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(54) **METHOD FOR COATING CELLULOSIC MATERIAL**

(57) The present invention relates to a method for coating cellulose material with essential oils that allows retarding the evaporation of these essential oils from the surface of the cellulose material. These oils are added to the cellulose material to provide it with antimicrobial and antioxidant properties. The method described in this invention delays the release of the active compounds during drying and during exposure of the cellulosic material to air.

The method disclosed herein comprises a chemical modification of a starch with a cyclodextrin, followed by dispersion of this modified starch at high temperatures, for finally being used in a coating step, together with the essential oil of interest. The method described herein does not require the use of surfactants or organic cosolvents to retard the evaporation of the essential oils added to the cellulosic material and according to its application.

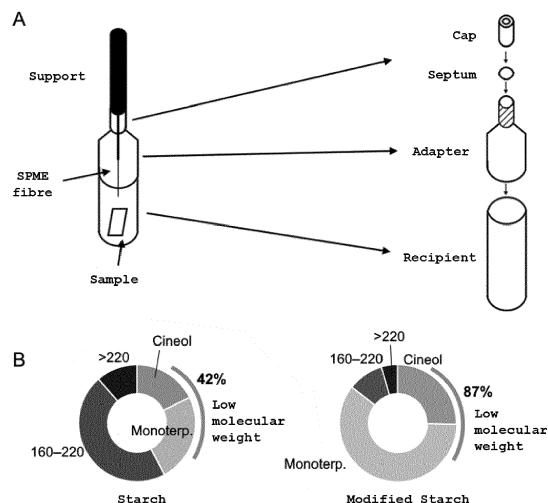


Fig. 4

Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to the area of consumer goods industries and specifically refers to a method for coating cellulosic material with essential oils for their application as antimicrobial and antioxidant materials.

BACKGROUND OF THE INVENTION

10 **[0002]** The usefulness of drug delivery systems and the distribution and emission of essential oils through cellulosic substrates, in the most diverse applications of, for example, antimicrobial and antioxidant action, should not be neglected [1], as evidenced by some previous studies. Among these systems, we have protective food packaging produced by coating paper with paraffin and cinnamon essential oil [2], a sheet of paper coated with a grapefruit seed extract rich in polyphenols [3] and the grafting of eugenol onto paper, while a polycarboxylic acid promotes crosslinking between cellulose chains [4], to name a few examples. A more recent work proposes antimicrobial wrapping paper with an essential oil of dill [6].

15 **[0003]** Active compounds in essential oils range from small molecules, such as monoterpenes and low molecular weight (MW) aldehydes [7], to non-volatile entities, including triterpenes, sterols, and polyphenols [8]. For example, eucalyptus essential oils are characterized by having terpenes and terpenoids in abundance. Of these, high MW compounds prevail in wood [9], while leaves mainly host low MW (<180 g/mol) compounds [7]. A major disadvantage of adding monoterpene compounds to paper by simple addition, either during sheet formation or as a coating component, is their tendency to evaporate along with water.

20 **[0004]** There is, for example, in the context of incorporating essential oils into cellulose and into water itself, as in CN102644217B [11], the solution of adding the essential oil or bacterial agent directly to the pulp mixture; and the immersion of the paper in the essential oil itself, as in CN109403142A [12]. However, the stability of papers with extracts and essential oils over time is, generally, not indicated.

25 **[0005]** The patent application EP0690170A1 [13] describes a process for coating paper, in which the aqueous coating consists of a starch modified through its reaction with an enzyme from the group of cyclodextrin glycosyl transferases, and which aims to make the surface of a paper sufficiently smooth and resistant.

30 **[0006]** Patent application CN111691224A [14] also describes this type of enzymes for the modification of starch and their application in paper production to increase the retention of starch and thus, consequently, the strength of the paper incorporating it.

35 **[0007]** There is thus a need for a method for coating cellulosic materials with essential oils to ensure the retardation of evaporation of these essential oils and other components of interest depending on their application, thereby ensuring their use for a longer time during the distribution and emission of essential oils in the most diverse applications such as, for example, antimicrobial and antioxidant action.

40 **[0008]** These applications find value at least in the following fields: public or private healthcare systems, including antiseptic printing papers, antiseptic posters for hospitals and antiseptic fibres for gowns; the food industry, in the context of containers with prolonged emission of natural active compounds; the pharmaceutical industry, e.g. to provide additional protection for pill boxes; and the paper and textile industries, to produce and supply the materials required in the mentioned applications.

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SUMMARY OF THE INVENTION

[0010] The present invention relates to a method for coating cellulosic material comprising the following steps:

a) obtaining a solid modified starch by means of a covalent bond of a starch with a cyclodextrin and a polycarboxylic acid;

b) redispersing the solid modified starch obtained in step a) in water, under agitation and heating at temperatures from 65 °C to 110 °C until the observation of a macroscopic homogeneity of the resulting mixture;

c) cooling the mixture resulting from step b) up to temperatures from 25°C to 60°C under continuous agitation;

d) adding 0,01-2,00 g of an essential oil to the resulting mixture of step c), under agitation until macroscopic homogeneity is observed in the resulting coating formulation;

e) coating with the coating formulation resulting from step d) through means for coating a surface of a cellulosic material.

[0011] According to a preferred embodiment, step a) comprises the following steps:

f) mixing a starch with a cyclodextrin and a polycarboxylic acid and in contact with a sodium hyposulfite catalyst, in aqueous medium and at a temperature of 25 °C to 70 °C until macroscopic homogeneity is observed for the resulting mixture;

g) evaporating water until the mixture resulting from step

f) has a moisture content of less than 10% and a solid modified starch is formed;

h) drying and heating, up to a temperature of 100 °C to 180 °C, of the solid resulting from step g);

i) washing the solid resulting from step h) with a mixture of water and ethyl alcohol until the resulting solid modified starch is isolated.

[0012] According to a preferred embodiment, step a) comprises the following steps:

j) mixing a starch with a cyclodextrin and a polycarboxylic acid and in contact with a sodium hyposulfite catalyst, in aqueous medium;

k) evaporating water until the mixture resulting from step j) has a moisture content of less than 10%;

l) drying and heating, up to a temperature of 80 °C to 180 °C, of the solid resulting from step k);

m) dissolving the cyclodextrin ester resulting from steps j), k) and l) in water, discarding its insoluble part, and later precipitation with an alcohol;

n) dissolution, in aqueous medium, of the cyclodextrin ester resulting from step m) by adding a starch and a sodium hypophosphite catalyst;

o) evaporating water until a solid is formed;

p) drying and heating, up to a temperature of 100 °C to 180 °C, of the solid resulting from step o);

q) washing the solid resulting from step p) with a mixture of water and alcohol until the resulting solid modified starch

is isolated.

