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**Antimikrobinen ionomeerikoostumus sekä sen käyttösovellukset**

**Antimikrobisk jononersammansättning och användningen därav**

**Antimicrobial ionomer composition and uses thereof**

(57) Tiivistelmä - Sammandrag - Abstract

Keksintö koskee polymeeristä antimikrobista koostumusta, menetelmää sen valmistamiseksi ja sen käyttösovelluksia.

Ionomeerikoostumus käsittää amiinifunktionaalisen polymeeriyhdisteen,

joka on saatettu reagoimaan hopeahalogenidin kanssa, valinnaisesti yhdessä stabilointiaineosan kanssa, kuten orgaanisen aineen kanssa, jossa on funktionaalinen sulfonamidiryhmä.

Ionomeerikoostumus voidaan aikaansaada saattamalla reagoimaan (i) ainakin yksi polyamiini ja hopeahalogenidi ja valinnaisesti ainakin yksi orgaaninen stabilointiaine tai (ii) ainakin yksi polyamiini, ainakin yksi ei-halogenidihopeasuola tai hopeakompleksi, vetyhalogenidi ja/tai alkalisen metallin halogenidisuola ja valinnaisesti ainakin yksi orgaaninen stabilointiaine. Tämä ionomeerikoostumus sopii käytettäväksi antimikrobisena pinnoitteena, antimikrobisena viimeistelyaineena, antimikrobisena lisäaineena ja antimikrobisena aineosana uusien antimikrobisten materiaalien muodostusta varten.

Denna uppfinning avser en polymer antimikrobisk sammansättning, ett förfarande för framsällning av densamma och användningarna därav. Jononersammansättningen omfattar en amin funktionell polymer förening, som reagerat med silverhalid, valbart tillsammans med en stabiliserande komponent, såsom ett organiskt ämne med en sulfonamid funktionell grupp. Jononersammansättningen kan erhållas genom att reagera tillsammans (i) åtminstone en polyamin och silverhalid och valbart åtminstone ett organiskt stabilisatorämne eller; (ii) åtminstone en polyamin, åtminstone ett ickehalogent silversalt eller silverkomplex, hydrogenn halid och/eller alkalimetallhalidsalt och valbart åtminstone ett organiskt stabilisatorämne. Denna jononersammansättning är lämplig för att användas som en antimikrobisk beläggning, antimikrobisk slutbehandling, antimikrobiskt tillsatsämne och som antimikrobisk komponent för att bilda nya antimikrobiska material.

## **ANTIMICROBIAL IONOMER COMPOSITION AND USES THEREOF**

### **Background of the Invention**

#### 5 **Field of the Invention**

The present invention relates to polymeric antimicrobial compositions. In particular the invention concerns novel antimicrobial ionomer compositions, methods of preparing the same and the uses thereof.

10

#### **Description of Related Art**

Antimicrobial technologies based on the bioactive properties of ionic silver are currently widely recognized as belonging to the most advanced solutions on the wide application  
15 field of antimicrobial materials both in the science community and the industries utilizing antimicrobial surface technologies. Ionic silver has a general status as a safe biocide in many applications. Also the wide antimicrobial spectrum of silver against most bacterial species, including the antibiotic resistant strains, e.g. MRSA and NDM-1 which currently generate a severe health treat to patients in the form of hospital infections, makes ionic  
20 silver particularly interesting.

Recently in the healthcare sector, strategies for improving hospital hygiene and preventing infections have been extended to cover the aspect of spreading of infections through various surfaces in the healthcare environments. Correspondingly the application of  
25 antimicrobial materials and coating technologies have been emphasized as a new complementary mean for together with other aspects contributing to the battle against hospital infections.

Multiple strategies have been utilized to form antimicrobially active, silver releasing  
30 surfaces on fibers and bulk material surfaces. Conventional strategies typically comprise attachment on the surfaces of silver containing particles, such as nanosilver, silver zeolite, silver zirconium phosphate and silver chloride containing titanium dioxide particles, by various chemical means, typically utilizing a carrier material. Another conventional method is to treat certain surface materials chemically in order to provide attachment of  
35 silver ions or silver containing particles on the surface.

Nanoparticulate silver (nanosilver) has recently been extensively studied emerged as a potentially hazardous material to health and environment, which again has increased pressure towards developing of new silver ion technologies

- 5 Liquid antimicrobial additives for liquid products, such as disinfection solutions, surfactants, paints, wax/polymer coatings, deodorizing solutions and cosmetic solutions, are typically based on utilization of silver citrate solutions or silver zeolite or particulate silver dispersions, colloidal silver.
- 10 To date, polymer carrier based silver technologies have not been studied or developed extensively. Technologies based on functional ionic polymers are rare.

International Published Patent Application WO2002/030204 discloses novel antibacterial agents, wherein the lone pair electrons of nitrogen atoms of amine compounds with high  
15 boiling point or water-soluble polymer with basic nitrogen at the backbone or side chain are coordinated with silver ion. Antibacterial and deodorizing solution comprising them are also disclosed.

