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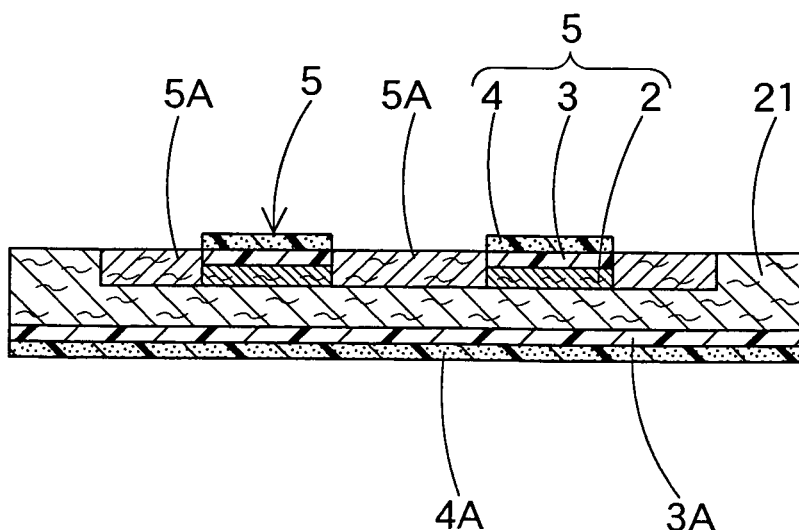
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(54) **Color-changing puzzle**

(57) The present invention provides (s) an aqueously color-changing puzzle. The aqueously color-changing puzzle is rich in convenience capable of easily changing the color by wetting and in durability, further is widely applicable. The puzzle piece includes a substrate(2), a water resistant resin layer(3) on the substrate(2), a po-

rous layer(4) on the water resistant resin layer(3). The porous layer(4) is made of a dispersion system of a low refractive-index pigment in a binder resin so that the transparency of the porous layer may differ between in the liquid-absorbing state and in the non-liquid absorbing state.

Fig. 2



Description

[0001] The present invention relates to an aqueously color-changing puzzle and an aqueously color-changing puzzle set using thereof. More particularly, the present invention relates to an aqueously color-changing puzzle having a puzzle piece whose colors are changed by wetting (attachment of water), and an aqueously color-changing puzzle set comprising an aqueously color-changing puzzle and a means for wetting (attaching water).

[0002] Conventionally, as a puzzle for showing color-changing, the puzzle in which designs have been formed with a thermally color-changing ink and reversible color-changing occurs by temperature changes has been disclosed (for example, see Patent Document 1).

[0003] The puzzle is an elaborate puzzle giving high interest for changing the designs by the temperature change, however, on the other hand, since the color-changing depends upon the temperatures, the color may not be changed at environmental temperatures. Moreover, even if the color-changing can be performed using a heating device or a cooling device, the operation is troublesome and it cannot be said that it is an easy means, moreover, it may return to the original state by the environmental temperatures even if the colors are changed. [Patent Document 1] Unexamined utility model publication (Kokai) No. H05-28388 Gazette

[0004] It is an object of the present invention to provide a simple, convenient and durable aqueously color-changing puzzle whose colors can change with application of water.

[0005] The present invention provides an aqueously color-changing puzzle, which has at least one puzzle piece having a water resistant resin layer on the substrate, and a porous layer where low-refractive-index pigments with binder resins have been adhered and fixed in a dispersed state and whose transparent property is different between in a liquid absorbing state and in a liquid non-absorbing state on the water resistant resin layer.

[0006] Further, the present invention provides the aqueously color-changing puzzle, which has further technical features: the water resistant resin layer is formed by image (s) selected from the letters, designs, symbols and numeric characters; the whole surface of the substrate is configured by being covered with the water resistant resin layer, the substrate is any one of a normal paper, a synthesized paper, a water resistant paper, a wood material, a plastic sheet, a foamed plastic sheet, a laminated sheet of a water resistant paper and a wood material, a laminated sheet of a synthesized paper and a foamed plastic sheet, a laminated sheet thereof. The aqueously color-changing puzzle is e.g. configured by further providing a water resistant coloring image on the porous layer, it is configured with at least 9 pieces or more of puzzle pieces and its number of puzzle pieces where the porous layer is provided occupies 30% or more of the whole puzzle pieces, or it is configured by being

equipped with a frame body.

[0007] Furthermore, the present invention provides an aqueously color-changing puzzle set comprising the aqueously color-changing puzzle and means for wetting (attaching water), the means for attaching water are selected from a writing tool or a coating tool having a brush, a fiber pen body or the like on the tip end portion or a writing tool or a coating tool which has a container holding water in a container and a fiber body or a brush for deriving out the water within the container.

[0008] The present invention can provide an aqueously color-changing puzzle, which is rich in convenience and durability capable of easily changing the color by attaching water and is excellent in application.

[0009] Fig. 1 is a cross-sectional view of a puzzle piece of the present invention.

[0010] Fig. 2 is a cross-sectional view of puzzle pieces holed on a frame body of the present invention.

[0011] As for a material of substrates configuring a puzzle pieces, it is not particularly limited, however, cellulose based material such as normal paper, water resistant paper, wood, hard board, particle board; synthesized paper, plastic sheet, foamed plastic sheet, rubber, synthesized leather and leather, preferably, paper, synthesized paper, water resistant paper, wood, plastic sheet or foamed plastic sheet may be used.

[0012] Moreover, as the substrates, a laminated sheet (laminated member) of same, similar or different materials may be also used; laminated member of normal paper and a water resistant paper, water resistant paper and wood material, synthesized paper and foamed plastic sheet and of plastic sheet and foamed plastic sheet are preferable.

[0013] It should be noted that as for the water resistant paper, a water resistant base paper manufactured by adding an appropriate amount of a water resistant agent such as a denaturant rosin based emulsion to the interior of pulp, or a water resistant paper for printing made of the water resistant base paper whose surface has been coated with a water resistant resin such as a synthesized rubber or an acrylic resin has been coated is applied.