[0013] According to a preferred embodiment, the polycarboxylic acid is a 1,2,3,4-Butanetetracarboxylic acid.

[0014] According to a preferred embodiment, the cyclodextrin is selected from the group consisting of alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin, hydroxypropyl-alpha-cyclodextrin, hydroxypropyl-beta-cyclodextrin, hydroxypropyl-gamma-cyclodextrin, methyl-alpha-cyclodextrin, methyl-beta-cyclodextrin, methyl-gamma-cyclodextrin, acetyl-alpha-cyclodextrin, acetyl-beta-cyclodextrin, acetyl-gamma-cyclodextrin, succinyl-alpha-cyclodextrin, succinyl-beta-cyclodextrin, succinyl-gamma-cyclodextrin and 7-beta-cyclodextrin sulfobutyl ether.

[0015] According to a preferred embodiment, step a) comprises the following steps:

r) mixing a starch with a beta-cyclodextrin and a polycarboxylic acid in aqueous medium;

s) heating to a temperature of 65 to 110 °C, under stirring for a time of 1 to 48 h;

t) precipitating the modified starch obtained in step s) by adding ethanol at a maximum temperature of 25 °C, and then drying to obtain a solid modified starch.

[0016] According to a preferred embodiment, the polycarboxylic acid is 1,2,3,4- acid tetracarboxylic butane.

[0017] According to a preferred embodiment, the coating formulation of step d) has 0,01 to 0,50 mmol of a cyclodextrin per gram of starch.

[0018] According to a preferred embodiment, the cellulosic material is a paper product.

[0019] According to a preferred embodiment, the cellulosic material is a textile material.

[0020] According to a preferred embodiment, the essential oil is selected from the group consisting of essential oils of wood, leaves, and fruits of plants.

[0021] According to a preferred embodiment, the coating medium consists of a roller coating.

[0022] According to a preferred embodiment, the mean for coating a surface of a cellulosic material consists of dipping the cellulosic material in an aqueous dispersion of the coating formulation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023]

Figure 1. Proton magnetic resonance spectra of the two-step cross-linking intermediate product compared with native cyclodextrin and 1,2,3,4-butanetetracarboxylic acid (BTCA) .

Figure 2. A) ATR-FTIR spectra of native starch (infra) and modified starch (supra). B) Condensed structural formulas of a substituted and unsubstituted monomer, highlighting an ester bond (star) and a free carboxyl group (ring). C) Schematic of the coating layer. As an example, a 1,8-cineole molecule (bottom right) tends to form an inclusion complex with cyclodextrins.

Figure 3. Color diagrams (gamut) of papers with eucalyptus essential oil, containing, besides the oil itself, native starch (A) or modified starch (B). The number in the center of each graph means the gamut area.

Figure 4. Evaluation of the ability of papers coated with essential oils to emit volatile active compounds. A) Experimental setup for solid phase microextraction. B) Proportion of 1,8-cineole and of different groups of volatile compounds. The numbers express molecular weight (g/mol). The "low molecular weight" compounds are 1,8-cineole itself and all those with a molecular weight below 160 g/mol.

Figure 5. Evaluation of the antioxidant power of hydroxytyrosol in comparison with the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH) (A) and of papers containing hydroxytyrosol in addition to modified starch or modified starch (B). The concentration in mg/mL refers to the paper in the MeOH/DCM extraction phase.

DETAILED DESCRIPTION OF THE INVENTION

[0024] The approach of the present invention involves the use of cyclodextrins to prolong the ability of cellulosic material to emit volatile active compounds in time.

[0025] A cyclodextrin is any cyclic oligosaccharide, composed of anhydroglucose units joined by α -1,4-type bonds, and with their functional groups oriented such that it has a hydrophobic cavity and a hydrophilic exterior. The most common compounds in this family are, but not limited to, alpha-cyclodextrin, with 6 anhydroglucose units; beta-cyclodextrin, with 7 units; the gamma-cyclodextrin, with 8 units, and the respective cyclodextrins functionalized with the

hydroxypropyl group, that is, hydroxypropyl-alpha-cyclodextrin, hydroxypropyl-beta-cyclodextrin, hydroxypropyl-gamma-cyclodextrin, functionalized with the methyl group, that is, methyl-beta-cyclodextrin, methyl-gamma-cyclodextrin, functionalized with the acetyl group, i.e. acetyl-alpha-cyclodextrin, acetyl-beta-cyclodextrin, acetyl-gamma-cyclodextrin, and functionalized with the succinyl group, i.e. succinyl-alpha-cyclodextrin, succinyl-beta-cyclodextrin, succinyl-gamma-cyclodextrin.

[0026] In the context of the present invention, native cyclodextrin refers to a cyclodextrin that has not been subjected to chemical modification.

[0027] In the context of the present invention, chemical modification refers to the process by which the molecular structure of a starch is modified through a reaction, incorporating cyclodextrins by covalent bonds.

[0028] Covalent bond is a region of high electron density between two atomic nuclei, wherein the electron clouds of the interacting atoms overlap. In the context of the present invention, the covalent bonds generated involve, at least, one oxygen atom of a polycarboxylic acid and one carbon atom of a carbohydrate, namely cyclodextrin and/or starch. In the context of the present invention, polycarboxylic acid is an organic compound with more than one carboxyl group, -COOH, such as citric acid, 1,2,3,4-butanetetracarboxylic acid, maleic acid or fumaric acid.

[0029] In the context of the present invention, starch consists of a polysaccharide of glucose units having alpha-1,4 and alpha-1,6 linkages. Modified starch in this invention refers to any starch derivative which contains, by means of covalent linkages, alpha-, beta- or gamma-cyclodextrin structures, such that at least one anhydroglucose unit of the starch is linked to a cross-linking agent which, in turn, is linked to an anhydroglucose unit of the cyclodextrin. Native starch, in turn, refers to starch that has not undergone any chemical modification.

