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(54) Title: HARD COATING COMPOSITION

(57) Abstract: A hard coating composition capable of being applied to the modification of a surface of plastic material that is being widely used in household appliances, the hard coating composition including an inorganic dispersion solution that is composed of at least one hydrolytically decomposable silane compound and an inorganic oxide particle, and an organic resin solution that is composed of a photo-curable acrylic-based compound and various additives capable of providing a functionality, such as a surface improving agent and an anti-static agent, the hard coating composition providing pH of between 4 and 6.



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Description

Title of Invention: HARD COATING COMPOSITION

Technical Field

- [1] Embodiments of the present disclosure relate to a hard coating composition, and more particularly, to a hybrid coating composition configured to be applicable on a surface of plastic material of household appliances.

Background Art

- [2] The plastic material, such as, PMMA (polymethylmethacrylate), PET (polyethyleneterehthalate), and PC (polycarbonate) are being used because they are lightweight, provided with superior durability, and easily molded by heat. However, the plastic material is provided with low surface hardness, and due to the limit in the physical/chemical characteristic thereof poor abrasion resistance and solvent resistance, a wider use of the plastic material is limited.
- [3] As to resolve the difficulties as such, various types of functional hard coating material are being developed. Particularly, the development of the coating material using organic/inorganic hybrid material being produced through a sol-gel processing is being a mainstream.
- [4] A hard coating material may be divided into an organic coating material using melamine, acryl, and urethane, inorganic coating material using silicon-based material, and organic/inorganic hybrid coating material that uses by combining inorganic-based material and organic-based material.
- [5] A coating composition that is composed of the inorganic material such as silicon material, when compared to the organic-based coating material, is provided with superior surface hardness and abrasion resistance. However, such a coating is provided with brittleness, and at the same time, a thick film coating may be difficult due to the generation of a crack such as an evaporation of a solvent in a drying process and a hardening process.
- [6] As to overcome the difficulty as such, a development of hybrid coating material that uses organic/inorganic material is being taken place.
- [7] However, the organic/inorganic hybrid coating material and the coating composition that may be used in coating of transparent plastic material are less sufficient in forming a coating layer having a satisfactory material characteristic, and since the hardness of the coating layer is low and the adhesion between the coating layer and the plastic substrate is low, making such as a product may be difficult.

Disclosure of Invention

Technical Problem

[8] Therefore, it is an aspect of the present disclosure to provide a hard coating composition including an inorganic dispersion solution that is composed of at least one hydrolytically decomposable silane compound and an inorganic oxide particle, and an organic resin solution that is composed of a photo-curable acrylic-based compound and various additives capable of providing a functionality, such as a surface improving agent and an anti-static agent, the hard coating composition providing pH of between 4 and 6.

[9] Additional aspects will be set forth in part in the description which follows and, in part, will be obvious from the description, or may be learned by practice of the disclosure.

Solution to Problem

[10] In accordance with one aspect, a hard coating composition includes a surface-modified Boehmite nano particle of 5 to 50 weight %, a photo-hardening-type acrylate compound of 10 to 50 weight %, an organic solvent of 30 to 70 of weight %, and a photo-initiator of 1 to 10 weight %, wherein the hard coating composition is provided with a pH thereof between 4 to 6.

[11] A surface of the Boehmite nano particle may be modified with an alkoxy silane compound, and the alkoxy silane compound includes at least one of an acrylic-based alkoxy silane compound and a vinyl-based alkoxy silane compound.

[12] The photo-hardening-type acrylate compound may include at least one of acrylate monomer, urethane acrylate, polyester acrylate, polyether acrylate, and acrylic acrylate.

[13] The organic solvent may include at least one of methanol, ethanol, isopropanol, normal-propanol, butanol, isobutanol, ethyl-cellosolve, methyl-cellosolve, butyl-cellosolve, butyl-acetate, diacetone alcohol, methyl-ethyl ketone, propylene glycol, isopropyl alcohol, and ethylene-glycol isopropyl alcohol.

[14] The photo-initiator may include at least one type of a benzo-phenone type, an acetone-phenone type, a benzoin-ether type, benzyl-ketal type, a thioctic-xanthone type, and an anthraquinone type.

[15] The hard coating composition may further include a surface improving material or an anti-static material, or the like.

[16] The pH may be controlled through at least one of monoethanolamine, diethanolamine, and triethanolamine.

[17] The Boehmite nano particle may be acicular.

