off and thermally stabilizing the deposited material.

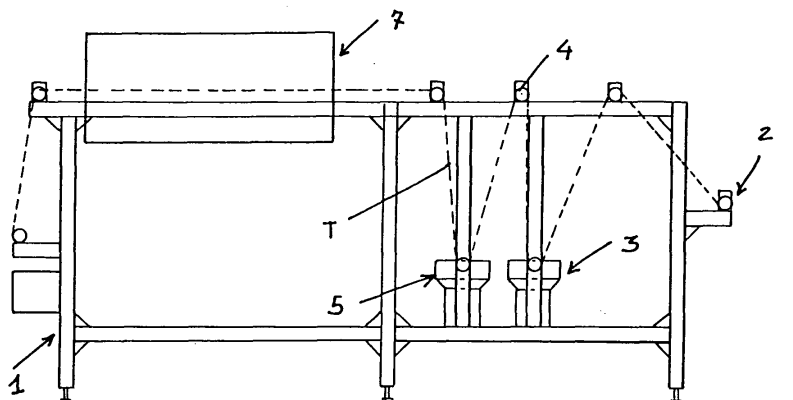


FIG. 1

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a method for surface covering technical-fabric fibers, in particular for screen printing processes.

[0002] As is known, in screen printing processes, the surface to be printed upon is entrained with a comparatively high speed between the printing cylinder and a further cylinder operating as a bearing surface.

[0003] The ink is supplied by an ink supplying system arranged inside the first cylinder, thereby providing a continuous type of printing system.

[0004] The fabric material to be used for making the printing surface must have a high flexure stiffness, a large size and a high mechanical stability, and a good resistance against corrosion, as well as a thin thickness.

[0005] All the above mentioned properties are at present achieved by using steel and nickel fabric materials, which have a high cost.

[0006] Moreover, the use of steel and nickel represents a limit for a diffusion of the rotary screen printing technique, as well as its extension to other application fields, and negatively affects the cost of the screen printed articles.

SUMMARY OF THE INVENTION

[0007] Accordingly, the aim of the present invention is to overcome the above mentioned problems, by providing a method for surface covering technical-fabric fibers, in particular for screen printing processes, allowing to stiffen, by increasing the flexure modulus, already made technical fabric materials comprising polymeric fibers, by depositing inorganic oxides, even of an organically modified type, and by directly continuously applying the process on the already existing material.

[0008] Within the scope of the above mentioned aim, a main object of the present invention is to provide such a method allowing the mesh size to be held unaltered, in particular without altering the original fabric material geometry, and this by a process operating at a temperature mating the characteristics of the polymer and finished fabric material.

[0009] Another object of the present invention is to modify the wetting properties of the surface, to broaden the selection of printing paste and ink materials.

[0010] Yet another object of the present invention is to introduce, into the oxide layer used for stiffening the material, nanometric particle dispersions, even of a metal type, and having such a resistivity as to promote a rejection of atmospheric dust materials and reduce to a minimum a possible accumulation of electric charges, by immediately dispersing the latter.

[0011] According to one aspect of the present invention the above mentioned aim and objects, as well as yet other objects, which will become more apparent herein-

after, are achieved by a method for surface covering technical-fabric fibers, in particular for screen printing processes, characterized in that said method comprises:

a starting step of preparing a base solution formed by at least a molecular precursor of Si, Al, Ti, Zr oxides, a polar organic solvent, either of a protic or an aprotic type, water to promote hydrolysis and condensing of said precursors, with the presence of an acid pH reaction acid and of a surface active agent; an actuating step of surface actuating fabrics having an opening larger than 50 μm and a fiber diameter larger than 10 μm by a reaction with a concentrated mineral acid and a following treatment in concentrated H_2O_2 ; a covering step for covering the processed fabric by dipping it into said base solution, upon ageing the latter for a time period adapted to induce rheologic properties for providing a homogeneous covering with a covering thickness less than 2 μm ; and an end thermal processing step for evaporating the solvent off and thermally stabilizing the deposited material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Further characteristics and advantages of the present invention will become more apparent hereinafter from the following detailed disclosure of a method for surface covering technical-fabric fibers, in particular for screen printing processes, which is illustrated, by way of an indicative, but not limitative, example in the accompanying drawings, where:

Figure 1 is a schematic side elevation view showing an apparatus which can be used for carrying out the inventive method;

Figure 2 is a further side elevation view of said apparatus;

Figure 3 shows a schematic cross-sectional view of the processed fabric material; and

Figure 4 is a top plan view of the processed fabric material.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] With reference to the above mentioned figures, the method for surface covering technical-fabric fibers, in particular for screen printing processes or applications, according to the present invention, comprises a starting step of preparing a base solution formed by at least a molecular precursor of Si, Al, Ti, Zr oxides, optionally modified by M-R (M = Si, Al, Ti, Zr; R = alkyl or aryl) linkages or mixtures thereof, at least a polar organic solvent, either of a protic or an aprotic type, and water as required for promoting hydrolysis and condensation of said precursors in the presence of an acid pH reaction acid and of a surface active agent.

