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Remarks:
Amended claims in accordance with Rule 137(2) EPC.

(54) **Composition for paper deacidification, process to obtain it and method for its application**

(57) This invention relates to a new chemical composition comprising nanoparticles of hydroxyapatite, suspended in solution of carboxymethyl cellulose (50% : 50%) in isopropylic alcohol as solvent, this composition being used for paper deacidification purposes, by the anihilating the paper acidity from pH = 4.5 to alkaline range pH = 7.2.

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Description

Backgroung of the invention

[0001] The present invention relates to a new chemical composition based on a suspension of hydroxyapatite nanoparticles (HA) in carboxymethyl-cellulose (CMC) in alcoholic solution (isopropylic alcohol), used for paper deacidification, by acidity anihilation from 4.5 to 7.2. There are shown the composition preparation, the process to obtain it and method for its application.

State of the art

[0002] The paper degradation, due to an excessive acidity (due to chemical or biological action), is reflected by the yellow tonalities appearance accompanied by an increased brittlement of the paper, which is transformed into a very fragile substance that is destroyed at the slightest touch. The acid hydrolysis of cellulose that occurs during aging, represents about 95% of the paper damages, and is considered as the most significant cause of deterioration of cellulosic materials. Acid attack causes a random attack on hemi-acetal bonds between different constituents of cellulose molecules. This reaction will weaken the molecules, leading to the brittlement of cellulosic materials.

[0003] The most frequently encountered paper damages are:

- Increased acidity (due to either pollutants or inks used to print) which led to a decreased mechanical strenght until the holes appearance. This is accompanied by the erosion and brittlement, thinning, making them transparent.
- Staining appearance of brown, yellowish, green, pink, purple, orange spots, accompanied by a deeper unvisible degradation, due to different fungi and in particular, due to some pigments produced by them;
- "foxing: or the appearance of some redheads-brownish spots of 0.5-5 mm diameter, due to the fungi, and in particular due to the cessation of their action. These foxing spots may be produced by the moulds, too, which generally live unnoticed in the paper, and become visible by their smell and by the brown color marked upon paper permeability.

[0004] The processes employed to remove paper acidity are known as paper deacidification purposes. In spite of the investigations carried out so far, the issue of the paper deacidification is far from being resolved. Some methods of mass deacidification purposes have been developed and improved, but nevertheless no one can say that any of them meet fully the criteria of featured quality in the field, such as pre-selection of the material to be restored, drying, duration of treatment, the effect of the inks, color, paper covers, acidity neutralization, final pH, alkaline reservoir, risks to the restorer and reader, the impact on the environment, the cost of the equipment and the cost of treatment.

[0005] Up to now, the main discoveries in the field are:

In the German Patent DE19921616 (A1), it is used a neutralizing method of the acidity of historical paper using a dispersion of calcium carbonate or magnesium carbonate (1.2% mass percent) with organic acid as stabilizer in cyclohexane. But, this method uses an organic solvent (cyclohexane, with a high degree of flammability and toxicity) existing the ignition danger of the material (book) during the treatment. In addition, the treated material is hardly drying and can assign on some certain foxing area.

In the patents AU2003215817 and W003082742, Preparation process of nano and micro-particles of metal oxides and hydroxides including those from Group II, nano and micro-particles thus obtained and their use in ceramic industries, textiles and paper, are presented only the synthesis methods of these nanoparticles, mentioning only their potential application in the fields referred to above;

Patent US2005042380 (A1), entitled: Basic suspension, preparation and deacidification process of the paper, which dealt with basic type suspensions, Li_2O Na_2O, K_2O, MgO, CaO, SnO, SnO_2, PbO, Pb_2O, Pb_2O_3, PbO, BiO, Bi_2O_3, Sb_2O_3 or their mixtures, as well as hydroxides with sizes ranging from 10 nm to 500 nm and paper deacidification by materials imersion into some bath with suspensions of oxides and bases above-mentioned. This method has the side effect of cellulose depolimerization, due to strong alkaline conditions.

In the paper entitled; "Conservation and restoration of records and books' authors: Carmen Crespo and Vicente Vinas, addressed a number of restoration methods of deteriorated papers, including the application of calcium hydroxide and magnesium hydroxide in solution, barbotating of carbon dioxide, on the paper surface so a layer of carbonate of the two metals above mentioned could be formed. The method has as drawbacks:

- formation of carbonate in the form of solid non-uniformly distributed and easily exfoliated on the paper surface;
- the use of carbon dioxide, which can lead to the formation of carbonic acid, which would increase the acidity of treated paper with stronger destructive effects on this paper.
- The generated carbonates could cover the used pigments belonging to figures or drawings from the paper and could produce lightening, making harder the color reviving.

