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(54) Title: WATER-BASED INK COMPOSITION FOR FINE POINTED BALLPOINT PEN AND FINE POINTED BALLPOINT PEN

(57) Abstract: Provided is a water-based ink composition for a fine pointed ballpoint pen characterized by blending an ink composition comprising at least water, a colorant and a water soluble solvent with at least one kind of ultra fine particles selected from the group consisting of alumina, titanium oxide, silica, silicon carbide and tungsten carbide each having an average particle diameter of less than 0.1 μm, wherein a blending amount of the ultra fine particles is 0.002 to 2 % by weight based on the ink composition, particularly preferably an ink composition having a viscosity of 50 to 2000 mPas (25° C) which is measured at 1 rpm by means of a corn and plate type rotational viscometer (1°34'R24 corn). Further, provided is a fine pointed ballpoint pen having a ball of a diameter of 0.4 mm or less, filled with the water-based ink composition described above.

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DESCRIPTION

WATER-BASED INK COMPOSITION FOR FINE POINTED BALLPOINT PEN AND FINE POINTED BALLPOINT PEN

Technical Field

The present invention relates to a water-based ink composition for a ballpoint pen, specifically to a water-based ink composition for a ballpoint pen which is excellent in abrasion resistance of a ball housing seat in a fine pointed ballpoint pen tip having a ball whose diameter is 0.5 mm or less, particularly 0.4 mm or less, drawn line quality, an ink discharge property and stability with the passage of time and a fine pointed ballpoint pen.

Background Art

In writing with a ballpoint pen, an ink is transferred onto a writing face by rotation of a ball, and there have so far been problems that a part (a ball-housing seat) which holds a ball and is brought into contact with it in the inside of a ballpoint pen tip is abraded as the ball rotates so that an ink discharge port is clogged or a caulking part which holds the ball is

brought into contact with a paper face to cause inferior writing such as starving and failure in writing. Accordingly, it has been tried to add a water soluble cutting oil and a surfactant as an abrasion resistant agent to an ink for a ballpoint pen or to blend the ink with a solid lubricant such as boron nitride, a wax emulsion or resin particles. However, satisfactory effects have not necessarily been obtained for abrasion resistance of a housing seat in a ballpoint pen tip.

Further, it is proposed (for example, Japanese Patent Application Laid-Open No. 206066/2002) as a measure for abrasion of a ball housing seat in a ballpoint pen tip to add fine particles having a particle diameter of 0.1 μm or more and 30 μm or less such as alumina, silicon carbide and chromium oxide each having a new Moh's hardness of 4 or more to an ink composition. However, this has involved problems that the writing feeling is deteriorated and that the quality of the drawn lines is reduced by a phenomenon (directional error) in which an ink discharge amount becomes uneven depending on a writing direction and a phenomenon (skipping) in which rotation of a ball is temporarily stopped and the ball slips on a paper face to break the drawn line. In particular, in a fine pointed ballpoint pen having a ball diameter of 0.5 mm or less, such a satisfactory effect

for inhibiting abrasion of a housing seat that a certain writing quality level can be exhibited is not obtained in some case. The following is considered as the reason therefor. In the case of a fine pointed ballpoint pen, a ball housing seat has a small area as compared with those of ordinary ballpoint pens, and therefore the housing seat has a large load exerted per unit area so that it has a high frictional resistance and is notably abraded. Further, it has a small ink discharge port and is liable to cause failure in writing due to clogging. In addition, a fine pointed ballpoint pen has a ball having a small diameter and has a small part in which the ball protrudes from a pen tip, and therefore the abrasion of the housing seat makes the ball-protruding part further smaller, so that a caulking part which holds the ball come into contact with a paper face to cause markedly problems including inferior writing such as starving and failure in writing. Thus, a fine pointed ballpoint pen stays in the condition that abrasion is accelerated, and in addition thereto, it has a small tolerance to abrasion in which the quality of writing can be maintained. Accordingly, it is liable to cause the serious inconvenience that it can not write before exhausting an ink, and a large problem has been involved in designing a fine pointed ballpoint pen. In particular, in the case

of a fine pointed ballpoint pen whose ball has a diameter of 0.4 mm or less, frictional resistance is further increased, and therefore abrasion in a housing seat is notably caused. In addition thereto, it is difficult to allow the ball to rotate smoothly, and therefore there have been involved the serous problems that the writing feeling is deteriorated and that the quality of the drawn lines is reduced by directional error and skipping.