[0014] The method comprises the further step of surface actuating fibers of fabric materials having an opening from 50 μm and a fiber diameter from 10 μm , by a chemical reaction in the presence of an acid which can comprise concentrated H_2SO_4 or other mineral acid; and then a further step of performing a following treatment by concentrated H_2O_2 .

[0015] According to a further embodiment, the actuation can also be carried out by a cold-plasma process or treatment.

[0016] Then, the thus processed fabric material is covered by dipping it into the base solution, upon ageing the latter for such a time as to induce rheologic properties suitable to provide a homogeneous covering of the individual fibers, with a covering thickness not larger than 2 μm .

[0017] Then, the solvent is evaporated off and the deposited material is thermally stabilized, by a thermal process designed as not to modify the original geometry of the fabric material and increase the elastic modulus of the deposited material, with a consequent stiffening of the fabric.

[0018] In particular, in a case of a deposit based on silicone oxide, the base solution can comprise RSiX_3 , where R is an alkyl or aryl, X is an halogen or OR, in a concentration from 5 to 150 g/l SiO_2 (as a rated value), preferably from 20 to 50 g/l SiO_2 (as a rated value) and acidified H_2O which has been acidified with an acid pH reaction acid, in such an amount as to provide a molar ratio $\text{Si}/\text{H}_2\text{O}$ at least equal to 2.

[0019] In a case of a surface actuation of polyester fabrics by means of an acid reaction, the first solution can comprise S_2SO_4 , from 10 to 50%, and preferably 20%, and the second solution can comprise H_2O_2 , from 30 to 120 volumes, preferably 120 volumes, at a temperature from 25°C to 90°C, preferably 40°C.

[0020] In the case of a deposit based on Al oxide, the base solution can comprise $\text{Al}(\text{OR})_{3-x}(\text{X})_x$, where R represents an alkyl or aryl and X an organic chelating anion and x can have values from 0 to 1.

[0021] For deposits based on Ti or Zr oxides, the base solution can comprise $\text{Ti}(\text{or Zr})(\text{X})_x(\text{OR})_{4-x}$, where R represents an alkyl or aryl and X an organic chelating anion, and x can assume values from 0 to 1.

[0022] A second aspect of the present invention provides to stiffen the fabric by using the base inorganic oxide deposit and by controlling the reaction rheology to provide the base solution as the processed fabric is contacted by a mineral acid.

[0023] This aspect is achieved, in case of a silicone oxide based deposit, in which the molar ratio of precursor/water/solvent/surface active agent in the reaction for the base solution varies from 1/1/2/0.1 and 1/4/6/1, the pH of H_2O is acid due to the presence of mineral acids or not, and the solvent is an alcohol, or an ether, or other bipolar solvents, to achieve a viscosity at least larger than 2 Pa.s.

[0024] To control the rheology, with respect to the for-

mation of a deposit homogeneously present on the weft and warp fibers, constitutes a further aspect of the present invention, and this is achieved by including in the base solution a surface active agent, thereby providing wetting properties suitable to concentrate the deposit on the fibers both in a horizontal and in a vertical direction, without closing the fiber mesh.

[0025] For a silicon oxide based deposit, the molar ratio RSiX_3 /surface active agent is preferably of 1/0.1.

[0026] The stabilizing of the deposit is performed in the final or end method step, by heating the material to cause the solvent to be evaporated off, and complete the chemical reactions of the precursors with water while holding unaltered the geometric arrangement of the fabric material; this can be carried out by a heating process, by using different heating techniques, preferably by IR illuminating or heating.

[0027] The invention provides the advantage that the above disclosed method steps are so performed as to provide a continuous process in a well controlled environment, without interfering against other optional or possible technologies as applied to technical fabric materials for screen printing applications.