- US Published Patent Application No. 2009246258 discloses antimicrobial and odor  
20 adsorbing fabric substrate having a surface coating. The coating contains silver compounds and combination thereof, a hyperbranched polyethyleneimine derivative, potassium citrate, inorganic chloride, a polyurethane binder, and a cross-linking agent. The silver compounds are selected from the group consisting of silver zirconium phosphate, silver zeolite, silver glass, and any mixtures thereof or a conductive silver containing nanoparticles. ion-  
25 exchange resins, zeolites, or, possibly substituted glass compounds. According to publication hyperbranched polyethyleneimine derivative, abbreviated "h-PEI", comprises at least one hyperbranched polyethyleneimine linked to one or more linear hydrocarbon groups having 5 to 30 carbons. The preferred silver containing compounds are silver zirconium phosphate available from Milliken & Company under the trade name  
30 ALPHASAN, silver zeolite available from Sinanen under the trade name ZEOMIC, and silver glass available from Ishizuka Glass under the trade name IONPURE. Inorganic chlorides are preferred, especially magnesium chloride and ammonium chloride. A range of ratios from 1:10 to 5:1 (chloride to silver ion). The h-PEI derivatives also suffered from discoloration and it was found that potassium citrate reduced or eliminated the yellowing  
35 of the h-PEI.

### **Summary of the Invention**

The present invention aims at providing an antimicrobial ionomer composition, which  
5 comprises an amine functional cationic polymer and silver halide.

According to the invention, an antimicrobial amorphous ionomer composition can be  
obtained by a process comprising reacting at least one amine functional polymer and a  
silver halide. Alternately, the composition can be obtained by a process comprising  
10 reacting a amine functional polymer and at least one silver non-halide salt or complex  
compound and hydrogen halide or an alkali metal or alkaline earth metal or ammonium  
halide salt.

Thus, in a first preferred embodiment the antimicrobial ionomer composition is obtained  
15 by reacting together in a solvent matrix

- at least one polymer exhibiting functional amine groups, and
- a silver halide.

In another preferred embodiment, the present antimicrobial ionomer composition is  
20 obtained by reacting together in a solvent matrix

- at least one polymer exhibiting functional amine groups,
- at least one organic silver salt or complex compound and
- hydrogen halide, an alkali metal or alkaline earth metal halide salt or ammonium  
halide salt, or a combination thereof.

25 In further preferred embodiments, the present antimicrobial ionomer composition is further  
balanced and controlled by including stabilizing components in the composition. In further  
preferred embodiments, the stabilizing components comprise a sulfonamide group  
containing organic substance(s). In some embodiments, said stabilizer substance may be  
30 the counter-anion or ligand of said at least one organic silver salt or complex compound.

In some embodiments, said antimicrobial composition includes additional components,  
such as cross-linking agents, hydrophobic modifiers, water repellents, various stabilizers  
and surfactants.

35

The preparation methods disclosed above can also be combined.

The antimicrobial ionomer composition according to the invention can be used for coating of a great variety of host surfaces.

5

More specifically, the present ionomer compositions are mainly characterized by what is stated in the characterizing part of claim 1.

10

The method according to the present invention is characterized by what is stated in the characterizing part of claim 25.

The use of the ionomer compositions is characterized by what is stated in claim 30.

15

The invention provides considerable advantages. Generally, the novel composition is suitable for use as an antimicrobial coating, antimicrobial finish, antimicrobial additive and as antimicrobial component for formation of new antimicrobial materials.

20

The novel antimicrobial ionomer compositions are particularly useful for coating of various substrates, such as fiber, fabric and bulk material surfaces, including various synthetic semisynthetic and natural fibers, woven fabrics, nonwoven fabrics, knitted fabrics, papers, various polymer surfaces, metal surfaces, various coating surfaces, wood surfaces and fiber. The novel antimicrobial ionomer compositions are particularly useful for antimicrobial wet wipes, hand sanitizer liquids and cosmetics.

25

The ionomer composition according to the present invention provides an enhanced antimicrobial effect, optical performance and stability which surpasses that of known antibacterial compositions comprising different silver sources mixed with polyamine polymers. It appears that halide carrying ionomers of polyamine and silver provide enhanced adhesion properties, antimicrobial activity, control of silver-ion release and optical performance. The ionomer composition according to the present invention is preferably free of particles.

30

Next the invention will be examined more closely with the aid of a detailed description and with reference to a number of working examples.

### **Detailed Description of Preferred Embodiments**

The present invention discloses novel antimicrobial compositions comprising ionomers of amine functional polymers (i.e. polymers exhibiting functional amine groups) and metal  
 5 halides. According to a preferred embodiment of the ionomer composition according to the invention, the composition is produced in – and it therefore also comprises – a solvent matrix, preferably comprising alcohols, such as methyl alcohol or ethyl alcohol, or water and combinations thereof.

10 In a first preferred embodiment, the ionomer compositions are obtained by reacting together at least one amine functional polymer (ionomer prepolymer, carrierpolymer) and silver halide. In another preferred embodiment the ionomer compositions are obtained by reacting together at least one amine functional polymer (ionomer prepolymer, carrier  
 15 polymer), at least one non-halide silver salt or complex compound and hydrogen halide and/or alkali metal or alkaline earth metal (in the following jointly designated “alkaline metal”) halide salt.

In one embodiment, an amine functional polymer “carrier”polymer is reacted together with either silver halide or a silver salt or complex compound, however in the latter case the  
 20 composition is halidized with either hydrogen halide or alkaline metal halide salt in order to obtain the ionomer composition characteristic to the invention. In a preferred embodiment, at least one stabilizer component/substance is included in the system (composition). With both routes the obtained product possesses similar essential properties independent of variations in the proton or alkaline metal cation or alkaline metal salt  
 25 concentrations.

In a preferred embodiment of the invention, said amine functional ionomer prepolymer comprises a branched polyethyleneimine, a linear polyethyleneimine or a mixture of  
 30 corresponding polyethyleneimines of different qualities with different properties with regard to e.g. molecular weights and primary:secondary:tertiary -amine ratios. Also copolymers of polyethyleneimines are useful.

