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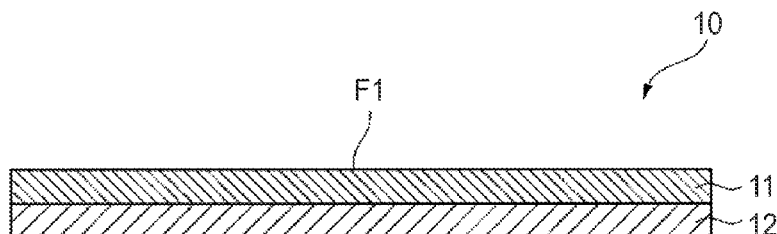


FIG. 1

(57) Abstract: A print media for water-based ink comprising a base, and an ink reception layer with a surface not facing the base to be used as the printing surface provided on one side of the base, wherein the ink reception layer includes; a hydrophilic first resin and a second resin having a thermal adhesive property a micro-phase separation structure in the printing surface, which is formed by the first resin and the second resin; and the second resin contains an acrylic polymer with a quaternized amino group.



**PRINT MEDIA FOR WATER-BASED COLOR INK JET PRINTING  
AND METHOD FOR MANUFACTURING SAME**

Field of Invention

5           The present invention relates to a print media, particularly for water-based color ink jet printing, and a method for manufacturing the same.

Background

10           As conventional print media, various products such as paper, synthetic paper, and a resin film are known. These print media are affixed to various objects, and used by, for example, providing adhesive on the print media, applying double-sided adhesive tape, etc.

          In recent years, a configuration of print media has become well known wherein the printing surface also functions as the adhesion surface and without requirement for the application of an adhesive over the print image. Illustrative examples are disclosed in the following: D1 -  
15   Japanese Patent Laid-Open No. 2004-276613; D2 - Japanese Patent Laid-Open No. 11-165457; D3 - Japanese Patent Laid-Open No. 2008-087276; D 4 - Japanese Patent Laid-Open No. 2008-087324; and D5 - Japanese Patent Laid-Open No. 2011-255650.

          The need exists for water-based ink jet receptive media that exhibit improved resistance to image bleed, resistance to water absorption and damage, particularly for use with high speed  
20   printing applications.

Summary of the Invention

          The present invention provides improved ink jet receptive print media and methods for making such media.

25

          In brief summary, a print media of the invention comprises a base having a first surface and an ink reception layer on at least a portion of the first surface of the base. In accordance with the invention: (1) the ink reception layer has a printing surface defined by micro-phase separation of a blend of a first resin component composition and a second resin component composition; (2) the  
30   first resin component is hydrophilic; and (3) the second resin component comprises an acrylic polymer with a quaternized amino group and exhibits thermal adhesive characteristics. It has been surprisingly found that ink reception layers with printing surface or area defined by a micro-phase separation structure as described herein provide unexpected and advantageous results.

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As described herein, the first and second resin components exhibit a micro-phase separation structure in the printing surface.

Briefly summarizing, the method for manufacturing print media of the invention comprises: (1) providing a base having a first surface; (2) providing a blend of a first resin component composition and a second resin component composition; (3) applying the blend to at least a portion of the first surface of the base to form a coating thereon; and (4) removing solvent from the coating such that micro-phase separation of the first resin component and second resin component occurs.

The media provided by the invention offer a surprising combination of significant advantages, including good, high resolution receptivity to water-based inks, resistance to image bleed, resistance to water absorption and water damage, and good adhesion properties, i.e., the printing surface will adhere to desired adherends. They are well suited for use in high speed printing applications and can be used to make articles with high quality, high resolution, durable images thereon.

Heretofore, the prior art, e.g., such as described in References D1-D4, did not provide print media capable of desired performance and capability. Reference D5 purports to disclose media exhibiting desired performance and capabilities, but the media disclosed therein were found to exhibit dye bleeding with water-based ink was applied with a high-speed jet printing of more than 25 mm/sec, it caused dye bleeding.

In accordance with the present invention, the printing surface has a plurality of first micro-phase isolation regions that contain more of the first resin component than the second resin component and a second micro-phase isolation region which contains more of the second resin component than the first resin component, surrounds each of the micro-phase isolation regions in approximately the shape of a ring, and is relatively convex.

The present invention also provides a print media for water-based ink comprising a base having a first surface and an ink reception layer on at least a portion of the first surface of the base wherein: (1) the ink reception layer has a printing surface defined by micro-phase separation of a blend of a first resin component composition and a second resin component composition; (2) the first resin component is hydrophilic; and (3) the second resin component comprises an acrylic polymer with a quaternized amino group and exhibits thermal adhesive characteristics; wherein the printing surface is made up of a matrix of first domains the majority fraction of which is first resin component and second domains the major fraction of which is second resin component;

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wherein the second domains substantially surround each first domain and the second domains are relatively convex;

wherein there is a difference in height between the first domains and the second domains from about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ ; and

5 wherein the first domains have an average diameter of about 100  $\mu\text{m}$  or less.

Reference to any prior art in the specification is not, and should not be taken as, an acknowledgment, or any form of suggestion, that this prior art forms part of the common general knowledge in Australia or any other jurisdiction or that this prior art could reasonably be expected to be ascertained, understood and regarded as relevant by a person skilled in the art.

10 As used herein, except where the context requires otherwise, the term "comprise" and variations of the term, such as "comprising", "comprises" and "comprised", are not intended to exclude other additives, components, integers or steps.

#### Brief Description of the Drawings

15 The invention is further explained with reference to the drawing wherein:

Fig. 1 is a schematic cross-sectional view showing one illustrative embodiment of a print media of the present invention;

Fig. 2 is a schematic cross-sectional view showing another illustrative embodiment of a print media of the present invention;

20 Fig. 3 is a schematic cross-sectional view showing yet another illustrative embodiment of

a print media of the present invention;

Fig. 4 is a figure showing the surface of the print media obtained in Example 1 as observed with an optical microscope;

Figs. 5a and 5b are figures showing the result when the non-contact surface coarseness of the print media obtained in Example 1 is measured with a measuring instrument;

Fig. 6 is a figure showing the result when the surface of the print media 2 obtained in Comparison Example 1 as observed with an optical microscope; and

Figs. 7a and 7b are figures showing the result when the non-contact surface coarseness of the print media obtained in Comparison Example 1 is measured with a measuring instrument.

Figs. 1-3 are not to scale and Figs. 1-7 are intended to be merely illustrative and not limiting.

Key to reference numerals:

Component Feature	Reference Numerals
Print Media	10, 20, 30
Ink Reception Layer	11, 21, 31
Base	12, 22, 32
Support Layer	23, 34
Anti-grime Layer	33
Printing Surface	F1, F2, F3

#### Detailed Description of Illustrative Embodiments

Hereinafter, the preferred embodiments of the present invention will be described while referring to the attached drawings.

Unless otherwise indicated, all numbers expressing quantities of ingredients, properties such as molecular weight, reaction conditions, and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about". Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings of the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques. Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations,

the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical value, however, inherently contains certain errors necessarily resulting from the standard deviations found in their respective testing measurements.

Weight percent, percent by weight, % by weight, and the like are synonyms that refer to the concentration of a substance as the weight of that substance divided by the weight of the composition and multiplied by 100.

The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5). As used in this specification and the appended claims, the singular forms "a", "an", and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

In the print media of the invention, the printing surface is defined by micro-phase separation of the blend of the first resin component composition and the second resin component composition. It has been discovered that the resultant printing surface is made up of a matrix of first domains the majority fraction of which is first resin component and second domains the major fraction of which is second resin component and that these domains have a physical configuration and combination of characteristics which result in surprising performance.

In typical embodiments, the ink reception layer has a plurality of first micro-phase isolation regions that contain more of the first resin component than the second resin component and a second micro-phase isolation region which contains more of the second resin component than the first resin component, surrounds each of the first micro-phase isolation regions in approximately the shape of a ring (i.e., the substantially completely enclosing cells), and is relatively convex.

As a result of the characteristic uneven surface properties between the first micro-phase isolation regions and the second micro-phase isolation regions resulting from the micro-phase separation, when during printing the tendency of water-based inks is reduced, resulting information of a clear printed image without any blurriness, even instances of high-speed printing of more than 25 mm/sec (for example, 100 mm/sec).

In some preferred embodiments, the first resin component comprises polyalkylene oxide. In such embodiments, the print characteristics and adhesion of the printing surface are improved because the polyalkylene oxide imparts improved receptiveness to water-based inks in conjunction with an adhesive property.

In some embodiments, the acrylic polymer of the second resin component comprises a phenoxy group. Resultant ink reception layers made with this component provide improved adhesion of the ink reception layer to desired adherends and impart improved water resistance to images printed thereon.

