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(54) **NANO-STRUCTURED SURFACE COATING PROCESS, NANO-STRUCTURED COATINGS AND ARTICLES COMPRISING THE COATING**

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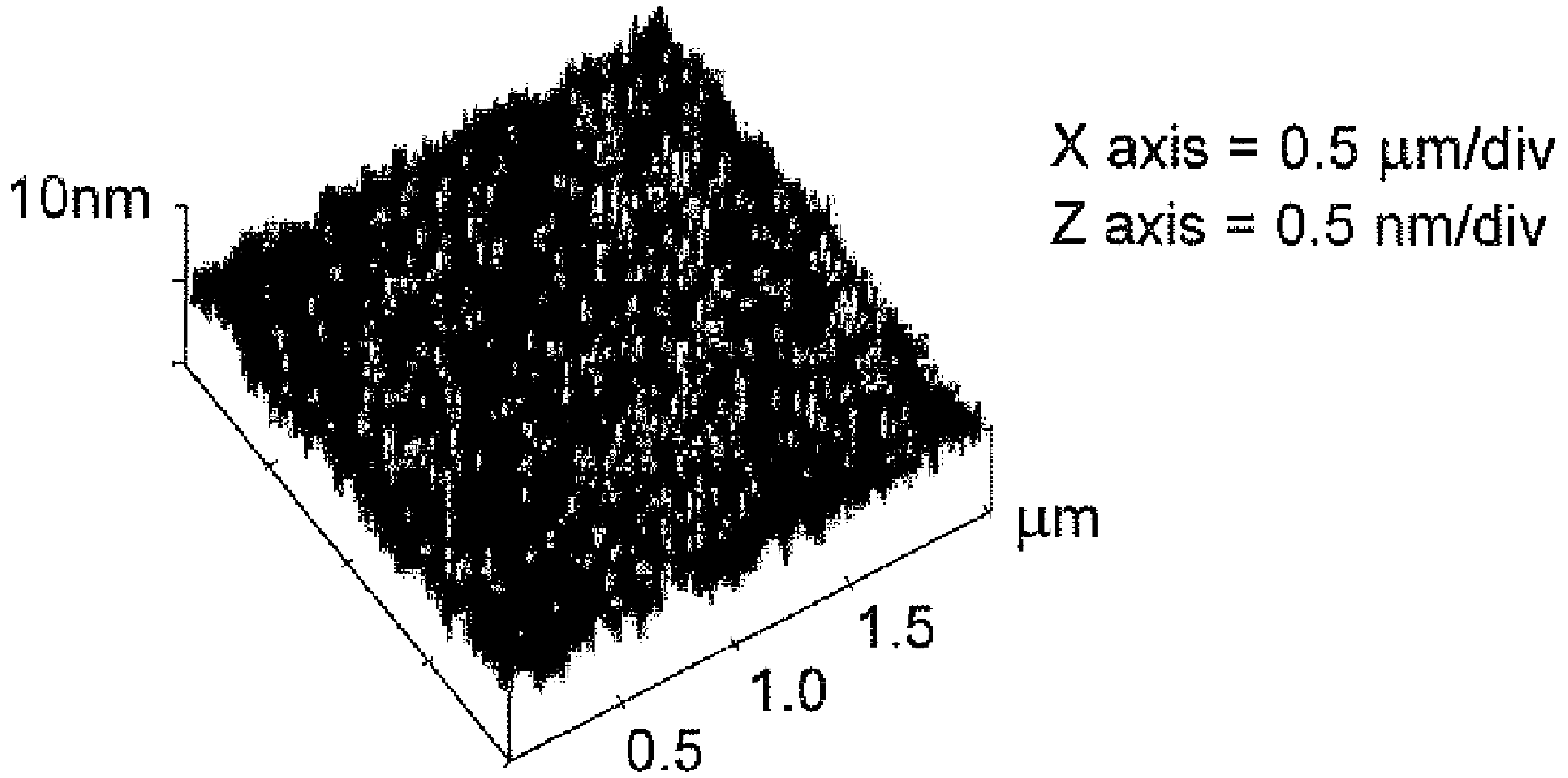
(57) **ABSTRACT**

The invention relates to a new process for the preparation of nano-structured and/or nano-porous surfaces, coatings having a nano-structured and/or nano-porous surface and articles comprising said coatings. The invention also relates to the use of coatings according to the invention, in particular as anti-reflective coatings. The process for the preparation of the surface nano-structured and/or nano-porous coatings is a process comprising the steps of

- a) applying a mixture to a substrate which mixture comprises
  - i) reactive nano-particles
  - ii) at least one solvent
  - iii) optionally a compound having at least one polymerisable group, in an amount that results in an increase in the transmission of at least 0.5%, for at least part of the electromagnetic spectrum between 400 and 800 nm, after the mixture has been applied and cured on a transparent substrate, in comparison with the same substrate without a coating
- b) inducing crosslinking and/or polymerisation in the mixture applied to the substrate.