[0030] In the context of the present invention, volatile active compound means any organic compound having, at 25 °C, a vapor pressure equal to or greater than 0.01 kPa, and which is commercially appreciated for having antioxidant, antimicrobial, anti-inflammatory, cytotoxic, or other types of activity of health interest, for the preservation of food, or for the preservation of the material itself. In the context of the present invention, macroscopic homogeneity refers to the observation of a single phase with the naked eye, without using any diffractometers, microscopes, spectrophotometers, or other instruments to differentiate between a continuous phase and a dispersed phase, either because dissolution is complete or because the dispersed particles are not appreciable to the naked eye.

[0031] In the context of the present invention, cellulosic material includes paper material and textile material.

[0032] In the context of the present invention, paper material relates to, for example and not limited to, tissue paper, packaging paper, printing and writing paper or any paper that may have a starch coating.

[0033] In the context of the present invention, textile material includes textile-based materials that may include a starch treatment, such as, for example and not limited to, cotton or rayon.

[0034] In the context of the present invention, essential oils are liquids, consisting of natural active or aromatic compounds, which are extracted from plant material such as, but not limited to, woods, leaves, and fruits. The essential oils considered in the present invention have at least one volatile active compound.

[0035] Means for coating a surface of a cellulosic material, in the context of the present invention, relates to means for applying and evenly distributing coatings to a substrate, whether by bonding press, curtain coating, roller and/or scraper coating, printing, or dipping. Roller coating considers the application of a coating to a substrate by means of one or more rollers of, for example, but not limited to, rubber or steel.

[0036] In the context of the present invention, retarding the evaporation of essential oils on the surface of cellulosic materials means preserving, for 7 days or more, volatile active compounds which, without modifications to conventional coating processes, would completely evaporate together with water during drying or during the first 7 days.

[0037] In the context of the present invention, moisture content refers to the amount of water in a solid material, which can be determined gravimetrically, either by means of a thermobalance or by drying in an oven until constant weighting.

[0038] The present invention thus relates to a method for coating a cellulosic material comprising the steps of chemically modifying a starch with cyclodextrins, obtaining a modified starch, followed by the step of redispersing this modified starch in water and using the aqueous dispersion in any of the steps of coating a cellulosic material. The method allows protection of volatile active compounds that would otherwise evaporate together with water during drying and by exposure to air of the final product. The described method allows the retardation of the evaporation of essential oils on the surface of cellulosic materials.

Examples

I) Modified starch

[0039] The modified starch was synthesized by cross-linking, via ester linkages, in one or two steps. In one form of realization of the invention, a starch was mixed with beta-cyclodextrin, 1,2,3,4-butanetetracarboxylic acid and in contact with the sodium hyposulfite catalyst in an aqueous medium at 25-70 °C. After observation of macroscopic homogeneity, most of the water was evaporated until the mixture showed a moisture content <10%, either by being dried at room

temperature for more than 18 h or by being heated. The solid was then placed in an oven at 100 - 180 °C for 2-20 min. Washes were carried out with a mixture of water and alcohol until it was possible to isolate the modified starch. This form of surface modification of the starch is called one-step cross-linking.

[0040] In an experimental option, a cyclodextrin ester was previously obtained. In the two-step cross-linking, cyclodextrin was mixed with 1,2,3,4-butanetetracarboxylic acid (BTCA) and in contact with the catalyst sodium hypophosphite in an aqueous medium at 25-70 °C. After observation of complete dissolution, most of the water was evaporated until the mixture had a moisture content of less than 10%, either by being dried at room temperature for more than 18 h or by being heated. The solid was then placed in an oven at temperatures between 80 and 180 °C for 1 to 10 min. The product, named cyclodextrin ester, was isolated by dissolving it in water, by rejecting the insoluble part, and by subsequent precipitation with an alcohol. In a second step, a starch was mixed with the cyclodextrin ester and in contact with the sodium hyposulphite catalyst in aqueous medium at temperatures from 25 to 70 °C. After observation of macroscopic homogeneity, most of the water was evaporated. The solid was then placed in an oven at 140-180 °C for 2-20 min. Washes with a water-alcohol mixture succeeded in isolating the modified starch obtained by two-step cross-linking.

[0041] The substitution of the main starch derivatives with cyclodextrin is shown quantified in Table 1. The gravimetric method is based on the difference in weight of the native starch and the modified starch. The spectrophotometric method is based on the absorption of phenolphthalein, which forms a 1:1 complex with beta-cyclodextrin.

[0042] Proton nuclear magnetic resonance spectra are shown in Figure 1 for beta-cyclodextrin, polycarboxylic acid and for the cyclodextrin ester. They allow to calculate the average degree of substitution of the cyclodextrin ester, which, in the case of having carried out the first esterification at 140 °C for 10 min and the second esterification at 160 °C for 5 min, is 2,410,1.

[0043] Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) are shown in Figure 2 for native and modified starch. The most relevant absorption bands, due to the elongation of a carbon-oxygen double bond that is not in the native starch, are marked. This figure also shows the condensed structures of the substituted starch monomer. An example of an ester bond, with an absorption band at 1718 cm⁻¹, is marked with a star. An example of a free carboxyl group, with an absorption band at 1560 cm⁻¹, is marked with a ring.

Table 1. Quantification of beta-cyclodextrin content in modified starch. The first number is provided by spectrophotometric determination; the second number corresponds to gravimetric estimation.

Type of cross-linking	Cross-linking time	Amount of beta-cyclodextrin/ (mmol/g)
One-step	10 min	0.20-0.24
Two-steps	5 min	0.11-0.11
	10 min	0.14-0.16

II) Coating

[0044] As the modified starch has a higher molecular weight than the starting starch, in one embodiment of the invention, this was compensated for by prior hydrolysis. Prior to the cross-linking reaction, the molecular weight of the polymer to be modified should be lower than the molecular weight of the polymer commonly used for paper coating. The modified starch was redispersed in water under strong stirring and was heated to 65-110 °C. After 5-30 min, and upon observation of macroscopic homogeneity, it was allowed to cool to 25-60 °C without stopping the stirring. 0,01-2,00 g of an essential oil was added, and the suspension continued under stirring until macroscopic homogeneity was again observed.

[0045] In one experimental option, the modified starch together with the essential oil, thus constituting the coating formulation, was placed on the paper by coating with one or two rolls. In an experimental option, the modified starch and essential oil were placed on the paper by dipping it in an aqueous dispersion of modified starch and essential oil.