[0014] It is configured such that a water resistant resin layer on the substrate is provided so that the strength as a puzzle piece may not be damaged by water filtration. It should be noted that in the case where a resin layer or a coloring layer to be formed on the substrate is poor in water resistance, since there is a fear that since a blur might be generated at the time when water is attached by the component in the relevant layer being eluted and transferred to the porous layer and a stain might be generated at the time when it is in a dry state, the troubles can be also solved by forming a water resistant resin layer.

[0015] As a resin used for the water resistant resin layer, it is preferable that a oil soluble resin and its hardened matter are used, however, a water insoluble resin obtained by combining a water soluble resin and a cross-linking agent, drying and curing it or a water insoluble

resin obtained by drying and curing a resin emulsion which has been dispersed into water may be also used.

[0016] As the resin, isobutylene-maleic anhydride copolymer, acrylonitrile-acrylic styrene copolymer, acrylonitrile-styrene copolymer, acrylonitrile-butadiene-styrene copolymer, acrylonitrile-chlorinated polyethylene-styrene copolymer resin, ethylene-vinyl chloride copolymer, ethylene-vinyl acetate copolymer, ethylene-vinyl acetate-vinyl chloride graft copolymer, vinylidene chloride, vinyl chloride resin, vinyl chloride - vinylidene chloride copolymer, chlorinated polyethylene, chlorinated polypropylene, polyamide, high density polyethylene, medium density polyethylene, linear low density polyethylene, polyethylene, terephthalate, polybutylene terephthalate, polycarbonate, polystyrene, styrene-butadiene copolymer, high impact polystyrene resin, polypropylene, polymethyl styrene resin, polyacrylic ester resin, methyl methacrylate resin, epoxy acrylate resin, alkyl phenol resin, rosin denatured phenol resin, rosin denatured alkyd resin, phenol resin denatured alkyd resin, epoxy denatured alkyd resin, styrene denatured alkyd resin, acryl denatured alkyd resin, amino alkyd resin, vinyl chloride-vinyl acetate resin, polyvinyl butyral resin, styrene-butadiene resin, epoxy resin, unsaturated polyester resin, polyurethane, silicone resin, cellulose acetate, cellulose nitrate, cellulose acetate butylate, vinyl acetate resin, urea resin, polybutadiene and ethyl cellulose are listed.

[0017] Even if the substrate is a material having the water resistance, in the case where it is a material into which water infiltrates, troubles occurring by water impregnating the substrate by means of providing the water resistant resin layer can be prevented, that is, the storage property can be prevented from being damaged by maintaining the puzzle piece in the moisture state by bad drainage even after it has been used, the occurrence of mildew can be prevented and the damage of the desired color-change effect by the component of the porous layer infiltrating in the relevant substrate at the time when the porous layer is formed can be prevented.

[0018] Moreover, even if the substrate has the water resistance not for making water infiltrate into it, in the case where the surface has convex and concave portions, since the color-change property is damaged by inhibiting a uniform formation of a porous layer, it is useful that the smooth surface is formed with the water resistant resin layer.

[0019] Furthermore, since the image can be visually recognized in a state where the porous layer is in a liquid absorbing state, the intellectual training can be also given as well as the mode change is excellent by the water resistant resin layer forming a coloring water resistant resin image selected from letter, design, symbol and numeric character.

[0020] It should be noted that it is preferable that from the viewpoint of the substrate strength, the storage property, the occurrence of mildew and the formation of the uniform porous layer, the water resistant resin layer has

covered the entire upper surface of the substrate, and it is preferable that the coloring water resistant resin image has similarly covered the entire upper surface of the substrate.

[0021] The state where the coloring water resistant resin image has covered the entire upper surface of the substrate means the fact that the other water resistant resin layer has been formed even on the portion where the images on the substrate has not been formed.

[0022] It is made up by providing a porous layer on the water resistant resin layer and the color tone of the underlying layer can be visually recognized by the porous layer absorbing water and it becoming transparent or translucent.

[0023] The porous layer is a layer in which a low-refractive-index pigment has been solidified and fixed in a dispersed state as well as a binder resin, as a low-refractive-index pigment, silicic acid and its salts, baryte powder, barium sulfate, barium carbonate, calcium carbonate, plaster, clay, talc, alumina white and magnesium carbonate are listed, as for these described above, the refractive indexes are in the range from 1.4 to 1.8, when water is absorbed, it shows an excellent transparency.

[0024] It should be noted that as salts of the silicic acid; aluminum silicate, aluminum potassium silicate, aluminum sodium silicate, aluminum calcium silicate, potassium silicate, calcium silicate, calcium sodium silicate, sodium silicate, magnesium silicate and magnesium potassium silicate are listed.

[0025] Although the particle diameter of the low-refractive-index pigment is not particularly limited, it is preferable to use the pigment whose particle diameter is in the range from 0.03 to 10 micrometer.

[0026] Moreover, two kinds or more of the low-refractive-index pigments may be used in combination.

[0027] It should be noted that as a low-refractive-index pigment which is preferably used, finely particulate silicic acid is listed.

[0028] The finely particulate silicic acid is manufactured as a noncrystalline amorphous silicic acid, depending upon its method of manufacturing, these are largely classified into one manufactured by a dry method using a vapor phase reaction such as thermal decomposition of halogenated silicon such as silicon tetrachloride (hereinafter, it is referred to as dry method finely particulate silicic acid) and one manufactured by a wet method using a liquid phase reaction such as decomposition by acid such as sodium silicate (hereinafter, it is referred to as wet method finely particulate silicic acid), any one of these may be used, however, in the case where a wet method finely particulate silicic acid has been used, since hiding property in the normal state is larger comparing to the series of a drying method finely particulate silicic acid, it is possible that the mixture ratio of the binder resin with respect to silic acid in a fine particle shape is made larger, and the coating strength of a porous layer can be enhanced, therefore, it is more preferably used.