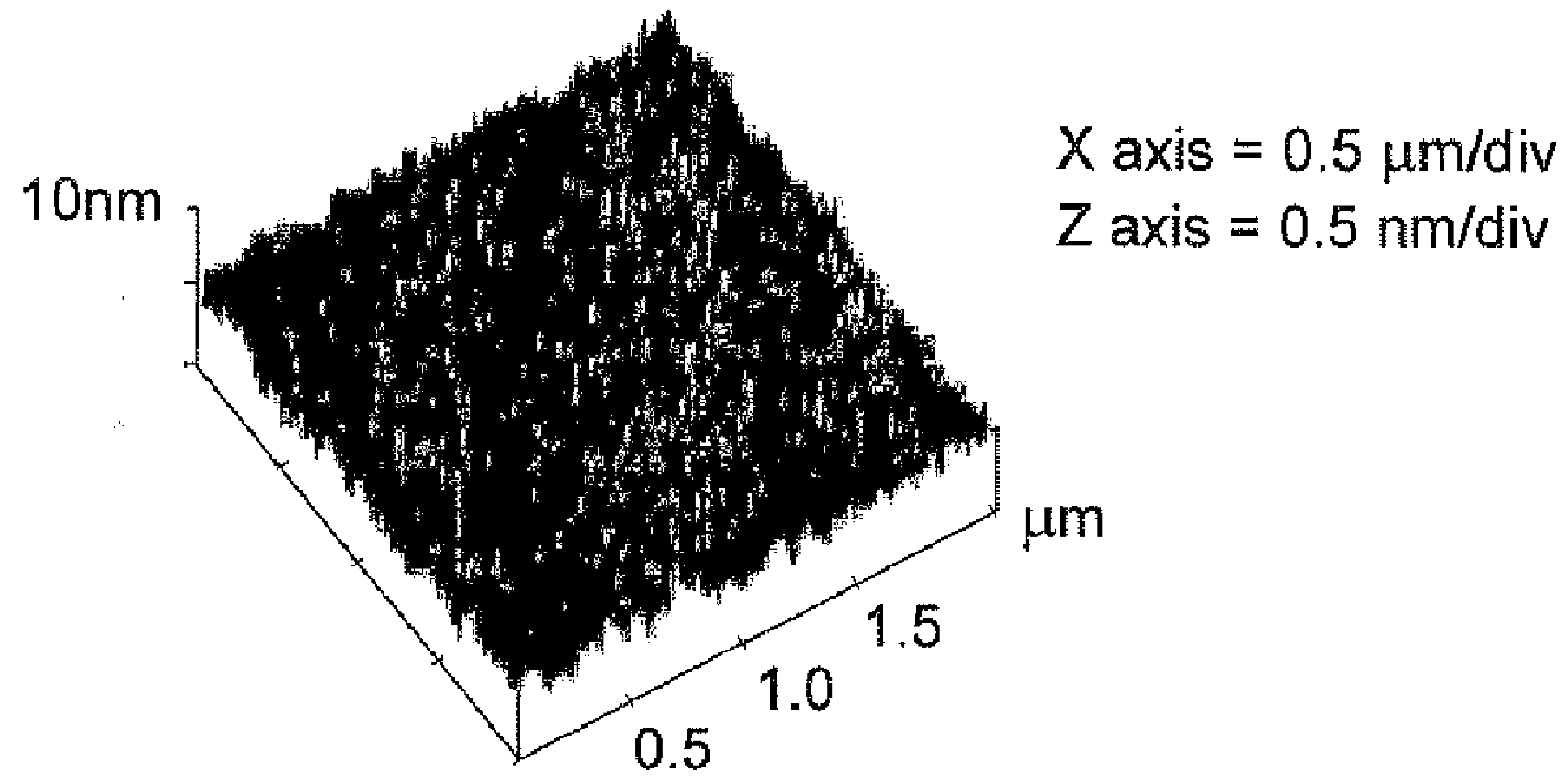


Fig. 1A

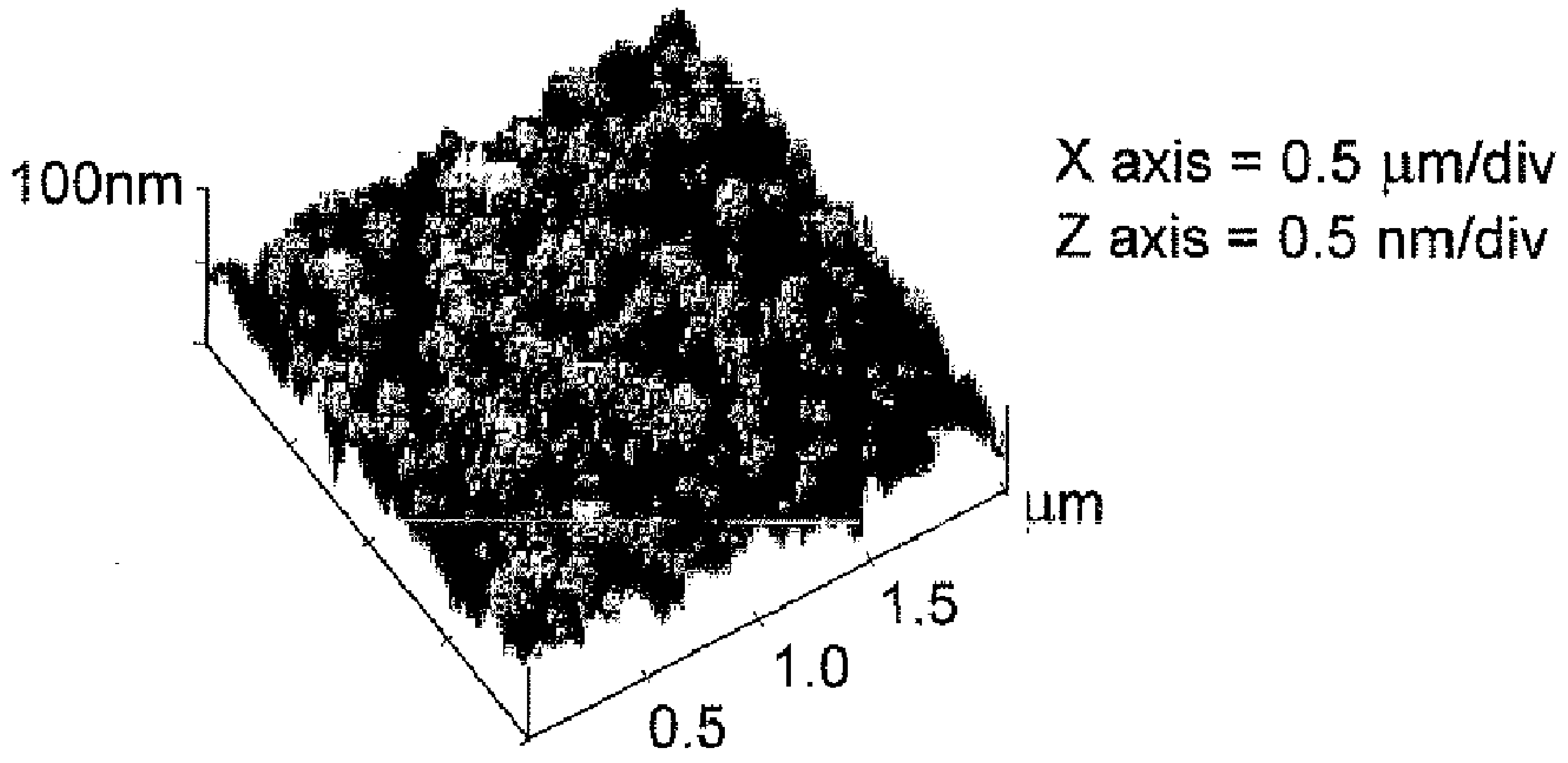
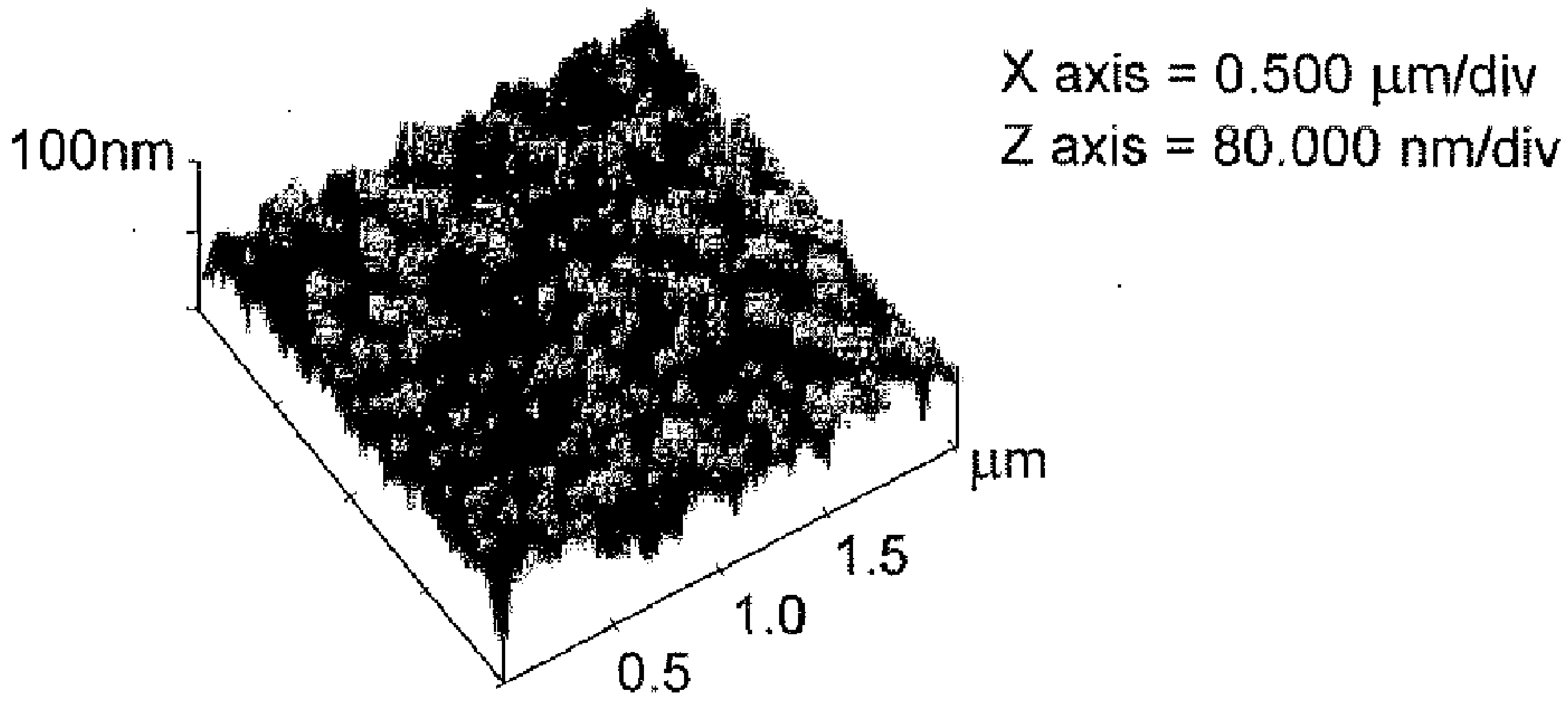