[0046] Table 2 shows the surface and optical properties of the paper coated by this method, with and without essential oil, compared with uncoated paper and the paper coated with unmodified starch. The modified starch did not produce any reduction in whiteness and even good printing properties were maintained. However, the reduction in air permeability or Gurley porosity as well as the reduction in roughness from the base paper were slightly less than using native starch. Anyway, in formulations containing essential oil, the differences between starch and modified starch are minor in the case of permeability or not significant in the case of roughness.

[0047] The substitution of native starch by modified starch had no significant effects on the printing quality using inkjet printers, as can be observed in Figure 3. The gamut area values were similar and correspond, in both cases, to a good color fixation.

Table 2. Average mass difference of coated paper compared to uncoated paper, D65 whiteness, opacity, Bendtsen roughness and Gurley porosity or permeability. In the latter case, the time shown, corresponding to the 100 mL air step, is greater when permeability is lower, and vice-versa.

Coating	Mass gain, g/m ²	D65 whiteness	Opacity, %	Roughness mL/min	Gurley porosity, s
No coating	0	144.9	94.2	416	13.58
Starch	2.89	145.9	94.2	330	25.57
Modified starch	2.18	147.9	94.3	446	16.09
Starch and oil	3.62	146.4	94.2	430	20.06
Modified starch and oil	3.82	145.2	94.5	421	14.94

III) Evaporation of water and volatile compounds

[0048] The volatile active compounds of the essential oils which were incorporated into the paper by coating were eventually released into the air, under the usual conditions of ambient temperature and humidity, either in the case of a conventional starch coating or in the case of the coating with the modified starch which is described in this invention. The difference is the speed with which these compounds were evaporated, which was lower in the case of the modified starch. Therefore, cellulosic materials coated with formulations consonant with this invention can be used as long-lasting emitters of active compounds, e.g., to ensure food preservation without using sulfites, iron bags or synthetic preservatives.

[0049] The permanence of volatile active compounds in the coated paper could be directly evaluated using a gas chromatograph coupled to a mass spectrometry detector (GCMS). The equipment used consisted of: Agilent Technologies 7820A chromatograph; Agilent Technologies 5975 detector; G43 stationary phase; helium as carrier gas.

[0050] An essential oil from eucalyptus wood was used because it contained not only volatile active compounds, but also compounds with a vapor pressure lower than 0.01 kPa at 25 °C. More specifically, this essential oil contained, as determined using the mentioned equipment: α -pinene: 55 mg/g; monoterpenes other than α -pinene: 3 mg/g; monoterpenoids (1,8-cineol, α -terpineol and α -terpinyl acetate): 202 mg/g; sesquiterpenes (aromadendrene and others): 125 mg/g; epiglobulol 95 mg/g; globulol: 295 mg/g; β -eudesmol: 35 mg/g; other sesquiterpenoids: 118 mg/g; esters: 40 mg/g; alkanes: 13 mg/g; aromatic hydrocarbons: 8 mg/g.

[0051] Papers coated with this essential oil and with different starches, namely the modified starch in the present invention and the native starting starch, were exposed to air for 1 to 7 days at a temperature of 23 °C and a relative humidity of approximately 50%. The same operation was carried out for papers coated with hydroxytyrosol extracted from olives, evaluating the effects of modified and unmodified starch.

IV) Evaluation of the capacity to emit volatile active compounds

[0052] To study the ability of paper with essential oils, and with native and modified starches, to release the bioactive compounds from these oils, the configuration of Figure 4A was constructed. Headspace Solid Phase Microextraction (HS-SPME) consists of exposing a SPME fiber consisting of polydimethylsiloxane, divinylbenzene and Carboxen® to the vapors released from a sample of paper coated according to Example 1 and with native starch. The exposure time to air, at a temperature of 23 °C and a relative humidity of approximately 50%, was 24 h. The exposure time to the fibre, also at 23 °C, but in a system closed to the transport of matter, was 6 h. Then, the fibre was inserted in the gas chromatograph, using the same column and configuration used for the determination of the oil composition, as mentioned above.

[0053] During the first day of drying, the greatest release of compounds with a tendency to evaporate together with water occurred, namely monoterpenes and monoterpenoids, including 1,8-cineole. Therefore, as presented in Figure 4B, after one day of exposure, the equilibrium of the vapor in contact with the sample was still very rich in volatile active compounds, i.e., of low molecular weight; however, a large part of these compounds was lost in contact with air in the case of native starch.

[0054] The hypothesis of protection of volatile active compounds by functionalization of starch with cyclodextrins was confirmed with a liquid-solid extraction using ethanol as solvent. Table 3 shows the composition obtained after an extraction with ethanol, containing fluorobenzene at a concentration of 1 mg/mL. In both cases, with native starch and modified starch, high amounts of lower vapor pressure compounds, namely epiglobulol, globulol and aromadendrene,

were still present after the week of exposure. However, as shown in Table 3, no low molar mass compounds were detected by GCMS, except α -terpinyl acetate, which was found in very similar proportion in both cases. The chemical modification with cyclodextrins, therefore, allowed to keep significant amounts of 1,8-cineole, α -pinene and α -terpineol, which are otherwise lost in contact with the atmosphere.

Table 3. Compounds extracted with ethanol after 7 days of exposure to air. Quantities are expressed as mg per mg of fluorobenzene, which was used as internal standard.

Starch	Monoterpenoids			Sesquiterpenoids		Terpenes	
	1,8-cineole	α -Terpineol	α -Terpinyl acetate	Epiglobulol	Globulol	α -Pinene	Aromadendrene
Native	0.000	0.000	0.131	0.214	0.479	0.000	0.461
Modified	0.115	0.063	0.127	0.151	0.521	0.013	0.677

V) Retention of antioxidant properties

[0055] Figure 5 refers to the evaluation of the antioxidant capacity, understood in terms of inhibition of the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH). In a first step, papers coated according to Example 2, together with papers where native starch was used instead of modified starch, were exposed to air, and out of reach of sunlight or other sources of ultraviolet radiation, at a temperature of 23 °C and a relative humidity of approximately 50%. After 4 days of exposure, hydroxytyrosol was extracted from the papers with a mixture of methanol and dichloromethane (MeOH/DCM, 50%, v/v), incubating the samples at 35 °C for 24 h.