[18] The Boehmite nano particle may have a size from 1nm to 20nm.

[19] The surface modification of the Boehmite nano particle may be performed at a temperature between 60°C and 80°C.

- [20] In a case when the surface of the Boehmite nano particle is being modified, the pH of the solvent having the dispersed Boehmite nano particle may be controlled at between 3 and 5.
- [21] In accordance with another aspect, a product having a surface coated with a hard coating composition is characterized by having the hard coating composition that includes a surface-modified Boehmite nano particle of 5 to 50 weight %, a photo hardening-type acrylate compound of 10 to 50 weight %, an organic solvent of 30 to 70 weight%, and a photo-initiator of 1 to 10 weight %.
- [22] A pH of the hard coating composition may be between 4 and 6.
- [23] A surface of the Boehmite nano particle may be modified with an alkoxy silane compound, and the alkoxy silane compound may include at least one of an acrylic-based alkoxy silane compound and a vinyl-based alkoxy silane compound.
- [24] The photo hardening-type acrylate compound may include at least one of acrylate monomer, urethane acrylate, polyester acrylate, polyether acrylate, and acrylic acrylate.
- [25] The organic solvent may include at least one of methanol, ethanol, isopropanol, normal-propanol, butanol, isobutanol, ethyl-cellosolve, methyl-cellosolve, butyl-cellosolve, butyl-acetate, diacetone alcohol, methyl-ethyl ketone, propylene glycol, isopropyl alcohol, and ethylene-glycol isopropyl alcohol.
- [26] The photo-initiator may include at least one type of a benzo-phenone type, an acetone-phenone type, a benzoin-ether type, benzyl-ketal type, a thioctic-xanthone type, and an anthraquinone type.
- [27] The product may further include a surface improving material or an anti-static material.
- [28] The pH may be controlled through at least one of monoethanolamine, diethanolamine, triethanolamine and triethylamine.
- [29] The Boehmite nano particle may be acicular.
- [30] The Boehmite nano particle may have a size from 1nm to 20nm.
- [31] The surface modification of the Boehmite nano particle may be performed at a temperature between 60°C and 80°C.
- [32] In a case when the surface of the Boehmite nano particle is being modified, the pH of the solvent having the dispersed Boehmite nano particle may be controlled at between 3 and 5.

Advantageous Effects of Invention

- [33] In accordance with one aspect, a hard coating composition is capable of enhancing the surface hardness and the abrasion resistance, both of which are regarded as drawbacks of plastic panel, without reducing the transparency of the plastic material

for household appliances such as a washing machine, an air conditioner, and a refrigerator.

- [34] In addition, since the adhesiveness with a plastic panel is superior, the hard coating composition may be used in various areas.

Best Mode for Carrying out the Invention

- [35] Inorganic nano particles of a hard coating composition in accordance with one embodiment may be obtained by performing a peptization after a hydrolysis of a metallic alkoxide, such as methoxide, ethoxide, isopropoxide, and butoxide, is performed in water.

- [36] In more detail, first, after obtaining a sediment in the form of a metallic hydrate having a cohesive form by performing a hydrolysis on a metallic alkoxide in an excess amount of water, and a strong acid such as a nitric acid or a hydrochloric acid is added to the sediment to perform a reaction for a number of hours at a temperature between 70°C and 100°C, preferably between 80°C and 90°C, so that a stable inorganic nano-sol having a size in nano units may be produced.

- [37] Most of the commercialized coating composition liquid having inorganic particle is used together with an organic binder, or is used in a manner to be dispersed in an organic solvent using a silane coupling agent.

- [38] In a case when a large amount of the organic binder is used, the content of the organic material is increased, and thus the surface hardness is reduced, and in a case when a reduced amount of the organic matter is used, since a dispersion may be difficult, the hard coating composition may not be used as a coating liquid, and thereby the production of hard coating material provided with superior surface hardness only by having a silica and a silane coupling agent is limited.

- [39] Thus, the hard coating composition in accordance with one embodiment, as to produce a hard coating composition having higher hardness, is configured to use Boehmite, which is an inorganic nano particle, having higher surface hardness than the hardness of silica.

- [40] A silane compound that is used on the modification of the surface of the inorganic nano particle is an alkoxy silane compound, and particularly, may be selected from an acrylic-based alkoxide silane compound or a vinyl-based alkoxy silane compound.

- [41] The Boehmite nano particle may be an aciform.