Further, a fine pointed ballpoint pen having a ball of small diameter tends to be reduced in an ink discharging property due to a small area of an ink-discharge port, so that the ink is usually reduced in a viscosity. However, when fine particles are blended in the ink, the particles having a large specific gravity settle down with the passage of time to bring about serious problems such as a deterioration in the writing feeling, reduction in the ink discharging property and inferior writing due to clogging caused by the settling down, and therefore it has been desired to solve them in an early stage.

Thus, in a fine pointed ballpoint pen having a ball of such a small diameter as 0.5 mm or less, only addition of fine particles having a particle diameter of 0.1 μm or more and 30 μm or less is unsatisfactory for inhibiting abrasion in the housing seat, and there has been the

problem that brought about are reduction in the drawn line quality, deterioration in the writing feeling, reduction in the ink discharging property and inferior writing due to clogging caused by settling down.

An object of the present invention is to provide a water-based ink composition for a fine pointed ballpoint pen which inhibits abrasion in a housing seat and is excellent in an ink discharging property and stability with the passage of time and which has smooth writing feeling and makes it possible to write for long time and a fine pointed ballpoint pen.

Disclosure of the Invention

Intensive researches repeated by the present inventors on abrasion resistance of a housing seat, drawn line quality, writing feeling, settling resistance of fine particles and stability with the passage of time in a fine pointed ballpoint pen having a ball of small diameter in order to solve the problems described above have resulted in finding that the problems can be solved by adding a specific amount of ultra fine particles selected from the group consisting of alumina, titanium oxide, silica, silicon carbide and tungsten carbide each having an average particle diameter of less than 0.1 μm to an ink and reducing an ink viscosity to a specific

value or lower. Thus, the present invention has come to be completed.

That is, the present invention relates to:

(1) a water-based ink composition for a fine pointed ballpoint pen characterized by blending an ink composition comprising at least water, a colorant and a water soluble solvent with at least one kind of ultra fine particles selected from the group consisting of alumina, titanium oxide, silica, silicon carbide and tungsten carbide each having an average particle diameter of less than 0.1 μm, wherein a blending amount of the ultra fine particles is 0.002 to 2 % by weight based on the ink composition,

(2) the water-based ink composition for a fine pointed ballpoint pen as described in the above item (1), having a viscosity of 50 to 2000 mPa·s (25°C) which is measured at 1 rpm by means of a corn and plate type rotational viscometer (1°34'R24 corn) and

(3) a fine pointed ballpoint pen having a ball of a diameter of 0.4 mm or less, filled with the water-based ink composition as described in the above item (1) or (2).

Use of the above water-based ink composition of the present invention for a fine pointed ballpoint pen removes reduction in the drawn line quality such as directional error and skipping and avoids damaging of the

writing feeling, the ink discharging property and the stability with the passage of time. In addition thereto, it elevates an abrasion resistant effect at the ballpoint pen tip and makes it possible to extend the writing distance. The particularly marked effect is suitably exhibited in a fine pointed ballpoint pen having a ball of a diameter of 0.4 mm or less, further 0.28 mm or less.

Best Mode for Carrying Out the Invention

The best mode for carrying out the present invention shall be explained below in details.