[0056] A 0,5 mM solution of DPPH was prepared in the above-mentioned mixture, MeOH/DCM. 2,5 mL of this solution was mixed with 0,5-2,5 mL of the extracts in MeOH/DCM. More MeOH/DCM was added until the volume was adjusted to 5 mL and the flask was kept out of light. After 1 h, the absorbance at 520 nm was calculated using a Shimadzu spectrophotometer, UV-2450. The negative control assay was performed by an identical extraction with MeOH/DCM of the papers coated with native starch and modified starch, but without active compounds. Similarly, hydroxytyrosol itself was evaluated, directly using this compound extracted from the olive (fruit and leaves) instead of the paper extracts.

[0057] Figure 5A revealed a low IC₅₀ value for the extract used, confirming its strong antioxidant capacity. Figure 5B showed that after 4 days of exposure to air, papers containing modified starch retained higher antioxidant power than those coated with native starch.

Example 1

[0058] Prior to modification, and to compensate for subsequent cross-linking, the molecular weight of the starch normally used in surface treatments was reduced by hydrolysis with α -amylase: 0,45 μ L of standard enzyme solution per gram of starch, 80 °C, 10 min, denaturation with zinc sulphate.

[0059] 8 g beta-cyclodextrin, 6 g BTCA and 3 g sodium hypophosphite were mixed in 50 mL of water. Under stirring, it was heated to 60 °C. The solution was poured over a metal container, where it was allowed to dry for 24 h. Then, the container was inserted into an oven at 140 °C for 10 min. The resulting solid was redissolved with 100 mL of water; the particles not dissolved at 60 °C were discarded. 8 g of depolymerized corn starch and 3 g of sodium hypophosphite were added to the solution. The new suspension was poured over the metal container, where it was allowed to dry for 24 h. Then, the rack was inserted into an oven at 160 °C for 5 min. This modified starch was obtained in two-steps and was washed with a mixture of water and ethanol, 50% v/v. This modified starch contained 0,11 mmol of cyclodextrin per gram of polymer.

[0060] 2,25 g of modified starch was suspended in 15,4 mL of water at 20 °C. It was heated to 90 °C under vigorous stirring and left at 90 °C for 15 min or until macroscopic homogeneity was observed, while replenishing water to compensate for evaporation losses. Without stopping stirring, it was allowed to cool down to 50 °C and 0,25 g of an essential oil of eucalyptus wood was added. Quickly, the drops of oil became imperceptible to the naked eye and the mixture was apparently homogeneous. The mixture was then used to coat a sheet of paper using a Mathis roller coater at 6 m/min and under infrared radiation. The coated sheet was dried on a metal plate by means of a thermoventilator at 50-60 °C for 20 min. This sheet had a mass gain of 3,1-4,5 g/m² compared to the uncoated sheet.

Example 2

[0061] 8 g of beta-cyclodextrin, 6 g of BTCA and 3 g of sodium hypophosphite were mixed in 50 mL of water. Under stirring, it was heated to 60 °C. The solution was poured over a metal container, where it was allowed to dry for 24 h.

Then, the rack was inserted into an oven at 160 °C for 10 min. The resulting modified starch obtained in one-step was washed with a mixture of water and ethanol, 50% v/v. This modified starch contained 0,20-0,24 mmol of cyclodextrin per gram of polymer.

[0062] A modified starch suspension was prepared as in the previous example. Instead of essential eucalyptus oil, 0,25 g of hydroxytyrosol, a compound with higher antioxidant activity, was added. An uncoated sheet of paper was impregnated in the modified starch and hydroxytyrosol suspension by means of the "KSV Nima Dip Coater" equipment for 20 s. This sheet had a mass gain of 7-9 g/m² compared to the uncoated sheet.

Example 3

[0063] 8 g starch, 8 g beta-cyclodextrin and 6 g 1,2,3,4-butanetetracarboxylic acid were mixed in 60 mL water and stirred under heating at 70 °C.

[0064] The long reaction at high temperature and low pH produced significant hydrolysis of cyclodextrin and starch, resulting in the presence of non-cyclic oligosaccharides, unreacted acid, and a lower viscosity than expected for its consistency. To separate the unwanted compounds, the modified starch was isolated by precipitation, adding 100 mL of ethanol at room temperature (20 °C to 23 °C), and keeping the suspension, without stirring, at room temperature (20 °C to 23 °C) for at least 60 min. The ethanol/water soluble phase was discarded.

[0065] The collected solid was then redispersed, preparing a solution consonant with the previous examples. 0,25 g of essential oil of eucalyptus leaves was added. The mixture was then used to coat a sheet of paper by means of the coater mentioned above, at 6 m/min and under infrared radiation. The coated sheet was dried on a metal plate by means of a thermoventilator at 50-60 °C for 20 min. The resulting paper sheet had a mass gain of 1,5-2 g/m² compared to the uncoated sheet.

Claims

1. A method for coating cellulosic material comprising the following steps:

- a) obtaining a solid modified starch by means of a covalent bond of a starch with a cyclodextrin and a polycarboxylic acid;
- b) redispersing the solid modified starch obtained in step a) in water, under agitation and heating at temperatures from 65 °C to 110 °C until the observation of a macroscopic homogeneity of the resulting mixture;
- c) cooling the mixture resulting from step b) up to temperatures from 25°C to 60°C under continuous agitation;
- d) adding 0,01-2,00 g of an essential oil to the resulting mixture of step c), under agitation until macroscopic homogeneity is observed in the resulting coating formulation;
- e) coating with the coating formulation resulting from step d) through means for coating a surface of a cellulosic material.

2. The method according to claim 1, wherein the step a) comprises the following steps:

- f) mixing a starch with a cyclodextrin and a polycarboxylic acid and in contact with a sodium hyposulfite catalyst, in aqueous medium and at a temperature of 25 °C to 70 °C until macroscopic homogeneity is observed for the resulting mixture;
- g) evaporating water until the mixture resulting from step f) has a moisture content of less than 10% and a solid modified starch is formed;
- h) drying and heating, up to a temperature of 100 °C to 180 °C, of the solid resulting from step g);
- i) washing the solid resulting from step h) with a mixture of water and ethyl alcohol until the resulting solid modified starch is isolated.