In other embodiments said amine functional polymer comprises other polyamines, such as polyvinylamine, polyacrylamine, polyarylamine, polyethyleneimine,  
 35 polyhexamethylenebiguanidine and polyvinylpyridine. Combinations of various amine

functional polymers may be applied for obtaining the antimicrobial ionomer compositions characteristic to the invention.

5 The amine functional polymer preferably comprises or consists of a potentially branched poly(ethyleneimine) having a molecular weight (Mw) between 200 and 3,000,000, in particular about 750 to 2,000,000.

10 As further examples, the following embodiments can be mentioned: compositions wherein the amine functional polymer is polyvinylamine or copolymer having 30–100 mol-% of vinylamine, in particular embodiments wherein the amine functional polymer is graft polymer of polyvinylamine with ethyleneimine; compositions wherein the amine functional polymer is a graft polymer of polyamidoamine with ethyleneimine; compositions wherein the amine functional polymer is a polyarylamine copolymer; compositions wherein the amine functional polymer is polyacrylamine.

15

Compositions wherein the polymer components are internally cross-linked through at least one cross-linking agent are also contemplated.

20 In some embodiments, said stabilizer component comprises one or more organic substances capable of promoting the stability of silver moieties within the composition against various stressors, such as UV-radiation, heat, moisture, redox reactions, pH and other factors which may cause unfavorable changes to the compositions in accordance with the invention. The unfavorable effects include discoloration, particle formation and other unfavorable effects in the essential chemical structure of the compositions and  
25 correspondingly e.g. in the state appearance of the composition.

In one preferred embodiment of the invention, said stabilizer comprises at least one substance or compound carrying sulfonamide functional group(s).

30 In another preferred embodiment, said stabilizer substance or combination of stabilizer substances are selected from the group comprising saccharin, cyclamic acid, sulfadiazine and acesulfame.

In a particularly preferred embodiment said stabilizer substance comprises saccharin.

35

In some embodiments said stabilizer substance may comprise e.g. organic acids (such as carboxylic acids, sulfonic acids and amino acids), phosphates, esters, aldehydes, ketones, zwitterionic compounds, titanates and their organic derivatives, silanes and their organic derivatives and organosulphur compounds.

5

Saccharin (o-sulfobenzimide; 1,2-benzothiazole-3(2H)-one 1,1-dioxide) is one of the most widely used artificial sweetening agents. The imino hydrogen of saccharin is acidic. The molecule can easily be converted into the corresponding nitranion. The coordination chemistry of the saccharinato anion is very versatile. It offers multiple coordination sites to  
10 metallic centers.

A typical silver compound, silver saccharinate (usual form: silver saccharinate dihydrate) is a solid white powder with limited solubility properties. Silver saccharin may typically be produced through precipitation by reacting acidic form saccharin and silver nitrate, or  
15 from sodium saccharin and silver nitrate in certain solvent compositions depending on the molecular state of saccharin.

In some embodiments, the free amine functional groups of said amine functional polymer,  
20 which in a preferred embodiment comprises polyethyleneimine, have a function in attachment of said composition to host materials (materials wherein the ionomer composition of the invention is added to provide antimicrobial functionality) and material surfaces (surfaces coated with material comprising the ionomer composition of the invention). When used as an additive, attachment to host material/host matrix may be  
25 achieved through adhesion, e.g. ionic bonding or covalent bonding, between amine groups of the amine functional polymer backbone part of the ionomer composition according to the invention and a molecular structure of a second material or interactions the like.

In one preferred embodiment the solvent matrix comprises ethyl alcohol or methyl alcohol  
30 or isopropanol or water or combinations thereof. Mixtures of solvents may be used, such as aqueous alcoholic solutions/mixtures. Said antimicrobial ionomer composition can be extracted from said solvent matrix for further use e.g. through evaporating the solvent. Typically a more practical and economical solution is, however, to design further processes for using the composition directly with a solvent matrix containing the ionomer  
35 composition as a starting material.



According to another embodiment of the invention, the silver cation is delivered into the ionomer composition as a non-halide silver salt or silver complex, which reacts with amine functional polymer(s), in a preferred embodiment polyethyleneimine, followed by  
5 chloridization of the composition with hydrogen halide or alkaline metal halide salt or combinations thereof. In association with the latter embodiment, suitable non-halide silver salts or silver complexes include e.g. silver nitrate, silver acetate, silver stearate, silver oxide, silver saccharinate, silver imidazole, silver citrate, silver methacrylate and silver sulfadiazine. In some embodiments, the chemical properties of the counter-ions (anions) of  
10 the specific silver salts are utilized in stabilization of the composition and in controlling the migration of silver ions from the composition.

The silver content of the ionomer composition is about 0.01 to 50 %, in particular about 1 to 30 %, preferably about 1.5 to 25 % by weight of the total dry weight of the composition.  
15 The dry weight in this case is defined as the total weight of the composition when the mass of the solvent matrix is excluded from the calculation.

In a preferred embodiment, the ionomer composition according to the invention is obtained by a process, which comprises the following steps:

20 First, an alcoholic or aqueous solution of polyethyleneimine (PEI) is provided. In some embodiments, the optimal ratio (w/w) between PEI and solvent ranges from 1:0.5 to 1:5, depending on the desired amount of the ionic silver compound, which is to be fed into the solution in the next step. Also, the assessment of the optimal solvent ratio depends on the  
25 molecular weight of polyethyleneimine to be used and the viscosity of the solution. The reaction between PEI and solvent is typically exothermic. In a preferred embodiment, the mixture is cooled to standard temperature or below (i.e. the mixture is cooled to 25 °C or less, typically however to a temperature above the melting point of the liquid part of the mixture).