Fig. 1B



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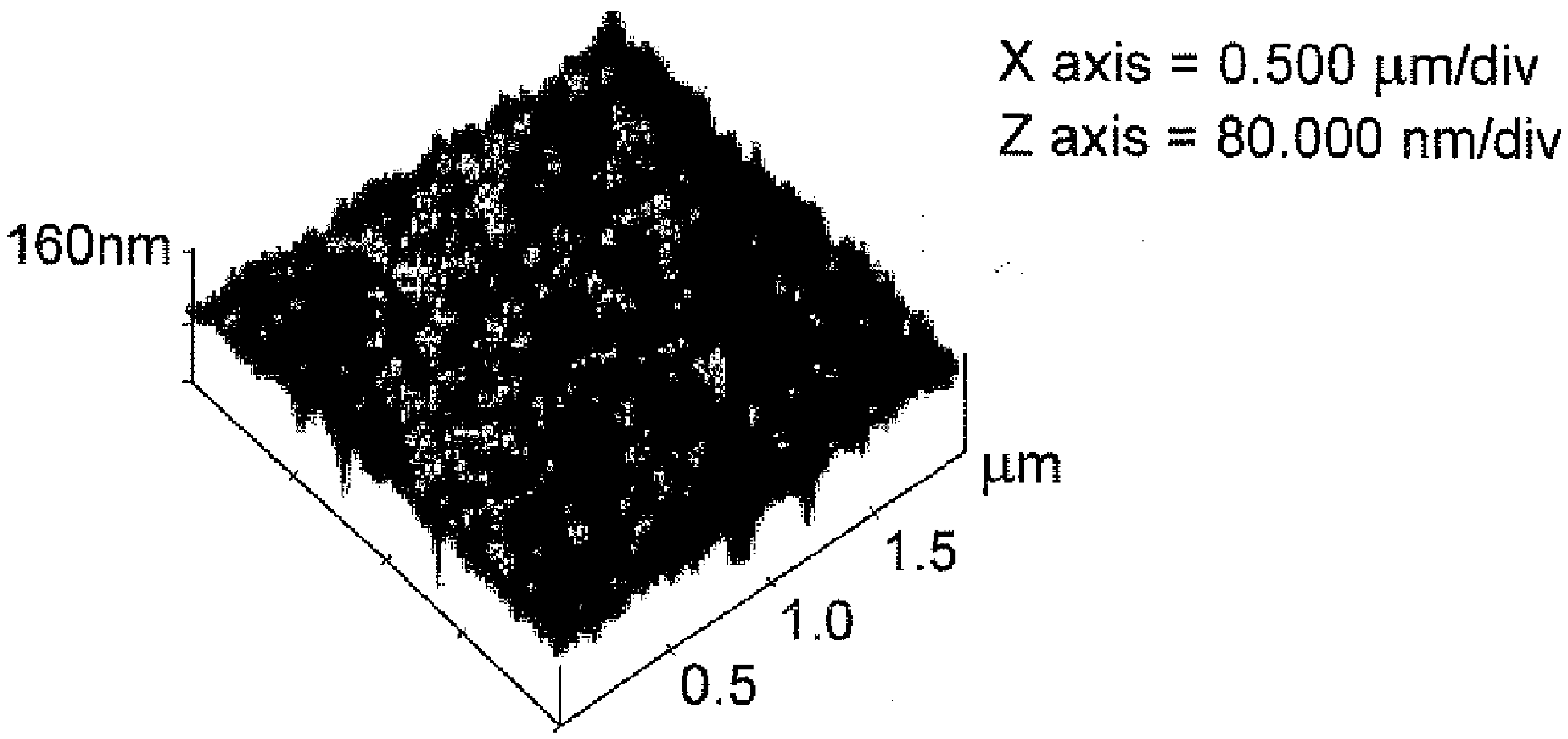
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Z axis = 80.000 nm/div
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µm
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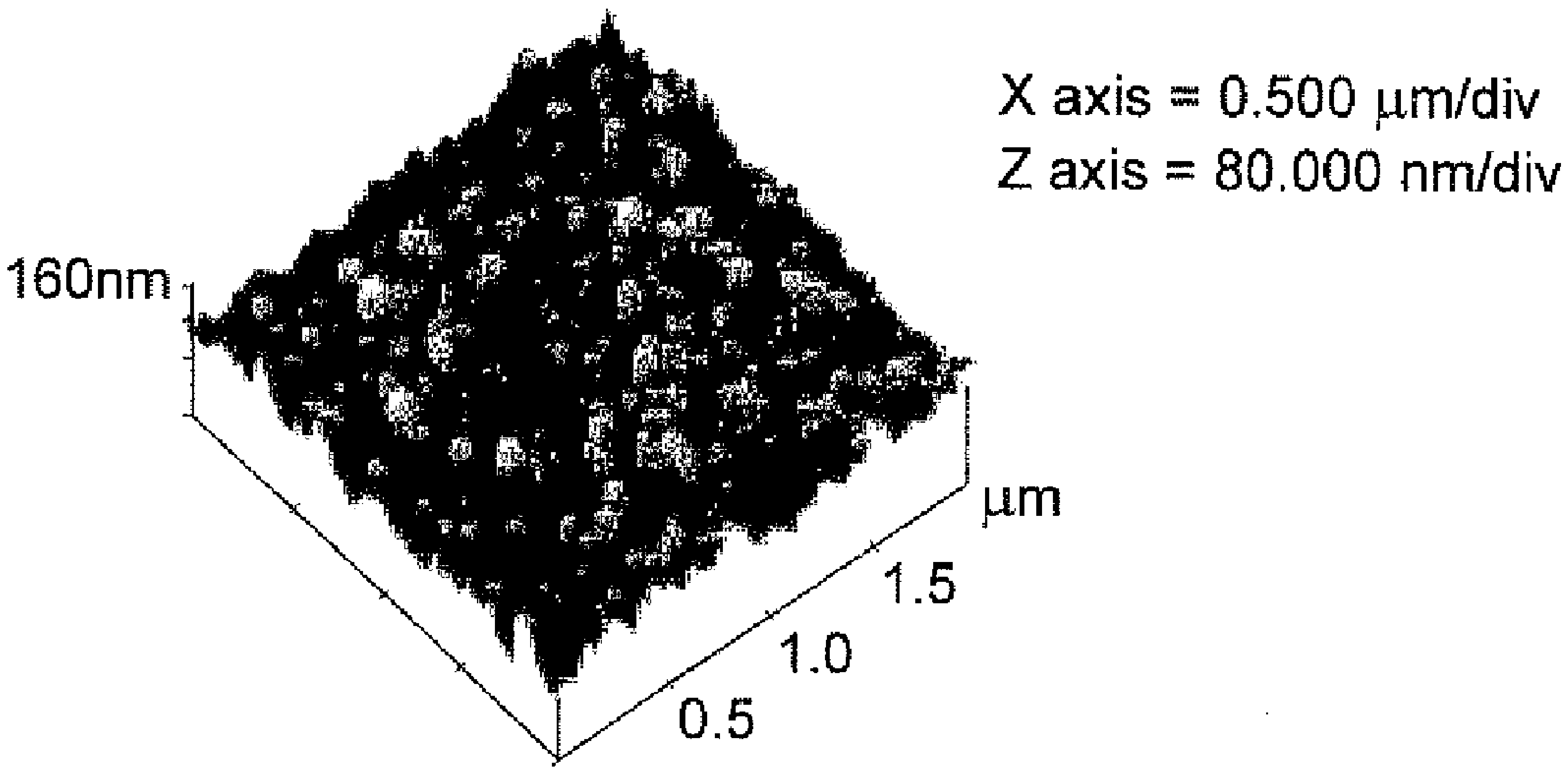
1.0
0.5

Fig. 1D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µm
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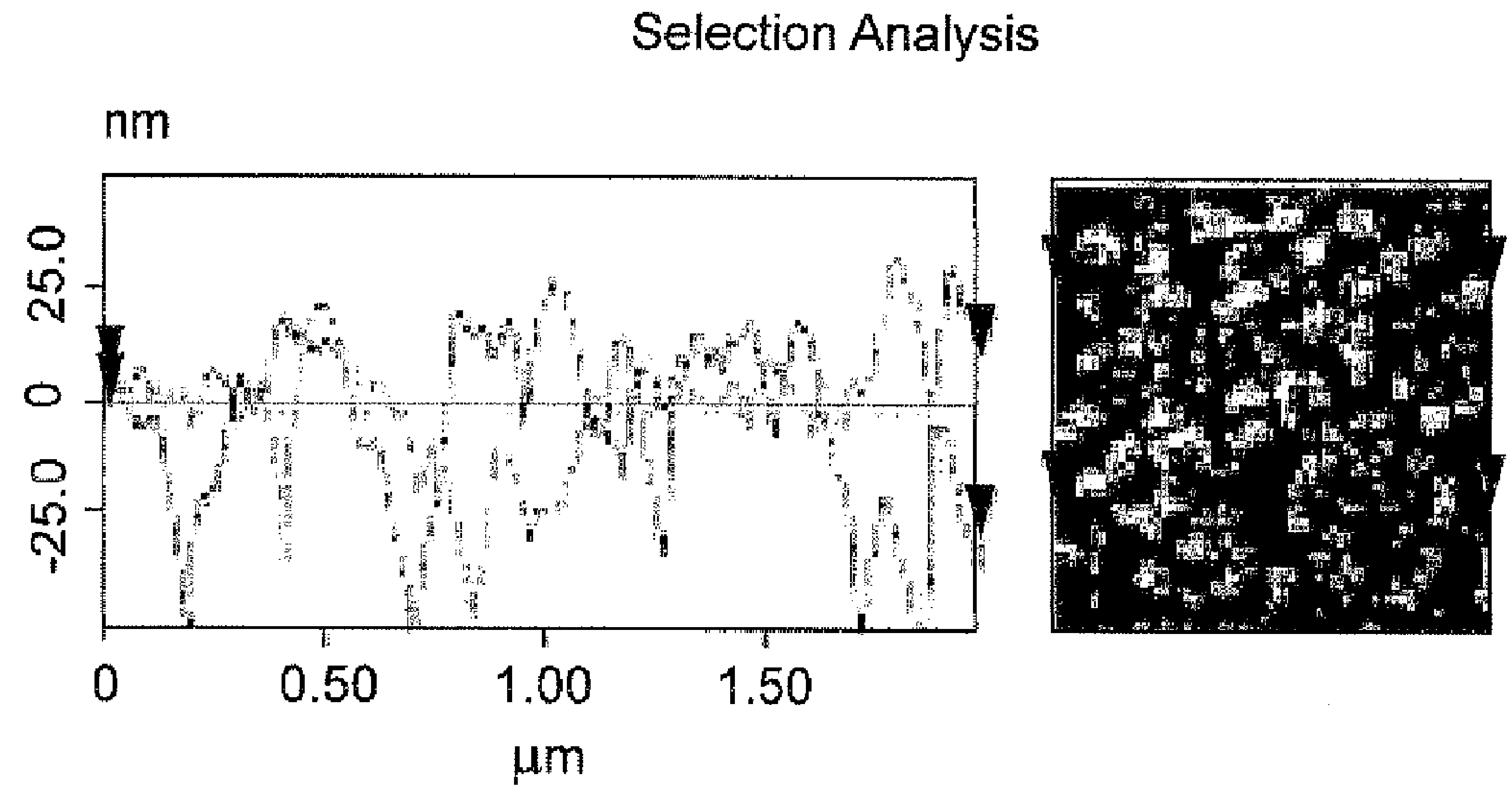
0.5