The fine particles of alumina, titanium oxide, silica, silicon carbide and tungsten carbide contained in the ink composition of the present invention comprising at least water, a colorant and a water soluble solvent have to be very fine in order to inhibit the housing seat from being abraded and improve dispersion stability thereof in the ink composition, and they are preferably ultra fine particles having an average particle diameter of less than 0.1 μm and have preferably a spherical form in order to enhance the writing feeling. The ultra fine particles referred to herein mean fine particles having a particle diameter of 0.001 to less than 0.1 μm.

Ultra fine particle alumina preferably used includes aluminum oxide C (primary particle diameter:

0.013 μm) manufactured by Nippon Aerosil Co., Ltd., Nano Tec Al_2O_3 (primary particle diameter: 0.033 μm) manufactured by C. I. Kasei Co., Ltd. and Taimicron TM-100J (primary particle diameter: 0.014 μm) manufactured by Taimei Chemicals Co., Ltd. Ultra fine particle titanium oxide includes titanium oxide P25 (primary particle diameter: 0.03 μm) manufactured by Nippon Aerosil Co., Ltd. and TTO-55A (primary particle diameter: 0.05 μm) manufactured by Ishihara Sangyo Kaisha Ltd.

In the present invention, a content of the ultra fine particles selected from the group consisting of alumina, titanium oxide, silica, silicon carbide and tungsten carbide each having an average particle diameter of less than 0.1 μm is preferably 0.002 to 2 % by weight, more preferably 0.05 to 1 % by weight based on the ink composition. The ultra fine particles may be used alone or in combination of two or more kinds thereof in the above range.

In the case of a fine pointed ballpoint pen having a ball of a diameter of 0.5 mm or less, fine particles having a particle diameter of 0.1 μm or more are less liable to provide a satisfactory effect for inhibiting a housing seat from being abraded. Further, in a fine pointed ballpoint pen having a ball of a diameter of 0.4 mm or less, brought about are inferior writing caused by

abrasion of a housing seat, deterioration in the writing feeling, reduction in the drawn line quality and clogging by settling which is liable to cause failure in writing. Particularly in the case of a fine pointed ballpoint pen having a ball of a diameter of 0.28 mm or less, reduction in an ink-discharge port and a decrease of a ball-protruding part and an increase in abrasion resistance notably reduce a writing performance with the passage of time. Accordingly, it is an essential requisite in a fine pointed ballpoint pen to use the ultra fine particles having an average particle diameter of less than 0.1 μm. If the content exceeds 2 % by weight, the writing feeling and the discharge property are reduced, and the abrasion resistance is deteriorated in a certain case.

The ink composition of the present invention described above has a viscosity of 50 to 2000 mPa·s (25°C), preferably 100 to 1000 mPa·s (25°C) which is measured at 1 rpm by means of a corn and plate type rotational viscometer (1°34'R24 corn). If the above viscosity is less than 50 mPa·s (25°C), the ultra fine particles described above bring about settling with the passage of time, and the ink is likely to cause bobbling and bring about failure in writing in a certain case. On the other hand, if the above viscosity exceeds 2000 mPa·s

(25°C), the discharge property is reduced to deteriorate the writing feeling in a certain case, and therefore both ranges are not preferred.

The water-soluble solvent in the ink composition of the present invention is used for the purpose of, for example, preventing freezing of the ink at a low temperature and drying of the ink at a pen tip. To be specific, it includes glycols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, polyethylene glycol, 1, 3-butylene glycol, thiodiethylene glycol and glycerin, ethylene glycol monomethyl ether and diethylene glycol monomethyl ether, and they can be used alone or in a mixture. A use amount thereof is 5 to 50 % by weight, preferably 10 to 30 % by weight based on the ink composition.

The ultra fine particles can be inhibited from coagulating and settling down by adding a dispersant for enhancing the stability with the passage of time. Nonionic and anionic surfactants and water-soluble resins are used as the dispersant. The water-soluble resins include synthetic water-soluble resins such as polyvinyl alcohol, polyacrylic acid, acrylic acid copolymers, maleic acid resins, polyvinylpyrrolidone, polyethylene oxide, water-soluble acryl resins and water-soluble styrene-acryl resins and water-dispersing emulsions of

acryl resins, alkyd resins, vinyl resins, polyester resins, styrene resins, maleic acid resins and urethane resins. They are preferably blended after they are converted in advance to water-dispersed matters (slurry) by means of a disperser.