5 In some embodiments, the relative proportions of first resin component and second resin component is such that in the resultant ink reception layer the first resin component constitutes 30 to 60 mass % with respect to a 100 mass % of the total of the first resin component and the second resin component. In this formulation, a good balance between the high-speed printing characteristic of the printing surface and water resistance of the printed image can be achieved.

10 The other aspect of the present invention relate to the method for manufacturing a print media for water-based ink. The method for manufacturing a print media for water-based ink comprises applying a blend containing the first resin component, the second resin component, and a solvent to the base and form a coating on the base, and removing solvent from the coating such that micro-phase separation of the first resin component and the second resin component occurs.

15 According to this manufacturing method, the printing surface is the print media which functions as the adhesion surface and has both good adhesive property and print characteristics, and a print media for water-based ink with good water resistance and bleed characteristics of the printed image even when printed with aqueous dye ink can be easily obtained.

In some embodiments, the application solution may be a suspension including the first  
20 resin component and the second resin component. The ink reception layer formed by such an application solution makes it easy to form the micro-phase separation structure in the printing surface by using the first resin component and the second resin component.

Fig. 1 is a schematic cross-sectional view showing one illustrative embodiment of the print media of the present invention. The print media 10 has a base 12, and an ink reception layer  
25 11 and a surface F1, which does not face the base 12, i.e., is opposite thereto in the embodiment show, provided on one side of base 12 as the printing surface.

The ink reception layer 11 comprises, and may consist essentially of, a hydrophilic first resin component and a thermal adhesive second resin component, and has a micro-phase separation structure formed by the first resin component and the second resin component in the printing  
30 surface F1. The second resin component comprises an acrylic polymer with a quaternized amino group.

In the printing surface F1 of the print media 10, the first resin component can function as the water-based ink reception area, providing desired receptivity to imaging ink, e.g., ink jet applied



water-based inks, and the second resin component can function as the adhesion area, providing desired adhesion of the media to a desired adherend. Therefore, an image print with the water-based ink is possible on the printing surface F1, and it functions as the adhesion surface.

Further, since the print media 10 has the configuration described above, it has good adhesive property and good high-speed printing characteristic in the printing surface F1, it is suitable for use as a print media for high-speed jet printing of more than 25 mm/sec., for example.

In addition, in the print media 10, the printed image formed by using the water-based ink on the printing surface F1 becomes superior in water resistance and bleed resistance. Particularly, in the conventional print media (for example, the print media described in Reference D5), it was difficult to prevent dye bleeding in printed images when dye ink was used as water-based ink, however bleeding can be sufficiently suppressed even in printed images form by using aqueous dye ink according to this print media 10. Therefore, the print media 10 can be suitably used as a print media for aqueous dye ink.

While we do not wish to be bound by this theory, it is thought the following. The minute ink reception area made by the first resin component and the minute adhesion area made by the second resin component accomplish this complicated structure in the printing surface F1 due to the micro-phase separation. Therefore, the water-based ink infiltrates the ink reception area in points of impact, however the expansion (bleeding) due to the penetration from the ink reception area of the points of impact to the ink reception area other than the points of impact is obstructed by the adhesion area. Therefore is it thought that bleeding of the water-based ink in the print can be prevented, and a clear image can be formed. In addition, it is thought that the printed image becomes superior in water resistance since bleeding of the water-based ink is prevented for a similar reason even after water-based ink has been printed.

The second resin component comprises a quaternized amino group in the printing surface F1. Therefore, the fixation of the dye becomes very superior, and dye bleeding is controlled in the interface with the ink reception area and the adhesion area when printed with aqueous dye ink. Note that, it is thought that if the dye is an acid dye, then this fixation is obtained even more conspicuously, and the bleed is controlled even more conspicuously. This is why the print media 10 can be particularly suitable for use as a print media for acid dye ink.

Here, the term micro-phase separation structure means the first resin component and the second resin component exhibit a microscopic phase separation structure. For example, when at least one of the first resin component and the second resin component makes an independent phase in the printing surface F1, and the average diameter of the phase is equal to or less than 100  $\mu\text{m}$ , it

may be said that it is a micro-phase separation structure. Note that, the average diameter of the phase can be found by adding together the arbitrary number and the average diameter of 10 to 100 phases observed with a surface optics micrograph and electron micrograph.

The micro-phase separation structure should preferably have an average diameter of the independent phase described above which is equal to or less than the dot diameter of water-based ink provided in the printing surface F1. For example, when printing so that the average diameter of the ink dot is equal to or less than 30  $\mu\text{m}$ , 20  $\mu\text{m}$ , or 10  $\mu\text{m}$  in the inkjet printing, the independent phase described above should preferably be a minute size equal to or less than average a diameter of 30  $\mu\text{m}$ , 20  $\mu\text{m}$ , or 10  $\mu\text{m}$ . Thereby making it possible to form an even clearer image.

As will be understood, the minimum of the average diameter of the independent phase described above is not particularly limited, and may be more than 0.01  $\mu\text{m}$  and in some embodiments even more than 0.1  $\mu\text{m}$ .

Island structure, cylinder structure, lamellar structure, and cocontinuum structures are given as examples of micro-phase separation structures. Specifically, an island structure where the first resin component having the hydrophilicity is in the shape of an island, and the second resin component constitutes the sea around it is desirable.

The first resin component is hydrophilic. What this means is that, the first resin component has a property to make it capable of absorbing water-based ink. For example, when water has been dripped on the resin component surface to sufficiently to cover a wide area, and the resin component absorbs the drops of water within a few seconds (for example, five seconds), it can be said that the resin component is hydrophilic.

In illustrative embodiments, the first resin component may comprise one or more of a polyalkylene oxide, hydrophilic acrylic acid resin, polyvinyl alcohol, polyvinylpyrrolidone, hydrophilic polyurethane resin, hydrophilic ethylene vinyl alcohol.

Preferably the first resin component contains a polyalkylene oxide. In this case, the print and adhesion characteristics of printing surface F1 become even better, since the polyalkylene oxide is superior in the receptiveness of the water-based ink and has an adhesive property. Polyethylene oxide, polypropylene oxide, ethylene oxide, and propylene oxide co-polymer, are given as the polyalkylene oxide.

Within the first resin component, polyalkylene oxide is preferably more than 80 mass %, and more preferably, more than 90 mass % of the total mass thereof. In addition, the first resin component may be a polyalkylene oxide.

The second resin component is a thermal adhesive resin component and contains at least

an acrylic polymer with a quaternized amino group.

The acrylic polymer may further include a phenoxy group. By this, the adhesive property of the printing surface and water resistance of the printed image improve even more.

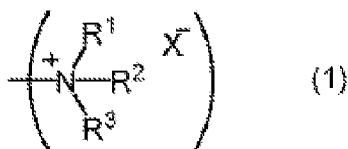
The acrylic polymer may be a polymer of which the monomer component includes an acrylic monomer with a quaternized amino group. In addition, the monomer component may further include an acrylic monomer with a phenoxy group, alkyl (meth)acrylate, or (meth)acrylic acid.

For example, an acrylic monomer with a quaternized amino group and a polymer of the monomer component including alkyl (meth)acrylate and (meth)acrylic acid are given as one form of the acrylic polymer, and the monomer component may include an acrylic monomer with a phenoxy group.

Here, the ratio of acrylic monomer with a quaternized amino group in the monomer component can be a 3 to 13 mass % or it can be 5 to 11 mass %. In addition, the ratio of alkyl (meth)acrylate in the monomer component, can be 20 to 90 mass %, and should preferably be 25 to 70 mass %, and more preferably be 30 to 60 mass %. Further, the ratio of the (meth)acrylic acid of the monomer component may be 1 to 8 mass %. Furthermore, the ratio of the acrylic monomer with the phenoxy group in the monomer component, may be 0 to 70 mass %, and should preferably be 10 to 65 mass %, and more preferably be 20 to 60 mass %.

In this embodiment, the total of the alkyl (meth)acrylate and acrylic monomer with the phenoxy group in the monomer component may be 60 to 94 mass %, and should preferably be 70 to 90 mass %.

For example, the group expressed with the following formula (1) is given as the quaternized amino group.



In the formula,  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  are independently an alkyl group or aryl group and the  $\text{X}^-$  is the monovalent anion.  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^3$  should preferably each be an alkyl or phenyl group, more preferably an alkyl group, and even more preferably an alkyl group of  $\text{C}_{1-2}$  (an alkyl group with a carbon number of one or two).

The expressed monovalent anion which is an  $\text{X}^-$  is not particularly limited, however examples such as a halogenide ion (a chloride ion, a bromide ion, an iodide ion) is given. Of these, a chloride ion is more preferable due to its easily availability.