Fig. 1E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1.00
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µm

Fig. 2A

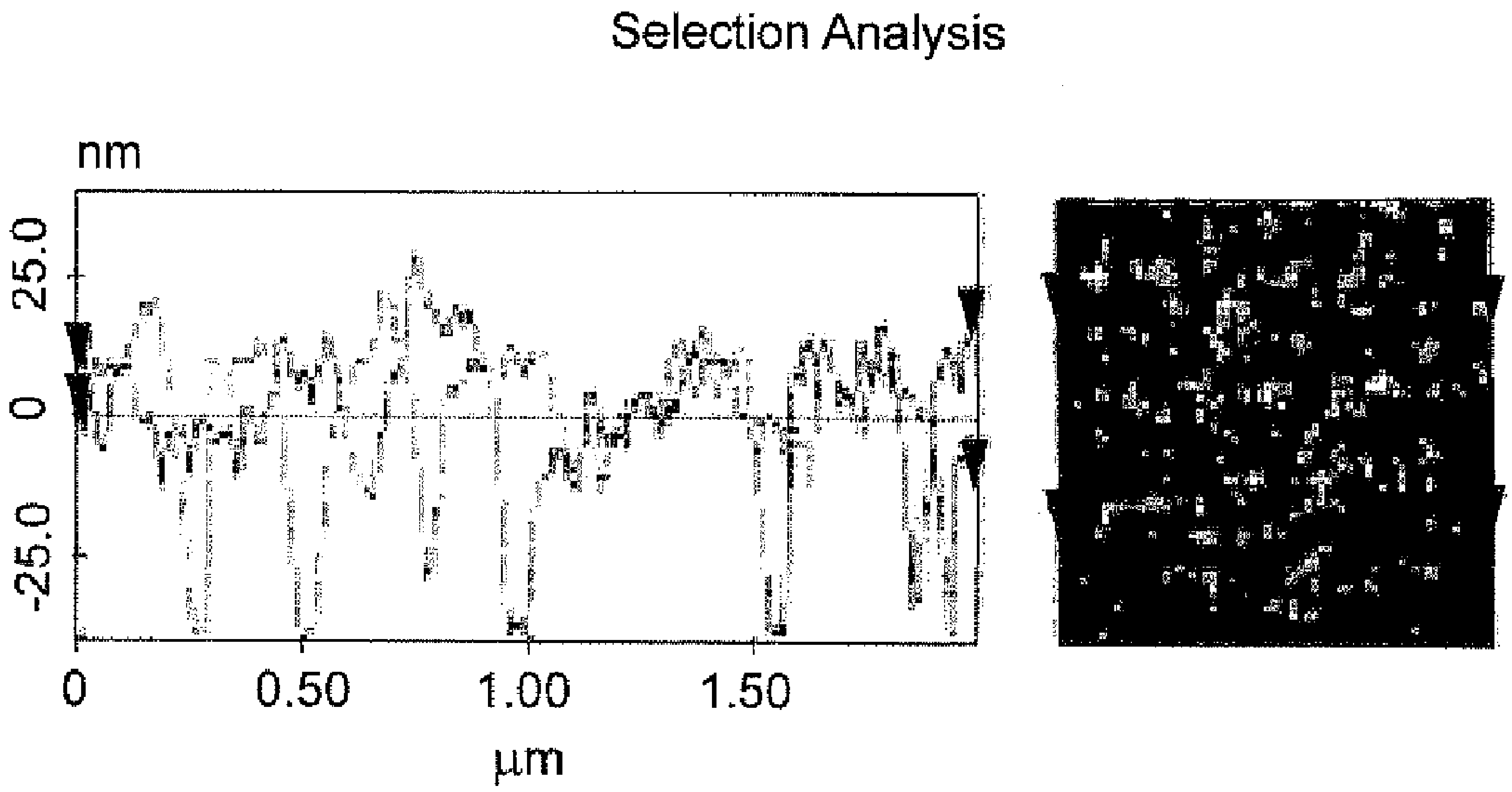
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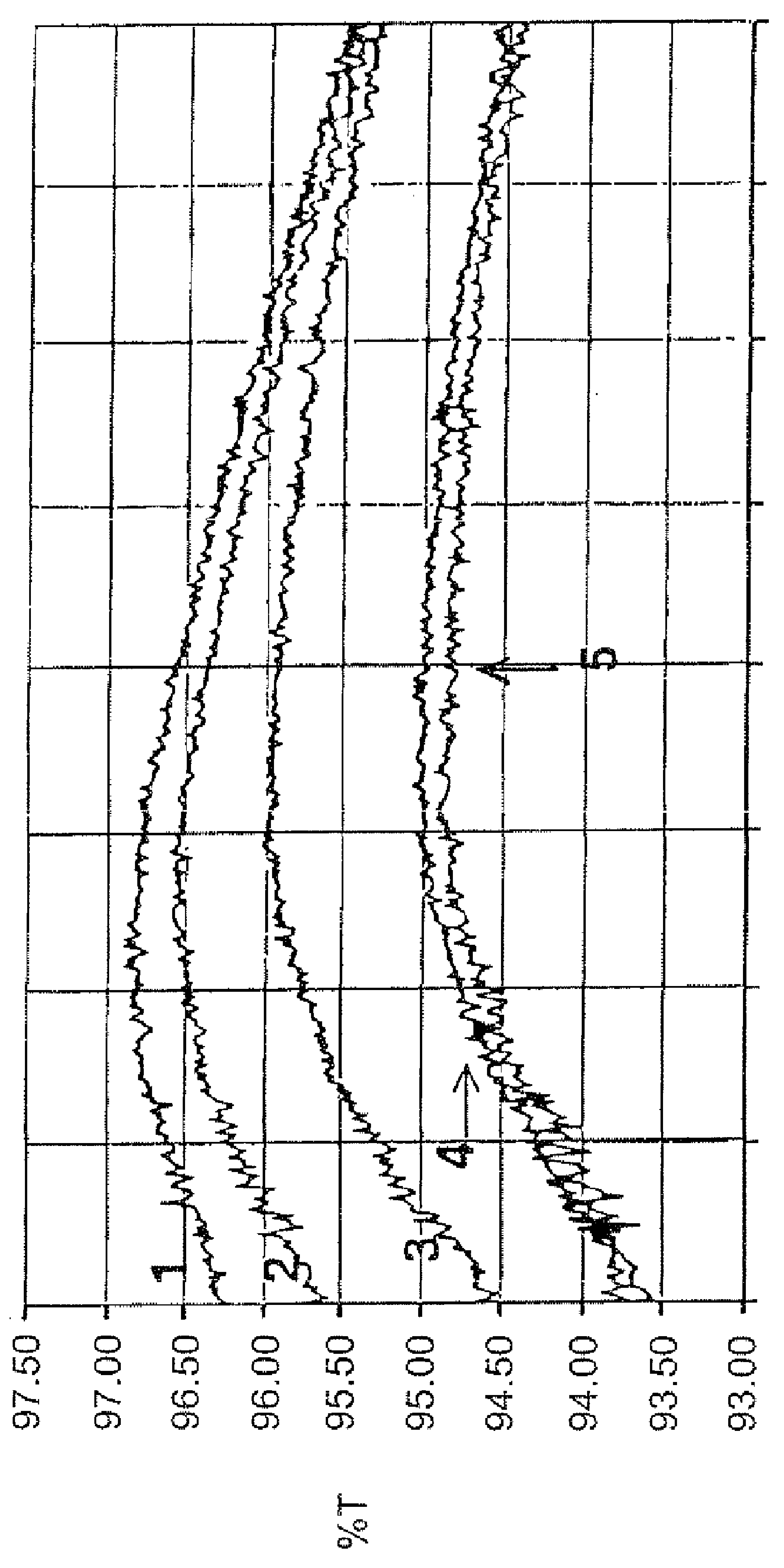
Fig. 2B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93.50
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550
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650
700
750
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NM
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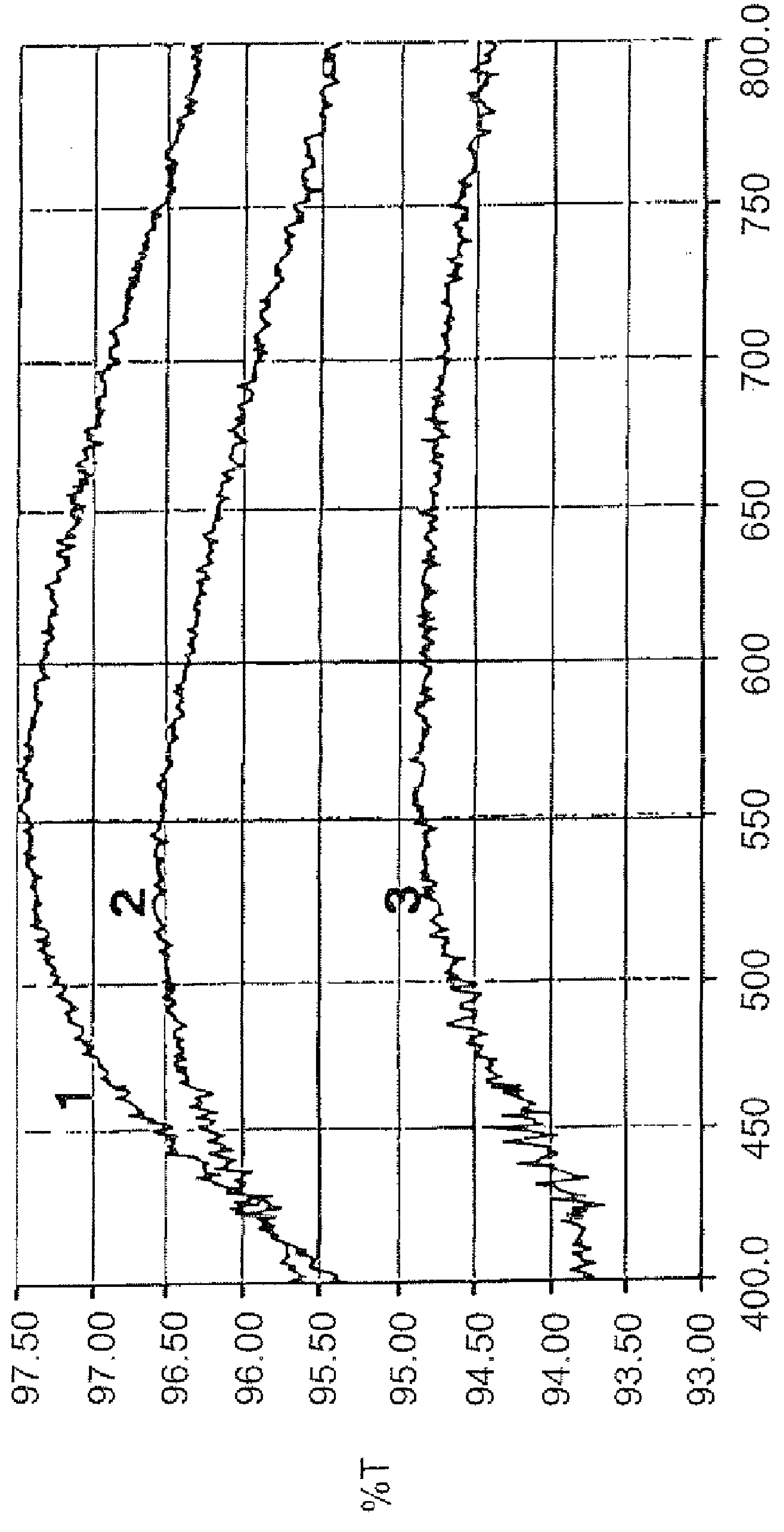
2
3
4
5