The colorant used for the ink composition of the present invention includes pigments and/or water-soluble dyes. The kind of the pigments shall not specifically be restricted, and optional ones selected from inorganic and organic pigments which have so far conventionally been used for a water-based ink composition can be used.

The inorganic pigments include, for example, carbon black and metal powders.

Further, the organic pigments include, for example, azo lakes, insoluble azo pigments, chelate azo pigments, phthalocyanine pigments, perylene and perinone pigments, anthraquinone pigments, quinacridone pigments, dye lakes, nitro pigments and nitroso pigments. To be specific, capable of being used are phthalocyanine blue (C. I. 74160), phthalocyanine green (C. I. 74260), hansa yellow 3G (C. I. 11670), disazo yellow GR (C. I. 21100), permanent red 4R (C. I. 12335), brilliant carmine 6B (C. I. 15850) and quinacridone red (C. I. 46500). Plastic pigments constituted from styrene and acryl resin particles can be used as well. Further, hollow resin

particles having voids in the inside of the particles can be used as a white pigment or as a pseudo resin colored with a dye for pleochroic uses.

Any of direct dyes, acid dyes, food dyes and basic dyes can be used for the water-soluble dyes.

The examples of the direct dyes shall be described below. They include C. I. direct black 17, ditto 19, ditto 22, ditto 32, ditto 38, ditto 51 and ditto 71, C. I. direct yellow 4, ditto 26, ditto 44 and ditto 50, direct red 1, ditto 4, ditto 23, ditto 31, ditto 37, ditto 39, ditto 75, ditto 80, ditto 81, ditto 83, ditto 225, ditto 226 and ditto 227 and direct blue 1, ditto 15, ditto 71, ditto 86, ditto 106 and ditto 119.

The examples of the acid dyes shall be described below. They include C. I. acid black 1, ditto 2, ditto 24, ditto 26, ditto 31, ditto 52, ditto 107, ditto 109, ditto 110, ditto 119 and ditto 154, C. I. acid yellow 7, ditto 17, ditto 19, ditto 23, ditto 25, ditto 29, ditto 38, ditto 42, ditto 49, ditto 61, ditto 72, ditto 78, ditto 110, ditto 127, ditto 135, ditto 141 and ditto 142, C. I. acid red 8, ditto 9, ditto 14, ditto 18, ditto 26, ditto 27, ditto 35, ditto 37, ditto 51, ditto 52, ditto 57, ditto 82, ditto 87, ditto 92, ditto 94, ditto 115, ditto 129, ditto 131, ditto 186, ditto 249, ditto 254, ditto 265 and ditto 276, C. I. acid violet 18 and ditto

17, C. I. acid blue 1, ditto 7, ditto 9, ditto 22, ditto 23, ditto 25, ditto 40, ditto 41, ditto 43, ditto 62, ditto 78, ditto 83, ditto 90, ditto 93, ditto 103, ditto 112, ditto 113 and ditto 158 and C. I. acid green 3, ditto 9, ditto 16, ditto 25 and ditto 27.

A great part of the food dyes is included in the direct dyes or the acid dyes, but one example thereof which is not included therein includes C. I. food yellow 3.

The examples of the basic dyes shall be described below. They include C. I. basic yellow 1, ditto 2 and, ditto 21, C. I. basic orange 2, ditto 14 and ditto 32, C. I. basic red 1, ditto 2 and, ditto 9 and ditto 14, C. I. basic brown 12 and C. I. basic black 2 and ditto 8.