N,N-Dimethylaminoethyl (meth)acrylate quaternized with methyl chloride, N,N-dimethylamino propyl (meth)acrylate quaternized with methyl chloride, N,N-dimethylamino ethyl (meta)acrylic amide quaternized with methyl chloride, and N,N-dimethylamino propyl (meta)acrylic amide quaternized with methyl chloride are suitable for use as an acrylic monomer with a quaternized amino group.

Phenoxy ethyl (meth)acrylate is given as the acrylic monomer with the phenoxy group. C<sub>1-16</sub> alkyl (meth)acrylate is preferable, and C<sub>1-10</sub> alkyl (meth)acrylate is more preferable as the alkyl (meth)acrylate. Here, "C<sub>1-16</sub>" and "C<sub>1-10</sub>" shows the carbon number of the alkyl group excluding the (meth)acryloyl group.

The second resin component may contain hydrophobic resin component as the thermal adhesive resin component excluding the acrylic polymer. For example, the second resin component may contain polyester, hydrophobic polyurethane resin, polyester urethane resin, and ethylene vinyl acetate. Note that, to hydrophobic means to have a property to repel water-based ink. For example, it could be said that it is a hydrophobic resin if almost all of the drops of water are repelled when the water is dropped on the resin the surface.

Preferably, within the second resin component, the acrylic polymer described above constitutes more than 50 mass %, and more preferably more than 60 mass % thereof. In some instances, the second resin component may consist essentially of the acrylic polymer.

The first resin component content in the ink reception layer 11 can be a 20 to 70 mass %, and can also be 30 to 60 mass % with regards to the gross weight of a 100 mass % of the first and the second resin component. By this, it is thought that the existence ratio of the ink reception area in the micro-phase separation structure of printing surface F1 and the adhesion area becomes suitable, and a good balance between the high-speed printing characteristic of the printing surface F1 and water resistance of the printed image can be achieved. At this time, for example, clear printed images with no bleeding can be obtained even in high-speed printings of more than 100 mm/sec.

In the printing surface F1, the ratio ( $S_1/S_2$ ) of the total area ( $S_1$ ) of the ink reception area made by the first resin component and total area ( $S_2$ ) of the ink reception area made by the second resin component may be, for example, 0.2 to 4.0, and it may be 0.4 to 1.5. Print characteristics, adhesive property and water resistance become even more superior by being provided with an ink reception area and adhesion area at such area ratio.

The ink reception layer 11 can be set to 10 to 40  $\mu\text{m}$  as well as 20 to 30  $\mu\text{m}$  for example. The ink reception layer 11 manufactured to become such a thickness has even better print and

adhesion characteristics of printing surface F1. The reason for such an effect is not always clear, however, it is thought that the adhesive strength of the second resin component is effectively expressed with a thickness of more than 15 $\mu$ m, and good adhesive strength can be secured. The micro-phase separation structure that is homogeneous, and is formed easily when it is less than 40  $\mu$ m.

The ink reception layer 11 should have optical transparency. According to such ink reception layer 11, the image printed on the printing surface F1 can be viewed from surfaces other than the printing surface F1. In this case, it is preferable for a base 12 (to mentioned later) to be added, and to have optical transparency.

The ink reception layer 11 may have a first micro-phase isolation region that contains more of the first resin component than the second resin component, and a second micro-phase isolation region that contains more of the second resin component than the first resin component, surrounds the first micro-phase isolation region in approximately the shape of a ring and is relatively convex. In this way, bleeding is prevented effectively in the region interface, and high-speed printing characteristics are largely improved by placing the region (the second micro-phase isolation region) where there is relatively a lot of the second resin component around the region (the first micro-phase isolation region) where there is relatively a lot of the first resin component.

Note that, "to contain more of the first resin component than the second resin component" means that the area ratio of the surface made by the first resin component occupying the region is bigger than the area ratio of the surface made by the second resin component. Further, "relatively convex" means that the region is at least higher than the adjacent first aspect isolation region.

There should preferably be a plurality of first micro-phase isolation regions and should preferably be approximately in the shape of a ring surrounding each of the second micro-phase isolation regions. That is to say, the ink reception layer 11 should preferably have a structure where the second micro-phase isolation region is surrounded around the first micro-phase isolation region and that this structural unit has a repeated unevenness structure in the printing surface F1 as one unit.

In other words, in the printing surface F1, the ink reception layer 11 should preferably have an unevenness structure with a concave part and a convex part surrounding the concave part in approximately the shape of a ring, wherein the concave part forms the first micro-phase isolation region that contains more of the first resin component than the second resin component, and the convex part forms the second micro-phase isolation region that contains more of the second resin

component than the first resin component.

In this manner, it is thought that the retention of the water-based ink in the printing surface F1 improves, and that the print characteristics further improve by the convex part making the second micro-phase isolation region surrounding the outside of the concave part, which makes the first micro-phase isolation region, to resemble the outer rim of a volcanic crater.

In addition, the first micro-phase isolation region includes more of the first resin component and has good absorption of the water-based ink. It is thought that the water-based ink maintained by concave part settles in the ink reception layer 11 due to the high absorbency of the first micro-phase isolation region by making the micro-phase isolation region with the concave portion.

Further, the second micro-phase isolation region includes more of the second resin component, and there is relatively little of the first resin component. It is thought that the superior adhesive property and water resistance are realized due to the convex portion where this kind of second micro-phase isolation region comes into contact by being adhered on the object.

The shape of the first micro-phase isolation region may be approximately in the shape of a circle, oval or polygon, but is typically circular in shape. The diameter of the first micro-phase isolation region may be for example, 10  $\mu\text{m}$  to 500  $\mu\text{m}$  or 50  $\mu\text{m}$  to 300  $\mu\text{m}$ .

The second micro-phase isolation region relatively forms a convex; however the difference ( $h_2 - h_1$ ) between the average height  $h_1$  of the adjacent first micro-phase separation structure and the average height  $h_2$  of the second micro-phase isolation region may typically be 1  $\mu\text{m}$  to 30  $\mu\text{m}$ , and in some instances may be 2  $\mu\text{m}$  to 20  $\mu\text{m}$ .

Note that, the second micro-phase isolation region, should preferably surround the first micro-phase isolation region in the shape of a ring; however it does not have to be in a completed circle, as long as the second micro-phase isolation region is formed around the first micro-phase isolation region in approximately the shape of a ring.

The base 12 should have a surface where it is possible to provide an ink reception layer 11. Note that, in the print media 10, the base 12 makes the shape of film, but the base does not always have to be shape of film used in the present invention.

Paper, synthetic paper, resin film or a resin sheet made from resins such as polyvinyl chloride resin, polyolefin resin, acrylic acid resin, polyester, and polyurethane resin can be used as the base 12. The base may be single layer or multilayer and should provide sufficient dimensional stability for formation of a ink reception layer thereon and subsequent handling and processing of the print media. Those skilled in the art will be able to readily select suitable material for the base

taking into account desired flexibility, tear strength, stretch properties, elasticity, weight, etc.

It is preferable for base 12 to have optical transparency. The image printed on the printing surface F1 can be seen through the ink reception layer 11 and the base 12 due to both the base 12 and the ink reception layer 11 having optical transparency.

5 Uses of the print media for water-based ink according to the present embodiment will be described below. Note that, the use of a print media for water-based ink of the present invention is not a limited to the following embodiment.

10 With the print media 10, a clear image can be printed on the printing surface F1 using water-based ink and the printing surface F1 also functions as the adhesion surface. Therefore, the print media 10 can be adhered to an object easily without any extra adhesion processing.

For example, the print media 10 is suitable for uses as a film affixed to IC cards, photo identification cards, etc. In this case, for example, first an image to be displayed on an IC card is printed on the printing surface F1, and then heat laminated with the printed surface F1 and IC card facing opposite of one another.

15 In such a use, IC cards having a clear image can be produced quickly because the print media 10 is superior in print characteristics, adhesive property and water resistance. In addition, the produced IC cards also become superior in water resistance.

20 In addition, for example, if the print media 10 is going to be peeled off after being applied on the IC card, the minute ink reception area gets destroyed, and the print content becomes illegible due to the micro-phase separation structure in the printing surface F1 of the print media 10. Therefore, according to the print media 10, the IC cards can be prevented from being reused for unauthorized purposes.

25 In addition, the print media 10 can be adhered on objects having unevenness or curved surfaces to be used as a decorative film. In this case, a heat extensibility base should preferably be used for the base 12 of the print media 10. For example, such a print media 10 can be adhered on objects having unevenness or curved surfaces to take the shape while heating the print media 10 with a dryer or the like.

30 The print media 10 may have a support layer on the other surface of the base 12 on the area, depending on the use, to support the print media 10 and improve the handling characteristics. Such a situation is shown Fig. 2.