3. The method according to claim 1, wherein the step a) comprises the following steps:

- j) mixing a starch with a cyclodextrin and a polycarboxylic acid and in contact with a sodium hyposulfite catalyst, in aqueous medium;
- k) evaporating water until the mixture resulting from step j) has a moisture content of less than 10%;
- l) drying and heating, up to a temperature of 80 °C to 180 °C, of the solid resulting from step k);
- m) dissolving the cyclodextrin ester resulting from steps j), k) and l) in water, discarding its insoluble part, and later precipitation with an alcohol;
- n) dissolution, in aqueous medium, of the cyclodextrin ester resulting from step m) by adding a starch and a

sodium hypophosphite catalyst;

o) evaporating water until a solid is formed;

p) drying and heating, up to a temperature of 100 °C to 180 °C, of the solid resulting from step o);

q) washing the solid resulting from step p) with a mixture of water and alcohol until the resulting solid modified starch is isolated.

4. The method according to any one of the preceding claims, wherein the polycarboxylic acid is a 1,2,3,4-Butanetetracarboxylic acid.

5. The method according to any one of the preceding claims, wherein the cyclodextrin is selected from the group consisting of alpha-cyclodextrin, beta-cyclodextrin, gamma-cyclodextrin, hydroxypropyl-alpha-cyclodextrin, hydroxypropyl-beta-cyclodextrin, hydroxypropyl-gamma-cyclodextrin, methyl-alpha-cyclodextrin, methyl-beta-cyclodextrin, methyl-gamma-cyclodextrin, acetyl-alpha-cyclodextrin, acetyl-beta-cyclodextrin, acetyl-gamma-cyclodextrin, succinyl-alpha-cyclodextrin, succinyl-beta-cyclodextrin, succinyl-gamma-cyclodextrin and 7-beta-cyclodextrin sulfobutyl ether.

6. The method according to claim 1, wherein the step a) comprises the following steps:

r) mixing a starch with a beta-cyclodextrin and a polycarboxylic acid in aqueous medium;

s) heating to a temperature of 65 to 110 °C, under stirring for a time of 1 to 48 h;

t) precipitating the modified starch obtained in step s) by adding ethanol at a maximum temperature of 25 °C, and then drying to obtain a solid modified starch.

7. The method according to claim 6, wherein the polycarboxylic acid is 1,2,3,4- acid tetracarboxylic butane.

8. The method according to any one of the preceding claims wherein the coating formulation of step d) has 0,01 to 0,50 mmol of a cyclodextrin per gram of starch.

9. The method according to any one of the preceding claims, wherein the cellulosic material is a paper product.

10. The method according to any one of claims 1 to 5, wherein the cellulosic material is a textile material.

11. The method according to any one of the preceding claims, wherein the essential oil is selected from the group consisting of essential oils of wood, leaves, and fruits of plants.

12. The method according to any one of the preceding claims, wherein the coating medium consists of a roller coating.

13. The method according to any one of the preceding claims, wherein the mean for coating a surface of a cellulosic material consists of dipping the cellulosic material in an aqueous dispersion of the coating formulation.