The above colorants each may be used alone or in combination of two or more kinds thereof. A content thereof falls in a range of usually 0.5 to 30 % by weight, preferably 1 to 15 % by weight based on the total ink composition. If the ink composition having a content exceeding 30 % by weight is stored over a long period of time, the pigment is coagulated or the dye is deposited to clog the pen tip, so that failure in writing is brought about. If the content is less than 0.5 % by weight, coloring is weakened or a hue of the lines is uncertain, and therefore it is not preferred.

When the pigment is used as the colorant, a dispersant has to be used. This dispersant has action to adsorb on the surface of the pigment to enhance an affinity of the pigment with water and stably disperse the pigment in water, and nonionic and anionic surfactants and water-soluble resins are used as the dispersant. A water-soluble polymer is preferably used.

It is effective and preferred to add a small amount of a thickener to the water-based ink composition of the present invention for the purpose of elevating a viscosity of the ink in order to inhibit particularly the ultra fine particles from settling down. The thickener which can be added is preferably a shear thinning property-providing agent which provides pseudo-plasticity for controlling a discharge property of the ink and inhibiting in the fine particles from settling down, and publicly known compounds can be used. Preferred is, for example, at least one selected from the group consisting of synthetic polymers, natural rubber, cellulose and polysaccharides.

To be specific, it includes, for example, gum arabic, succinoglycan, welan gum, tragacanth gum, guar gum, locust bean gum, alginic acid, carrageenan, gelatin, casein, xanthan gum, dextran, methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, carboxymethyl

cellulose, sodium glycolate starch, propylene glycol alginate, polyvinyl alcohol, polyvinylpyrrolidone, polyvinyl methyl ether, poly(sodium acrylate), carboxyvinyl polymers, polyethylene oxide, copolymers of vinyl acetate and polyvinylpyrrolidone, cross-linking type acrylic acid polymers and salts of styrene-acrylic acid copolymers. A content thereof is preferably 0.1 to 0.6 % by weight, more preferably 0.1 to 0.4 % by weight in terms of a solid content based on the total amount of the ink composition.

In the ink composition of the present invention, a pH-controlling agent, a rust preventive, a preservative·fungicide and a lubricant may be added if necessary. The lubricant includes nonionic compounds such as fatty acid esters of polyhydric alcohols, higher fatty acid esters of sugar, polyoxyalkylene higher fatty acid esters and alkylphosphoric acid esters, anionic compounds such as alkylsulfonic acid salts of higher fatty acid amides and alkylarylsulfonic acid salts, all of which are used as well for a surface treating agent for pigments, derivatives of polyalkylene glycols, fluorine base surfactants and polyether-modified silicones. The rust preventive includes benzotriazole, tolyltriazole, cyclohexylammonium nitrite and saponins, and the pH-controlling agent includes ammonia, urea,

triethanolamine, aminomethylpropanol and sodium hydroxide. The preservative or fungicide includes phenol, sodium omadine, sodium benzoate and benzimidazole base compounds.

Conventionally known methods can be adopted for producing the water-based ink composition of the present invention, and it is obtained, for example, by blending the prescribed amounts of the respective components described above and stirring and mixing them by means of a stirrer such as a homomixer and a disper. Further, coarse particles contained in the ink composition may be removed, if necessary, by filtering or centrifugal separation.

A mechanism in which the ultra fine particles selected from the group consisting of alumina, titanium oxide, silica, silicon carbide and tungsten carbide inhibit the ball-housing seat from being abraded is not certain, and it is considered that in a fine pointed ballpoint pen, the ultra fine particles of less than 0.1 μm are buried into the ball housing seat by virtue of a large pressure at the same time as the ink discharges as the ball rotates in writing, so that a surface hardness of the housing seat is increased to inhibit the abrasion of the housing seat brought about by rotation of the ball. The above effect does not disturb the rotation of the ball since the ultra fine particles are evenly present in

the ink interposed between the ball and the housing seat in writing. Accordingly, it is considered that the water-based ink composition of the present invention stably inhibits the ball-housing seat from being abraded and provides good writing feeling and no damage to the drawn line quality.