Fig. 3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750
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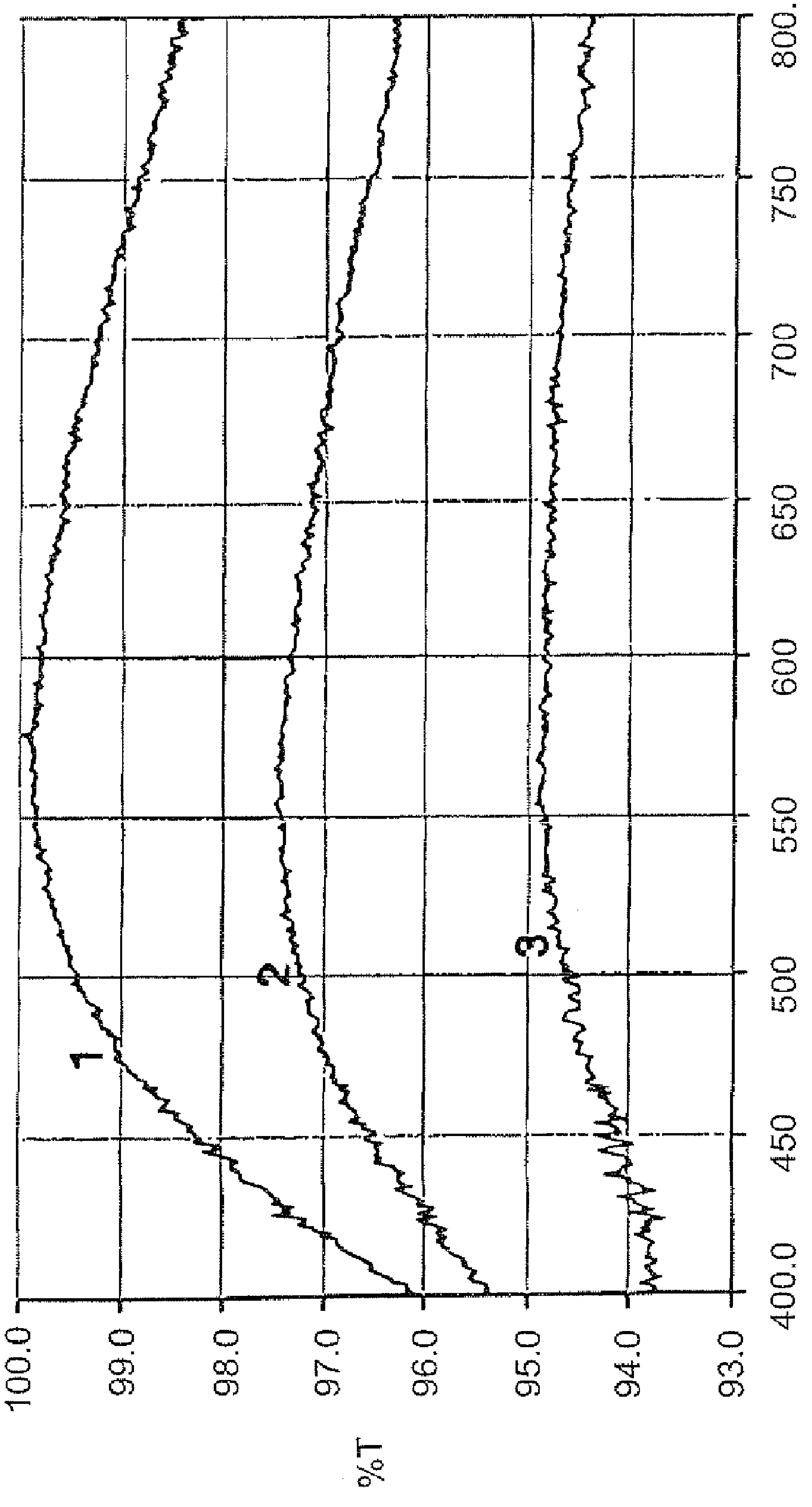
NM
1
2
3

Fig. 4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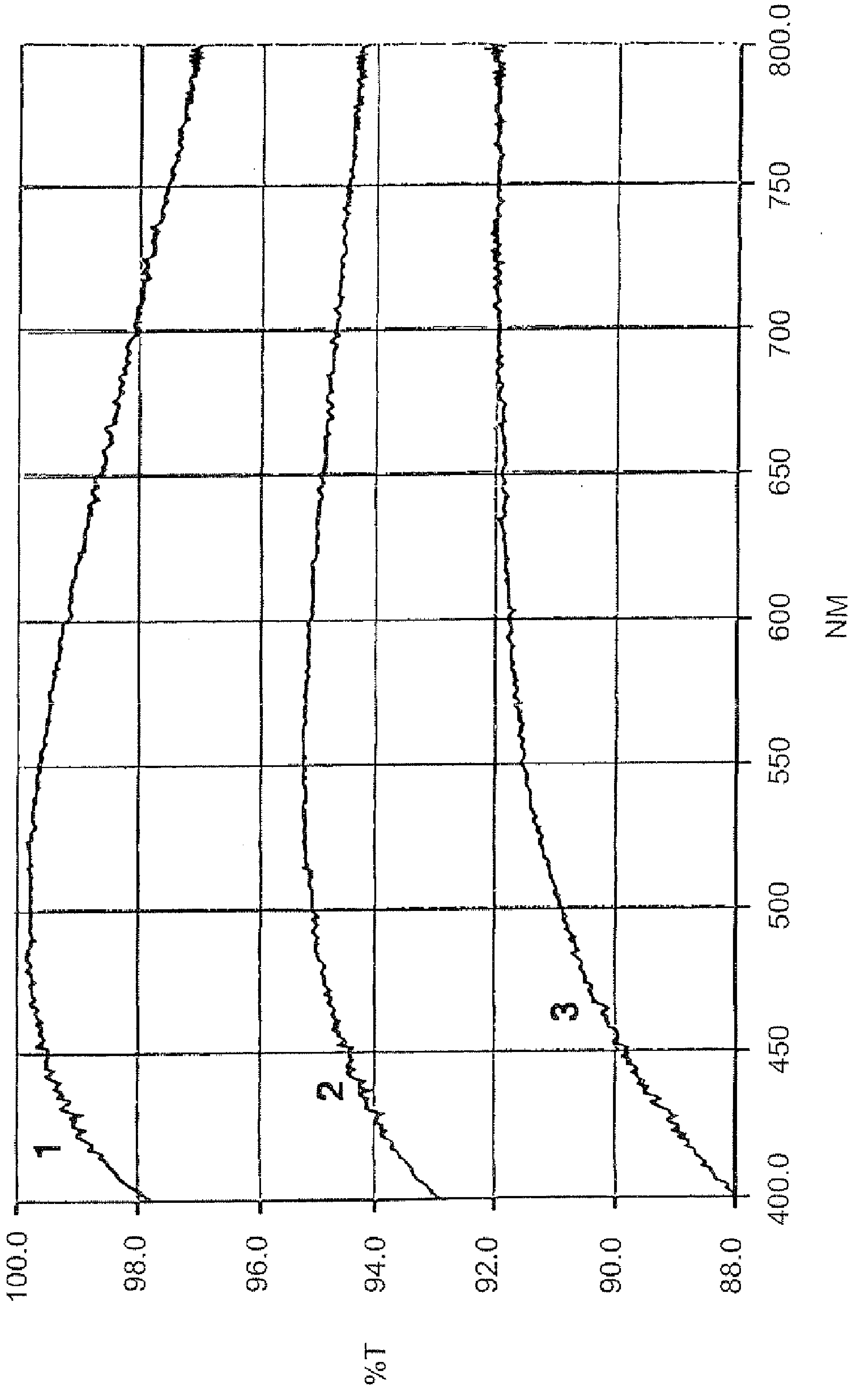
NM
1
2
3

