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(54) **Title:** METHOD OF PREPARATION OF BIOACTIVE PACKAGING MATERIALS

(57) **Abstract:** The method of preparation of bioactive packaging materials consists in surface activation of packaging materials based on synthetic polymers or polymeric materials of natural sources by thin-layer polymer coating containing an immobilized conservation substance.

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Method of preparation of bioactive packaging materials

Field of technology

The expanding centralization of activities and internationalization of large markets resulting in increasing distribution distances increases the demand for products with a longer shelf life. The production technology itself, such as thermal processing, does not know how to reliably resolve this request without adverse effects on organoleptic properties. Hence, producers are required to use preservatives allowing the required shelf life to be attained in combination with technological processing. This contradicts the increasing requirements for healthy nourishment promoting natural foods where preservatives are eliminated. In addition, there is an appreciable percentage of our population suffering from excessive sensitivity to these substances. In relation with this issue, attention has been paid to minimum application of preservatives and using other methods than to the overall volume of foods during their production, however with the present efficiency being retained.

Current status of technology

At present, preservatives are usually added directly to the whole volume of foods during their production. An integral part of most foods is their packaging. Its prime functions include allowing the batching of products in rational quantities, allowing distribution or informing the customer on the composition of products, but also protection of these products against adverse effects of the surrounding environment as they most cause damage. Thanks to these properties, packaging represents a suitable carrier for the fixation of preservatives, which particularly in the area of touching packaging of packed goods may significantly contribute to its protection without their application to the whole volume of the packed products.

To prepare bioactive coating materials, a method of built-in antimicrobial agents in the internal structure of the packaging was described; in most cases, the agent was an additive to polymeric melt or the method consisted in

dissolution followed by integration. Thermal methods are used in adding thermally stable antimicrobial agents, e.g. zeolites substituted by silver. The antimicrobial agents not resistant to high temperatures used in the production of polymers may be fixed on the packaging surface, whereas their adsorption may be improved by the addition of certain dissolvents or by modification of the polymer structure. In addition to pure adsorption, antimicrobial agents immobilise on the packaging surface through a covalent link as well. This type of preparation of bioactive packaging requires the availability of functional groups on the packaging surface and also in the structure of the immobilized antimicrobial agents, which participate in the production of the relevant covalent link. In addition to the requirement specified above, additives that participate in joining the packaging surface with antimicrobial agent should be used in some cases when immobilizing. These spacers allow adequate movement flexibility of the linked agent, allowing direct contact with the microorganisms on the surface of the packaged food. The immobilization of the antimicrobial agents on the internal surface of the packaging using the covalent link is technically somewhat complex, however the only sorption is not sufficiently strong for most of the preservatives and building in these agents to the internal structure of the packaging in its full volume represents needlessly high consumption of preservatives, which is reflected in higher expenses.

Summary of the invention

The above-mentioned drawbacks are resolved by the method of preparing the bioactive preservatives depending on the invention consisting in the fact that the packaging material – based on synthetic polymers (polyethylene and its co-polymers, e.g. ionomers, polypropylene and its co-polymers, polyamide and its co-polymers, polyethyleneterephthalate etc.) as well as polymeric natural-resource materials (particularly polysaccharides – starch or cellulose, proteins – collagen and homo- or heteropolymeric amino acids, glycoproteins, waxes etc.) – is coated with the polymer layer containing the immobilized preservative. To coat the substances, a polymer is used based on

polyethylene and its copolymers and/or polypropylene and its copolymers and/or polybutadiene and its copolymers and/or copolyamide and its copolymers and/or polyacrylate and its copolymers and/or polyvinylchloride and/or polyvinylacetate and/or polyesters and/or polymeric resins in the form of solutions or dispersions in water or organic solvent and mixtures thereof or in the form of disperse varnishes and dissolvent varnishes.

It is advantageous to use biologically degradable polymers such as copolyamide of amides of caproic and lauric acids.

The polymers and preservatives are applied on the surface of the packaging materials in the form of a solution in organic dissolvent by coating or spraying or submersing the whole packaging materials in the solution prepared in this way followed by evaporation of the organic solvent (e.g. ethanol) at temperatures from 10 to 120 °C.

In case of application of preservatives built-in to the applied varnish, it is advantageous to use aqueous emulsions based on vinylacetates, polyesters, acrylates, ethylene copolymers and polymeric resins for the applied varnish and the dissolution print varnishes depending on the type of preservative agent. The application of these varnishes containing preservatives is carried out using flex or intaglio printing.

The preservative is selected from the group of microbicide and bacteriostatic preservatives and/or fungicides. The preservatives may be based on antibiotics and/or compounds of silver and/or phenol derivatives and/or bacteriocins and/or esters of p-hydroxybenzoic acid and/or monoglycerides of fat acids and/or benzoic acid and/or sorbic acids and/or chitosane and/or (2,4,4-trichloro-2-hydroxydiphenylether) and/or lysozyme and/or nisine and/or hexamethylenetetramine. For food purposes, preservatives legislatively approved for the preservation of foods should be used.