The print media 20 shown in Fig. 2 has a base 22, and an ink reception layer 21 and a surface F2, which does not face the base 22, provided on one side of base 22, and a support layer 23 provided on the other side of the base 22. Note that, the base 22 and the ink reception layer 21 in

the print media 20 is equivalent to the base 12 and the ink reception layer 11 in the print media 10.

The print media 20 is superior in the handling characteristics because the base 22 and the ink reception layer 21 are supported by the support layer 23. With the print media 20, for example, the support layer 23 can be peeled after the water-based ink printed image has been formed and only the base 22 and the ink reception layer 21 can be adhered on the object.

The print media 10 may have an anti-grime layer on the other surface of the base 12 on the area, depending on the use, to prevent dirt and grime from getting attached to most outer surface after the print media 10 has been adhered on the object. Such the situation is shown Fig. 3.

The print media 30 shown in Fig. 3 has a base 32, an ink reception layer 31 with a surface F3 that is not faced with the base 22 that is provided on one side of base 32 as the printing surface, and grime layer 33 provided on the other side of the base 32. Note that, the base 32 and the ink reception layer 21 in the print media 30 is equivalent to the base 12 and the ink reception layer 11 in the print media 10. For example, the anti-grime 33 can be formed from a resin composition containing fluorine resin.

In addition, the print media 30 may also have a support layer 34 to support the base 32, ink reception layer 31 and anti-grime 33. With the print media 30, for example, the support layer 34 can be peeled after the water-based ink printed image has been formed and only the base 32, ink reception layer 31 and anti-grime 33 can be adhered on the object.

Next, an example of the print method for a print media for water-based ink according to this embodiment will be described.

The method to print water-based ink on the printing surface F1 of the print media 10 is not particularly limited; however ink jet printing is preferable. A printed image can be formed quickly if ink jet printing is performed, and the above-described IC card can be produced even more quickly.

The printing speed of the jet printing may be more than 25 mm/sec, more than 50 mm/sec, or even more than 100 mm/sec. Advantages of the present invention include that clear images can be formed on media of the invention without suffering bleeding of the ink even with such a printing speed since the print media 10 is superior in high-speed printing characteristics in the printing surface F1.

The water-based ink to be used for print is not limited in particular, but it may be aqueous dye ink, or it may be acid dye ink. According to the print media 10, when dye ink is used, bleeding can be sufficiently controlled.

Next, the manufacturing method of the print media for water-based ink according to this



embodiment will be described. Note that, the print media for water-based ink of the present invention is not limited to the print media produced by the following manufacturing method.

This manufacturing method comprises a step to apply a solution containing the first resin component, the second resin component and a solvent to the base and form a coating on the base,  
5 and a step to remove the solvent from the coating and allow micro-phase separation of the first resin component and the second resin component.

According to this manufacturing method, the printing surface is the print media which functions as the adhesion surface and has both good adhesive property and print characteristics, and a print media for water-based ink (refer to print media 10 for a specific example) with good water  
10 resistance and bleed characteristics of the printed image even when printed with aqueous dye ink can be easily obtained.

In the application solution of the first process, the first resin component and the second resin component may be dissolved in a solvent and may be dispersed as resin component fine particles in the solvent to form the suspension (the term "solvent" is used herein to refer to such  
15 embodiments wherein the subject fluids would more precisely be referred to as liquid media, liquid fraction, etc.).

The solvent may be such that the first resin component and the second resin component are dissolved or capable of being dispersed uniformly in the application solution, and an organic solvent may be suitably used. Aromatic types such as benzene, toluene, and xylene; ketones such  
20 as acetone, and methyl ethyl ketone; esters such as ethyl acetate, and butyl acetate; alcohols such as methanol, and ethanol are given as examples of the organic solvent. These can be combined together or used individually. In addition, a mixture of water or water and alcohol can be used as a solvent in this manufacturing method.

The application solution may be heated if necessary. For example, the application  
25 solution may be heated to 30 to 60°C to let the first resin component and the second resin component dissolve.

In one situation of this manufacturing method, the application liquid may be a suspension including the first resin component and the second resin component. The ink reception layer formed with such an application solution makes the characteristic unevenness shape having the  
30 concave part and the peak-shaped convex part surrounding the concave part in the printing surface, and further improves the water resistance and bleeds characteristics of the printed image if it is formed to a convex and concave shape.

The resin fine particles can be formed by using the lytic difference between the first resin

component and the second resin component and allowing the partial separation of the first resin component and/or the second resin component when mixing the first solution and the second solutions together.

For example, when the first resin component is a polyalkylene oxide, the first resin  
5 component can be allowed to dissolve at 40°C in the mixture solvent of methyl ethyl ketone / toluene / methanol (weight ratio 2/1/1). In addition, the acrylic polymer which is the second resin component can be allowed to dissolve at room temperature (for example, 20°C) in a mixture solvent of the acetone / methanol.

For example, by mixing the first solution of 40°C where the first resin component was  
10 allowed to dissolve in a mixture solvent (2/1/1) of the methyl ethyl ketone / toluene / methanol and the second solution of 20°C where the second resin component was allowed to dissolve in the mixture solvent of the acetone / methanol at room temperature (20°C), an application solution containing the above-described resin fine particles can be obtained.

When the first resin component is a polyalkylene oxide, the first solution, should  
15 preferably contain methyl ethyl ketone, toluene and methanol as a solvent, and it should preferably be heated to 35 to 60°C. On the other hand, the second solution should preferably contain methyl ethyl ketone or acetone and methanol as a solvent, and the temperature should preferably be 15 to 30°C.

The density of the first resin component in the first solution should preferably be 10 to 20  
20 mass %, and more preferably be 14 to 16 mass %. In addition, the density of the second resin component in the second solution should preferably be 30 to 40 mass %, and more preferably be 33 to 38 mass %.

The coating can be applied by applying the application solution on one side of the base. The application method of the application liquid is not particularly limited, and well known  
25 methods such as the knife coat method, spin coat method, roll coat method, silkscreen coat method, and gravure coat method can be used.

Preferably the coating should be formed so that the thickness of the ink reception layer formed after the second process becomes 10 to 40 µm. When the coating is formed to become such a thickness, the printing surface of the ink reception layer to be obtained becomes even more  
30 superior in print characteristics and its adhesive property.

The solvent is removed from the coating in the second process. A method to volatilize and remove the solvent by heating, and an air-drying method are given as methods to remove the organic solvent. In the second process, the solvent of the coating does not always have to be

entirely removed, and the ink reception layer may contain some of the solvent.

As will be understood, print media of the invention may be formed in sheet or roll form.

As described above, a suitable embodiment of the present invention was explained; however present invention is not limited to the above-described embodiment. For example, with the present invention, the printed image formed with the water-based ink on the printing surface F1 of the print media 10 may be a decorative film. In addition, the present invention may be a decorative item (for example, an IC card having a printed image) wherein the print media 10 with the printed image formed by the water-based ink on the printing surface F1 is adhered on the object (for example, main body an IC card).

### Examples

Hereinafter, the present invention will be described in more detail with reference to the following illustrative.

Acrylic Polymer B1: 33 mass % of methyl acrylate (below expressed as "MA" depending on the case.), 55 mass % of phenoxy ethyl acrylate (below expressed as "PhEA" depending on the case), 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride (below expressed as "DMAEA-Q" depending on the case), and 2 mass % of acrylic acid (below expressed as "AA" depending on the case) was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. Note that, a water solution of 79 mass % for the solidity was used as DMAEA-Q. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B1 was obtained.

Acrylic Polymer B2: 43 mass % of methyl acrylate, 45 mass % of phenoxy ethyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. Note that, a water solution of 79 mass % for the solidity was used as DMAEA-Q. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20

hours, and a 35 mass % solution of the acrylic polymer B2 was obtained.

Acrylic Polymer B3: 23 mass % of methyl acrylate, 65 mass % of phenoxy ethyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. Note that, a water solution of 79 mass % for the solidity was used as DMAEA-Q. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B3 was obtained.

Acrylic Polymer B4: 73 mass % of methyl acrylate, 15 mass % of phenoxy ethyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. Note that, a water solution of 79 mass % for the solidity was used as DMAEA-Q. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B4 was obtained.

Acrylic Polymer B5: 33 mass % of 2-ethyl hexyl acrylate (below expressed as "2EHA" depending on the case.), 55 mass % of phenoxy ethyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. Note that, a water solution of 79 mass % for the solidity was used as DMAEA-Q. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B - 5 was obtained.

Acrylic Polymer B6: 29 mass % of methyl acrylate, 55 mass % phenoxy ethyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. Note that, a water solution of 79 mass % for the

solidity was used as DMAEA-Q. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymersization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B6 was obtained.