Fig. 5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750
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NM
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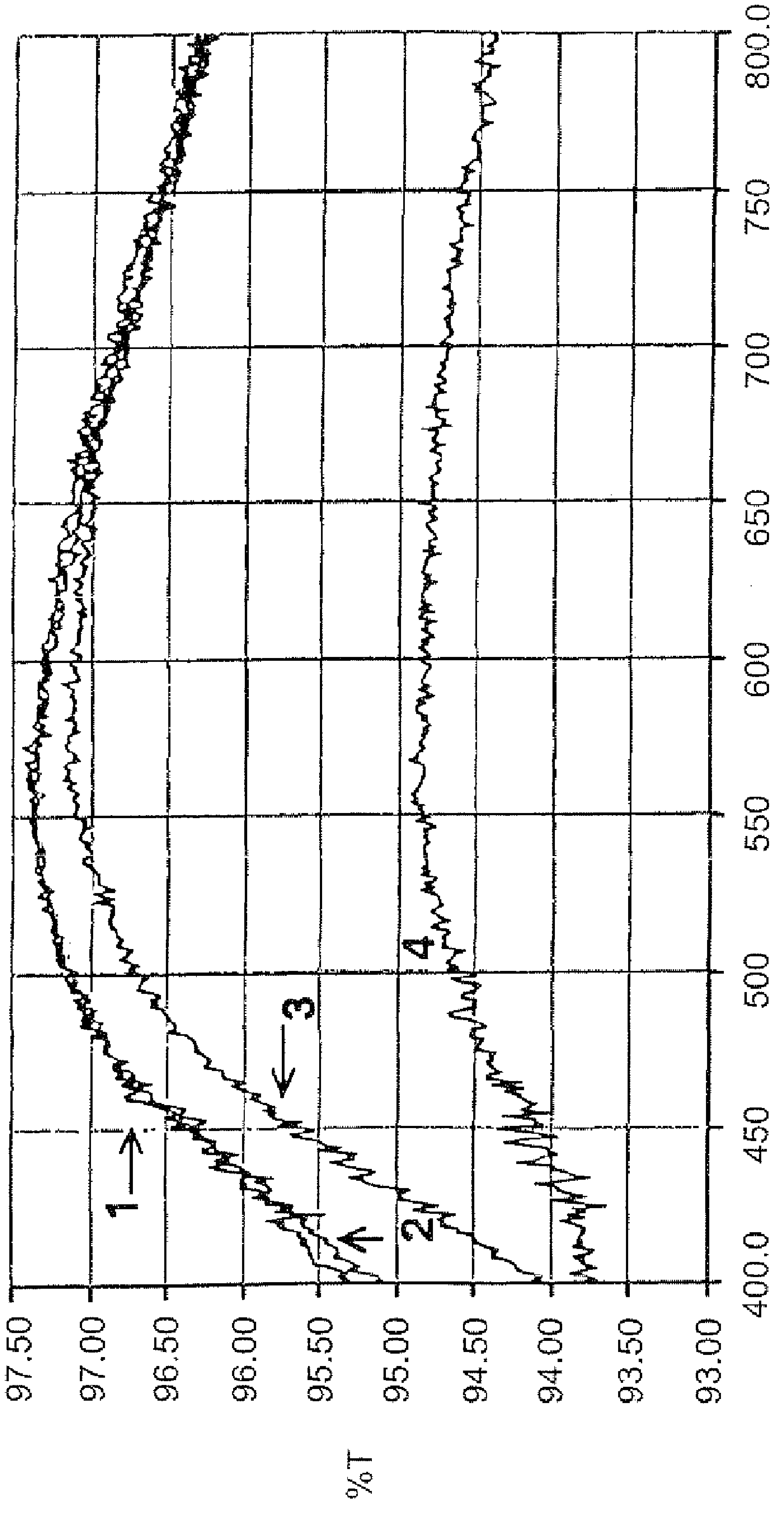
2
3

Fig. 6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94.00
93.50
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400.0
450
500
550
600
650
700
750
800.0
NM
1
2
3
4

Fig. 7

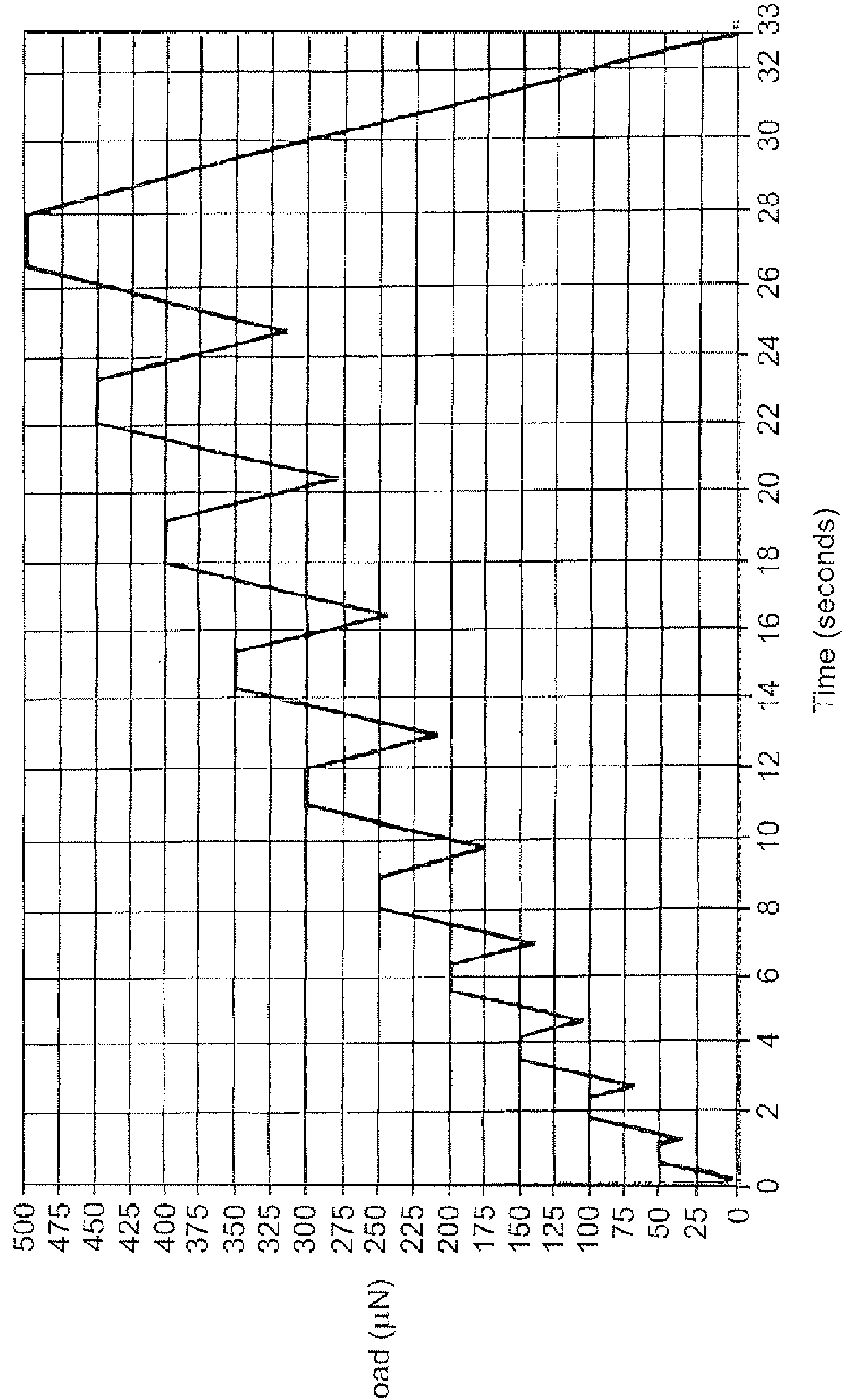
Load (µN)
500
475
450
425
400
375
350
325
300
275
250
225
200
175
150
125
100
75
50
25
0
Time (seconds)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
33

Fig. 8

# NANO-STRUCTURED SURFACE COATING PROCESS, NANO-STRUCTURED COATINGS AND ARTICLES COMPRISING THE COATING

**[0001]** This application is a divisional of commonly owned copending U.S. application Ser. No. 10/557,243, filed on Nov. 16, 2005, which is the national phase application under 35 USC §371 of PCT/NL2004/00329, filed May 13, 2004, and claims the benefit of priority from EP 04075534.0, filed Feb. 20, 2004, ER 04075534.0, filed May 20, 2003, and U.S. Provisional Application Ser. No. 60/471,746, filed May 20, 2003, the entire contents of which is hereby incorporated by reference.