An advantage of the preparation of bioactive packaging materials as specified above, in addition to easy application and preparation of the polymers or varnishes coated containing the preserving agents, is the increased resistance level of the packaging against water, air humidity and mechanical stress,

which is particularly important for packaging based on biodegradable polymers as their use is limited by high hydrophilic nature and low level of mechanical resistance. Their biological degradability remains unchanged. The antimicrobial effect caused by the preservatives applied is determined by their concentration in the applied solution or dispersion, the quantity of the polymer or varnish coated, the temperature of evaporation of the organic dissolvent and the temperature of external environment.

Examples of the invention design

The invention is documented by examples of its use without limiting thereof.

Example 1

Solution of nisine or esters of hydroxybenzoic acid or of anhydride of benzoic acid or Triclosan (2,4,4- trichloro-2-hydroxydiphenylether) in ethanol is brought almost to the boil, adding copolyamide 6/12 formed by polymerization of a starter consisting of 59 mol. % hexane-6-lactam, 40 mol. % dodecane-12-lactam and 1 mol. % of the initiation mixture (1 mol. % of non-aqueous hexane-6-lactam and phosphoric acid in proportion 1:1) in such a quantity to create 3 – 9% solution. Packaging material based on starch prepared by thermal expansion or based on polymeric films or layered packaging material is surface coated by dipping it in a prepared hot ethanol solution of copolyamide followed by evaporation of the solvent in a flow of hot air.

Example 2

To a solution of monolaurine (monoglyceride of lauric acid) or of fungicides such as Benomyl (methyl(1-(butylcarbamoyl)-2-benzimidazole carbamate) or Imazalil (1-[2(2,4-dichlorophenyl)-2-(2-propenyloxy)ethyl]-1H-imidazole) or permethrine (3-phenoxybenzyl(1RS)-cis,trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate) in organic solvent, flex or intaglio printing, dissolvent varnish is added and the solution is applied to the packaging based on polymeric films or layered packaging material in the form of flex or intaglio printing.

Example 3

The dispersion of Ag-zeolites or of chitosan or of fungicides such as Benomyl or Imazalil or of hexamethylenetetramine in polyvinylacetate and/or polyethylene or polybutadiene and its copolymers or in polymeric resins is hot-coated onto the layered packaging material based on treated paper or layered packaging material followed by evaporation of the aqueous part in a flow of hot air.

Example 4

A solution of esters of hydroxybenzoic acid or of anhydride of benzoic acid or of Triclosan (2,4,4-trichloro-2-hydroxydiphenylether) in organic solvent is added to the dispersive varnish and the disperse is applied on the packaging material based on polymeric films or of packaging materials of natural sources (e.g. expansion-modified starch or starch with cellulose or collagen or homo- or heteropolymeric amino acids or glycoproteins or waxes etc.) by spraying following evaporation of the solvent.

Example 5

An aqueous solution of lysozyme or of nisine or of potassium sorbate and/or sodium benzoate or water-soluble fungicides or hexamethylenetetramine is added to an aqueous dispersion of polyethylene or polypropylene or polyvinylchloride or polyvinylacetate and this dispersion is used for dipping packaging materials based on paper or modified cellulose or synthetic polymers or layered packaging materials. Upon withdrawal, the dispersion applied on the packaging material is left to dry freely or in a flow of hot air.

Industrial application

The method of preparation of bioactive packaging materials based on synthetic plastic materials or polymeric materials from natural sources is applicable particularly for packaging foods and everywhere where there is a danger of microbial contamination or spoilage of packed substances through the activity of microorganisms. An important advantage of the preparation of

bioactive packaging materials is the fact that the activation of the packaging material does not limit the existing technology of the packaging material production as the polymer or varnish layer with the preservative is applied onto the finished packaging material.

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PATENT CLAIMS

1. The preparation of bioactive packaging materials based on synthetic polymers or polymeric materials of natural sources is **characterised** by coating of packaging material with a thin layer of polymer containing immobilized preservatives.

2. The method of preparation of bioactive packaging materials according to claim 1 is **characterised** by using a polymer based on polyethylene and its copolymers and/or polypropylene and its copolymers and/or polybutadiene and its copolymers and/or copolyamide and its copolymers and/or polyacrylate and its copolymers and/or polyvinylchloride and/or polyvinylacetate and/or polyesters and/or polymeric resins in the form of solutions or dispersions in water or organic solvents and mixtures thereof or in the form of disperse varnishes and dissolvent varnishes.

3. The method of preparation of bioactive packaging materials according to claims 1 and 2 **characterised** by an application of a solution or dispersion of a polymer with preservatives on packaging material by spraying and/or coating and/or submersing the packaging material in such solution or dispersion and/or flex or intaglio printing followed by evaporation of the solvent under room or increased temperature.

4. The method of preparation of bioactive packaging materials according to claim 1 is **characterised** by the preservative selected from the group of microbicide and/or bacteriostatic preservatives and/or fungicides; the preservatives are antibiotics based and/or silver compounds and/or phenol derivatives and/or bacteriocins and/or esters of p-hydroxybenzoic acid and/or monoglycerides of fat acids and/or benzoic acid and/or sorbic acid and/or chitosan and/or (2,4,4-trichloro-2-hydroxydiphenylether and/or lysozyme and/or nisine and/or hexamethylenetetramine.