The publication: Nanoparticules of Mg $(OH)_2$: Synthesis and applications in conservation of

paper, authors: Giorgi, R., Bozzi, C., Dei Gabbiani, C., Ninham, B. W., Baglioni, P. Langmuir 21, 8495-8501 (2005), some alternative preparation methods of $Mg(OH)_2$ and the reagents effect on the quality of this hydroxide is shown; its use in the deacidification of some paper samples by transforming it into the corresponding carbonate on the paper surface, is presented, too.

The paper "A new method for deacidification of paper-based on calcium hydroxide dispersed in aqueous environments," authors: Giorgi, R., Dei, Schettino, L., Baglioni, P, published in Preprint of the IIC Baltimore Congress 2002, Work of Art on Paper, Books, Documents and Photographs: Techniques and Conservation, 69, Baltimore (2002) where the application of calcium hydroxide in suspension, is shown. Unfortunately, calcium hydroxide, magnesium hydroxide, barium hydroxide in aqueous solutions, intense used in the last decade, induce undesirable side effects due to the strong alkaline conditions which causes cellulose depolimerization subsequently the treatment. In addition, for paper samples with alkaline reservoir, which have undergone the deacidification process, atmospheric CO_2, weak acid, is causing a pH decreasing of the solutions used for deacidification purposes with more than 1.5 pH units. It contributes to a mild dissolution of alkaline-earth inorganic metals carbonates present in the system.

In the book "Preservation technologies of books", the U.S. Congress, Office of the promotion of technology, Washington, D. C., there are presented some problems and their solutions for some books. An additional reliable process, from Preservation Technologies, Inc., used MgO with particles sizes between 0.1 and 0.9 microns, a surfactant and perfluoroheptan as solvent.

The method Wei T 'O, leads to good results about pH, but has no good results of homogeneity of the alkaline reservoir; due to the lower reagents solubility in methanol, they produce some side-effects. Alkaline reservoir that remained in the paper is relatively low, so that after a short time requires a repetition of the deacidification process.

U.S. patent 5091111 and U.S. Patent 5208072**,** deals with a composition for paper deacidification containing 0.1-20% methyl magnesium carbonate in an organic solvent which does not attack the paper, but requires special precautions due to its toxicity.

The patent U.S. 5770148**,** refers to an improved deacidification method, for the paper printed books and other printed material containing cellulose, by treating the material with metallic basic oxides, hydroxides or salts dispersed in hidrofluoreter, alone or in combination with perfluorinated transportors, in presence of surfactants.

US patent 6676856 presents improvements to the composition and method for preservation of cellulosic materials by using metal organic carbonates solutions, alcohols C_1-C_4, with a moisture content of less than 100 ppm, and 86-99% solvent with a moisture content of less than 100 ppm.

In the patent**:** RO126570 (A2) entitled: **Composition and process for treatment, chemical restoration and biological disinfection of historical paper surface with hydroxyapatite nanoparticles,** it is presented the preparation and application of a suspension of hydroxyapatite nanoparticles in isopropylicalcohol, in a concentration of 0.08 ... 0.8% for chemical restoration and biological desinfection (for Aspergillus Ş i Penicillium fungi) for the surface of a deteriorated paper.

Detailed description of the invention

[0006] For this invention was used hydroxyapatite (HA) in the form of nanoparticles prepared by grinding of a hidroxyapatite powder in a vibrator vessel, until it has reached a size of about 30 nm. In order to avoid lowering alkali reservoir of the paper supporting deacidification, HA in the form of nano-powder was mixed with a solution of carboxymethyl-cellulose (CMC) in isopropylicalcohol 50%: 50% (percentage by weight), and the obtained suspension is applied on the surface of the acid attack damaged paper.

[0007] By using carboxymethyl-cellulose (CMC), a super- activation of hidroxyapatite (HA) is intended by strengthening of electrostatic and hydrogen bonding between the two components, in order to get a smoothing paper surfaces where it is applied this suspension. Generally, HA has hydrogen atoms bound to oxygen atom. On the other hand, the functional groups that contain pairs of positive charged ions of calcium and clusters of six atoms of oxygen negative charge associated with phosphate crystal triplets, generating hexagonal crystals with a columnar shape with Ca: P = 1.67. The ions Ca, P and hydroxyl groups, are located on the HA surface. At the contact with CMC takes place an electrostatic attraction between Ca^{2+} ions from HA with the carboxyl anions, from the CMC structure, which is not a classical ionic exchange interaction, being more intense in an acidic medium [Bernardi, G. Hydroxyapatite Chromatography of proteins, Methods Enzymol 22, 32-339 (1971)]. This means that, in the acidic environment of degraded paper, the two components will form a compact powder between them and with the paper support.