[0028] With reference to the accompanying figures, the apparatus for carrying out the above disclosed method comprises a framework 1, including a fabric material T feeding assembly 2, said fabric material T being engaged by cylinders and, through transmission pulleys, being fed to a starting immersion or dipping station 3.

[0029] At said immersion station, the fabric material is immersed or dipped into the impregnating solution and then conveyed, through the transmission pulleys 4, to a following impregnating station 5, if the first impregnation is not suitable to provide a sufficient thickness deposit.

[0030] The outlet fabric from each immersion station is then impinged upon by a hot air jet, provided by a blowing device 6, for removing any excess liquid and to facilitate the mesh opening.

[0031] Then, the fabric material is conveyed into an IR beam oven, generally indicated by the reference number 7, where said fabric material is dried and size stabilized, as an end processing step.

[0032] The above disclosed method can be carried out in a lot of different manners, as disclosed in the following operating Examples.

[0033] Example 1: the polyethyleneglycole terephthalate fabric, having fibers with a diameter of 20 μm and a mesh opening of 60 μm , is used in the form of a web having a width of 5 cm, wound up and then distended by pulleys and braking cylinders pertaining to the apparatus inlet assembly 2.

[0034] The actuation is performed by dipping the fabric material into a solution comprising H_2SO_4 , 10% by weight at 50°C, and with such a sliding speed as to provide a suitable contact between the web and solution, for a time period of substantially 1 minute.

[0035] The outlet web is then immersed into a solution, at a temperature of 25°C, containing 120 volume H_2O_2 ,

with a contact time identical to that of the preceding treatment.

[0036] The web is then introduced into a silicon oxide precursor solution upon ageing the latter for 24 hours, correspondingly to the station 3 shown in figure 1.

[0037] This solution is prepared by mixing 165.8 ml of $\text{CH}_3\text{Si}(\text{OEt})_3$ with 789.3 ml absolute ethanol and 44.9 ml of 0.1 M HCl, to provide a molar ratio $\text{H}_2\text{O}/\text{Si}=3$ and a SiO_2 rated concentration of 50 g/l.

[0038] The solution is left under a high speed stirring condition obtained by a magnetic stirring device for 2 hours and then a $\text{NH}_4\text{O}_3\text{SO}(\text{CH}_2)_{11}\text{CH}_3$ surface active agent is added in an amount of 8 ml/solution liter.

[0039] The solution is left under a high speed stirring condition for further 22 hours, before using it.

[0040] The web is immersed into this solution with such a sliding speed as to assure a contact time between the web and solution of a centimeter/sec.

[0041] The outlet sample is subjected to a hot ventilating air, at a temperature of 120°C, blown perpendicularly to the with of the web, with an air flow rate of a liter/sec for a web meter.

[0042] The web is collected onto spindles and held in web vessels.

[0043] The flexure modulus increase which is thereby obtained corresponds to about 30% with respect to a non-processed fabric material.

[0044] Example 2: the polyester fabric material, including fibers having a diameter of 31 μm and mesh openings of 50 μm is used in the form of a web or strip having a width of 25 cm, supplied in a wound up condition and then distended by pulleys and braking cylinders.

[0045] Said web, actuated by causing it to pass through an air atmospheric cold plasma, is then introduced into a precursor solution comprising silicon oxide and titanium oxide, which has been subjected to an ageing process for 4 hours.

[0046] The SiO_2 precursor solution is prepared by mixing 165.8 ml $\text{CH}_3\text{Si}(\text{OEt})_3$ with 789.3 ml absolute ethanol and 44.9 ml of 0.1 M HCl so as to provide a molar ratio $\text{H}_2\text{O}/\text{Si}=3$, and rated SiO_2 concentrations of 50 g/l.

[0047] The solution is left under stirring (provided by a magnetic stirrer device) for 2 hours.

[0048] A $\text{Ti}(\text{OisoPr})_4$ solution is prepared by mixing 186.3 ml of this compound with 738.1 ml of 2-propanol, 64.3 ml of acetylacetone and 11.3 ml of 0.1 M HCl, so as to provide a molar ratio $\text{H}_2\text{O}/\text{Ti}=1$.

[0049] This solution is left under stirring for about 1 hour.

[0050] The two solutions are reunited by using volumetric ratios adapted to provide a rated molar ratio of $\text{TiO}_2\text{SiO}_2=1/3$ and a rated TiO_2 concentration of 10 g/l, and a rated SiO_2 concentration of 40 g/l.