Acrylic Polymer B7: 88 mass % of methyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. Note that, a water solution of 79 mass % for the solidity was used as DMAEA-Q. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymersization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B7 was obtained.

Acrylic Polymer B8: 58 mass % of methyl acrylate, 35 mass % of phenoxy ethyl acrylate, 5 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymersization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B8 was obtained.

Acrylic Polymer B9: 33 mass % of methyl acrylate, 55 mass % of phenoxy ethyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate (third grade amine expressed as "DMAEA" depending on the case.) and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymersization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B9 was obtained.

Acrylic Polymer B10: 43 mass % of methyl acrylate, 55 mass % of phenoxy ethyl acrylate and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58

acetone mass % and 34.49 methanol mass % and the solution was reacted. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B10 was obtained.

Acrylic Polymer B11: 28 mass % of methyl acrylate, 55 mass % of phenoxy ethyl acrylate, 15 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 2 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B5 was obtained.

Acrylic Polymer B12: 25 mass % of methyl acrylate, 55 mass % of phenoxy ethyl acrylate, 10 mass % of N,N-dimethylamino ethyl acrylate quaternized with methyl chloride, and 10 mass % of acrylic acid was uniformly dissolved in a mixture solvent of 148.58 acetone mass % and 34.49 methanol mass % and the solution was reacted. This reaction solution was poured into a pressure and heat-resisting glass container, and nitrogen was passed through the reaction solution while stirring it for 10 minutes to performed deoxidation after having added 0.1 mass % of azobisisobutyronitrile as a start agent. Then, an interpolymerization reaction was performed by warming it at 50°C for 20 hours, and a 35 mass % solution of the acrylic polymer B5 was obtained.

The ratios (mass ratios) of the monomer unit which constitutes the acrylic polymers B1 to B10 are shown in following Table 1.

Table 1

Acrylic Polymer	MA	2EHA	PhEA	DMAEA-Q	DMAEA	AA
B1	33	—	55	10	—	2
B2	43	—	45	10	—	2
B3	23	—	65	10	—	2
B4	73	—	15	10	—	2
B5	—	33	55	10	—	2
B6	29	—	55	10	—	6

Acrylic Polymer	MA	2EHA	PhEA	DMAEA-Q	DMAEA	AA
B7	88	—	—	10	—	2
B8	58	—	35	5	—	2
B9	33	—	55	—	10	2
B10	43	—	55	—	—	2

#### Example 1

AQUA COKE® (from Sumitomo Seika Chemicals Co., Ltd., a polyalkylene oxide, 100 mass % for solidity) was dissolved at 40°C in a mixture solvent (mass ratio 2/1/1) of the methyl ethyl ketone / toluene / methanol and a solution A1 with a solid density of 15 mass % was produced as the first resin component. In addition, a solution with 35 mass % of the acrylic polymer B1 (hereinafter referred to as the solution B1) was used as the second resin component.

A solution A1 and a solution B1, which were 40°C, were mixed so that the mass ratio of the first resin component and the second resin component became 60/40, and a mixture C1 was produced.

A print media 1 was obtained by applying the solution C1 on a polyethylene terephthalate film (a PET film) having a thickness of 50μm using the knife coat method, and allowing the solution C1 to dry for 10 minutes in an oven set to 80°C to form the ink reception layer on the PET film. Then, the thickness of the ink reception layer formed after drying was adjusted to become 25 μm. Note that, the thickness of the ink reception layer is adjusted by adjusting the gap between the PET film surface and the knife surface.

When the obtained print media 1 was observed with a surface optical microscope, the ink reception layer of print media 1 had a near uniform micro-phase separation structure in the printing surface. The result is shown in Fig. 4.

In addition, the printing surface of the ink reception layer of the obtained print media 1 was measured with a non-contact surface coarseness-measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. The result is shown in Fig. 5. From the result shown in Fig. 5, the unique unevenness structural arrangement was confirmed, wherein the structural unit consisting of the first micro-phase isolation region approximately in the shape of a circle, and the second convex-shaped micro-phase isolation region surrounding that outer periphery in approximately a ring shape. In other words, it was confirmed that the unique unevenness structure was formed such that the second micro-phase separation structure rose up in the shape of a

peak and surrounded the first micro-phase isolation region in approximately the shape of a circle.

The micro-phase separation structure of the printing surface formed the island structure, and the average diameter of the island was about 5  $\mu\text{m}$ . In addition, the diameter of the first micro-phase isolation region in approximately the shape of a circle was roughly 50 to 300  $\mu\text{m}$ , and the difference ( $h_2 - h_1$ ) between the average height  $h_1$  of the first micro-phase separation structure and average height  $h_2$  of the second micro-phase isolation region was roughly 25 to 30  $\mu\text{m}$ .

In addition, from the surface observation with the atomic force microscope (AFM), it was confirmed that there was more of the first resin component than the second resin component in the first micro-phase isolation region, and more of the second resin component than the first resin component in the second micro-phase isolation region. To be specific, that existence was confirmed from the crystal orientation state displayed by the first resin component.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 1 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Example 2

In addition, other than using a solution with 35 mass % of the acrylic polymer B2 (hereinafter referred to as the solution B2) instead of the solution B1, as the second resin component, the print media 2 was obtained similar to that of Example 1.

When the obtained print media 2 was observed with a surface optical microscope, the ink reception layer of print media 2 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 2 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. From a result of the measurement with the non-contact surface coarseness measuring instrument, it was confirmed that a multiple arranged unique unevenness structures with a first micro-phase isolation region, and a second convex-shaped micro-phase isolation region surrounding the outer periphery of the first micro-phase isolation region in approximately a ring shape was formed similar to that of Example 1 even in the printing surface of the ink reception layer of the print media 2.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 2 according to the following evaluation method. The evaluation results are as shown in Table 2.



### Example 3

In addition, other than using a solution with 35 mass % of the acrylic polymer B3 (hereinafter referred to as the solution B3) instead of the solution B1, as the second resin component, the print media 3 was obtained similar to that of Example 1.

5 When the obtained print media 3 was observed with a surface optical microscope, the ink reception layer of print media 3 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 3 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to  
10 measure the surface coarseness of the printing surface. From a result of the measurement with the non-contact surface coarseness measuring instrument, it was confirmed that a multiple arranged unique unevenness structures with a first micro-phase isolation region, and a second convex-shaped micro-phase isolation region surrounding the outer periphery of the first micro-phase isolation region in approximately a ring shape was formed similar to that of Example 1 even in the printing  
15 surface of the ink reception layer of the print media 3.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 3 according to the following evaluation method. The evaluation results are as shown in Table 2.

### Example 4

20 In addition, other than using a solution with 35 mass % of the acrylic polymer B4 (hereinafter referred to as the solution B4) instead of the solution B1, as the second resin component, the print media 4 was obtained similar to that of Example 1.

When the obtained print media 4 was observed with a surface optical microscope, the ink reception layer of print media 4 had a near uniform micro-phase separation structure in the printing  
25 surface.

In addition, the printing surface of the ink reception layer of the obtained print media 4 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. From a result of the measurement with the non-contact surface coarseness measuring instrument, it was confirmed that a multiple arranged  
30 unique unevenness structures with a first micro-phase isolation region, and a second convex-shaped micro-phase isolation region surrounding the outer periphery of the first micro-phase isolation region in approximately a ring shape was formed similar to that of Example 1 even in the printing surface of the ink reception layer of the print media 4.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 4 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Example 5

5 In addition, other than using a solution with 35 mass % of the acrylic polymer B5 (hereinafter referred to as the solution B5) instead of the solution B1, as the second resin component, the print media 5 was obtained similar to that of Example 1.

10 When the obtained print media 5 was observed with a surface optical microscope, the ink reception layer of print media 5 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 5 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. From a result of the measurement with the non-contact surface coarseness measuring instrument, it was confirmed that a multiple arranged  
15 unique unevenness structures with a first micro-phase isolation region, and a second convex-shaped micro-phase isolation region surrounding the outer periphery of the first micro-phase isolation region in approximately a ring shape was formed similar to that of Example 1 even in the printing surface of the ink reception layer of the print media 5.

20 In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 5 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Example 6

25 Other than replacing solution C1 and using mixture C2 prepared by mixing solution A1 and solution B1, which were 40°C, so the mass ratio of the first resin component and the second resin component became 50/50, the print media 6 was obtained similar to that of Example 1.

When the obtained print media 6 was observed with a surface optical microscope, the ink reception layer of print media 6 had a near uniform micro-phase separation structure in the printing surface.