[0008] In our invention, the two components of the composition HA: CMC at the primary contact, are interacting only by weak hydrogen bonds.The interaction between CMC with HA in this composition is visible in FTIR spectra through the widening of OH group bands (3500-3000 cm^{-1}). By laying this composition on the paper with high acidity (pH 4.5), the electrostatic binding of the two components will be favored, too, forasmuch due to acidic pH, Ca^{2+} ions located on the surface of HA come

into contact with the -COO^{2-} anions from the CMC surface. The electrostatic link between these two components is stabilizing and neutralizing the paper pH where it is sprayed (visible at 1460 cm^{-1} band of the FTIR spectrum, attributed to ionic pair -$Ca^{2+}COO^{2-}$). For this reason, the atmospheric CO_2 has the ability to react with none of these two components, the risk of transformation of pH paper from the basic range to acidic one, is practically null.

Novelty and advantages of the invention consist in:

[0009]

- the use of hydroxyapatite nanoparticles suspension $Ca_{10}(PO_4)_6(OH)_2$ in carboxymethyl cellulose (CMC) alcoholic solution (isopropylic alcohol) 50%: 50% (percentage by weight), the solution being sprayed on the acidic paper surface;
- layering on paper involves the hydrogen bonds between the H atoms and OH groups existing in the structures of the two components, as well as electrostatic binding of the two components favoured by acidic medium of the paper (pH 4.5), because in the field of the acidic pH, Ca^{2+} ions located on the HA surface are coming into contact with the COO^{2-} ions from the CMC surface, forming ion-pairs $COO^{2-}Ca^{2+}$. For this reason, the atmospheric CO_2 has the ability to react with none of these two components, the risk of transformation of pH paper from the basic range to acidic one, is practically null.
- isopropylicalcohol has a low toxicity, it is volatile, has a low surface tension and is environment friendly.

[0010] In comparison with existing methods up to this point and used in many book deposits and libraries, the composition hidroxyapatite: carboxymethyl cellulose prepared by us, has the following advantages:

- (1) the nanoparticules of HA and CMC are not toxic, being recognized as biocompatibile materials;
- (2) has minor disadvantages in terms of used solvent: Wei t 'O method is using CFC (freon);
- (4) the paper treatment with nanoparticles is not followed by carbonatation of the applied reagents, and there is no risk for the disappearance of paper alkaline reservoir and the reappearance of paper acidity.

[0011] Further, this invention is described in figures 1-5:

Figure 1 present FTIR spectra for indidual components of this composition with hydrogen bonds evidence (a) and the evidence of $COO^{2-}Ca^{2+}$ bond (b)

Figure 2, shows micrograms obtained by scanning electron microscopy (SEM) and atomic force microscopy (AFM) of untreated paper samples (left side a,b) and the samples of paper sprayed with HA: CMC 50% - 50% (isopropylic alcohol) (right side a,b);

Figure 3 shows the AFM topology of untreated acid paper;

Figure 4 shows the AFM topology paper after treatment with HA: CMC = 50%: 50% in isopropylic alcohol

Figure 5 presents the visual evidence of an acidic paper samples before (left) and after treatment (right) with HA: CMC = 50%: 50% in isopropylic alcohol.

[0012] There follows an example of the invention.

[0013] **Example 1.** Operations have been carried out by the treatment of a yellowed, lightened and brittled paper sample:

1. Removing the dust by a mechanical operation that was made with a soft brush, poor ventilation in the fume hoods;
2. Treatment of smoothing by mechanical tools with a soft brush and a bone palette knife;
3. Mechanical cleaning: dry powder gum and eraser;
4. Removing the dry wax with a scalpel;
5. 0.2 g HA nano-powder was mixed with 100 ml isopropylicalcohol containing 0.2 grams carboxymethyl cellulose (CMC) 50%: 50% (percentage by weight), and the obtained suspension is applied by a spray on the surface of a deteriorated paper. The spraying suspension HA: CMC has been applied by rotating movements in successive circles from left to right and from top to bottom;
6. the paper in question is left to dry in the air at room temperature, so that to achieve new bonds between sprayed nanoparticles with cellulose fibers from the paper, in order to make the paper more consistent and strength. Drying will occur 24 hours at room temperature.
7. After the application of uniform flow of HA-CMC in isopropylicalcohol, and drying, the paper was the subject of physico-chemical investigations, such as: FTIR, scanning electron microscopy (SEM) and atomic force microscopy (AFM). On the one hand, it could be observed, the topology of HA nanoparticle in CMC suspension, their size and homogeneity of the HA:CMC sample sprayed on paper, on the other hand.
8. The efficiency of presented composition in this invention is determined by pH measurements, too. For pH measurement, weighing 0.5 grams of not printed paper, subjected to ultrasonication defibrilation (for 15-20 minutes) with a special ultrasonicator in sealed tubes. After defibrilation, the pH has been measured continuously to a constant value. The measurements were carried out in triplicate. For the