[0029] As described above, as a finely particulate sil-

ic acid used for satisfying the hiding property in the normal state of a porous layer, it is preferable that the finely particulate silicic acid using a wet method is used. The structures are different between the finely particulate silicic acid using a drying method and the finely particulate silicic acid using a wet method, the finely particulate silicic acid using a drying method forms the three-dimensional structure in which the silicic acid is densely bonded with each other, in contrast to this, the finely particulate silicic acid using a drying method has a so called two-dimensional structure portion in which a long molecular sequence has been formed by silicic acid being condensed. Therefore, since the molecular structure becomes rough when comparing to the finely particulate silicic acid using a drying method, in the case where the finely particulate silicic acid using a wet method has been applied to a porous layer, it is estimated that diffuse reflection property of the light in the dry state is more excellent comparing to a system using the finely particulate silicic acid using a drying method, hence, the hiding property in the normal state becomes larger.

[0030] Moreover, since the infiltrating medium is water when considering the safety and cost, it is preferable that the low-refractive-index pigment contained in the porous layer has the hydrophilic property in an appropriate degree. The finely particulate silicic acid using a wet method is preferable, since it has high hydrophilic property, because there are a large number of hydroxyl groups existing as silanol group on the particle surface therein comparing to those in the finely particulate silicic acid using a drying method.

[0031] In the case where the finely particulate silicic acid using a wet method is used as a low-refractive-index pigment, the amount of coating depends upon the kind, the properties such as particle diameter, specific surface area and oil absorption

of the finely particulate silicic acid using a wet method. In order to satisfy both of hiding property in the normal state and the transparency in the liquid-absorbing state, however, it is preferable that the amount of coating is in the range from 1 g/m² to 30g/m², and more preferably in the range from 5 g/m² to 20 g/m². In the case where it is in the range less than 1 g/m², it is difficult to obtain the sufficient hiding property in the normal state, and it is difficult to obtain a sufficient transparency at the time when it absorbs water when it exceeds over 30 g/m².

[0032] The low-refractive-index pigment is dispersed in a vehicle containing a binder resin (as binder), and coated on the water resistant resin layer, and then, the volatile component is dried to form a porous layer.

[0033] As the binder resin, urethane based resin, nylon resin, vinyl acetate resin, acrylic ester resin, acrylic ester copolymer resin, acrylic polyol resin, vinyl chloride-vinyl acetate copolymer, maleic acid resin, polyester, styrene resin, styrene copolymer, polyethylene, polycarbonate, epoxy resin, styrene-butadiene copolymer, acrylonitrile-butadiene copolymer, methyl methacrylate-butadiene copolymer, butadiene resin, chloroprene resin, melanin

resin and emulsions of them, casein, starch, cellulose derivatives, polyvinyl alcohol, urea resin, phenol resin and epoxy resin are listed.

[0034] Since the porous layer has the mixture ratio of the binder resin with respect to the coloring agent is small when it is compared to the general coating film which has been conventionally known, it is difficult to obtain a sufficient coating strength. Hence, in a use requiring the abrasion resistant property, it is preferable that a urethane resin or a nylon resin is used as the above-described binder resin, or at least it contains these resins.

[0035] As the urethane resin (polyurethane), polyester based polyurethane, polycarbonate based polyurethane and polyether based polyurethane are listed, and two kinds or more of these may be also used in combination. Moreover, a urethane emulsion resin in which the resin has been emulsified and dispersed in water, a colloid dispersion type (ionomer type) urethane resin in which it is self-emulsified by ion group of itself of the urethane resin (urethane ionomer) having the ionic property without requiring an emulsifying agent and dissolved or dispersed in water may be also used.

[0036] It should be noted that as for the urethane resin, either of aqueous urethane resin or oily urethane resin may be used, however, it is preferable that an aqueous urethane resin, especially, an urethane emulsion resin or a colloid dispersion type urethane based resin is used.

[0037] The urethane resin can be singly used, however, according to the performance required for the kind and coating of the supportive body, the other binder resin may be used accompanying with the urethane resin. In the case where a binder resin is used in combination except for the urethane resin, in order to obtain a practical coating strength, it is preferable that the urethane resin is contained 30% by solid content weight ratio or more in the binder resin of the porous layer.

[0038] In the binder resin, if it is a crosslinking resin, its coating strength can be further enhanced by adding an optional crosslinking agent and making it crosslink.

[0039] Referring to the binder resins, there are binder resins whose hydrophilic property is large and small, however, the infiltration time into the porous layer, the infiltration degree, the delay and speed up of the drying after its infiltration can be regulated. Furthermore, the infiltration performance described above can be also controlled by appropriately adding a dispersion agent.

[0040] The porous layer can be formed by means of a conventionally known method, for example, printing means such as a screen printing, offset printing, gravure printing, a coater, a pad application printing and a transcription, means such as a brush coating, a spray coating, an electrostatic coating, an electrodeposition coating, a continuous flow curtain coating, a roller coating and a dip coating:

[0041] Furthermore, in the porous layer, a metal brightening pigment such as titanium dioxide coating mica, iron oxide-titanium dioxide coating mica, iron oxide coating mica, guanine, sericite, basic lead carbonate, acidic lead

arsenate and bismuth oxychloride can be added, or the color-changing can be also made various by adding a general die, or a pigment.

[0042] On the porous layer of the puzzle piece formed as described above, if it is necessary, a water resistant coloring image can be also provided by a water resistant ink containing a general die or a pigment, a fluorescent die or a pigment.

[0043] It should be noted that by providing and arranging the water resistant coloring image on the upper layer of the porous layer, the porous layer becomes rich in mode change in a liquid-absorbing state and a puzzle which is excellent in ornament decorating property especially in a dry state can be obtained as well.