30 Next a solid ionic silver source is fed into the solution and mixed. Eg. silver halide reacts with PEI solution while increase of viscosity indicates ionomer formation. Depending on silver content and PEI:solvent ratio, a transparent, yellowish or almost colorless silver ionomer composition is formed.

35

The silver content of the ionomer composition may be controlled by regulating the amount of the silver source reacted with the PEI-solution, in one embodiment silver chloride.

Typically the silver compound is used at 0.1 to 10,000 parts by weight, preferably about 10 to 1,000 parts by weight for each 100 parts by weight of the ionomer prepolymer. Thus,

5 typically the weight ratio of the silver compound to the ionomer prepolymer is about 1:100 to 100:1.

Optionally thereafter a stabilizer compound, in a preferred embodiment acid form saccharin and/or sodium saccharin and/or potassium acesulfame, is fed into the

10 composition. When mixed together with the ionomer solution formed by the PEI and silver chloride, said acid form saccharin or sodium saccharin solubilizes into the ionomer solution forming a stable ionomer composition. The stabilizer compound is used in amounts of 1 to 50 parts by weight for each 100 parts by weight of a combination of silver compound with polymer compound. Typically, the weight ratio between the silver  
15 compound and the stabilizer compound is about 1:10 to 10:1.

In another preferred embodiment, a solution of PEI and alcoholic or aqueous solution is first produced and cooled down as described previously. Thereafter solid silver saccharin is delivered into the polymer solution and mixed. Silver saccharin solubilizes into the PEI  
20 solution and forms a transparent, yellowish or almost colorless solution of silver ionomer complex. The silver content of the composition may be controlled eg. through the amount of silver saccharin.

Thereafter, in a preferred embodiment, an aqueous solution of hydrochloric acid is  
25 supplied. In one preferred embodiment the molar amount of the chloride anion is equivalent to the molar amount of silver cations. When the solution of PEI and silver saccharin is chloridized, a momentary white precipitation can be observed suggesting that at least a part of the silver cation is precipitated from the soluble PEI-silver complex by the chloride anion, however, the assumed silver chloride precipitation is quickly reacted  
30 further. The latter phenomenon also suggests that silver chloride has a tendency to form unique ionic bonds with the amine functional groups of polymers. However, this is only one possible explanation for the observed phenomenon and should not be interpreted as in any way limiting on the scope of the invention.

35 The molecular structure of the silver cation source, typically a silver salt or complex, has

naturally a role in production of silver ionomer, through the introduction of the corresponding counter-ion (anion) or ligand into the system and through the specific interactions with the ionomer composition.

- 5 An interesting phenomenon observed in association with the invention at hand is, that surprisingly, the presence of halide anions, in a preferred embodiment, chloride anions, in the amine functional silver ionomer produces an enhanced antimicrobial effect when compared to ionomers comprising solely a PEI having its amine groups reacted with silver ions.

10

In a preferred embodiment, polyethyleneimines (PEIs) are applied as amine functional polymers in accordance with the invention. PEIs belong to the class of polyamines and cationic polymers having the highest cationic charges per weight. The structures of homopolymeric polyethyleneimines always follow the pattern: one amine nitrogen and two carbon groups.

15

- In general, PEIs adhere to various polar surfaces very effectively. Branched PEIs comprising cationic anchor points (amines) allow fixation of the molecules to various surfaces and substrates with exceptionally high adhesion. In some embodiments of the invention, the amine groups of the ionomer composition may be cross-linked to various surfaces. Resulting from the strong surface active character, the ionomer composition according to the invention can be applied as e.g. an additive in substrates and adhesives and as building blocks in a polymer matrix. Like amine functional polymers, the ionomer compositions according to the invention are soluble in polar solvents and miscible with e.g. water, ethyl alcohol and methyl alcohol at any concentration.

25

- In some embodiments the properties of the ionomer composition according to the invention are controlled through chemically bonding the amine groups of the amine functional polymer according to the composition with various additive compounds and compositions suitable for a specific application of the ionomer composition. In some embodiments, the additives may include anionic, non-ionic and other non-covalently bonded compounds (such as non-ionic surfactants, conjugate bases of carboxylic acids, zwitterionic compounds etc.) or organic compounds (e.g. epoxy or isocyanate functionalized organic compounds) covalently bonded with the amine groups of the composition.

35

In some embodiments, the ionomer compositions according to the invention may be cross-linked internally and/or to and/or within host surfaces, materials and compositions. In some embodiments, the applicable cross-linking agents include e.g. substances with isocyanate,  
5 epoxy, aziridine, titanate, silane and acrylate functionalities.

Through the adhesive character of the ionomer composition according to the invention at hand, the composition functions well as thin films and monomolecular layers. Retrieved from the properties of PEIs, 1 mg of the ionomer composition according to the invention,  
10 may cover an area of close to 2 m<sup>2</sup> of a nonporous surface with a monomolecular layer.

The ionomer compositions according to the invention are directly compatible with cationic or nonionic systems. The PEI-backbone with cationic amine groups may break down anionic dispersions or naturally depending on the chemical environment, produce modified  
15 dispersions or emulsions containing the composition according to the invention. Anionic surfaces adhere strongly to the composition due to ionic charges. In some embodiments, anionic or nonionic additives may be incorporated into the composition according to the invention for enhancing and improving compatibility of the ionomer composition with e.g. anionic systems.