determination of the pH was used a pH-meter with a calibrated glass electrode. If at the primary contact between the paper and composition, the pH paper was 4.5, after treatment, its pH became 7.2. It has been stable for several months, without any visual changes of the paper.

Claims

1. composition of the invention that consists of: hydroxyapatite and carboxymethyl cellulose (50%-50%) (weight percentages), in 100 ml isopropylic alcohol;

2. the process of getting the composition according to claim 1, **characterized in that** it consists in the following stages: production of a suspension of carboxymethyl cellulose in isopropylic alcohol, producing nanoparticles of hydroxyapatite, the combination of components in the following proportions: 0.2 g HA, 0.2 g CMC, 100 ml of isopropylic alcohol by vigorous shaking.

3. the application procedure of composition according to claim 1, **characterized in that** it consists of the following stages: removing the dust, mechanical smoothing by mechanical tools, mechanical cleaning, removing of deposits of dry wax, and applying such composition by spraying on the surface of the damaged paper, inducing the paper deacidification, with anihilating the paper acidity from pH = 4.5 to alkaline range pH = 7.2, followed by drying for 24 hours at room temperature.

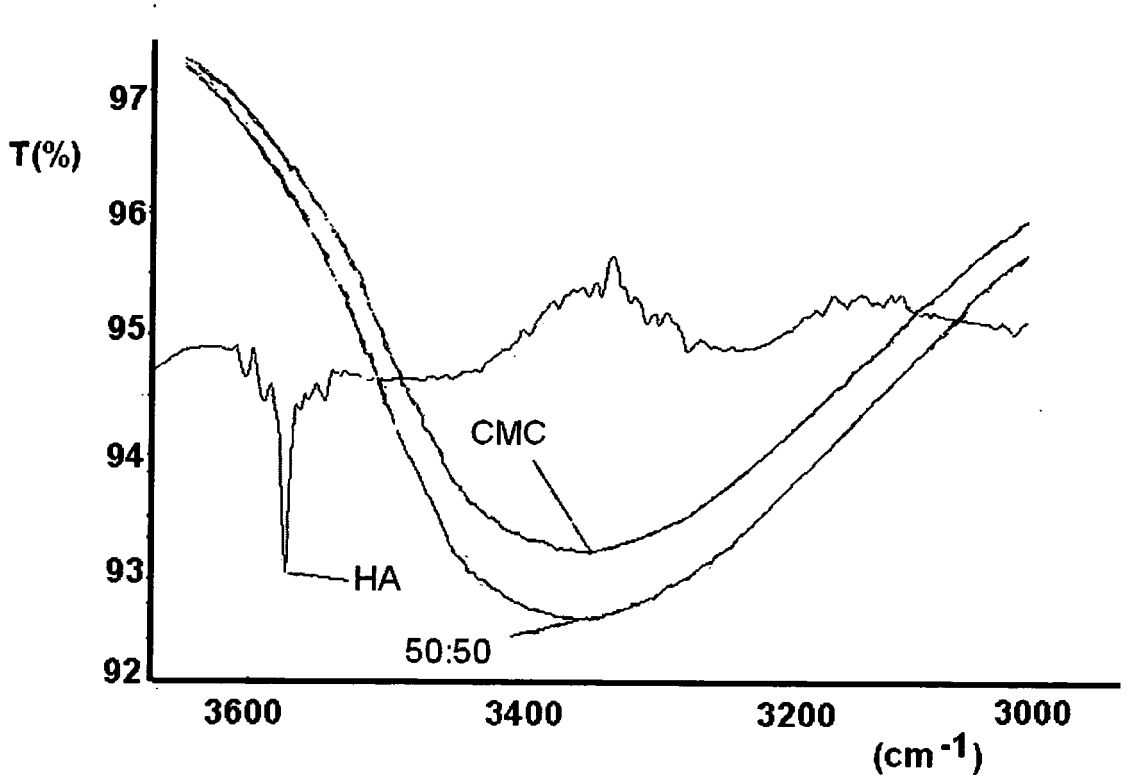
Amended claims in accordance with Rule 137(2) EPC.