[0044] The water resistant layer may be transparent or translucent and in that case, the substrate may be colored and further printed images such as patterns (designs), letters or numerals on it.

[0045] The puzzle piece in which the porous layer has been provided may be one of a plurality of puzzles, however, in order to give the changing characteristic to the puzzle at the time when it has been completed, it would be better that the porous layer has been provided in a plurality of the puzzle pieces.

[0046] As a concrete configuration for giving the changing characteristic to the puzzle, it is preferable that it comprises at least 9 pieces or more of puzzle pieces 5, and the number of pieces of the puzzle pieces in which a porous layer 4 has been provided is 30% or more of whole puzzle pieces and the mode change becomes poor in the case where the number of puzzle pieces 5 in which a porous layer has been provided is 30% or less.

[0047] As the form of the puzzle, a puzzle comprising only a plurality of puzzle pieces and a puzzle comprising a plurality of puzzle pieces 5, 5A and a frame body 21 into which the puzzle pieces 5, 5A are to be fitted are listed. (See Fig. 2)

[0048] And a porous layer 4A may be provided on the rear surface of the frame body 21, optionally providing a water resistant layer between them (see Fig. 2). Therefore, the puzzle becomes rich in playing characteristics, because the colors of the frame body 21 can be changed by applying water thereto.

[0049] Moreover, the surface of puzzle may be a flat surface or other surfaces, for example, the surface may also have the convex and concave portions for giving stereoscopic property by fitting together these puzzle pieces.

[0050] As a means for wetting the aqueously color-changing puzzle (water attachment means), a means for making a user's contact on the puzzle after wetting his or her hand or finger with water, a means for bringing a writing tool or a coating tool having e.g. a brush or a fiber pen body on the tip end portion in contact with the puzzle, a means for containing water within the container and bringing a writing tool or a coating tool in which a fiber body and a brush for deriving water within the container in contact with the puzzle, a means for making a sponge

containing water and bringing it in contact with the puzzle; a means for brining the container containing water nearby or bringing in contact with the puzzle and deriving water from the container and making water attach; a means for making a stamp in which a foamed body having a continuous bubble or independent bubble has been fixed on the pressing surface water-contained and making water attach to the puzzle; means for making water attaching to the stamp in which the pressing surface made of a plastic or rubber is formed on a rough surface and bringing the pressing surface in contact with the puzzle are listed.

[0051] An aqueously color-changing puzzle set is obtained by combining the water attachment means (means for wetting) and an aqueously color-changing puzzle.

[0052] It should be noted that as a preferable water attachment means, a writing tool or a coating tool in which a plastic porous body or a fiber-formed body having continuous pores has been applied as a pen tip member is used, the writing images can be easily formed, and the practical usability can be enhanced.

(Examples)

[0053] Hereinafter, Examples will be exemplified. It should be noted that the part(s) in Examples indicate(s) part(s) by weight.

(Example 1)

Preparation of aqueously color-changing puzzle :

[0054] On a white color coat paper having the thickness of 3 mm as the substrate of a puzzle, the screen printing has been performed using a blue color printing ink containing an oily acrylic resin and the water resistant resin layer has been provided by drying and curing.

[0055] Subsequently, on the water resistant resin layer, a porous layer has been formed by the screen printing using a white color ink for printing that 15 parts of finely particulate silicic acid manufactured by a wet method as a low-refractive-index pigment [trade name: Nipsil E-200A, manufactured by Nippon Silica Industrial Co., Ltd.], 50 parts of an aqueous urethane resin as a binder [trade name: Hydran AP-10, polyester based urethane resin, solid content 30% manufactured by Dainippon Ink & Chemicals Inc.], 30 parts of water, 0.5 parts of silicon based anti-foaming agent, 3 parts of a water based ink thickening agent, 1 portion of ethylene glycol, and 2 parts of an epoxy based crosslinking agent have been uniformly mixed and agitated, whereby a sheet has been obtained.

[0056] Aqueously color-changing puzzle pieces have been obtained by cutting the sheet.

[0057] After the aqueously color-changing puzzle has been assembled by fitting together the aqueously color-changing puzzle pieces, when water was attached to a white color porous layer, the porous layer absorbed water

and became transparent, and a blue color expressed by the underlying water resistant resin layer was visualized.

[0058] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original white color.

[0059] The above appearance change could be repeatedly performed, trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

(Example 2)

Preparation of aqueously color-changing puzzle set:

[0060] An aqueously color-changing puzzle set was obtained by combining the aqueously color-changing puzzle obtained in Example 1 and a writing brush as a means for attaching water.

[0061] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces, when water dipped in a writing brush was attached to a white color porous layer, the porous layer absorbs water and became transparent and a blue color expressed by the underlying water resistant resin layer was visualized.

[0062] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, as the porous layer was dried, it became gradually white color and it returned to the original white color after about 10 minutes.

[0063] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has been generated even if water was applied, and the durability was excellent.

(Example 3)

Preparation of aqueously color-changing puzzle:

[0064] The screen printing of the letter of "A" has been performed with the blue color printing ink containing oily acryl resin on a white color coat paper having the thickness of 2 mm as the substrate of the puzzle, and the coloring water resistant resin layer (image) has been provided by drying and curing it.

[0065] Subsequently, on the coloring water resistant resin layer, a porous layer has been formed by the screed printing using a white color ink for printing that 15 parts of finely particulate silicic acid manufactured by a wet method as a low-refractive-index pigment [trade name: Nipsil E-200A, manufactured by Nippon Silica Industrial Co., Ltd.], 50 parts of an aqueous urethane resin as a binder resin [trade name: Hydran AP-10, polyester based urethane resin, solid content 30% manufactured by Dain-

ippon Ink & Chemicals Inc.], 30 parts of water, 0.5 parts of silicon based anti-foaming agent, 3 parts of a water based ink thickening agent, 1 part of ethylene glycol, and 2 parts of an epoxy based crosslinking agent have been uniformly mixed and agitated, whereby a sheet has been obtained.