Examples

The present invention shall more specifically be explained below with reference to examples, but the present invention shall by no means be restricted by these examples.

Examples 1 to 9 and Comparative Examples 1 to 9

Water-based ink compositions corresponding to Examples 1 to 9 and Comparative Examples 1 to 9 were obtained in the form of homogeneous solutions by blending components 1 to 13 described below by means of a stirrer in amounts (% by weight) suitably combined as shown in Table 1.

1-a. Colorant (pigment): carbon black

1-b. ditto (dye): Red No. 105

2-a. Shear thinning property-providing agent: xanthan gum

2-b. ditto: cross-linking type polyacrylic acid

3-a. Water-soluble organic solvent: glycerin

3-b. ditto: propylene glycol

4. Lubricant: phosphoric acid ester alkyl ether

5. Rust preventive: benzotriazole

6. Preservative: 1,2-benzoisothiazoline-3-one

7. pH-controlling agent: triethanolamine

8-a. Alumina: primary particle diameter 0.033 μm

8-b. ditto: primary particle diameter 0.013 μm

8-c. ditto: primary particle diameter 0.7 μm

9-a. Titanium oxide: primary particle diameter 0.05 μm

9-b. ditto: primary particle diameter 0.03 μm

9-c. ditto: primary particle diameter 0.27 μm

10. Silicon carbide: primary particle diameter 0.04 μm

11. Tungsten carbide: primary particle diameter 0.06 μm

12. Water-soluble resin: styrene-acryl acid salt copolymer

13. Refined water

In respect to measurement of the viscosity by means of a corn and plate type rotational viscometer, the viscosity value was measured at 25°C and a revolution number of 1 rpm of an ST rotor (1°34'R24 corn) by means of a corn and plate type rotational viscometer EMD manufactured by Tokimec Inc.

Ballpoint pen tips having a ball of the respective ball diameters were mounted in tubes (PP-made tubes

having an inner diameter of 3.4 mm) and polypropylene-made coupling members each mounted in UM-151 manufactured by Mitsubishi Pencil Co., Ltd., and they were charged with the water-based ink compositions obtained in the examples and the comparative examples and ink followers and subjected to centrifugal treatment (500 G, 5 minutes) to be defoamed. Then, they were assembled into ballpoint pens and subjected to various writing tests shown below.

The writing tests were carried out in the following manners, and all the evaluation tests were carried out each by five ballpoint pens.

1) Abrasion resistance test: helical writing of 1000 m (writing end) was carried out by a machine writing test and evaluated according to the following criteria:
Writing conditions: 100 gf, writing angle 75 degrees, writing speed 4.5 mm/minute

◎: no problems in all samples and writable

○: a little starving observed but writable up to writing end

△: starving observed but writable up to writing end

▲: at least one pen has thin written lines and is incapable of writing because of reduction in a discharge amount

× : all are incapable of writing in the middle of

writing because of marked abrasion

2) Writing feeling test: writing feeling was sensorily evaluated by round writing and judged according to the following criteria:

◎: very smooth

○: smooth

△: scratch feeling felt

×: inferior

3) Written line quality: written lines obtained by helical writing of 200 m in a machine writing test were evaluated according to the following criteria.

Writing conditions: 100 gf, writing angle 75 degrees, writing speed 4.5 mm/minute

◎: good

○: a little shade observed but good

△: a little skipping observed

▲: skipping and a little directional error observed

×: directional error observed over the whole lines

4) Centrifugal resistance: the pen was subjected to centrifugation by means of a centrifugal separator (800 G, 10 minutes), and then the writing property thereof was evaluated by the frequency of rounds having a diameter of

about 1.5 cm according to the following criteria:

◎: writable from the beginning without any problem

○: starving slightly observed in the beginning but recovered within a frequency of 5 times in writing rounds

△: starving observed at a frequency of 5 to 10 times in writing rounds but recovered after that