1. A composition for paper deacidification (preservation by safeguards measures in front of potential attacks of chemical / biological damages / degradation and conservation by treatment applied to stop and prevent the development processes of damage / degradation), which consists in its treatment, by contact paper with our nano-aqueous suspension organic / inorganic nanoparticles;

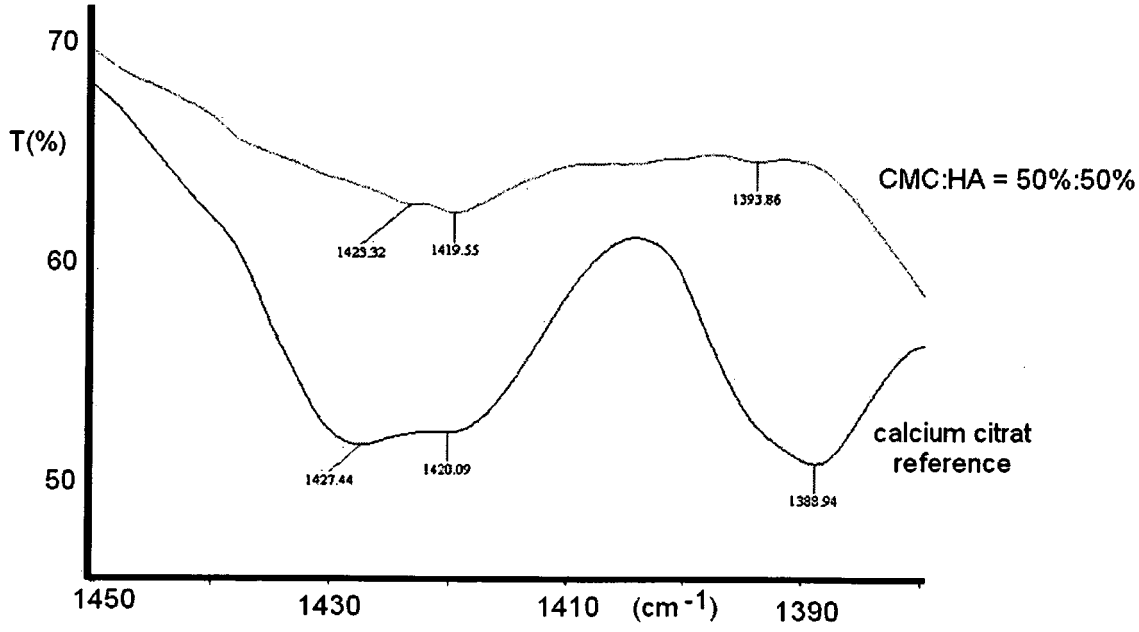
2. A process of prucing the composition according to claim 1, which comprises hydroxyapatite and carboxymethyl-cellulose (50% - 50%) (weight percentages) in 100 ml of isopropyl alcohol;

3. A process for obtaining this composition, according to claim 2, which comprises the following steps: producing the suspension of carboxymethyl-cellulose in isopropyl alcohol, producing hydroxyapatite nanoparticles, combining components obtained in the following proportions: 0.2 g HA 0.2 g CMC, 100 ml isopropyl alcohol by shaking them vigorously.

4. An application method of the composition according to claim 2, which comprises the following stages: removing the dust, mechanical smoothing by mechanical tools, mechanical cleaning, removing of deposits of dry wax, and applying such composition by spraying on the surface of the damaged paper, inducing the paper deacidification, with anihilating the paper acidity from pH = 4.5 to alkaline range pH = 7.2, followed by drying for 24 hours at room temperature.


T(%)
97
96
95
94
93
92
CMC
HA
50:50
3600
3400
3200
3000
(cm-1)

(a)


70
T(%)
60
50
1425.32
1419.55
1393.86
CMC:HA = 50%:50%
1427.44
1420.09
1388.94
calcium citrat
reference
1450
1430
1410
(cm-1)
1390

(b)

Figure 1.