[0066] Eight sheets of aqueously color-changing puzzle pieces have been obtained by cutting the sheet.

[0067] Furthermore, the aqueously color-changing puzzle comprising the aqueously color-changing puzzle pieces, 8 sheets of non-color-changing puzzle pieces on which an image (non-color-changing image) of the product composed of the initials of "A" has been printed and a frame body was obtained.

[0068] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces within the frame body, when water was attached to the white color porous layer, the porous layer absorbed water and became transparent and the letter of "A" which is blue color expressed by the underlying layer of the coloring water resistant resin layer is visualized.

[0069] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it returned to the original white color.

[0070] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0071] Furthermore, on all of 8 sheets of the non-color-changing puzzle pieces, the image of the product initiated from the letter "A" has been printed, since the letter of "A" emerges by applying water to the aqueously color-changing puzzle pieces, it has been admitted that it was a puzzle whose applicability was excellent, which may be used as an intellectual training tool after it has been assembled as well as it has the playing characteristics enjoyed at the time when the puzzle is assembled.

(Example 4)

Preparation of aqueously color-changing puzzle set

[0072] An aqueously color-changing puzzle set was obtained by combining the aqueously color-changing puzzle obtained in Example 3 and a coating tool for containing water within the axial cylinder as means for attaching water and coating water from the fiber pen body by deriving out water within the container.

[0073] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces within the frame body within a frame body, when water was coated by bringing the pen body of the

coating tool in contact with the white porous layer, the porous layer absorbed water and became transparent and the letter of "A" in a blue color expressed by the underlying coloring water resistant resin image was visualized.

[0074] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it returned to the original white color.

[0075] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0076] Furthermore, on all of 8 sheets of the non-color-changing puzzle pieces, the image of the product initiated from the letter "A" has been printed, since the letter of "A" emerges by applying water to the aqueously color-changing puzzle pieces, it has been admitted that it is a puzzle set whose applicability is excellent, which may be used as an intellectual training tool after it has been assembled as well as it has the playing characteristics enjoyed at the time when the puzzle is assembled.

(Example 5)

Preparation of aqueously color-changing puzzle:

[0077] After the design of a bear has been process-printed using the respective dry offset inks of magenta color, cyan color, yellow color and black color on the white color coat paper as the substrate of the puzzle, the whole surface has been coated using an oil based colorless transparent polyester resin, and the water resistant resin layer was provided by drying and curing it.

[0078] Subsequently, on the coloring water resistant resin layer, a porous layer has been formed by performing a solid printing on the whole surface using a white color ink for printing that 15 parts of finely particulate silicic acid manufactured by a wet method as a low-refractive-index pigment [trade name: Nipsil E-200A, manufactured by Nippon Silica Industrial Co., Ltd.], 50 parts of an aqueous urethane resin as a binder resin [trade name: Hydran AP-10, polyester based urethane resin, solid content 30% manufactured by Dainippon Ink & Chemicals Inc.], 30 parts of water, 0.5 parts of silicon based anti-foaming agent, 3 parts of a water based ink thickening agent, 1 part of ethylene glycol, and 2 parts of an epoxy based crosslinking agent have been uniformly mixed and agitated.

[0079] Furthermore, the water resistant coloring image has been provided by printing the outline of the design of the bear using black color oily printing ink on the porous layer.

[0080] Subsequently, after the pasting working of a coated board paper having the thickness of 2 mm has been performed on the coat paper using an adhesive,

250 sheets of the aqueously color-changing puzzle pieces was obtained by cutting it.

[0081] After the aqueously color-changing puzzle having the outline of a bear has been completed by fitting together the color-changing aqueously color-changing puzzle pieces, when water was attached to the porous layer, the porous layer absorbed water and became transparent, and the design of the colorful bear expressed by the underlying layer was visualized.

[0082] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original white color.

[0083] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0084] Furthermore, since the puzzle piece was configured only by the black and white outline of the bear before water has been applied, the difficulty level at the time when it is assembled is increased and after it has been fixed together, the colorful design can be made emerge by applying water, and it has been admitted that it is a puzzle excellent in applicability and which can be played as an aqueously coloring drawing.

(Example 6)

Preparation of aqueously color-changing puzzle set:

[0085] An aqueously color-changing puzzle set was obtained by combining the aqueously color-changing puzzle obtained in Example 5 and a coating tool for containing water within the axial cylinder as means for attaching water and coating water from the fiber pen body by deriving out water within the container.

[0086] After the aqueously color-changing puzzle having the outline of a bear has been completed by fitting together the aqueously color-changing puzzle pieces, when water was coated by bringing the pen body of the coating tool in contact with the white porous layer, the porous layer absorbed water and became transparent and the colorful design of a bear expressed by the underlying layer was visualized.

[0087] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original puzzle of the outline of a bear.

[0088] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0089] Furthermore, since the puzzle piece was configured only by the black and white outline of the bear

before water was applied, the difficulty level at the time when it is assembled is increased and after it has been fixed together, the colorful design can be made emerge by applying water, and it has been admitted that it is a puzzle set excellent in applicability and which can be played as a coloring drawing whose colors are changed with water.

(Example 7)

Preparation of aqueously color-changing puzzle:

[0090] After the designs of the letters of "A" to "Z" and a product and a living organism initiated from the respective letters of "A" to "Z" have been process-printed using the respective ultraviolet ray curing type oily dry offset inks of magenta color, cyan color, yellow color and black color on the white color synthesized paper as the substrate of the puzzle, a water resistant resin layer was provided by drying and curing it.