×: starving caused at a frequency of 10 times or more in writing rounds

5) Writing property with the passage of time: the pen was left standing at 50°C for 2 weeks with the pen tip turned downward, and then the writing property with the passage of time was evaluated by writing rounds and the frequency thereof according to the following criteria:

◎: writable from the beginning without any problem

○: starving slightly observed in the beginning but recovered within a frequency of 5 times in writing rounds

△: starving observed at a frequency of 5 to 20 times in writing rounds but recovered after that

×: starving observed at a frequency of 20 times or more in writing rounds or incapable of writing

The evaluation results thereof are shown all

together in Table 1 in the case of Examples 1 to 9 and in Table 2 in the case of Comparative Examples 1 to 9.

Table 1

		Particle diameter μm	Example								
			1	2	3	4	5	6	7	8	9
Colorant	1-a		5		5	5	5	5		5	5
	1-b			6					6		
Thickener	2-a			0.15					0.25	0.4	0.05
	2-b		0.2		0.4	0.3	0.3	0.3			
Water-soluble solvent	3-a		20	10	20	10	10	20	10	10	10
	3-b			10		10	10		10	10	10
Lubricant	4		0.8	0.8	0.8	0.8	0.8	0.6	0.6	0.8	0.8
Rust preventive	5		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Preservative	6		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
pH-controlling agent	7		2	2	2	2	2	2	2	2	2
Alumina fine particle	8-a	0.033	0.05					0.8	0.1		
	8-b	0.013		0.3						0.4	
	8-c	0.7									
Titanium oxide fine particle	9-a	0.05			0.6						
	9-b	0.03									0.2
	9-c	0.27									
Silicon carbide fine particle	10	0.04				0.3					
Tungsten carbide fine particle	11	0.06					0.3				
Water-soluble resin	12		0.5	0.3	0.5	0.5	0.5	0.5	0.3	0.5	0.5
Refined water	13		rest	rest	rest	rest	rest	rest	rest	rest	rest
Viscosity (mPa·s)	1 rpm		256	858	1340	678	755	576	2125	3251	38
Abrasion resistance			◎	◎	◎	◎	◎	○	◎	◎	○
Writing feeling			◎	◎	△	◎	◎	◎	△	△	○
Written line quality			◎	○	◎	○	◎	◎	○	△	◎
Centrifugal resistance			◎	◎	◎	◎	◎	◎	◎	◎	△
Writing property with the passage of time			◎	◎	◎	◎	◎	◎	◎	◎	○
Ball diameter (mm)			0.28	0.18	0.4	0.2	0.28	0.5	0.28	0.28	0.28

Table 2

		Particle diameter μm	Comparative Example								
			1	2	3	4	5	6	7	8	9
Colorant	1-a		5			5	5	5	5	5	5
	1-b			6	6						
Thickener	2-a			0.15	0.15						
	2-b		0.22			0.3	0.22	0.22	0.22	0.3	0.3
Water-soluble solvent	3-a		20	10	10	20	20	20	20	20	20
	3-b			10	10						
Lubricant	4		0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Rust preventive	5		0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Preservative	6		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
pH-controlling agent	7		2	2	2	2	2	2	2	2	2
Alumina fine particle	8-a	0.033			0.001						
	8-b	0.013				3					
	8-c	0.7		0.5							
Titanium oxide fine particle	9-a	0.05									
	9-b	0.03									
	9-c	0.27					0.6	0.6	0.6		
Silicon carbide fine particle	10	0.04									
Tungsten carbide fine particle	11	0.06									
Water-soluble resin	12		0.3	0.2	0.2	0.5	0.5	0.5	0.5	0.3	0.3
Refined water	13		rest	rest	rest	rest	rest	rest	rest	rest	rest
Viscosity (mPa·s)	1 rpm		320	652	550	538	332	332	332	794	794
Abrasion resistance			×	▲	▲	△	▲	▲	△	×	▲
Writing feeling			△	×	△	×	×	▲	▲	○	○
Written line quality			△	▲	○	△	▲	▲	▲	○	○
Centrifugal resistance			◎	×	○	△	×	△	△	◎	◎
Writing property with the passage of time			◎	×	○	△	×	×	△	◎	◎
Ball diameter (mm)			0.18	0.18	0.2	0.28	0.28	0.4	0.5	0.38	0.5