**[0002]** The invention relates to a new process for the preparation of nano-structured and/or nano-porous surfaces, coatings having a nano-structured and/or nano-porous surface and articles comprising said coatings. The invention also relates to the use of said coatings, in particular as anti-reflective coatings, The drive for ever smaller features sizes in surfaces and coatings has been brought about through a desire to achieve attractive properties for applications in, for example micro-electronics, anti-reflective coatings for displays and super-hydrophobic or even self cleaning surfaces. The numerous techniques for preparation of nano-structured surfaces or coatings can be regarded as fitting into one of two classes.

**[0003]** The first class is know as the top down approach and is primarily concerned with the manufacture of progressively smaller and smaller feature sizes in photolithographic processes. Top down lithographic techniques are especially applied where regular and straight features are required as is the case for photo-resists in the microprocessor field. Manufacture of random, irregular structures and structuring via these techniques over large surface areas (d m$^2$ to m$^2$) is extremely difficult, time consuming and therefore expensive.

**[0004]** The second class of nano-structuring techniques can be regarded as so-called bottom up techniques and are usually based on phase separation, which can be achieved in two ways. Firstly, by phase separation of two incompatible polymers (e.g. Polymethylmethacrylate and Polystyrene, Steiner et al., Science, Vol 283, pg 520-522, 1999), during the evaporation of a solvent. After that the nano-structure is formed by removal of one of the polymers by a selective solvent, that dissolves only one of the polymers.

**[0005]** Secondly, phase separation can be induced by crosslinking a mixture of components where at least one component is capable of crosslinking and at least one other is not(Ibn-Elhaj and Schadt, Nature, Vol 410, pg 796-799, 2001). The mixture is homogeneous prior to crosslinking and the phase separation occurs during the formation of the crosslinked network. The nano-structure is formed by removal of the non-crosslinkable component. As phase separation is a dynamic process, the size and distribution of the features formed under both of the above techniques is strongly dependent on the rate or kinetics of the phase separation. Parameters such as temperature and in the case of photoinduced crosslinking the photo-initiator concentration and/or radiation intensity all will affect the feature size of the nano-structured coatings, Therefore processing is complicated and reproducibility is poor. Also the necessary washing to remove one of the components is a sizable hurdle in the commercialisation of such technologies, especially for large surface areas. Thus, there is a need for an simple technique that allows the manufacture of nano-structured coatings.

**[0006]** Surprisingly, a very elegant and simple process has now been found for the preparation of surface nano-structured and/or nano-porous coatings or films. The process according to the invention, which is a process for the preparation of nano-structured and/or nano-porous coatings, comprises the steps of

**[0007]** a) applying a mixture, which mixture comprises

**[0008]** i) reactive nano-particles, having reactive organic groups on their surface

**[0009]** ii) a solvent

**[0010]** iii) optionally a compound having at least one polymerisable group in an amount that is small enough to allow the formation of a nano-structured surface after cure of the formulation,

to a substrate,

**[0011]** b) polymerising the mixture on the substrate.

**[0012]** Surprisingly by simply using no or only a little of the compound having at least one polymerisable group, a coating or a film is obtained with the process of the present invention having a nano-structured surface. Furthermore the coating or film has favourable mechanical properties and adheres well on several substrates. The coating or film has a variety of applications, among which are films or coatings having super hydrophobic properties and especially coatings having anti-reflective properties.

**[0013]** From U.S. Pat. No. 2,601,123 a coating for reducing surface reflections is known for the coating of glass substrates. The coating however must be sintered at very high temperatures, so that it is not suitable for application on polymer substrates. Furthermore it relates to very old and abandoned technology.

**[0014]** It is known from U.S. Pat. No. 5,582,859 that anti-reflective properties may be obtained by preparing a multi-layer system of coatings in which each coating has a carefully selected thickness and refractive index. However, multilayer coatings suffer from two sets of problems. The first is that the anti-reflective performance of multilayer coatings suffers from angle-dependency (D, Chen, Solar Energy Materials & Solar Cells, 86 (2001) 313-336). This means that transmission will vary from the normal to oblique angles. Secondly, reproducible processing of such multilayer coatings with precisely controlled thickness and optical properties is difficult and therefore costly and time-consuming.

**[0015]** Also in U.S. Pat. No. 6,455,103 a similar multi-layer anti-reflective coating is applied, giving the same problems as explained above.

**[0016]** In DE 19746885 Al a process for coating a substrate with a mixture comprising reactive nanoparticles is disclosed. However there is no teaching given how to obtain the surface nano-structured and/or nanoporous coating of the present invention and the anti-reflective properties are poor.

**[0017]** Since the reactive nano-particles in step a) always have more than one reactive group on their surface, the polymerisation in step b results in the formation of a crosslinked phase, comprising the nanoparticles interconnected. Therefore, in this text, the terms polymerise or polymerisation is used interchangeably with cross-linking or cross-linked and polymerisable group is used interchangeably with cross-linking group.

**[0018]** Within the context of the invention the term surface nano-structured coatings refers to coatings having a surface roughness, and in which surface the dimensions of the features on the surface are larger than or equal to the smallest cross-sectional dimension of an individual nano-particle. Preferably the dimensions of the features are smaller than 1200 nm, more preferably smaller than 800 nm, still more preferably smaller than 400 nm, most preferably smaller than 300 nm. There also may be nanosized voids in the coating.

**[0019]** In the framework of this invention the term "nano-particles" is defined as particles of which the majority has a diameter of less than a micrometer. Within the framework of the invention a nano-particle is elongated when the aspect ratio, defined as the length divided by the diameter is greater than unity. The preparation of reactive nano-particles as such is known in the art, and has been described in e.g. U.S. Pat. No. 0,602,5455. In a preferred embodiment of the process according to the invention, all nano-particles are reactive.

**[0020]** The compound having at least one polymerisable group is in this text also referred to as both diluent or reactive diluent. In this text the term hard coat refers to a coating comprising nano-particular species, optionally reactive nano-particular species, in a crosslinked polymeric network, wherein the volume fraction of reactive diluent is such that there are no or at least hardly no void spaces and/or surface nano-structures present in the coating.

**[0021]** For obtaining the nano-structured surface it is important that no or a relatively small amount of the reactive diluent and optional further components is present in the coating obtained with the process according to the invention. If a too high amount of reactive diluent and optional further components is used, the nano particles will be embedded and a coating having a smooth surface and not having any pores will be obtained. Normally the amount of reactive diluent and eventually further components in the final coating (after evaporation of the solvent) as expressed in volume fraction may not exceed 1-(the random close packing volume fraction of the reactive nanoparticles). The skilled person can easily determine the amount of diluent and eventually further additives by varying the amount and measuring the surface roughness or a parameter as for instance the transmission or the reflection of the coating as a function of this amount. Above a certain concentration of reactive diluent (or optionally further additives) the surface roughness of the coating has vanished and no special anti-reflective properties are detected any more.

**[0022]** Furthermore the invention also relates to the mixture for the preparation of nano-structured and/or nano-porous coatings, the coatings or films obtained from the process according to the invention, articles comprising said coatings and the use of said coatings.

Reactive Nano-Particles

**[0023]** In a preferred embodiment, the majority of the nano-particles in the mixture according to the invention have a diameter of less than 400 nm, more preferably the majority of particles have a diameter of less than 50 nm. Most preferably all particles have a diameter of less than 50 nm. In a preferred embodiment, the majority of the nano-particles have a length in the range of 40 to 300 nm. Preferably, the particles used have such a dimensions that they do not (or not significantly) influence the transparency of the eventual coating. Most preferably the increase in haze of a transparent substrate comprising the coating in a thickness of 0.1 micrometer, compared to the substrate not yet comprising the coating is less than 2%, preferably less than 1%, most preferably less than 0.5%.

**[0024]** As will be obvious to anyone skilled in the art, the random packing density of the nanoparticular species is determined by the shape and the relative size and size distribution of the nano-particles. Hence it may be advantageous to use nano-particles of differing shapes and sizes to precisely control the size of the surface nano-structures and/or nano-pores.