[0091] Subsequently, only on the water resistant resin layer consisting of the designs of the product and living organism, a porous layer has been formed by performing a solid printing using a white color ink for printing that 15 parts of finely particulate silicic acid manufactured by a wet method as a low-refractive-index pigment [trade name: Nipsil E-200A, manufactured by Nippon Silica Industrial Co., Ltd.], 50 parts of an aqueous urethane resin as a binder resin [trade name: Hydran AP-10, polyester based urethane resin, solid content 30% manufactured by Dainippon Ink & Chemicals Inc.], 30 parts of water, 0.5 parts of silicon based anti-foaming agent, 3 parts of a water based ink thickening agent, 1 part of ethylene glycol, and 2 parts of an epoxy based crosslinking agent have been uniformly mixed and agitated.

[0092] Subsequently, after the pasting working of a coated-board paper having paper the thickness of 2 mm has been performed on the synthesized paper using an adhesive, 26 sheets of the aqueously color-changing puzzle pieces and 26 sheets of the non-color-changing puzzle pieces on which the letters from "A" to "Z" have been drawn were obtained by cutting it.

[0093] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces, when water was attached to the porous layer, the porous layer absorbed water and became transparent, and the design of the underlying layer was visualized.

[0094] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original puzzle.

[0095] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0096] Furthermore, since as for the puzzle piece, the letters drawn on the non-color-changing puzzle piece and the design of the aqueously color-changing puzzle pieces are communicated with each other and work together, it has been admitted that it is a puzzle excellent in applicability and which may be used as an intellectual training tool by applying water after these have been fitted together.

10 (Example 8)

Preparation of aqueously color-changing puzzle set:

[0097] An aqueously color-changing puzzle set was obtained by combining the aqueously color-changing puzzle obtained in Example 7 and a coating tool for containing water within the axial cylinder as means for attaching water and coating water from the fiber pen body by deriving out water within the container.

[0098] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces, when water was coated by bringing the pen body of the coating tool in contact with the white porous layer, the porous layer absorbed water and became transparent and the design of the underlying layer was visualized.

[0099] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original puzzle.

[0100] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0101] Furthermore, since as for the puzzle pieces, the letters drawn on the non-color-changing puzzle pieces and the designs drawn on the aqueously color-changing puzzle pieces are communicated with each other and work together, it has been admitted that it is a puzzle set excellent in applicability and which may be used as an intellectual training tool by applying water after these have been fixed together.

(Example 9)

Preparation of aqueously color-changing puzzle:

[0102] After the letters of numerical characters "1" to "10" and the designs on which the number of the products corresponding to the respective numerical characters has been drawn, have respectively been process-printed using the respective ultraviolet ray curing type oily dry offset inks of magenta color, cyan color, yellow color and black color on a transparent polyolefin sheet having the thickness of 25 micrometer as the substrate of the puzzle,

a water resistant resin layer was provided by drying and curing it.

[0103] Subsequently, only on the water resistant resin layer consisting of numerical characters from "1" to "10", a porous layer has been formed by performing a solid printing using a white color ink for printing that 12 parts of finely particulate silicic acid manufactured by a wet method as a low-refractive-index pigment [trade name: Nipsil E-200A, manufactured by Nippon Silica Industrial Co., Ltd.], 50 parts of an aqueous urethane resin as a binder resin [trade name: Hydran AP-10, polyester based urethane resin, solid content 30% manufactured by Dainippon Ink & Chemicals Inc.], 30 parts of water, 0.5 parts of silicon based anti-foaming agent, 3 parts of a water based ink thickening agent, 1 portion of ethylene glycol, and 2 parts of an epoxy based crosslinking agent have been uniformly mixed and agitated.

[0104] Subsequently, after the pasting working of a foaming polyolefin sheet having the thickness of 2 mm has been performed on the transparent polyolefin sheet side using an adhesive, 10 sheets of the aqueously color-changing puzzle pieces and 10 sheets of the non-color-changing puzzle pieces on which the letters from "1" to "10" have been drawn were obtained by cutting it.

[0105] It should be noted that as for the aqueously color-changing puzzle piece, the numerical characters expressed by the water resistant resin layer are slightly visually recognized in a dry state.

[0106] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces, when water was attached to the porous layer, the porous layer absorbed water and became transparent, and the letters of the underlying layer was visualized.

[0107] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original puzzle.

[0108] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0109] Furthermore, since as for the puzzle piece, the design drawn on the non-color-changing puzzle piece and the letters of the aqueously color-changing puzzle pieces are communicated with each other and work together, it has been admitted that it is a puzzle excellent in applicability and which may be used as an intellectual training tool by applying water after these have been fitted together.

(Example 10)

Preparation of aqueously color-changing puzzle set:

[0110] A aqueously color-changing puzzle set was ob-

tained by combining the aqueously color-changing puzzle obtained in Example 9 and a coating tool for containing water within the axial cylinder as means for attaching water and coating water from the fiber pen body by deriving out water within the container.

[0111] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces, when water was coated by bringing the pen body of the coating tool in contact with the white porous layer, the porous layer absorbed water and became transparent and the letter of the underlying layer was visualized.

[0112] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original puzzle.

[0113] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0114] Furthermore, since as for the puzzle piece, the design drawn on the non-color-changing puzzle piece and the letters of the aqueously color-changing puzzle pieces are communicated with each other and work together, it has been admitted that it is a puzzle set excellent in applicability and which may be used as an intellectual training tool by applying water after these have been fitted together.

(Example 11)

Preparation of aqueously color-changing puzzle set:

[0115] After the respective letters from "あ" (the first letter of the Japanese syllabary) to "ん" (the last letter, i.e. the fifteenth letter, of the Japanese syllabary) and the designs of the product or living organism initiated from the respective letters from "あ" (the first letter of the

Japanese syllabary) to "ん" (the last letter of the Japanese syllabary) have been process-printed using the respective ultraviolet ray curing type oily dry offset inks of magenta color, cyan color, yellow color and black color on a white color water resistant paper having the thickness of 0.5 mm as the substrate of the puzzle, a water resistant resin layer was provided by drying and curing it.