[0051] The obtained solution is added with a surface active agent $\text{NH}_4\text{O}_3\text{SO}(\text{CH}_2)_{11}\text{CH}_3$ in an amount of 10 ml/liter and said solution is held under a high speed stirring condition for 4 hours.

[0052] The web or strip is immersed into this solution

with such a sliding speed as to provide a contact time corresponding to 1 cm/minute.

[0053] The outlet sample is processed by processing air at a temperature of 100°C, with an air flow speed and air flow rate designed to subject said web to an air flow of 10 l/meter.

[0054] The, the thus processed web is conveyed to an IR beam dry oven, adapted to bring the sample surface temperature to 300°C.

[0055] The increase of the flexural modulus corresponds to about 120% with respect a non processed web.

[0056] From the above disclosure it should be apparent that the subject polyester fabric materials can be advantageously used, upon stiffening, for building rotary screen printing cylinders, without using metal fabrics, since hybrid organic-inorganic surface material are used thereon.

[0057] In this connection it should be further apparent that the advantages of the method according to the present invention are not limited to a stiffening of the fabric material.

[0058] Actually, a deposit at the joining weft and warp joining points is such as to advantageously improve the size stability of the fabric material and its resistance against the corrosive action of printing ink and paste materials.

[0059] Due to the high flexibility of the sol-gel process, the covering can be actuated to reduce or fully eliminate dust or powder deposits or for embedding therein other inorganic oxides or metal dispersions, designed for providing the fabric material with very good antistatic, electric conductivity or UV absorption properties.

[0060] Another application field would relate to a modification of the wetting properties, induced by the sol-gel oxide deposit.

[0061] Thus, it is possible to use printing paste or ink materials having particular rheologic characteristics, for a better printing definition.

[0062] The above disclosure has briefly disclosed only few of the main application fields of the invention, which, however do not limit the invention scope.

[0063] In the above disclosed processing method, the used oxide precursors, surface active agents or the activation of the surface fibers can be used in any other desired fields, for producing fabric materials based on polymeric fibers having any desired stiffness, mechanical stability, and corrosion and abrading resistance characteristics.

[0064] It should moreover be pointed out that the stiffening of the screen printing technical fabric by homogeneously depositing thereon inorganic oxides (on the surface of their fibers), does not modify the other features of the fabric material and, in particular, the fabric mesh openings.

[0065] Moreover, it is possible to provide deposits having mechanical stability and thickness homogeneity features in a range of 0.1 to 2 μm , jointly with a possibility of performing a continuous processing in a tightly closed

processing environment.

[0066] The invention, as disclosed, is susceptible to several modifications and variations, all of which will come within the scope of the invention.

[0067] Moreover, all the details can be replaced by other technically equivalent elements.

[0068] In practicing the invention, the used materials, as well as the contingent size and shapes, can be any, depending on requirements.

Claims

1. A method for surface covering technical-fabric fibers, in particular for screen printing processes, **characterized in that** said method comprises:

a starting step of preparing a base solution formed by at least a molecular precursor of Si, Al, Ti, Zr oxides, a polar organic solvent, either of a protic or an aprotic type, water to promote hydrolysis and condensing of said precursors, with the presence of an acid pH reaction acid and of a surface active agent; an actuating step of surface actuating fabrics having an opening larger than $50\mu\text{m}$ and a fiber diameter larger than $10\mu\text{m}$ by a reaction with a concentrated mineral acid and a following treatment in concentrated H_2O_2 ; a covering step for covering the processed fabric by dipping it into said base solution, upon ageing the latter for a time period adapted to induce rheologic properties for providing a homogeneous covering with a covering thickness less than $2\mu\text{m}$; and an end thermal processing step for evaporating the solvent off and thermally stabilizing the deposited material.

2. A method, according to the preceding claim, **characterized in that** said molecular oxide precursor is modified by M-R linkages, where M is equal to Si, Al, Ti, Zr and R comprises an alkyl or aryl or mixtures thereof.

3. A method, according to one or more of the preceding claims, **characterized in that** the mineral acid surface actuation is carried out by a processing by concentrated H_2O_2 .

4. A method, according to one or more of the preceding claims, **characterized in that** said surface actuation of said fabric materials is carried out by a cold plasma treatment in air or process gas at an atmospheric pressure.

5. A method, according to one or more of the preceding claims, **characterized in that** said end thermal processing step is carried out in order not to modify the original geometry of the fabric material and in-

crease the elastic modulus of the deposit, with a consequent stiffening of the fabric material.