- [42] The Boehmite nano particle is pre-processed by the acrylic-based alkoxide silane or the vinyl-based alkoxy silane, which are the organic silane coupling agents having an acrylic group and a vinyl group through a sol-gel method, so that hard coating liquid having an organic/inorganic nano particle hard coating composition liquid having superior dispersibility in organic solvent.

- [43] The coating composition as such, by the characteristic of the Boehmite having superior surface hardness, may be provided with an enhanced abrasion resistance when compared to silica, and may be provided with superior dispersibility with respect to the organic solution by a silane coupling agent.
- [44] The hybrid nano particle produced as such is provided with a structure of an Al-O-Si, and may form a coating film having high abrasion resistance after a hardening is performed.
- [45] In the present disclosure, the reaction to perform a modification of the surface of the Boehmite with a silane compound is proceeded in the range of pH 3 and pH 5.
- [46] The electrical charge of the surface of the Boehmite particle, which is charged with a strong positive (+) charge in an acid state, is approached to about 0 at the range of pH 6 to pH 7, in other words, the repulsive force on the surface of the Boehmite particle is reduced due to the loss of the electrical charge of the surface of the Boehmite particle, and thereby causing the cohesion of the sol.
- [47] That is, with respect to the Boehmite particle, since the partial positive charge of aluminum is shown at a relatively larger scale, in a case when a loss of the electrical charge of the surface is occurred, a nano-size particle has a tendency of showing a strong cohesion for stabilization as to recover the loss as such.
- [48] In addition, in a case when the surface of a particle is modified with an organic silane, a sol-gel method is being used, and the sol-gel method requires a reaction under an acid state serving as catalysis reaction to promote a hydrolysis reaction and a condensation reaction.
- [49] A photo-hardening-type acrylate compound of a hard coating composition in accordance with one embodiment may be selected from an acrylate monomer, a urethane acrylate, a polyester acrylate, a polyether acrylate, and an acrylic acrylate.
- [50] The acrylic compound, by performing a role as a cross-linking agent with respect to the modified particles, may be able to produce a further solid coating film, and in order to obtain the optimal coating layer, 10 to 65 weight parts of a modification particle and 35 to 90 weight parts of an acrylic-based monomer are required on a basis of 100 parts by weight of solid content of the coating liquid.
- [51] As for an initiator of a hard coating composition in accordance with one embodiment of the present disclosure, a conventional polymerization initiator, which is configured to enable a hardening while forming a radical when an UV is radiated, is used, and the initiator may include a benzo-phenone type initiator, an acetone-phenone type initiator, a benzoin-ether type initiator, a benzyl-ketal type initiator, a thioctic-xanthone type initiator, and an anthraquinone type initiator, and from the above initiators, the benzophenone, 1-hydroxy cyclohexyl phenyl ketone, and a - amino acetophenone may be used.

- [52] An UV initiator, by forming a radical as a weak coupling is broken by an UV during a chemical combination of the initiator, enables a fast and solid hardening to take place. The content of the initiator to obtain an optimal coating film, on a basis of 100 parts of solid content of the coating liquid, may be 3 to 10 weight parts, or preferably, 5 to 7 weight parts.
- [53] In addition, alcohol is used as a solvent to disperse the coating liquid. The acrylic-based alkoxy silane or the organic silane, which are added in the present embodiment may be able to maintain the stability of the inorganic nano particle in accordance with the addition of the alcohol-like solvent. Thus, even when the composition of the solvent is changed, the stability of the particle is maintained. As for the ratio of the added alcohol, which is a solvent, the ratio of the solid content of a coating liquid and the alcohol is provided to be from 3:2 to 2:3 in terms of a weight ratio.
- [54] The coating liquid as such, in a case when being coated on the substrates of various materials, may be able to form a strong, colorless, and transparent coating film by silanol generated by the hydrolysis of the acrylic-based alkoxide silane compound, or by the functional group of an acryl group of the acrylic based compound.
- [55] In addition, by considering the miscibility with water and the drying speed after a coating, the alcohol may be used by selecting more than one type of alcohol from methane, ethanol, 1-propanol, and 2-propanol.
- [56] By adding a TEA (triethanolamine) to the coating liquid that is ultimately produced in the present disclosure, the coating liquid may be produced having various pH.
- [57] As the pH is increased, the electrical charges of the surface of the Boehmite having an IEP (isoelectric point) at between 7 and 8 are reduced, and accordingly, the viscosity is enhanced. Through such, the thickness of the coating film may be controlled not only through an increase of the solid content but also through the controlling of the pH of the coating liquid without having to increase a solid content, the controlling of the pH of the coating liquid also enabling the enhancement of the hardness.
- [58] As to secure the transparency and the convenience of a processing while enhancing a surface hardness, the pH of the coating liquid is preferred to be adjusted in the range between 4 and 6.
- [59] The substrates at which the hard coating composition in accordance with one embodiment of the present disclosure may be used in a useful manner include the substrates that are formed of glass, stainless steel, ceramics, aluminum, and plastic, and by applying a coating on the substrates as such using a spin coating method, a deep coating method, a flow coating method, and a spray coating method, a coating film having high hardness and transparency may be formed.
- [60] Hereinafter, the descriptions will be provided more in detail through the following