[0116] Subsequently, only on the water resistant resin layer consisting of the respective letters, a porous layer has been formed by performing a solid printing using a white color ink for printing that 15 parts of finely particulate silicic acid manufactured by a wet method as a low-refractive-index pigment [trade name: Nipsil E-200A, manufactured by Nippon Silica Industrial Co., Ltd.], 50 parts

of an aqueous urethane resin as a binder resin [trade name: Hydran AP-10, polyester based urethane resin, solid content 30% manufactured by Dainippon Ink & Chemicals Inc.], 30 parts of water, 0.5 parts of silicon based anti-foaming agent, 3 parts of a water based ink thickening agent, 1 part of ethylene glycol, and 2 parts of an epoxy based crosslinking agent have been uniformly mixed and agitated.

[0117] Subsequently, after the pasting working of a coated cardboard having the thickness of 2 mm has been performed on the water resistant paper side using an adhesive, 50 sheets of the aqueously color-changing puzzle pieces and 50 sheets of the non-color-changing puzzle pieces consisting of the designs of products and living organisms were obtained by cutting these.

[0118] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces, when water was brought in contact with the porous layer, the porous layer absorbed water and became transparent and the letter of the underlying layer was visualized.

[0119] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original puzzle.

[0120] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0121] Furthermore, since as for the puzzle piece, the design drawn on the non-color-changing puzzle piece and the letters of the aqueously color-changing puzzle pieces are communicated with each other and work together, it has been admitted that it is a puzzle excellent in applicability and which may be used as an intellectual training tool by applying water after these have been fixed together.

(Example 12)

Preparation of aqueously color-changing puzzle set:

[0122] An aqueously color-changing puzzle set was obtained by combining the aqueously color-changing puzzle obtained in Example 11 and a coating tool for containing water within the axial cylinder as means for attaching water and coating water from the fiber pen body by deriving out water within the container.

[0123] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces and the non-color-changing puzzle pieces, when water was coated by bringing the pen body of the coating tool in contact with the white porous layer, the porous layer absorbed water and became transparent and the letter of the underlying layer was

visualized.

[0124] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it returned to the original puzzle.

[0125] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0126] Furthermore, since as for the puzzle piece, the design drawn on the non-color-changing puzzle piece and the letters of the aqueously color-changing puzzle pieces are communicated with each other and work together, it has been admitted that it is a puzzle set excellent in applicability and which may be used as an intellectual training tool by applying water after these have been fitted together.

(Example 13)

Preparation of aqueously color-changing puzzle:

[0127] After the designs of animals and the names of animals (letters) have been process-printed using the respective ultraviolet ray curing type oily dry offset inks of magenta color, cyan color, yellow color and black color on a white color water resistant paper having the thickness of 0.3 mm as the substrate of the puzzle, a water resistant resin layer was provided by drying and curing it.

[0128] Subsequently, only on the water resistant resin layer on which the names of animals have been printed, a porous layer has been formed by performing a solid printing using a white color ink for printing that 15 parts of finely particulate silicic acid manufactured by a wet method as a low-refractive-index pigment [trade name: Nipsil E-200A, manufactured by Nippon Silica Industrial Co., Ltd.], 50 parts of an aqueous urethane resin as a binder resin [trade name: Hydran AP-10, polyester based urethane resin, solid content 30% manufactured by Dainippon Ink & Chemicals Inc.], 30 parts of water, 0.5 parts of silicon based anti-foaming agent, 3 parts of a water based ink thickening agent, 1 portion of ethylene glycol, and 2 parts of an epoxy based crosslinking agent have been uniformly mixed and agitated.

[0129] Subsequently, after the pasting working of a wood material having the thickness of 10 mm has been performed on the water resistant paper side using an adhesive, 9 sheets of aqueously color-changing puzzle pieces that the non-color-changing designs of animals and a porous layer exist on the same puzzle piece were obtained by cutting it.

[0130] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces, when water was attached with the porous layer, the porous layer absorbed water and became transparent and the letter of the underlying layer

was visualized.

[0131] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it has returned to the original puzzle.

[0132] The above appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and even if the puzzle piece has been immersed for 24 hours in water at 24°C, no peelings have not been generated and the durability was excellent.

[0133] Furthermore, since as for the puzzle piece, the design and letters of animals drawn on the puzzle piece are communicated with each other and work together, it has been admitted that it is a puzzle excellent in applicability and which may be used as an intellectual training tool by applying water.

(Example 14)

Preparation of aqueously color-changing puzzle set:

[0134] An aqueously color-changing puzzle set was obtained by combining the aqueously color-changing puzzle obtained in Example 13 and a coating tool for containing water within the axial cylinder as means for attaching water and coating water from the fiber pen body by deriving out water within the container.

[0135] After the aqueously color-changing puzzle has been completed by fitting together the aqueously color-changing puzzle pieces, when water was coated by bringing the pen body of the coating tool in contact with the white porous layer, the porous layer absorbed water and became transparent and the letter of the underlying layer was visualized.

[0136] The appearance was visually recognized for about 3 minutes at room temperature of 24°C, however, it became gradually white color as the porous layer was dried, and after about 10 minutes, it returned to the original puzzle.

[0137] The appearance change could be repeatedly performed, the trouble such as a swelling of the substrate, a blur of the printing surface has not been generated even if water has been applied, and the durability was excellent.

[0138] Furthermore, since as for the puzzle piece, the designs and letters of animals drawn on the puzzle piece are communicated with each other and work together, it has been admitted that it is a puzzle set excellent in applicability and which may be used as an intellectual training tool by applying water.

(Example 15)

Preparation of aqueously color-changing puzzle:

[0139] An aqueously color-changing puzzle comprising an aqueously color-changing puzzle piece obtained in Example 3, 8 sheets of non-color-changing puzzle pieces on which an image (image whose colors are not changed) of a product item composed of an initial letter of "A" has been printed, and the frame body to which the said pieces are to be fitted and fixed was obtained.