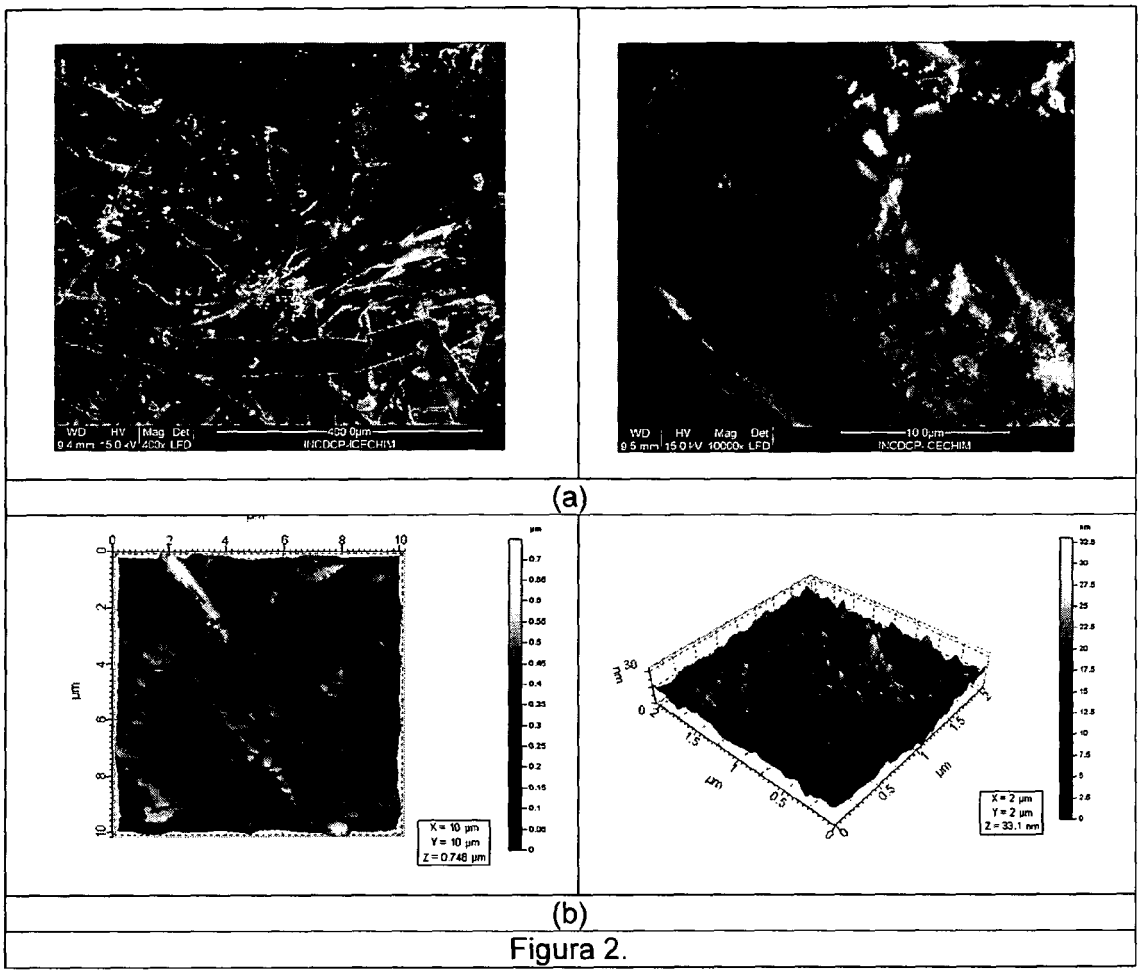
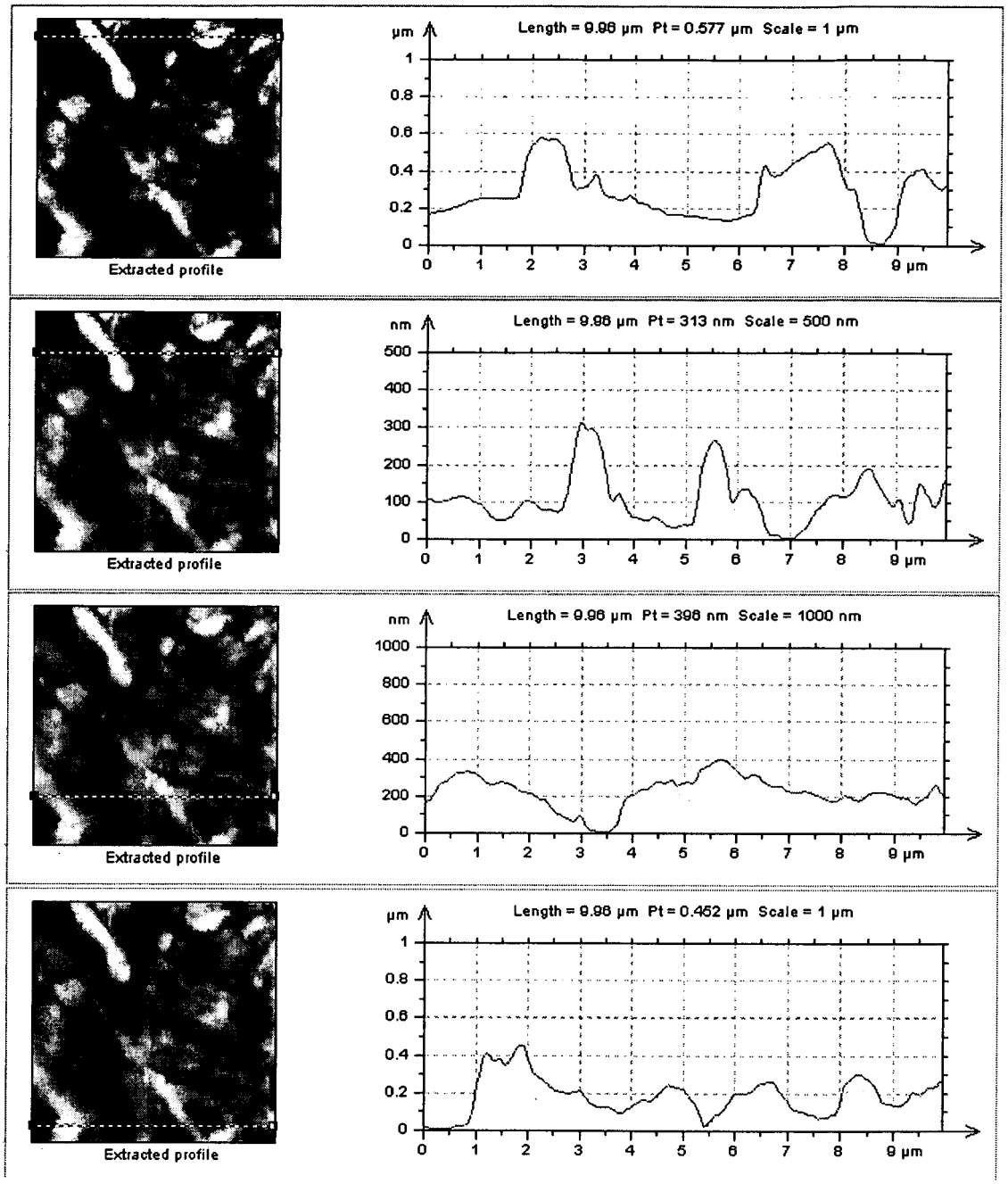