It can be found from the evaluation results shown in Table 1 and Table 2 that the water-based ink compositions meeting the conditions of the present invention are excellent in writing characteristics and abrasion resistance in a fine pointed ballpoint pen having a ball of a diameter of 0.5 mm or less. On the other hand, it is apparent that the water-based ink compositions which do not meet the conditions of the present invention are inferior in writing characteristics and abrasion resistance in a fine pointed ballpoint pen having a ball of a diameter of 0.5 mm or less. To be specific, the abrasion resistance is extremely inferior in Comparative Example 1, Comparative Example 8 and Comparative Example 9 in which the ultra fine particles according to the present invention are not added and Comparative Example 3 in which the addition amount thereof falls outside the lower limit in the present invention. It can be found that in Comparative Example 2, Comparative Example 5, Comparative Example 6 and Comparative Example 7 in which the fine particles having a primary particle diameter of 0.1 μm or more are added, the abrasion resistance does not reach a satisfactory level and various performances such as writing feeling, centrifugal resistance and a writing property with the passage of time are inferior and that such trend is more

notable in the pens having a smaller ball. Further, the writing feeling is markedly inferior in Comparative Example 4 in which an addition amount of the fine particles falls outside the upper limit in the present invention. Thus, it is apparent that the water-based ink compositions falling outside the scope of the present invention can not solve the problems in the present invention.

Industrial Applicability

The water-based ink composition of the present invention can suitably be used for a fine pointed ballpoint pen, particularly a fine pointed ballpoint pen having a ball of a diameter of 0.5 mm or less.

CLAIMS

1. A water-based ink composition for a fine pointed ballpoint pen characterized by blending an ink composition comprising at least water, a colorant and a water soluble solvent with at least one kind of ultra fine particles selected from the group consisting of alumina, titanium oxide, silica, silicon carbide and tungsten carbide each having an average particle diameter of less than 0.1 μm, wherein a blending amount of the ultra fine particles is 0.002 to 2 % by weight based on the ink composition.

2. The water-based ink composition for a fine pointed ballpoint pen as described in claim 1, having a viscosity of 50 to 2000 mPa·s (25°C) which is measured at 1 rpm by means of a corn and plate type rotational viscometer (1°34'R24 corn).

3. A fine pointed ballpoint pen having a ball of a diameter of 0.4 mm or less, filled with the water-based ink composition as described in claim 1 or 2.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/011653

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl⁷ C09D11/18,B43K1/08,B43K7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl⁷ C09D11/00-11/20,B43K1/08,B43K7/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Japanese Utility Model Gazette 1922-1996, Japanese Publication of Unexamined Utility Model Applications 1971-2004, Japanese Registered Utility Model Gazette 1994-2004, Japanese Gazette Containing the Utility Model 1996-2004

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI (DIALOG)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2002-206066 A(PENTEL CO., LTD.)2002.07.26,CLAIMS,EXAMPLES(FAMILY:NONE)	1-3
X	JP 11-80628 A(KAO CORPORATION)1999.03.26,CLAIMS,EXAMPLES(FAMILY:NONE)	1-3
X	JP 2003-73587 A(SAKURA COLOR PRODUCTS CORPORATION)2003.03.12,CLAIMS,EXAMPLES(FAMILY:NONE)	1-3
E,X	JP 2004-292757 A(PENTEL CO., LTD.)2004.10.21,CLAIMS,EXAMPLES(FAMILY:NONE)	1-3

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
02.11.2004	22.11.2004

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