[0140] It should be noted that, similar to Example 3, a coloring water resistant resin layer was provided using a blue color printing ink on the rear surface of the said frame body, and subsequently, a porous layer was formed using a white color ink for printing on the said coloring water resistant resin layer.

[0141] As for the said aqueously color-changing puzzle, similar to Example 3, colors of the puzzle pieces could be changed by applying water.

[0142] Moreover, the rear surface of the frame body could be made such that the axial cylinder as a means for attaching water contains water therein and derives out the water in the container so as to form a drawing design using the coating tool for coating water from a fiber pen body. Accordingly, an aqueously color-changing puzzle which is rich in playing characteristics can be obtained.

Claims

1. An aqueously color-changing puzzle comprising:

one or more puzzle piece(s);
the piece comprises a substrate, a water resistant resin layer on the substrate, and a porous layer on the a water resistant resin layer;

wherein the porous layer is made of a dispersion system of (a) low-refractive-index pigment(s) in (a) binder resin(s) so that the transparency of the porous layer may differ between in a liquid-absorbing state and in a non-liquid absorbing state.

2. The aqueously color-changing puzzle according to claim 1, in which said water resistant resin layer includes (a) colored image(s) selected among letters, designs, symbols and numeric characters.

3. The aqueously color-changing puzzle according to claim 1 or 2, in which the whole upper surface of said substrate is covered with the water resistant resin layer.

4. The aqueously color-changing puzzle according to any one of claims 1 to 3, in which said substrate is made of one of selected among normal paper, syn-

thesized paper, water resistant paper, wood material, plastic sheet, foamed plastic sheet, and laminated sheet thereof.

5. The aqueously color-changing puzzle according to any one of claims 1 to 4, further comprising (a) further colored water resistant image(s) provided on said porous layer. 5

6. The aqueously color-changing puzzle according to any one of Claim 1 to 5, in which said aqueously color-changing puzzle comprises at least 9 pieces or more of puzzle pieces, and the number of puzzle pieces in which a porous layer is provided occupies 30% or more of the whole puzzle pieces. 10
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7. The aqueously color-changing puzzle according to any one of claims 1 to 6, further comprising a frame body which holds the whole puzzle pieces. 20

8. The aqueously color-changing puzzle according to in claim 7, further comprising a porous layer on the rear surface of said frame body, in which the porous layer is made of a dispersion system of (a) low-refractive-index pigment (s) in (a) binder resin(s) so that the transparency of the porous layer may differ between in a liquid-absorbing state and in a non-liquid absorbing state. 25

9. An aqueously color-changing puzzle set comprising the aqueously color-changing puzzle according to any one of claims 1 to 8 and means for wetting. 30

10. The aqueously color-changing puzzle set according to claim 8, in which said means for wetting is selected from a writing tool or a coating tool having a brush or a fiber pen body on the tip end portion; and a writing tool or a coating tool having a water container and a fiber body or a brush for deriving out water within the container. 35
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Fig. 1

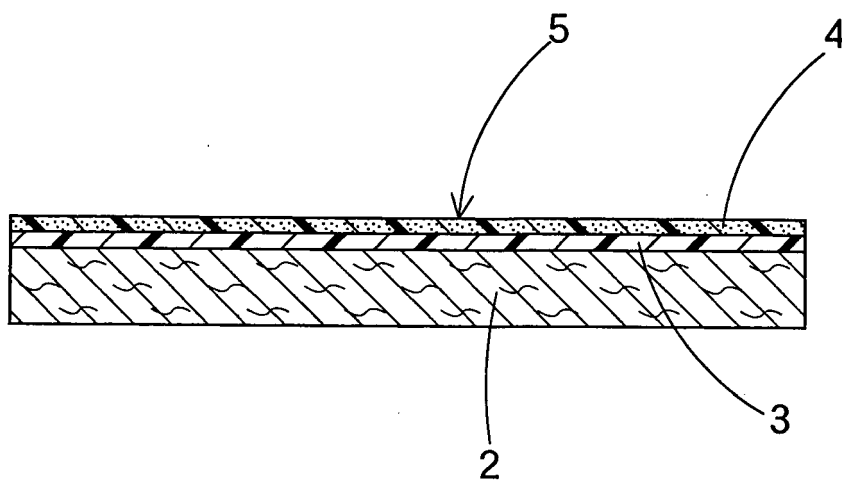
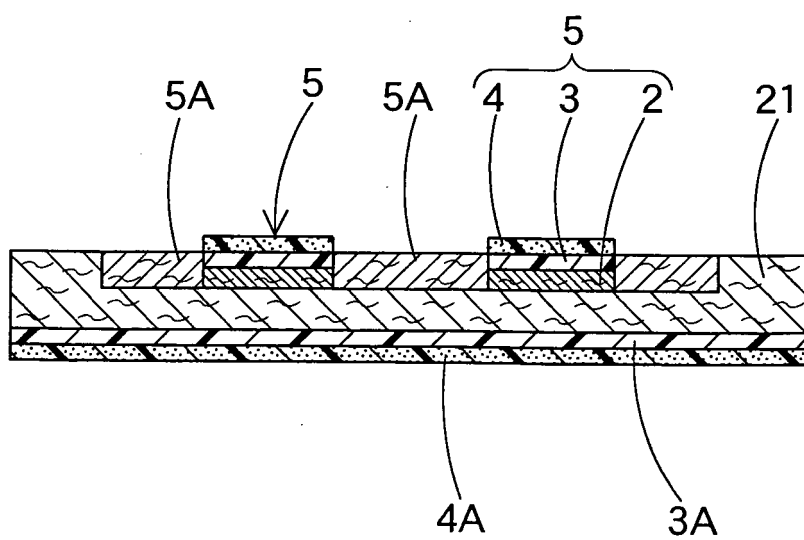


Fig. 2





European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 06 02 3751

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 4 September 2007	Examiner Lucas, Peter
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04-09-2007

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