20

In some embodiments, said antimicrobial ionomer composition according to the invention is applied as such or as including additional components, such as cross-linking agents, hydrophobic modifiers, water repellents, various stabilizers and surfactants, for coating of host surfaces such as fiber, fabric and bulk material surfaces, including various synthetic  
25 semisynthetic and natural fibers, woven fabrics, nonwoven fabrics, knitted fabrics, papers, various polymer surfaces, steel surfaces, various coating surfaces, wood surfaces and fiber, fabric and bulk material surfaces the like with the composition according to the invention.

In some embodiments, the ionomer compositions according to the invention adhere to a  
30 large variety of surfaces very effectively because of the cationic character of the PEI-backbone of the ionomer composition can be used for coating purposes of various substrates. Good adhesion is achieved to, for example, cellulosic products (e.g. cellulose, rayon and viscose), proteins, polyesters, polyamides, chlorine cont. polymers, silicates, silicium dioxide, iron, pigments, paper, wood, cotton, plants, skin, hair, films and fibers.  
35 Smooth polyolefin surfaces (PE, PP etc.) may be pretreated to bind certain substrates like

coatings, adhesives or polymer films. An effective pretreatment is an oxidative treatment, which produces an exceptionally strong adhesion.

Coating can be achieved through e.g. roll coating, spray coating or bath coating or  
5 processes the like. The ionomer composition can be diluted in e.g. alcohols or water or combinations thereof or in other suitable solvent compositions to obtain optimal solutions of the ionomer composition according to the invention in relation to the process in question and required thickness of the ionomer composition according to the invention. Substances assisting the attachment of said ionomer composition according to the invention to  
10 surfaces, e.g. cross-linking agents, primer agents or substances the like can be incorporated to the composition. Said assisting substances may be used e.g. as included in the solvent system. In some embodiment said host surfaces may be treated chemically to assist the attachment of the ionomer composition according to the invention, e.g. through oxidation, attachment of substrate/primer layers and methods the like. In some embodiments the  
15 ionomer composition of the invention may be covalently cross-linked to and on host surfaces.

Generally, after dilution, the silver concentration of the diluted composition is from 1/5 to 1/1000 parts by weight of that of the original composition.

20

In some other embodiments, the antimicrobial ionomer composition according to the invention is used as an antimicrobial additive in various liquid product matrixes (host materials) compatible with said antimicrobial ionomer composition. The antimicrobial ionomer composition according to the invention can be added into said host materials e.g.  
25 during a suitable unit process in association with their production processes, or as a finishing step, naturally depending on the material and process. According to the invention, new antimicrobial materials may be formed through the interaction of the antimicrobial ionomer composition according to the invention (when used as an antimicrobial additive) and said host material. In some embodiments said ionomer composition according to the  
30 invention is used as an additive for liquid product matrixes or intermediate product matrixes to form new antimicrobial materials and products.

The “liquid product matrixes” in this context mean any liquid product or intermediate product regardless of its use, its interaction with said antimicrobial additive composition  
35 and the final state of matter after usage. In some embodiments the ionomer composition of

the invention may be cross-linked with the components of the host matrix. Some exemplifying applications wherein said ionomer composition according to the invention can be used as an antimicrobial additive and/or component for formation of new antimicrobial materials include the following: detergents (e.g. cosmetic/hygienic  
5 detergents, shower gels, shampoos and industrial detergents), paints, varnishes, floor conditioners/polishes, adhesives, gelcoats, epoxy materials, polyurethanes, cosmetic products, disinfection substances (e.g. disinfection hand gels, hospital, public space and consumer applications, medical devices, liquids for moist wipes), seaming materials, medicinal products, toothpastes and applications the like.

10

The examples presented in the following are not meant to limit the scope of the invention.

#### **Example 1**

15

An antimicrobial composition according to the invention was produced in a solvent matrix. 2.0 grams of a branched polyethyleneimine (Lupasol WF, BASF, MW 25 000) was solubilized in 8 grams of ethyl alcohol and cooled down. The solution was reacted together with 0.295 grams of silver chloride by mixing said suspension at room temperature until a  
20 clear solution was formed. The obtained ionomer composition had a dry content (mass of the solvent excluded) of 22.3 % (w/w) and theoretical silver content of 9.7 % (w/w) of dry mass.

#### **Example 2**

25

An antimicrobial ionomer composition according to the invention was produced in a solvent matrix. Approximately 2.0 g of a branched polyethyleneimine (Lupasol G20 waterfree, BASF, molecular weight 1300) was mixed with 6 g of ethyl alcohol and cooled down. The solution was reacted with 0.724 g of silver saccharinate by mixing said  
30 suspension at room temperature until a clear solution was formed. The process was continued by adding of 2.49 ml of 1 M hydrochloric acid into said solution under continuous mixing. A clear solution of an optically clear ionomer composition was formed, having a dry content (w/w) of 25.0 % and theoretical silver content of 9.5 % (w/w) of dry mass.

35

**Example 3**

An antimicrobial ionomer composition according to the invention was produced in a solvent matrix. 1.0 grams of a branched polyethyleneimine (Lupasol G20 waterfree, BASF, molecular weight 1300) was solubilized to 3 grams of ethyl alcohol and cooled down. The solution was reacted together with 0.156 grams of silver saccharinate by mixing said suspension at room temperature until a clear solution was formed. The process was continued by diluting the intermediate composition to a total volume of 50 ml with EtOH. Finally, the product was chloridized by adding 0.570 ml of 1 M HCl under mixing conditions.