embodiments and comparative examples.

[61] <Embodiments>

[62] Production of Boehmite Nano particle and Modification of Surface of Boehmite Nano Particle

[63] Water of about 5L and aluminum isopropoxide of 2.45mol are placed in a reactor and then stirred to obtain sediment that is hydrolyzed. Then, a nitrate of about 0.288 mol is added, and by gradually increasing the temperature, a peptization reaction is induced. While maintaining the pH in the range of 3.6 and 4.0, a reaction is performed for about 6 hours at a temperature of 90 degrees, and the Boehmite sol, which is opaque, is obtained. By stirring the Boehmite nano sol obtained as such, the Boehmite sol is evaporated under a decompression to obtain Boehmite nano particles. As a result of the TEM analysis, the size of the Boehmite nano particle is provided with the size of several nanometers, while the compounded Boehmite is in match with the planes of the crystal lattice of each of (020), (120), (03 1), and (200) of a Boehmite phase of JCPDS (No. 31-1307) and is present in the form of a γ -AlOOH. Then, with respect to Boehmite nano particle obtained, distilled water of about 100mL and the Boehmite particle of about 83.33mmol are placed in a reactor, which is provided with a mechanical stirrer installed thereto, to produce the evenly dispersed Boehmite nano sol. Next, by adding the 3-(trimethoxysilyl) propyl methacrylate of about 47.34mmol and the triethoxyvinylsilane of about 12.34mmol to the dispersed liquid, and the temperature is increased to about 70 °C to induce the hydrolysis and the condensation reaction between the Boehmite and the organic silane for about 30 minutes, and thus sediment that is agglomerated at an inside the reactor is obtained. The sediment as such is formed by the lipophilic characteristic of the acrylate in water, and after the completion of the reaction, the Boehmite particle, which is surface-modified with an organic silane, is ultimately obtained by a filter apparatus.

[64] Embodiments 1 to 4

[65] A 60% solution is produced by dispersing the Boehmite particle, which is grafted with an organic group produced as above, and an acrylate compound (SC2153) in isopropyl alcohol at a weight ratio of about 45:55. Then, by adding 7 weight parts of 1-hydroxy cyclohexyl phenyl ketone (IRG-184) as an UV initiator with respect to the solid content, a coating liquid is produced. After then, by adding a triethanolamine at about 0.5 to 3 weight parts, final coating liquids having pH of 4, 4.5, 5, and 5.5 are produced

[66] Comparative Example 1

[67] Except that a 40% solution, which is provided with the surface-modified Boehmite particle and the acrylate compound dispersed isopropyl alcohol at the weight ratio of about 50:50, is being used, the comparison is performed using the same methods the

above embodiments 1 to 4.

[68] Comparative Example 2

[69] Except that a 50% solution, which is provided with the surface-modified Boehmite particle and the acrylate compound dispersed in isopropyl alcohol at the weight ratio of about 50:50, is being used, the comparison is performed using the same methods the above embodiments 1 to 4.