6. A method, according to one or more of the preceding claims, **characterized in that**, for a SiO_2 based deposit, said base solution comprises compounds of formula $\text{R}_x\text{SiX}_{4-x}$, where y is equal to 4 and x varies from 0 to 2 or mixtures of these compounds, where R is an alkyl or aryl, X an R group or halogen, acidified water which is acidified by an acid pH reaction acid in such an amount as to provide a molar ratio $\text{Si}/\text{H}_2\text{O}$ at least equal to 2.

7. A method, according to one or more of the preceding claims, **characterized in that**, for an Al oxide based deposit, said base solution comprises compounds of formula $\text{Al}(\text{OR})_x\text{B}_y$, where x is equal to 3 and y varies from 0 to 3, where R is an alkyl or aryl and B comprises a halogen or an organic chelating anion, or mixtures of these compounds, and such an water amount as to provide a molar ratio $\text{Al}/\text{H}_2\text{O}$ at least equal to 0.5, a molecular chelating agent in a ratio molecular chelating agent/Al varying from 0 to 2.

8. A method, according to one or more of the preceding claims, **characterized in that**, for a Ti(or Zr) based deposit, the base solution comprises compounds of formula $\text{Ti}(\text{or Zr})(\text{OR})_x\text{B}_y$ where x is 4 and y varies from 0 to 3, where R is an alkyl or aryl, B is a halogen or an organic chelating anion or mixtures thereof; water being moreover added in such an amount as to provide a molar ratio $\text{Ti}(\text{or Zr})/\text{H}_2\text{O}$ at least equal to 0.5, with a molecular chelating agent with a molecular chelating agent/Ti(or Zr) ratio varying from 0 to 3.

9. A method, according to one or more of the preceding claims, **characterized in that** said base solution is **characterized by** compound mixtures having $\text{Si}/\text{Al}/\text{Ti}/\text{Zr}$ molar ratios from 0 to 1 per element pairs, in such a concentration as to provide, by mixing, a homogeneous liquid.

10. A method according to one or more of the preceding claims, **characterized in that** the H_2O pH is acid and that the base solution solvent comprises an alcohol or other low boiling protic or aprotic polar organic solvents.

11. A method, according to one or more of the preceding claims, **characterized in that** the material deposited on said fabric is stabilized by a hot air flow processing with an evaporating of the solvent and being moreover hot processed by IR radiating beams in a processing oven.

12. A method, according to one or more of the preceding claims, **characterized in that** said covering com-

prises other inorganic oxides or metal dispersions, adapted to provide the fabric material with antistatic, electric conductivity, UV radiation absorption properties to improve the operating characteristics of the screen printing fabric materials.

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13. An apparatus for carrying out a method according to the preceding claim, **characterized in that** said apparatus comprises a bearing framework supporting a fabric material feeding assembly for feeding said fabric material to a starting immersion station including a base solution; said fabric material being entrained on transmission pulleys to feed said fabric material to an immersion station; downstream of said immersion station being provided a blowing device and at the outlet of said immersion station the fabric material being fed to an IR beam oven.

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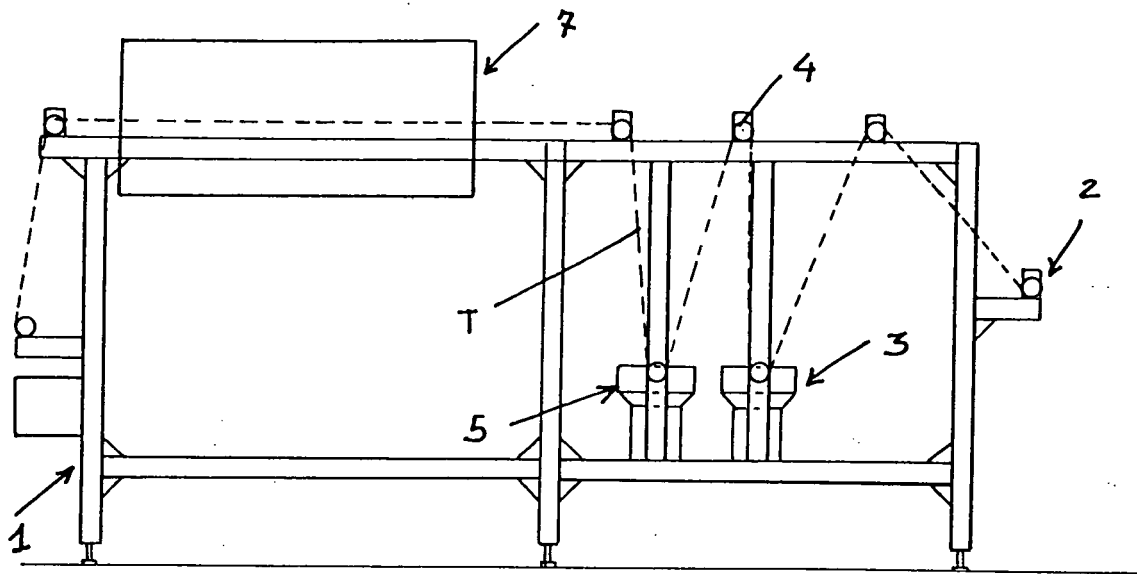