**Comparison example 4**

An antimicrobial composition was produced in a solvent matrix. 1.0 grams of a branched polyethyleneimine (Lupasol G20 waterfree, BASF, molecular weight 1300) was solubilized to 3 grams of ethyl alcohol and cooled down. The solution was reacted together with 0.156 grams of silver saccharinate by mixing said suspension at room temperature until a clear solution was formed. The product was diluted to a total volume of 50.570 ml with EtOH.

**Example 5**

An antimicrobial ionomer composition according to the invention was produced in a solvent matrix. 3.0 grams of a branched polyethyleneimine (Lupasol PS, BASF, molecular weight 750,000, concentration in water 33%) was mixed with 1 grams of ethyl alcohol and cooled down. The solution was reacted together with 0.156 grams of silver saccharinate by mixing said suspension at room temperature until a clear solution was formed. The intermediate composition was diluted to a total volume of 50 ml with EtOH. Finally, the composition was chloridized by adding 0.570 ml of 1 M HCl under mixing conditions.

**Comparison example 6**

An antimicrobial composition was produced in a solvent matrix. 3.0 grams of a branched polyethyleneimine (Lupasol PS, BASF, molecular weight 750,000, concentration in water 33%) was mixed with 1 grams of ethyl alcohol and cooled down. The solution was reacted

together with 0.156 grams of silver saccharinate by mixing said suspension at room temperature until a clear solution was formed. The product was diluted to a total volume of 50.570 ml with ethyl alcohol.

## 5    **Application Example 7**

The antimicrobial ionomer composition according to the invention produced as described in Example 2 was applied as an antimicrobial additive for an acrylic interior paint (Tikkurila Harmony, white, determined dry mass 88 % w/w). Two test batches were  
10    prepared by mixing the composition according to Example 2 and the paint in mixing ratios of 1:10 and 1:20, respectively. The resulting theoretical silver contents (% of dry weight) were correspondingly about 0.3 % and 0.14 %.

For both samples, test surfaces were prepared by painting two surfaces of a PVC film with  
15    the sample compositions and the allowed to dry at standard temperature for 48 hours. The antimicrobial efficacy of the paint surfaces against Methicillin Resistant *Staphylococcus Aureus* (MRSA) were determined following standard ISO 22196. As a result for the two paint surfaces, a reduction of >4log for MRSA was achieved.

## 20    **Application Example 8**

The antimicrobial ionomer composition according to the invention produced as described in Example 2 was applied as an antimicrobial additive for a waxed floor conditioning and polishing agent (Johnson Diversey, Jontec, determined dry mass 28.6 % w/w). A test batch  
25    was prepared by mixing the ionomer composition according to Example 2 and the paint in a mixing ratio of 1:10 resulting in theoretical silver content (% of dry weight) of 0.84 %. A test surface was prepared. A working solution was prepared by further diluting the test batch with tap water in a ratio of 1:20 (composition according to example 2: Jontec). The dilution was spread on a PVC film and let dry for 48 hours leaving a faint colorless dry  
30    material film on the surface. The antimicrobial efficacy of the conditioned surface against Methicillin Resistant *Staphylococcus aureus* (MRSA) was determined following standard ISO 22196. As a result for the surface treated with the diluted floor conditioner doped with the antimicrobial composition according to the invention, a reduction of >4log for MRSA was achieved.



### Application Example 9

The antimicrobial ionomer composition according to the invention produced in examples 3 and 5 and the compositions produced in comparative examples 4 and 6 were applied as an antimicrobial coating/ antimicrobial finish for knitted fabric. Four sample pieces (2,5x15 cm<sup>2</sup>) of a polyester-cotton blend (65%-35%) medical scrub fabrics were treated with the compositions obtained in examples 3 (AE91, 4 (AE92), 5 (AE93) and 6 (AE94). The sample fabrics were immersed into the diluted solutions for 30 seconds. The immersed samples were let dry overnight at room temperature on paper tissues. The antimicrobial efficacy against *Staphylococcus aureus* (ATCC 6538) was tested following ISO 20743 – standard. The results are presented in Table 1.

**Table 1**

Sample	Vinson's rating	Antimicrobial efficacy
AE91	4+(2mm)	Excellent
AE92	2	Fair
AE93	4+(2mm)	Excellent
AE94	2	Fair

According to the results presented in Table 1, the antimicrobial efficacies of chloridized ionomer compositions, turned out to be higher compared to the compositions obtained through reacting solely PEI and silver saccharinate.

### Application Example 10

A series of antimicrobial treatments was carried out for nonwoven polypropylene (19.9 g/m<sup>2</sup>) fabric (4 samples, CE101-CE104) and polyester-cotton (65%-35%) blend (212.5 g/m<sup>2</sup>) medical scrub fabric (4 samples, CE105-CE108). An antimicrobial ionomer composition according to the invention was produced in a solvent matrix. 2.0 grams of a branched polyethyleneimine (Lupasol G20 waterfree, BASF, molecular weight 1300) was solubilized to 6.0 grams of ethyl alcohol and cooled down. The solution was reacted together with 0.3 grams of silver saccharinate by mixing said suspension at room temperature until a clear solution was formed. The process was continued by adding 1.140 ml of 1 M hydrochloric acid into said solution. A clear solution of an optically clear ionomer composition was formed, having a dry content (w/w) of 24.8 % and theoretical

silver content of 4.7 % (w/w) of dry mass. A series of baths containing antimicrobial ionomer composition of the invention obtained previously were prepared. The bath compositions are presented in Table 2.