[70] The components of the coating composition produced at the embodiments and the comparative examples are shown on the [Table 1] below:

[71] Table 1

[Table 1]

Category	Modified Inorganic Particle	Acrylic-based Compound	Initiator	Organic Solvent	pH
Embodiment 1	0.9g	1.1g	0.14g	1.3g	4
Embodiment 2	0.9g	1.1g	0.14g	1.3g	4.5
Embodiment 3	0.9g	1.1g	0.14g	1.3g	5
Embodiment 4	0.9g	1.1g	0.14g	1.3g	5.5
Comparative Example 1	1.0g	1.0g	0.14g	3.0g	3.5
Comparative Example 2	1.0g	1.0g	0.14g	2.0g	3.5

[72] With respect to the coating composition, a PMMA panel, which is provided with the width and the length thereof at about 5 cm each, is thoroughly cleaned with Isopropyl Alcohol for the coating composition to be applied thereon, and through a spin coating method, a coating film is produced, and an UV hardening is performed after a natural drying process of about 10 minutes. After the completion of the above, the physical properties of the coating film are evaluated as follows:

[73] Transmittance /Haze

[74] By using a Hazemeter (NDH-5000), the total transmittance and a haze of a coating sample are measured.

[75] Transmittance (T) O : T > 90%, Δ : 75% < T < 90%, X : T < 75%

[76] Haze (H) O : H < 2%, Δ : 2% < H < 5%, X : 5% < H

[77] Pencil Hardness

[78] The pencil hardness is measured by inserting a pencil, which is prepared for a hardness measurement, into a pencil hardness tester (QM450A) at a 45-degree angle,

and by applying a certain weight (0.5kg) on the coating film that is formed on the PMMA substrate. As for the pencils, Mitsubishi pencils having the strengths of H-9H, F, HB, and B-6B are used. The hardness of the lead of each pencil occurring no scratch after three attempts is measured.

[79] Adhesiveness

[80] With respect to the adhesiveness test, a cross-cut test is used. By using a cross cutter, the coating film having the width and length of about 10mm is divided into 10x10 sections while each of the 100 sections is provided with the width about 1mm, and the length of about 1mm. Then, on the total of 100 sections, a strip of 3M scotch tape is placed and closely adhered by use of a hand. Next, the strip of 3M scotch tape is removed instantly from the 100 sections in a perpendicular direction to the direction of the strip of 3M scotch tape is placed on the 100 sections. At this time, by measuring the number of the rectangular sections that remain on the coating layer, the adhesiveness is evaluated.

[81] $\text{Adhesiveness} = \text{Number of Remaining Rectangular Sections} / 100$

[82] Abrasion Resistance

[83] With respect to the evaluation of the abrasion resistance, a printing abrasion tester is used. After fixing the coating layer sample to a tester, a friction ruler having a diameter of about 28mm is wrapped with a cotton cloth, and while applying a weight of about 2kg on the friction ruler, the abrasion is performed for about 2,000 times at the frequency of about 45 round trips in a minute. After the above process, the surface is investigated.

[84] O: No trace of peeling or abrasion, Δ: Minor abrasion occurred, X: Peeling of coated surface occurred

[85] The physical properties of the coating film that is produced according to the embodiments 1 to 4 as well as the comparative examples 1 and 2 are as follows:

[86] Table 2

[Table 2]

Category	Transmittance	Haze	Pencil Hardness	Adhesive-ness	Abrasion Resistance
Embodiment 1	○	○	7H	100/100	○
Embodiment 2	○	○	8H	100/100	○
Embodiment 3	○	○	9H	100/100	○
Embodiment 4	○	○	9H	100/100	○
Comparative Example 1	○	○	5H	100/100	○
Comparative Example 2	○	○	6H	100/100	○

[87] Although a few embodiments have been shown and described, it would be appreciated by those skilled in the art that changes may be made in these embodiments without departing from the principles and spirit of the disclosure, the scope of which is defined in the claims and their equivalents.