30 In addition, the printing surface of the ink reception layer of the obtained print media 6 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. From a result of the measurement with the non-contact surface coarseness measuring instrument, it was confirmed that a multiple arranged unique unevenness structures with a first micro-phase isolation region, and a second convex-shaped

micro-phase isolation region surrounding the outer periphery of the first micro-phase isolation region in approximately a ring shape was formed similar to that of Example 1 even in the printing surface of the ink reception layer of the print media 6.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 6 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Example 7

In addition, other than using a solution with 35 mass % of the acrylic polymer B6 (hereinafter referred to as the solution B6) instead of the solution B1, as the second resin component, the print media 7 was obtained similar to that of Example 1.

When the obtained print media 7 was observed with a surface optical microscope, the ink reception layer of print media 7 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 7 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. From a result of the measurement with the non-contact surface coarseness measuring instrument, it was confirmed that a multiple arranged unique unevenness structures with a first micro-phase isolation region, and a second convex-shaped micro-phase isolation region surrounding the outer periphery of the first micro-phase isolation region in approximately a ring shape was formed similar to that of Example 1 even in the printing surface of the ink reception layer of the print media 7.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 7 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Example 8

AQUA COKE® (from Sumitomo Seika Chemicals Co., Ltd., a polyalkylene oxide, 100 mass % for solidity) was dissolved at 40°C in a mixture solvent (mass ratio 2/1/1) of the methyl ethyl ketone / toluene / methanol and a solution A2 with a solid density of 15 mass % was produced as the first resin component. Other than using the solution A2 instead of the solution A1, the print media 8 was obtained similar to that of Example 1.

When the obtained print media 8 was observed with a surface optical microscope, the ink reception layer of print media 8 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 8 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. As a result of measurement with the non-contact surface coarseness measuring instrument, the unique unevenness structure observed with Example 1 was not observed in the printing surface of the ink reception layer of print media 8, and there were large mountain-shaped cells forming the surface structure.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 8 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Example 9

The solution A2 was prepared similar to that of Example 8. Then, a solution A2 and a solution B1, which were 40°C, were mixed so that the mass ratio of the first resin component and the second resin component became 30/70, and a mixture C3 was prepared.

Other than using the mixture C3 instead of the mixture C1, the print media 9 was obtained similar to that of Example 1.

When the obtained print media 9 was observed with a surface optical microscope, the ink reception layer of print media 9 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 9 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. As a result of measurement with the non-contact surface coarseness measuring instrument, the unique unevenness structure observed with Example 1 was not observed in the printing surface of the ink reception layer of print media 8, and there were large mountain-shaped cells forming the surface structure.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 9 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Example 10

The solution A2 was prepared similar to that of Example 8. In addition, a 35 mass % solution of the acrylic polymer B7 (hereinafter referred to as solution B7) was used as the second resin component. Then, a solution A2 and a solution B7, which were 40°C, were mixed so that the mass ratio of the first resin component and the second resin component became 40/60, and a mixture C4 was prepared.

Other than using the mixture C4 instead of the mixture C1, the print media 10 was obtained similar to that of Example 1.

When the obtained print media 10 was observed with a surface optical microscope, the ink reception layer of print media 10 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 10 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. As a result of measurement with the non-contact surface coarseness measuring instrument, the unique unevenness structure observed with Example 1 was not observed in the printing surface of the ink reception layer of print media 9, and there were large mountain-shaped cells forming the surface structure.

#### Example 11

In addition, other than using a solution with 35 mass % of acrylic polymer B8 (hereinafter referred to as solution B8) instead of the solution B1, as the second resin component, the print media 11 was obtained similar to that of Example 1.

When the obtained print media 11 was observed with a surface optical microscope, the ink reception layer of print media 11 had a near uniform micro-phase separation structure in the printing surface.

In addition, the printing surface of the ink reception layer of the obtained print media 11 was measured with a non-contact surface coarseness measuring instrument (from Zaygo) to measure the surface coarseness of the printing surface. From a result of the measurement with the non-contact surface coarseness measuring instrument, it was confirmed that a multiple arranged unique unevenness structures with a first micro-phase isolation region, and a second convex-shaped micro-phase isolation region surrounding the outer periphery of the first micro-phase isolation region in approximately a ring shape was formed similar to that of Example 1 even in the printing surface of the ink reception layer of the print media 11.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 9 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Comparison Example C1

The solution A2 was prepared similar to that of Example 8. Then, a solution A2 and a 35 mass % solution of acrylic polymer B9 (hereinafter referred to as solution B9) were mixed so that the mass ratio of the first resin component and the second resin component became 40/60, and a

mixture D1 was prepared.

Other than using the mixture D1 instead of the mixture C1, the print media 21 was obtained similar to that of Example 1.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 21 according to the following evaluation method. The evaluation results are as shown in Table 2.

Note that, it was confirmed that the print media 21 had a near uniform micro-phase separation structure in the printing surface when observed with a surface optical microscope. However, from the measurement result using a non-contact surface coarseness measuring instrument (from Zaygo), the unique unevenness structure observed with Example 1 was not observed in the printing surface, and there were large mountain-shaped cells forming the surface structure. The observation result of the surface optical microscope is shown in Fig. 6, and the measurement result of the non-contact surface coarseness measuring instrument is shown in Fig. 7.

#### Comparison Example C2

The solution A1 was prepared similar to that of Example 1. Then, a solution A1 and a 35 mass % solution of acrylic polymer B10 (hereinafter referred to as solution B10) were mixed so that the mass ratio of the first resin component and the second resin component became 40/60, and a mixture D2 was prepared.

Other than using the mixture D2 instead of the mixture C1, the print media 22 was obtained similar to that of Example 1.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 22 according to the following evaluation method. The evaluation results are as shown in Table 2.

Note that, it was confirmed that the print media 22 had a near uniform micro-phase separation structure in the printing surface when observed with a surface optical microscope. However, from the measurement result using a non-contact surface coarseness measuring instrument (from Zaygo), the unique unevenness structure observed with Example 1 was not observed in the printing surface.

#### Comparison Example C3

40 mass % of AQUA COKE® (from Sumitomo Seika Chemicals Co., Ltd., 100 mass % for solidity), and 40 mass % of hydrophobic Polyester Byron® 670 as the hydrophobic resin having a thermal adhesive property (from Toyobo Co., Ltd., Polyester), and 20 mass % of Polyurethane resin BYRON® UR-3200 (from Toyobo Co., Ltd., Polyester urethane resin, glass transition

temperature: -3°C, 30 mass % for solidity) was sufficiently churned to allow for dispersion in a mixture solvent of methyl ethyl ketone / toluene (mass ratio 1/1) at 60°C.

A print media 23 was obtained by casting the solution D3 on a polyethylene terephthalate film (a PET film) having a thickness of 50 µm using the knife coat method, and allowing the solution D3 to dry for 10 minutes in an oven set to 80°C to form the ink reception layer on the PET film. Then, the thickness of the ink reception layer formed after drying was adjusted to become 25 µm.

Note that, it was confirmed that the print media 23 had a near uniform micro-phase separation structure in the printing surface when observed with a surface optical microscope. However, from the measurement result using a non-contact surface coarseness measuring instrument (from Zaygo), the unique unevenness structure observed with Example 1 was not observed in the printing surface.

In addition, the print characteristics, water resistance, normal temperature adhesive strength and high temperature adhesive strength were evaluated for the print media 23 according to the following evaluation method. The evaluation results are as shown in Table 2.

#### Test Methods

Evaluation Of Printing Characteristics: A picture of a person and letters. were printed on the ink reception layer of the print media with a CANON® Inkjet Printer p-640L, using six colors of aqueous dye ink print, at a print speed of 25 mm/sec or 100 mm/sec. The printed image was visually evaluated on the 5 ranks described below. "D" represents that the printed image was most indistinct, the vividness of an image printed was shown by "C", "B", and "A" in the order of improvement, and "AA" was the score given to the printed image that was the most clear. Note that, the result obtained at a print speed of 25 mm/sec was evaluated as the "print characteristics", and the result obtained at a print speed of 100 mm/sec was evaluated as "high-speed printing characteristics".

Evaluation Of Bleeding Characteristics: An image was printed on the ink reception layer of the print media and evaluated similar to the printing evaluation. Then, a print media and a vinyl chloride resin card were positioned so that the printing surface of the print media and one side of the card were facing each other and then they were heat laminated (for one second at 120°C) using a roll type heat laminator. The printed image was visually observed to see if there was any blur after the sample was allowed to stand for a period of 7 days at 80°C. The evaluation was rated on the 5 ranks described below.

AA: Absolutely no change.

A: There is almost no change in comparison with the control.

B: There is noticeable change in comparison with the control.

C: There is noticeable blur.

D: Very obvious blur noticeable over the entire surface.

Evaluation Of Normal Temperature Adhesive Strength: An image was printed on the ink reception layer of the print media and evaluated similar to the printing evaluation. Then, a print media and a vinyl chloride resin card were positioned so that the printing surface of the print media and one side of the card were facing each other and then they were heat laminated (for one second at 120°C) using a roll type heat laminator.