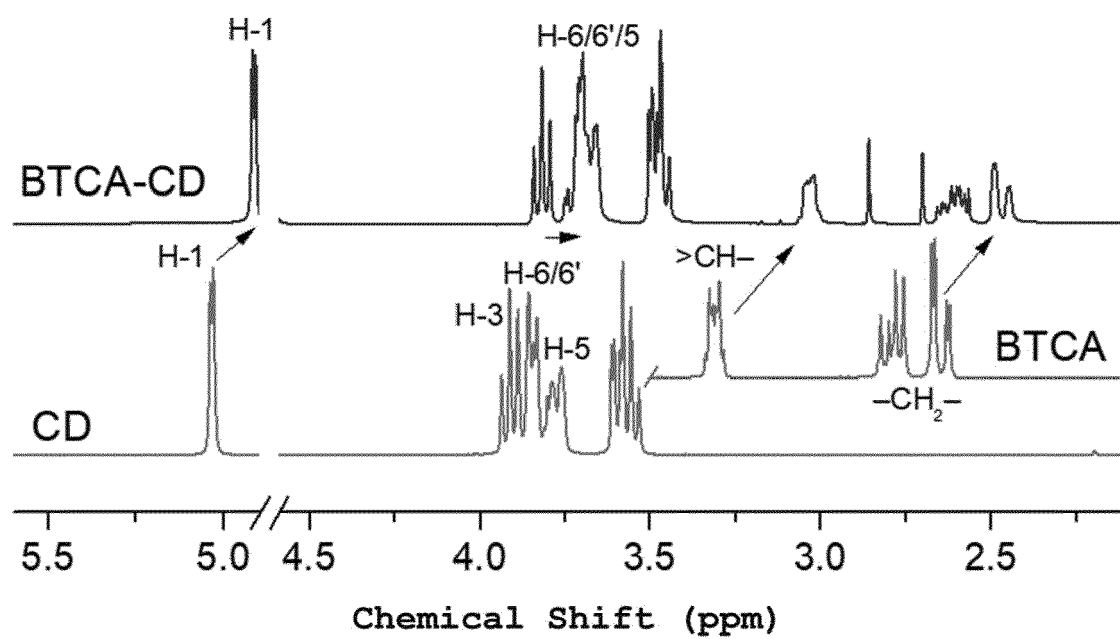


Fig. 1

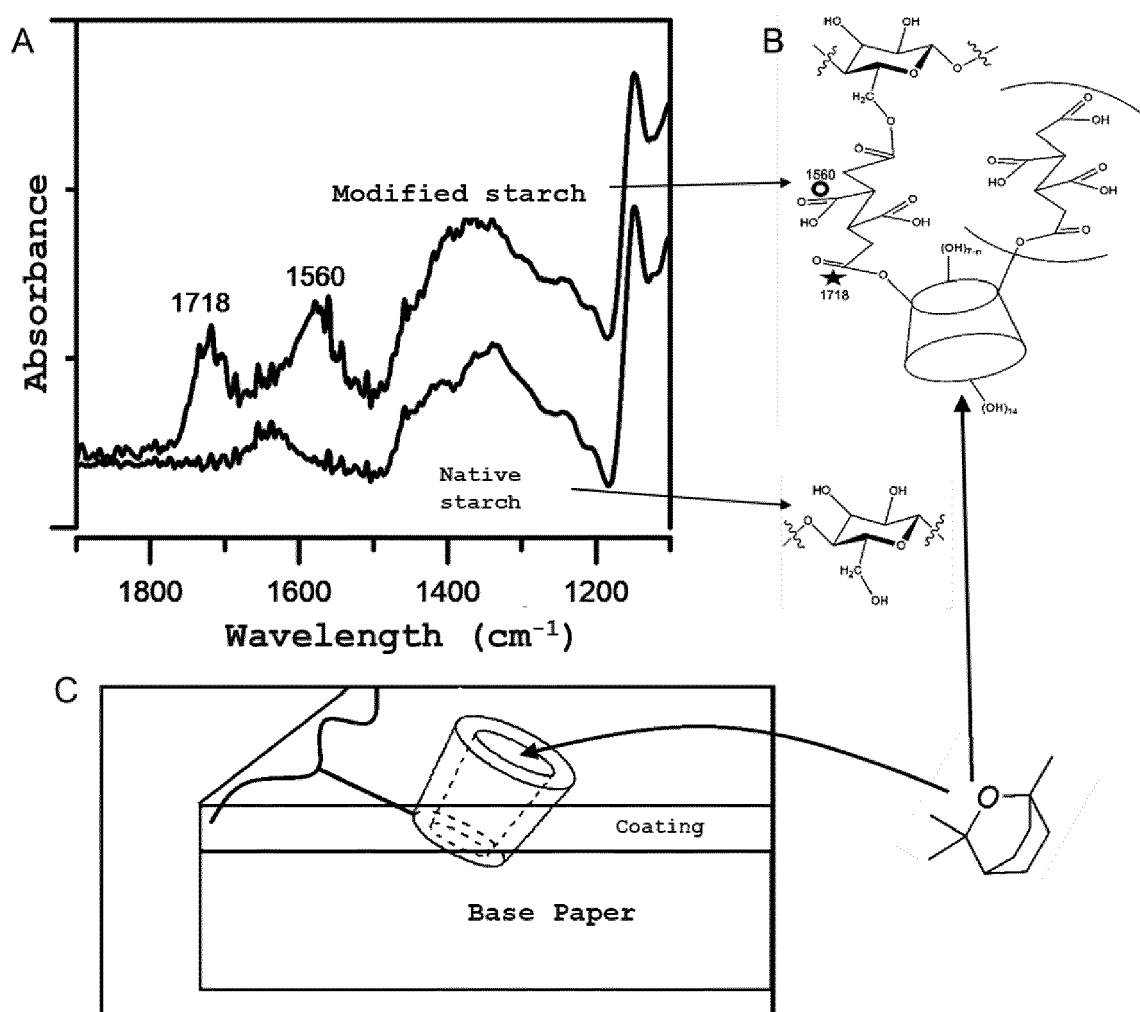


Fig. 2

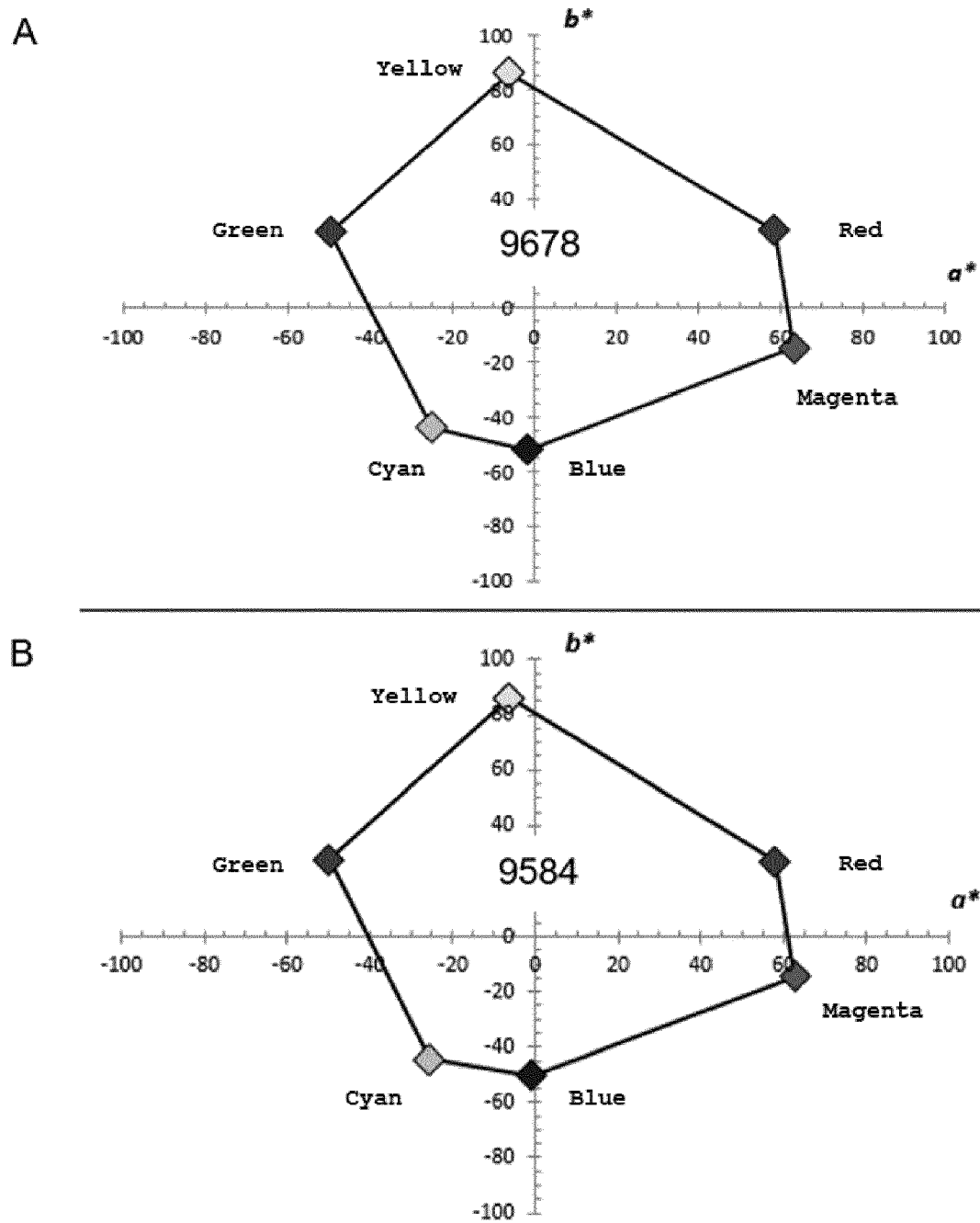


Fig. 3

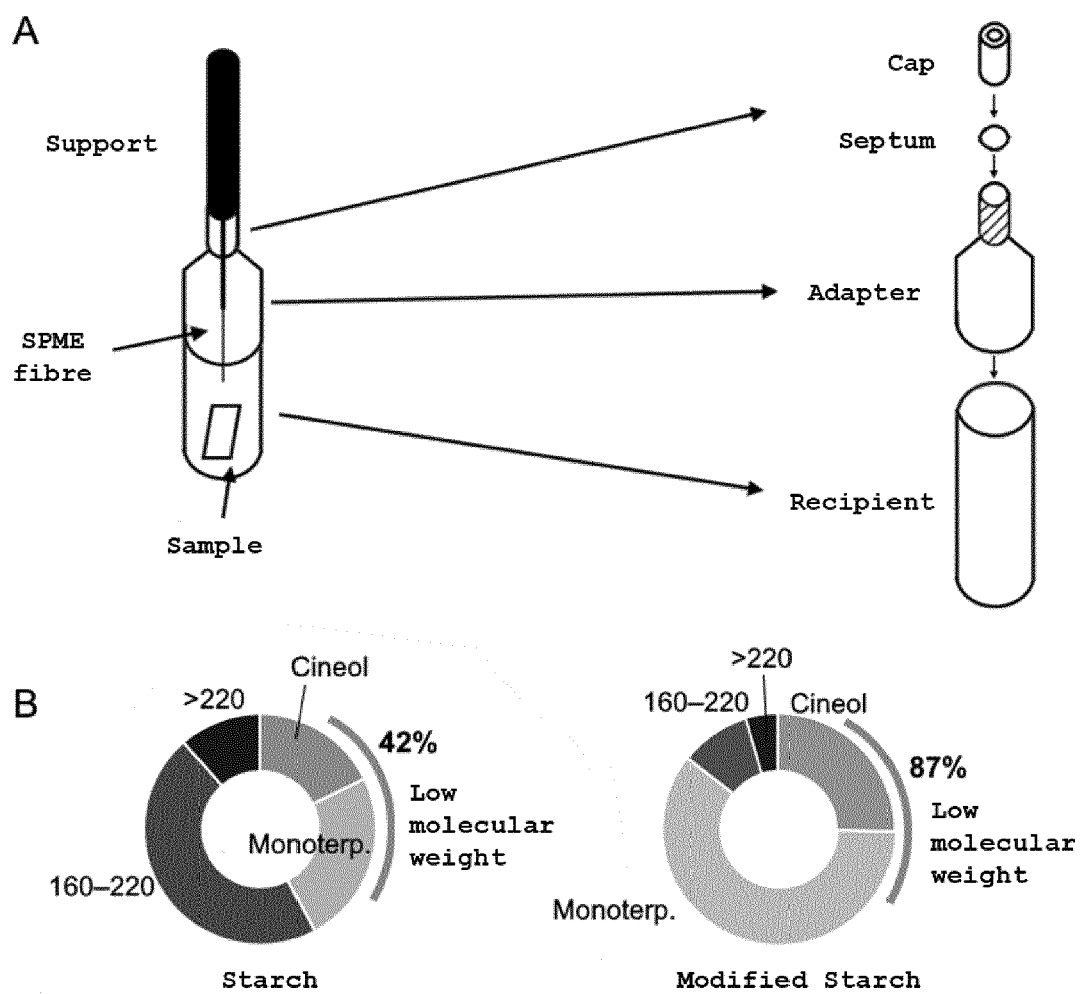


Fig. 4

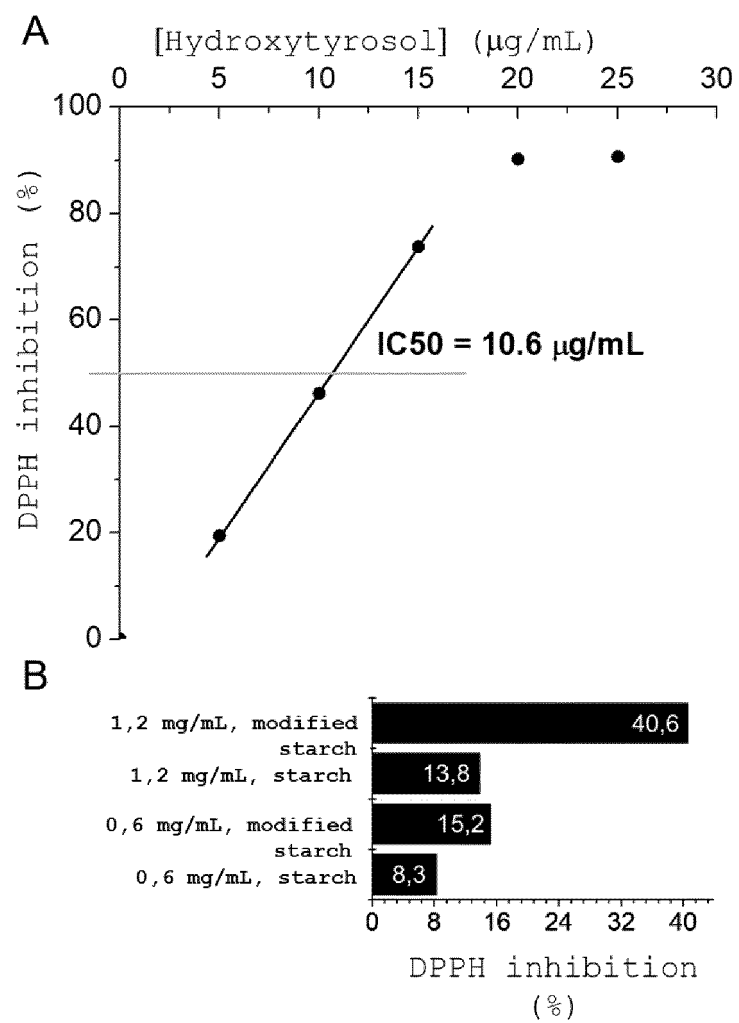


Fig. 5



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Application Number

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Place of search Munich		Date of completion of the search 22 August 2023	Examiner Karlsson, Lennart
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