Claims

- [Claim 1] A hard coating composition, comprising:
a surface-modified Boehmite nano particle of 5 to 50 weight %;
a photo-hardening-type acrylate compound of 10 to 50 weight %;
an organic solvent of 30 to 70 of weight %; and
a photo-initiator of 1 to 10 weight %.
- [Claim 2] The hard coating composition of claim 1, wherein the hard coating composition is provided with a pH thereof between 4 to 6.
- [Claim 3] The hard coating composition of claim 1 or 2, wherein:
a surface of the Boehmite nano particle is modified with an alkoxy silane compound, and
the alkoxy silane compound comprises at least one of an acrylic-based alkoxy silane compound and a vinyl-based alkoxy silane compound.
- [Claim 4] The hard coating composition of any one of claims 1 to 3, wherein:
the photo-hardening-type acrylate compound comprises at least one of acrylate monomer, urethane acrylate, polyester acrylate, polyether acrylate, and acrylic acrylate.
- [Claim 5] The hard coating composition of any one of claims 1 to 4, wherein:
the organic solvent comprises at least one of methanol, ethanol, isopropanol, normal-propanol, butanol, isobutanol, ethyl-cellosolve, methyl-cellosolve, butyl-cellosolve, butyl-acetate, diacetone alcohol, methyl-ethyl ketone, propylene glycol, isopropyl alcohol, and ethylene-glycol isopropyl alcohol.
- [Claim 6] The hard coating composition of any one of claims 1 to 5, wherein:
the photo-initiator comprises at least one type of a benzo-phenone type, an acetone-phenone type, a benzoin-ether type, benzyl-ketal type, a thioctic-xanthone type, and an anthraquinone type.
- [Claim 7] The hard coating composition of any one of claims 1 to 6, further comprising:
a surface improving material or an anti-static material.
- [Claim 8] The hard coating composition of any one of claims 1 to 7, wherein:
the pH is controlled through the use of at least one of monoethanolamine, diethanolamine, and triethanolamine.
- [Claim 9] The hard coating composition of any one of claims 1 to 8, wherein:
the Boehmite nano particle is acicular.
- [Claim 10] The hard coating composition of any one of claims 1 to 9, wherein:
the Boehmite nano particle has a size from 1nm to 20nm.

- [Claim 11] The hard coating composition of any one of claim 1 to 10, wherein: the surface modification of the Boehmite nano particle is performed at a temperature between 60°C and 80°C.
- [Claim 12] The hard coating composition of any one of claims 1 to 11, wherein: when the surface of the Boehmite nano particle is being modified, the pH of the solvent having the dispersed Boehmite nano particle is controlled at between 3 and 5.
- [Claim 13] A product having a surface coated with a hard coating composition, the hard coating composition being according to any one of claims 1 to 12.
- [Claim 14] A method of manufacturing a product, comprising:
coating the surface of the product using a hard coating composition,
wherein the hard coating composition is according to any one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR20 12/010748**A. CLASSIFICATION OF SUBJECT MATTER****C09D 4/02(2006.01)i, C09D 7/12(2006.01)1, C09D 133/04(2006.01)1, C09D 5/00(2006.01)1**

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)

C09D 4/02; C08K 3/20; B05D 1/36; B05D 3/08; C09D 7/12; C09D 183/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & keywords: hard coating, surface-modified Boehmite nanoparticle, U.V curing type coating composition, alkoxy silane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	(JENØN, s. j. et al.). Hard coating films based on organosilane-modified boehmite nanoparticles under UV/thermal dual curing. The Solid Films. 2008, Vol. 516, No. 12, pp. 3904-3909. See abstract; page 3904, right column, lines 3-11; page 3904, right column, lines 15-24; page 3905, left column, lines 1-11; page 3905, right column, lines 1-28.	1-3
X	(SEPEUR, s. et al.). UV curable hard coatings on plastics. The Solid Films. 1999, Vol. 351, No. 1/2, pp. 216-219. See abstract; page 216, right column, lines 1-7; page 216, right column, lines 13-22; page 217, left column, lines 8-26; page 217, right column, lines 23-43.	1-2
A	KR 10-2010-0125339 A (UNIVERSITY OF FLORIDA RESEARCH FOUNDATION, INC) 30 November 2010 See claims 1, 3, 5, 7-13, 18, 20, 25, 26; paragraphs [0002], [0005], [0009], [0011], [0013], [0021], [0023], [0029].	1-3
A	US 2004-0131793 A1 (BIER, P. et al.) 8 July 2004 See abstract; paragraphs [0044], [0048], [0078], [0079]; claims 1, 5, 6.	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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

28 FEBRUARY 2013 (28.02.2013)

Date of mailing of the international search report

28 FEBRUARY 2013 (28.02.2013)

Name and mailing address of the ISA/KR



Facsimile No. 82-42-472-7140

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2012/010748

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: **4-14**
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☒ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☒ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2012/010748

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6939908 B1 (SINGHAL, A. et al.) 6 September 2005 See abstract; column 1, lines 13-18; column 1, lines 23-28; column 2, lines 26-35; claims 1, 8, 10.	1-3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2012/010748

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP 2250226 A2	17.11.2010
		JP 2011-513553 A	28.04.2011
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		KR 10-2005-0061505 A	22.06.2005
		WO 2004-031272 A1	15.04.2004
US 6939908 B1	06.09.2005	None	