5 **Table 2**

Bath	Dilution (AM-comp.:EtOH)	AM-Comp. (g/l)	Ag (mg/l)
1	1:20	11.50	541
2	1:50	4.60	216
3	1:100	2.30	108
4	1:200	1.15	54

The fabric samples were treated with the antimicrobial ionomer composition by immersing the sample fabrics into the diluted solutions. Immersed samples were let dry on paper tissues absorbing part of the excess liquid. Resulted mass percentages of antimicrobial coatings and theoretical silver contents of the treated fabrics are listed in Table 3.

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**Table 3**

Sample/ Bath	Material	AM-Comp (%w/w)	Ag (mg/m <sup>2</sup> )
CE101/1	nonwoven PP	6.20	54
CE102/2	nonwoven PP	3.26	26
CE103/3	nonwoven PP	0.83	8
CE104/4	nonwoven PP	0.40	4
CE105/1	cotton-PE blend	1.55	155
CE106/2	cotton-PE blend	0.84	84
CE107/3	cotton-PE blend	0.39	39
CE108/4	cotton-PE blend	0.33	33

The antimicrobial efficacies of treated sample fabrics coated with the antimicrobial composition of the invention were tested against *Staphylococcus aureus* (ATCC 6538) following ISO 20743 –standard. The results are presented in Table 4.

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**Table 4**

Sample	Vinson's rating	Antimicrobial efficacy
CE101	4	Excellent
CE102	2	Fair
CE103	2	Fair
CE104	2	Fair
CE105	4 (+2)	Excellent
CE106	4 (+1)	Excellent
CE107	4	Excellent
CE108	4	Excellent

It must be noted, that the applied microbiological test has limitations when tested with a very lightweight fabrics, such as CE 101-104. By taking into account the limitations, very successful antimicrobial performances were achieved for all samples.

**Example 11**

An antimicrobial ionomer composition according to the invention was produced in a solvent matrix. 2.0 grams of a branched polyethyleneimine (Lupasol WF, BASF, MW 25,000) was solubilized in 8 grams of ethyl alcohol and cooled down. The solution was reacted together with 0.295 grams of silver chloride by mixing said suspension at room temperature until a clear solution was formed. The process was continued by adding 0.378 grams of saccharin and mixing until a clear solution was formed.

**Example 12**

An antimicrobial ionomer composition according to the invention was produced in a solvent matrix. 2.0 grams of a branched polyethyleneimine (Lupasol P, BASF, MW 750,000, concentration in water 50 %) was mixed with 5.460 grams of ethyl alcohol and cooled down. The solution was reacted together with 0.345 grams of silver chloride by mixing said suspension at room temperature until a clear solution was formed. The process was continued by adding 0.5 grams of saccharin. An ionomer composition with 14.1% w/w theoretical silver content (of dry weight) was produced.

**Example 13**

An antimicrobial ionomer composition according to the invention was produced in a solvent matrix. 160 grams of a branched polyethyleneimine (Lupasol WF, BASF, MW  
5 25,000) was solubilized to 640 grams of ethyl alcohol and cooled down. The solution was reacted together with 23.64 grams of silver chloride by initially homogenizing said product with a high shear homogenizer for one minute and further mixing said suspension at room temperature under agitation by a magnetic stirrer until a clear solution was formed. The process was continued by adding 35.21 grams of saccharin followed by mixing until a  
10 clear transparent composition was formed.

**Claims**

1. An antimicrobial ionomer composition which comprises an amine functional cationic polymer compound and silver halide.
2. The antimicrobial ionomer composition according to claim 1, further comprising a stabilizing component.
3. The antimicrobial ionomer composition according to claim 1, wherein silver halide is in molecular form.
4. The antimicrobial ionomer composition according to claim 1, wherein silver halide is silver chloride.
5. The antimicrobial ionomer composition according to any of claims claim 1 to 4, comprising at least one stabilizer substance selected from the group of organic substances carrying sulfonamide functional group(s), in particular the at least one stabilizer substance is selected from the group comprising saccharin, cyclamic acid, sulfadiazine, acesulfame and their alkali metal or ammonium salt or complex derivatives.
6. The antimicrobial ionomer composition according to any of claims 1 to 5, comprising a solvent matrix, preferably formed by alcohols, such as methyl, ethyl, propyl or butyl alcohol or water and combinations thereof.
7. The antimicrobial ionomer composition according to any of the preceding claims, wherein said amine functional polymer is selected from the group comprising; polyethyleneimine, polyvinylamine, polyacrylamine, polyhexamethylenebiguanidine, polyvinylpyridine and polyarylamine.
8. The antimicrobial ionomer composition according to any of the preceding claims, wherein said amine functional polymer comprises poly(ethyleneimine) having a molecular weight (Mw) between 200 and 3,000,000, in particular about 750 to 2,000,000.
9. The antimicrobial ionomer composition according to any of claims 1 to 8, obtainable by reacting together

- (i) at least one amine functional polymer and silver halide or;
- (ii) at least one amine functional polymer, at least one non-halide silver salt or complex compound, and hydrogen halide, or an alkaline metal or ammonium halide salt.

5 10. The antimicrobial ionomer composition according to claim 9, wherein

- (i) said at least one amine functional polymer and silver halide or;
  - (ii) said at least one amine functional polymer and at least one silver salt or complex compound and hydrogen halide, or alkaline metal or ammonium halide salt,
- are further reacted together with at least one stabilizer substance.