Figura 2.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µm
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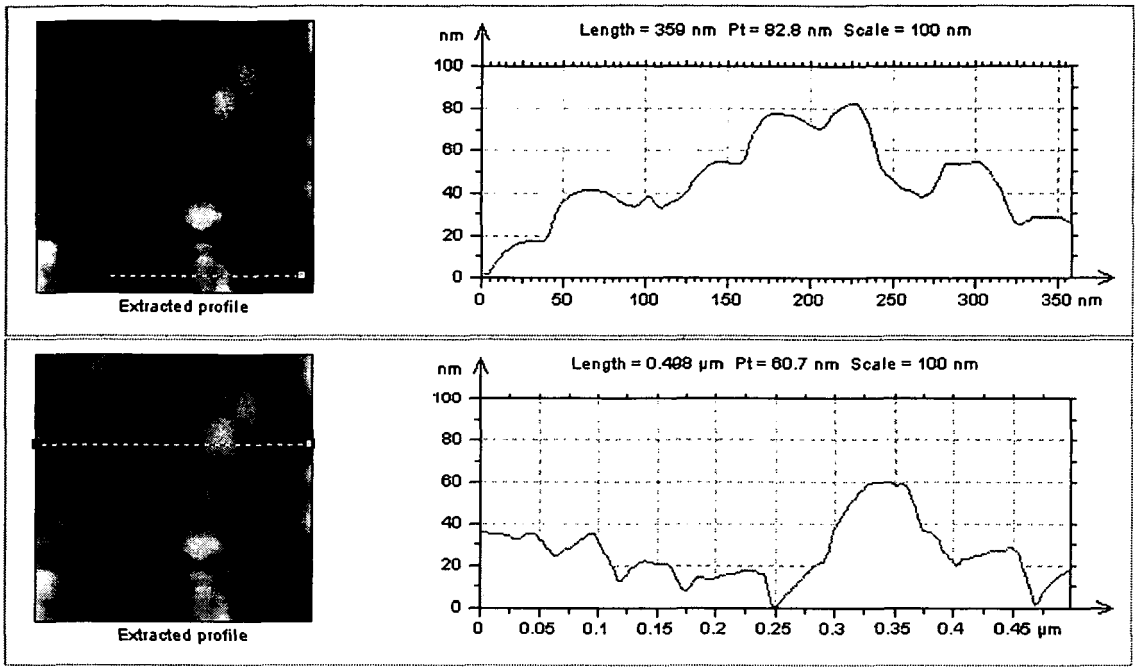
1
0.8
0.6
0.4
0.2
0
0 1 2 3 4 5 6 7 8 9 µm
Extracted profile
nm
Length = 9.96 µm Pt = 313 nm Scale = 500 nm
500
400
300
200
100
0
0 1 2 3 4 5 6 7 8 9 µm
Extracted profile
nm
Length = 9.96 µm Pt = 398 nm Scale = 1000 nm
1000
800
600
400
200
0
0 1 2 3 4 5 6 7 8 9 µm
Extracted profile
µm
Length = 9.96 µm Pt = 0.462 µm Scale = 1 µm
1
0.8
0.6
0.4
0.2
0
0 1 2 3 4 5 6 7 8 9 µm