FIG. 1

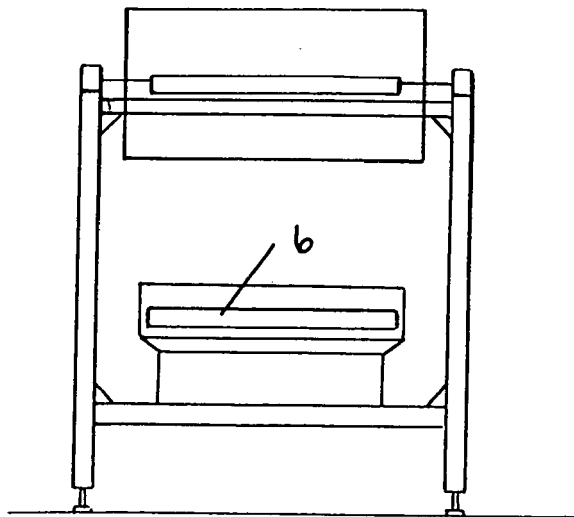


FIG. 2

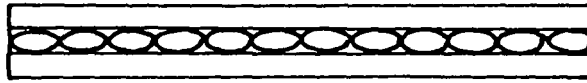


FIG. 3

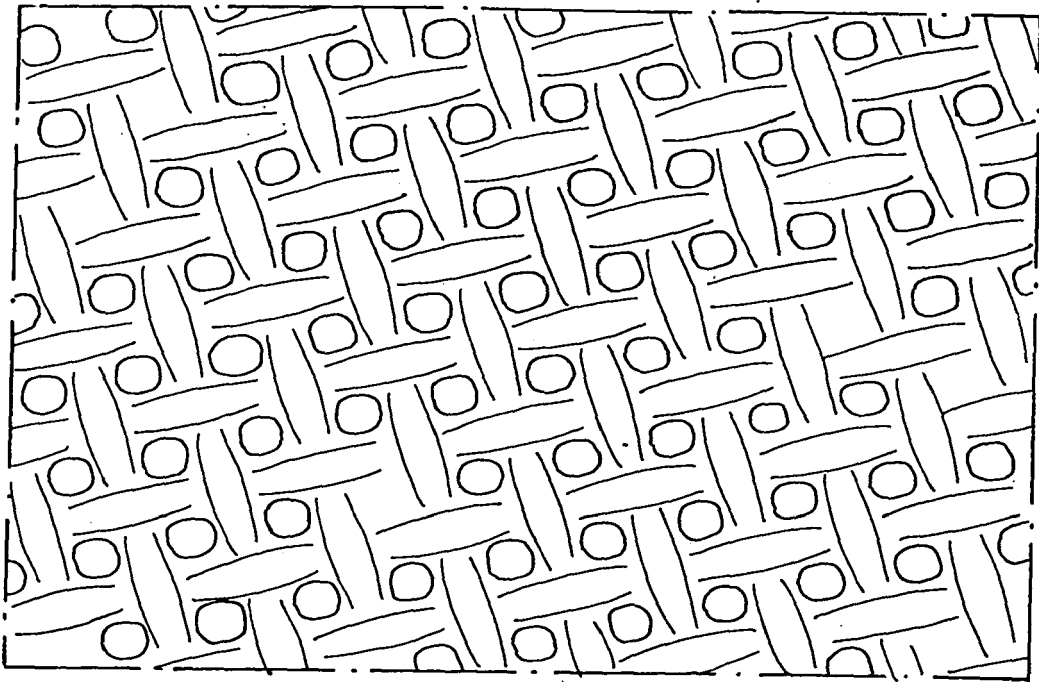


FIG. 4



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EUROPEAN SEARCH REPORT

Application Number
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EUROPEAN SEARCH REPORT

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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