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11. The antimicrobial ionomer composition according to claim 9, wherein the counter anion or ligand of said at least one silver salt or complex compound comprises an organic stabilizer substance.

15 12. The antimicrobial ionomer composition according to any of the preceding claims, wherein said silver halide comprises silver chloride, said hydrogen halide comprises hydrogen chloride and said alkaline metal halide salt comprises sodium chloride or potassium chloride.

20 13. The antimicrobial ionomer composition according to any of the preceding claims, wherein said reacting is carried out in a solvent matrix.

14. The antimicrobial ionomer composition according to any of claims 2 to 13, wherein said solvent matrix comprises alcohols, such as methyl, ethyl, propyl, butyl alcohol or  
25 water and combinations thereof.

15. The antimicrobial ionomer composition according to any of the preceding claims, wherein the amine functional groups of said amine functional polymer have a function as further attaching said composition to a molecular structure of a second material through  
30 non-covalent bonding or covalent bonding or coordinate bonding or combinations thereof.

16. The antimicrobial ionomer composition according to any of the preceding claims, wherein said amine functional polymer is polyvinylamine or copolymer having 30–100 mol-% of vinylamine.

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17. The antimicrobial ionomer composition according to any of the preceding claims, wherein said amine functional polymer is graft polymer of polyvinylamine with ethyleneimine.

5 18. The antimicrobial ionomer composition according to any of the preceding claims, wherein said amine functional polymer is graft polymer of polyamidoamine with ethyleneimine

19. The antimicrobial ionomer composition according to any of the preceding claims,  
10 wherein said amine functional polymer is polyarylamine copolymer

20. The antimicrobial ionomer composition according to any of the preceding claims, wherein said amine functional polymer is polyacrylamine

15 21. The antimicrobial ionomer composition according to any of the preceding claims, wherein said composition is internally cross-linked through at least one cross-linking agent.

22. The antimicrobial ionomer composition according to any of the preceding claims,  
20 wherein said composition is attached to a second material through at least one cross-linking agent.

23. The antimicrobial ionomer composition according to any of the preceding claims, wherein the silver content of the composition is about 0.01 to 50 %, in particular about 1 to  
25 30 %, preferably about 1.5 to 25 % by weight of the total weight of the composition.

24. The antimicrobial composition according to any of the preceding claims, wherein the weight ratio of the silver compound to the amine compound is about 1:100 to 100:1.

30 25. A method of producing a polymeric antimicrobial composition, comprising reacting together

- (i) at least one amine functional polymer and silver halide or;
- (ii) at least one amine functional polymer and at least one non-halide silver salt or complex compound and hydrogen halide and/or alkaline metal halide salt and;
- 35 (iii) optionally, at least one stabilizer substance.

26. The method according to claim 25, comprising reacting together in a solvent matrix
- (i) at least one amine functional polymer;
  - (ii) a silver halide and;
  - 5 (iii) optionally at least one stabilizer substance.
27. The method according to claim 25, comprising reacting together in a solvent matrix
- (i) a non-halide silver salt or silver complex
  - (ii) hydrogen halide or an alkaline metal halide salt or a combination thereof, and;
  - 10 (iii) optionally at least one stabilizer substance.
28. The method according to any of claims 25 to 27 carried out in a solvent matrix preferably comprising alcohols, such as methyl alcohol, ethyl alcohol or water and combinations thereof.
- 15 29. The method according to any of claims 25 to 28, wherein additive compounds are incorporated into said composition providing means for modifying the physical-chemical properties of said composition.
- 20 30. The use of an ionomer composition according to any of claims 1 to 24 for coating of host surfaces.
31. The use according to claim 30, comprising coating substrates selected from the group of fiber, fabric and bulk material surfaces, including various synthetic semisynthetic and
- 25 natural fibers, woven fabrics, nonwoven fabrics, knitted fabrics, papers, various polymer surfaces, steel surfaces, various coating surfaces, wood surfaces and fiber, fabric and bulk material surfaces.
32. The use according to claim 30 or 31, comprising coating a material selected from
- 30 cellulosic products (e.g. cellulose and viscose), proteins, polyesters, polyamides, chlorine cont. polymers, silicates, silicium dioxide, iron, pigments, paper, wood, cotton, plants, skin and hair.



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VIITEJULKAISUT		
Kategoria*)	Julkaisun tunnistetiedot ja tiedot sen olennaisista kohdista	Koskee vaatimuksia
X Y	WO 0015036 A1 (SURFACINE DEV COMPANY LLC) 23. maaliskuuta 2000 (23.03.2000) sivu 18, rivit 4-31; esimerkit 1, 2, 12-14; vaatimukset 1-79	1-4, 6-32 5
X Y	US 2009149583 A1 (LIN JIANG-JEN et al.) 11. kesäkuuta 2009 (11.06.2009) esimerkki 1; vaatimukset 1-26	1-4, 6-29 5
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Y	WO 2010083589 A1 (KANE BIOTECH INC et al.) 29. heinäkuuta 2010 (29.07.2010) sivu 8, rivit 18-27; vaatimukset 1 ja 5	5
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X	WO 2010108837 A1 (BASF SE et al.) 30. syyskuuta 2010 (30.09.2010) vaatimukset 1-16	1-4, 6-32
A	US 2005112151 A1 (HORNG LIOU L) 26. toukokuuta 2005 (26.05.2005)	