A peel strength of 180° (N/25 mm) was measured with a pull test machine at 23°C after the obtained measurement sample was left to stand for 24 hours at 23°C. The measurement condition was set at a tension speed of 200 mm/min. A measurement result was evaluated as "A" in a case of more than 15 N/25 mm or when the materials were damages, "B" in a case of between 15 - 10 N/25 mm, and "C" in cases of less than 10 N/25 mm.

Evaluation Of High Temperature Adhesive Strength: The measurement sample was obtained by the method similar to the evaluation of the normal temperature adhesive strength. A peel strength of 180° (N/25 mm) was measured with a pull test machine at 80°C after the obtained measurement sample was left to stand for 24 hours at 23°C. The measurement condition was set at a tension speed of 200 mm/min. A measurement result was evaluated as "A" in a case of more than 15 N/25 mm or when the materials were damages, "B" in a case of between 15 - 10 N/25 mm, and "C" in cases of less than 10 N/25 mm.

Evaluation Of Water Resistance: The measurement sample was obtained by the method similar to the evaluation of the normal temperature adhesive strength. Changes in the external appearance were visually confirmed after allowing the measurement sample to stand for 24 hours in water at room temperature (25°C). Note that, in the evaluation of the water resistance, cases where no changes were observed were ranked as "AA," cases where the ends of the laminate swelled by 3-5 mm width, but could be restored to the original state were ranked as "A", cases where the ends of the laminate swelled by 3-5 mm width, and could not be restored to the original state were ranked as "B", cases where the adhesive layer eluted were ranked as "C" and cases the film had burrs were ranked as "D".



Table 2

Example	Evaluation of anti-bleed characteristics	Evaluation of printing characteristics		Evaluation of adhesive strength		Evaluation of water resistance
		25 mm/sec	100 mm/sec	Normal Temp (25°C)	High Temp (80°C)	
1	A	AA	A	A	A	A
2	A	AA	A	A	A	A
3	A	AA	A	A	A	A
4	A	AA	A	B	A	B
5	A	AA	A	A	A	A
6	A	AA	A	A	A	A
7	A	AA	A	A	A	A
8	A	A	B	A	A	B
9	AA	A	C	B	B	B
10	A	A	C	B	B	B
11	A	AA	A	A	A	A
C1	D	A	C	B	B	C
C2	D	A	C	A	A	A
C3	C	B	C	A	A	C

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

5 1. A print media for water-based ink comprising a base having a first surface and an ink reception layer on at least a portion of the first surface of the base wherein: (1) the ink reception layer has a printing surface defined by micro-phase separation of a blend of a first resin component composition and a second resin component composition; (2) the first resin component is hydrophilic; and (3) the second resin component comprises an acrylic polymer with a quaternized amino group and exhibits thermal adhesive characteristics; wherein the printing surface is made up of a matrix of first domains the majority fraction of which is first resin component and second domains the major fraction of which is second resin component;

10 wherein the second domains substantially surround each first domain and the second domains are relatively convex;

wherein there is a difference in height between the first domains and the second domains from about 1  $\mu\text{m}$  to about 30  $\mu\text{m}$ ; and

15 wherein the first domains have an average diameter of about 100  $\mu\text{m}$  or less.

2. The print media of claim 1 wherein the first resin component comprises polyalkylene oxide.

20 3. The print media of claim 1 wherein the acrylic polymer has a phenoxy group.

25 4. The print media of claim 1 wherein the acrylic polymer is the product made by polymerization of the following components: 3 to 13 mass % of an acrylic monomer with a quaternized amino group; 20 to 90 mass % of alkyl (meth)acrylate; 0 to 70 mass % of acrylic monomer having a phenoxy group; and 1 to 8 mass % of (meth)acrylic acid.

5. The print media of claim 1 wherein the amount of the first resin in the ink reception layer is 20 to 70 mass % for a total of 100 mass % of the first resin and the second resin.

30 6. A method for manufacturing the print media of claim 1 comprising: (1) providing a base having a first surface; (2) providing a blend of a first resin component composition and a second resin component composition; (3) applying the blend to at least a portion of the first surface of the base to form a coating thereon; and (4) removing solvent from the coating such that micro-phase separation of the first resin component and second resin component occurs to yield a printing surface made up of a matrix of first domains the majority of which is first resin

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component and second domains the major fraction of which is second resin component, wherein the second domains substantially surround each first domain and the second domains are relatively convex.

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7. The method of claim 6 wherein the application liquid is a suspension including resin fine particles consisting of the first resin and the second resin.

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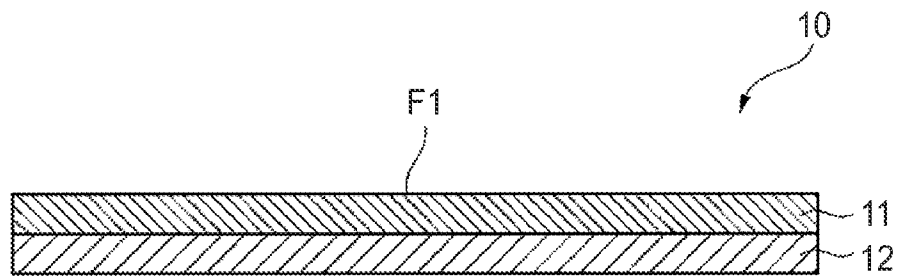


FIG. 1

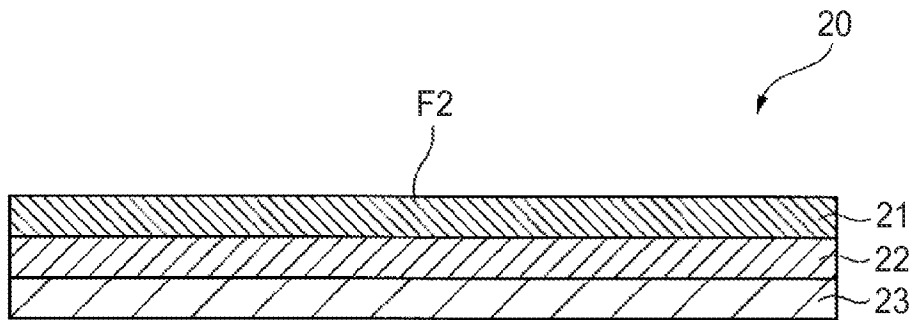


FIG. 2

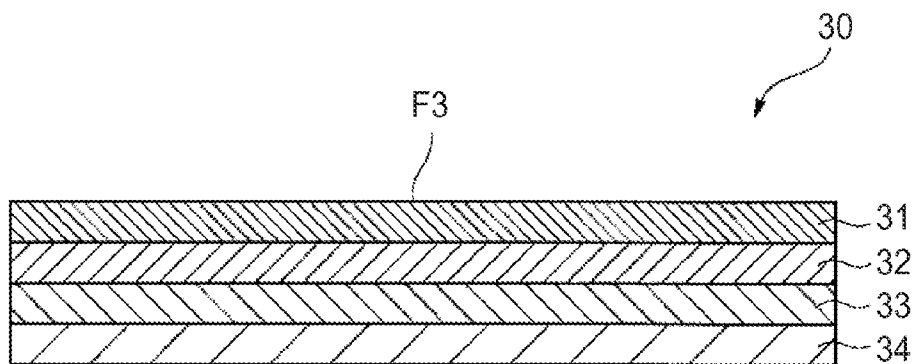
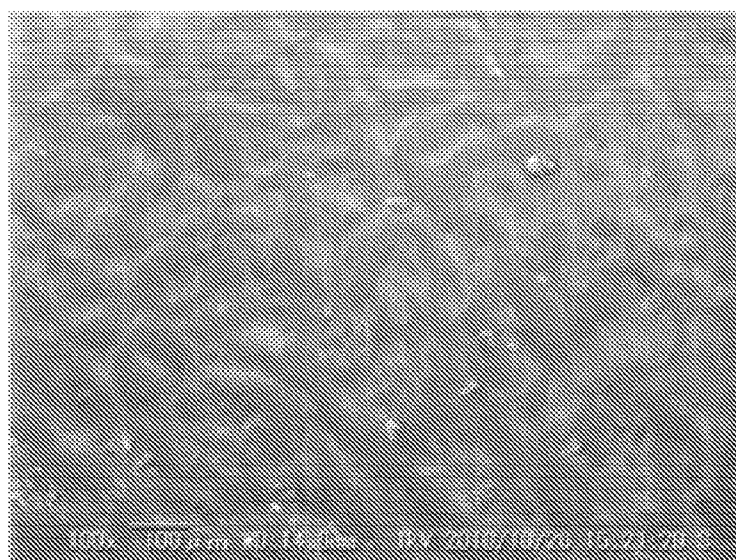