Figure 3.


Extracted profile
nm
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100
80
60
40
20
0
0
50
100
150
200
250
300
350 nm
Extracted profile
nm
Length = 0.498 µm Pt = 60.7 nm Scale = 100 nm
100
80
60
40
20
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45 µm

Figure 4.

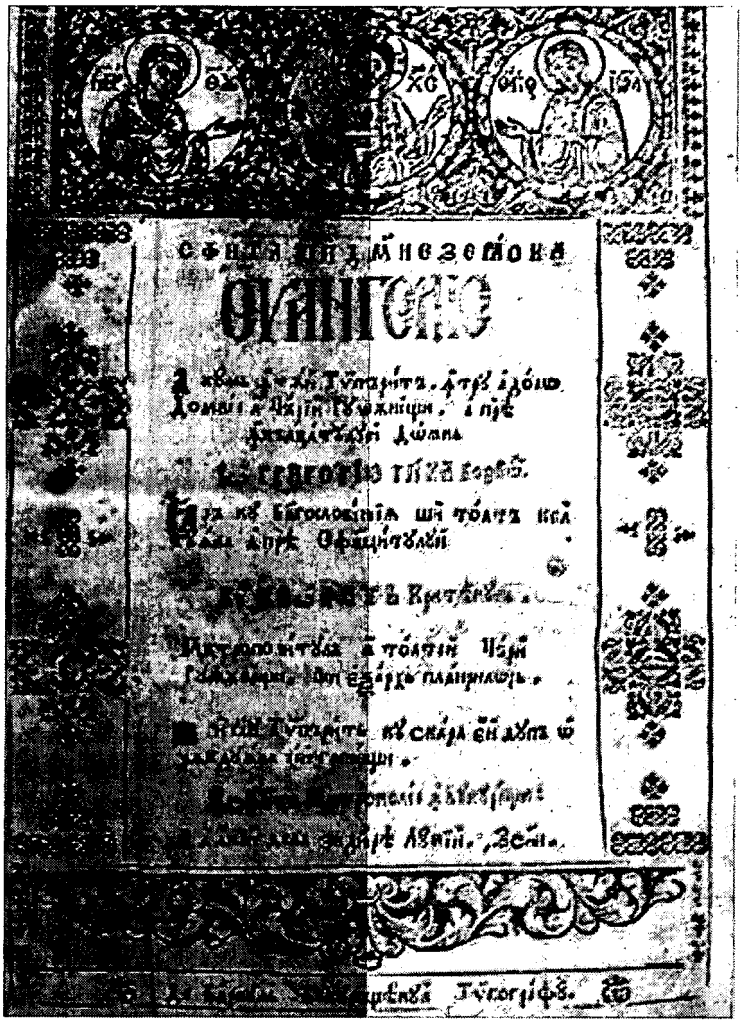

Figure 5.

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EUROPEAN SEARCH REPORT

Application Number
EP 11 46 4027

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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A	US 3 676 182 A (SMITH RICHARD DANIEL) 11 July 1972 (1972-07-11) * the whole document *	1-3	
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			TECHNICAL FIELDS SEARCHED (IPC)
			C09D D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	15 March 2012	Chindia, Evangelia

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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1

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