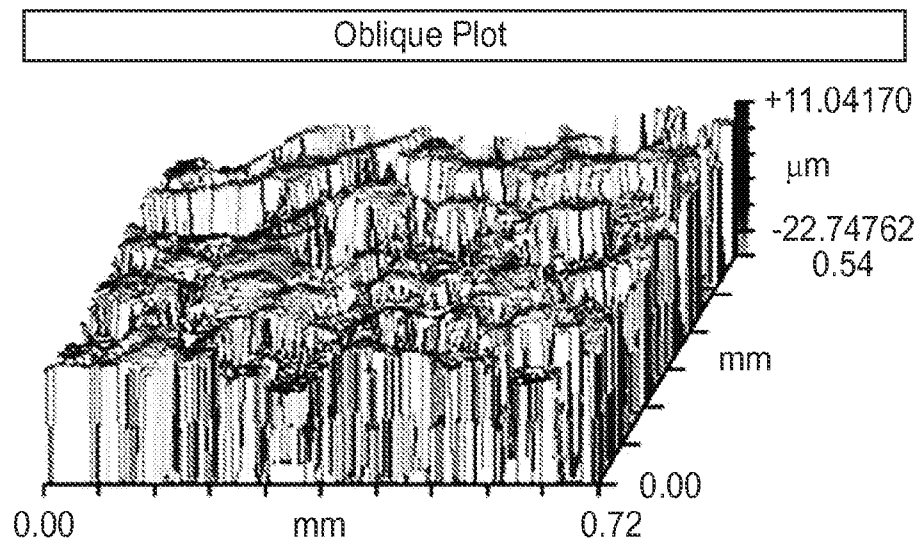
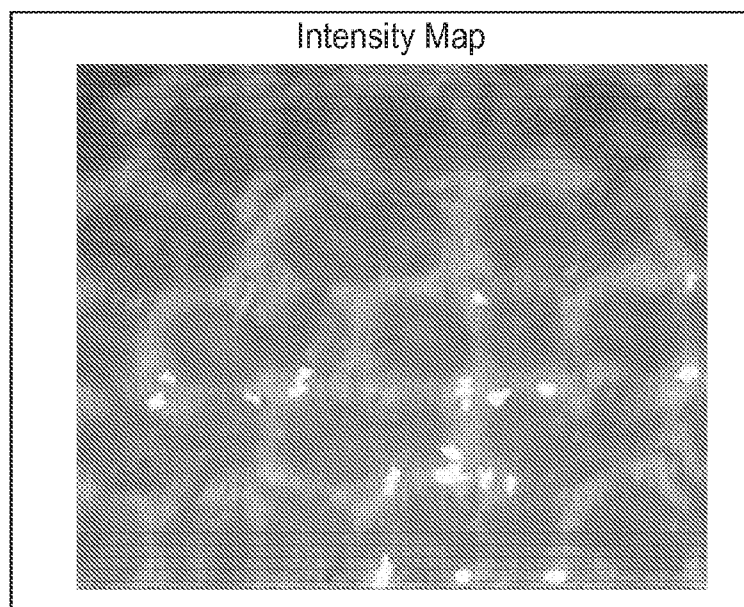
FIG. 3

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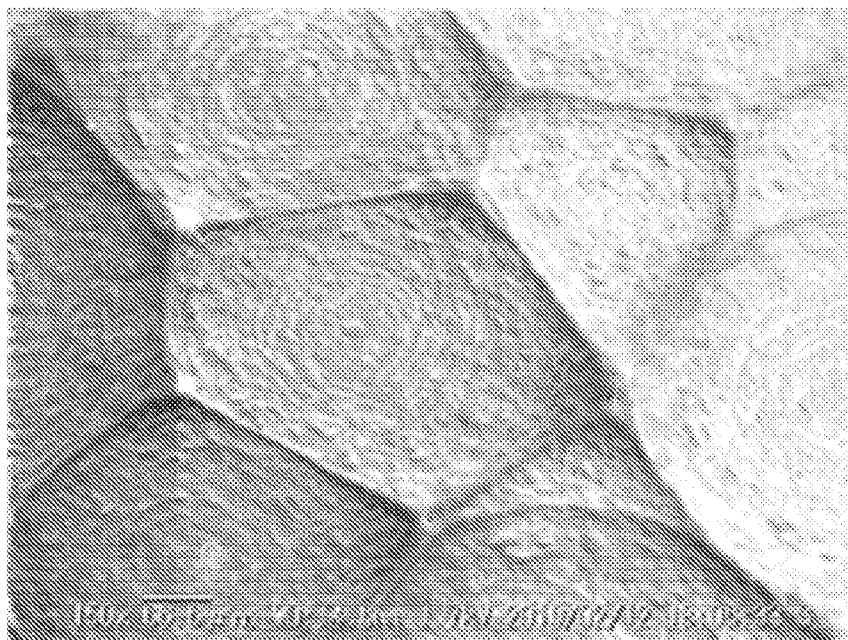


*FIG. 4*

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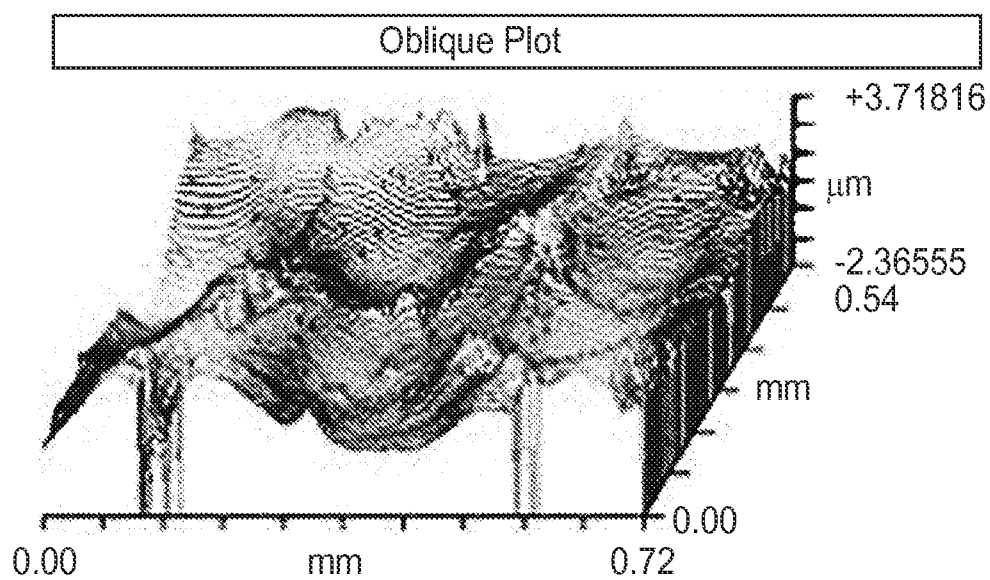
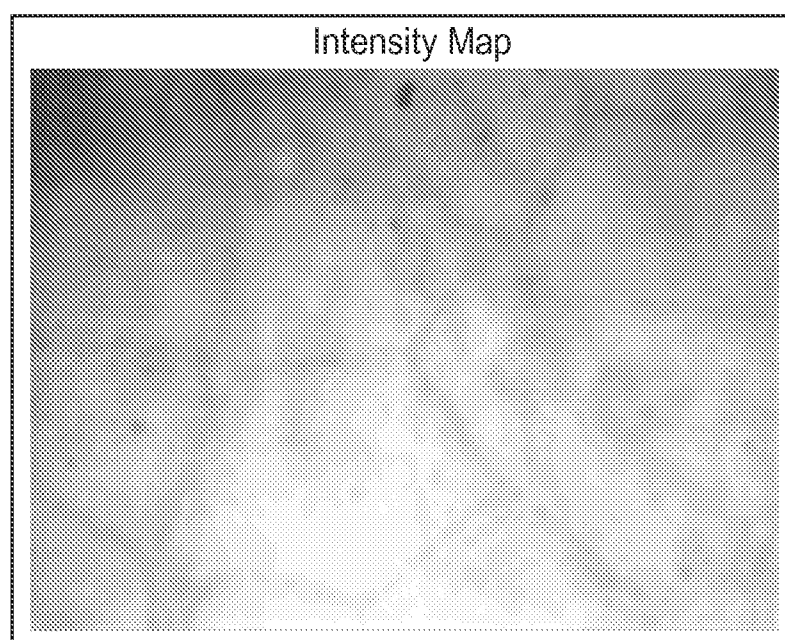
*FIG. 5a**FIG. 5b*

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*FIG. 6*

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*FIG. 7a**FIG. 7b*