**[0025]** In a preferred embodiment, the reactive nano-particles have an aspect ratio greater than 1, more preferably, they have an aspect ratio (length/diameter) greater than 3, still more preferably greater than 5, and most preferably, they have an aspect ratio of greater than 10. If elongated reactive nano-particles are used it is possible to obtain a coating having even further improved anti-reflective properties or to use a higher concentration of reactive diluent, which gives better mechanical properties to the coating. More preferably the nanoparticles are wormlike. Of a wormlike nano particle the primary axis is curved.

**[0026]** Methods for determining the particle dimension include optical or scanning electron microscopy, or atomic force microscopy (AFM) imaging.

**[0027]** For measuring the dimensions of the nano-particles the particles are in a very dilute mixture applied on a surface in a thin layer, so that at a SEM photographic image of the layer, the single nano-particles are observable. Than from 100 nanoparticles, ad random selected, the dimensions are determined and the average value is taken. In case of particles having an aspect ratio above 1, like worm-shaped nano-particles, the total length is determined, from one end to the other end, by following the primary axis as projected in the plane of the photo. For the diameter the longest straight line that can be drawn from one side of the particle to the other side, perpendicular to the primary axis is taken.

**[0028]** In the process according to the invention the coating may comprise either organic or inorganic nano-particles. Examples of organic nano-particles are carbon nano-tubes or nano-spheres. Preferably, the nano-particles are inorganic nano-particles. Suitable inorganic particles are for example oxide particles. Preferred oxide particles are particles of an oxide selected from the group of aluminum oxide, silicum oxide, zirconium oxide, titanium oxide, antimony oxide, zinc oxide, tin oxide, indium oxide, and cerium oxide. It is also possible to use a mixture of particles from different oxides or to use particles of mixed oxides. Most preferably, the nano-particles are particles of aluminum oxide, zirconium oxide or silicum oxide. The refractive index of the coating and effective refractive index of the coating/air interface can in part be tuned by the choice of oxide used.

**[0029]** The nano-particles have reactive organic groups on their surface, Such reactive nano-particles may or may not comprise additional, non-reactive organic groups, Additional non-polymerisable groups may be used to tune the overall polarity and thus the hydrophobicity or hydrophilicity of the particle and the resultant coating. In a preferred embodiment of the process according to the invention, all nano-particles are reactive nanoparticles. The reactive groups of the nano-particles, and if present, the polymerisable groups of the diluent may polymerise in a homopolymerisation reaction or a copolymerisation reaction. In such a case the reactive groups are polymerisable groups, A copolymerisation reaction is possible when in the mixture different groups are present that can polymerize, for example if the groups of the particles and of the reactive diluent are different, or if mixtures of reactive diluent and reactive/or particles are used that comprise such different groups. It is also possible that the reactive groups of the nanoparticles react with a polymer network that is formed by the polymerisation of one or more reactive diluents. Important however, is that the nanoparticles are chemically interconnected in a cross-linked phase.

**[0030]** Preferably the reactive groups of the reactive nanoparticles are polymerisable groups.

**[0031]** The preparation of reactive nano-particles as such is known in the art, and has been described in e.g. U.S. Pat. No. 0,6025,455.

Substrates

**[0032]** A wide variety of substrates may be used as a substrate in the process according to the invention. Suitable substrates are for example flat or curved, rigid or flexible substrates including films of for example polycarbonate, polyester, polyvinyl acetate, polyvinyl pyrollidone, polyvinyl chloride, polyimide, polyethylene naphthalate, polytetrafluoro ethylene, nylon, polynorbornene or amorphous solids, for example glass or crystalline materials, such as for example silicon or gallium arsenide. Metallic substrates may also be used. Preferred substrates for use in display applications are for example glass, palynorbornene, polyethersulfone, polyethyleneterphtalate, polyimide, cellulose triacetate, polycarbonate and polyethylenenaphtalate.

**[0033]** A free-standing single layer anti-reflective film obtainable by a process according to the invention may be obtained by preparing a film or coating on a substrate and subsequently removing the film or coating from the substrate after crosslinking. The removal of the film or coating from the substrate should always take place after the crosslinking.

Application of the Mixture to a Substrate

**[0034]** The mixture may be applied onto the substrate by any process known in the art of wet coating deposition. Examples of suitable processes are spin coating, dip coating, spray coating, flow coating, meniscus coating, capillary coating and roll coating.

**[0035]** Preferably the mixture according to the invention is applied in a single layer. In this case it is possible that the mixture is applied on a further coating, as long as this is not a coating according to the invention.

**[0036]** Typically, the reactive nano-particles are mixed with at least one solvent and, optionally crosslinking initiator and optionally a reactive diluent, to prepare a mixture that is suitable for application to the substrate using the chosen method of application.

Solvent

**[0037]** In principle, a wide variety of solvents may be used. The solvent preferably has the ability to form stable suspensions of the reactive nano-particles in order to facilitate a random close packing arrangement of the reactive nano-particles upon application, i.e. after evaporation of the solvent.

**[0038]** Nano-particles typically are added to the mixture in the form of a suspension. The same solvent as used in the suspension may be used to adjust the mixture so that it has the desired properties, However, other solvents may also be used.

**[0039]** Preferably the solvent used evaporates after applying the mixture onto the substrate. In the process according to the invention, optionally the mixture may after application to the substrate be heated or treated in vacuum to aid evaporation of the solvent.

**[0040]** Examples of solvent that may be suitable are 1,4-dioxane, acetone, acetonitrile, chloroform, chiorophenol, cyclohexane, cyclohexanone, cyclopentanone, dichloromnethane, diethyl acetate, diethyl ketone, dimethyl carbonate, dimethylformamide, dimethylsuiphoxide, ethanol, ethyl acetate, m-cresol, mono- and di-alkyl substituted glycols, N,N-dimethylacetamide, p-chlorophenol, 1,2-propanediol, 1-pentanol, 1-propanot, 2-hexanone, 2-methoxyethanol, 2-methyl-2-propanot, 2-octanone, 2-propanol, 3-pentanone, 4-methyl-2-pentanone, hexafluoroisopropanot, methanol, methyl acetate, methyl acetoacetate, methyl ethyl ketone, methyl propyl ketone, n-methylpyrrolidone-2, n-pentyl acetate, phenol, tetrafluoro-n-propanol, tetrafluoroisopropanol, tetrahydrofuran, toluene, xylene and water. Alcohols, ketones and esters based solvents may also be used, although the solubility of acrylates may become an issue with high molecular weight alcohols. Halogenated solvents (such as dichloromethane and chloroform) and hydrocarbons (such as hexanes and cyclohexene), may also be suitable. Preferably methanol, methyl ethyl keton or isopropanol are used.

**[0041]** Compound having at least one polymerisable group also called "diluent" or "reactive diluent")

**[0042]** In principle, a wide variety of materials are suitable to be used as the reactive diluent. The relative amount of reactive diluent with respect to the relative amount of reactive nano-particles must be so small that it allows formation of a nano-structured surface. A way of determining of a coating has a surface nano-structure and/or nano-pores, is to apply the coating to a transparent substrate, crosslinking, and subsequently measuring the transmission. Preferably the amount of reactive diluent and optional further components in the mixture is that low, that if applied as a coating at one side of a transparent substrate, in a thickness between 100-200nm, there is an increase in transmission of light at at least one wave length between 400 and 800 nm of at least 0.5% relative to the same substrate without the coating. Preferably the increase in transmission is at least 0.75%, more preferably at least 1%; still more preferably at least 1.5%, still more preferably at least 2%, still more preferably at least 2.5%, most preferably at least 3%. The exact amount of reactive diluent depends on the particle size, shape, and size distribution, and can thus not be given exactly. In case of elongated nano particles the amount of diluent may be less than 40 wt %, relative to the total weight of the mixture as applied in step a) of the process according to the invention, however without taking the solvent into account (total weight of solid). Preferably, the amount of diluent is less than 20 wt %. Although it is not necessary to use any diluent, the mechanical properties of the coating will generally be better when at least some diluent is present, e.g., at least 1 wt %, more preferably at least 2 wt. %, still more preferably at least 5 wt. %, most preferably at least 10 wt. %. With respect to this aspect the advantage of the elongated particles and of these especially the wormlike nano particles becomes evident, as it is possible with these particles to apply a relatively high amount of reactive diluent to obtain very favourable mechanical properties and yet still having a well developed nano-structured surface, resulting for example in good antireflective properties.

**[0043]** As mentioned, in principle a wide variety of materials are suitable to be used as the reactive diluent, for example monomers or oligomers having crosslinking groups. Monomers or oligomers having only one crosslinking group per molecule may be used, but preferably in combination with other crosslinking components that do have at least two crosslinking groups. Preferably monomers or oligomers having at least two or more crosslinking groups per molecule are used. It is also possible that the reactive diluent comprises a mixture of compounds that after the induction of crosslinking in step b, together form a crosslinked phase. The mixture may comprise compounds that are by itself crosslinking, such as for example different acrylates or it may comprise compounds that will not crosslink by itself but which form a crosslinked phase in combination with another compound after initiation of the crosslinking reaction, for example copolymerising systems comprising electron rich and electron poor double bonds such as for example maleate/vinyl ether copolymerising systems.

**[0044]** Examples of monomers suitable for use as a reactive diluent and having at least two crosslinking groups per molecule include monomers containing (meth)acryloyl groups such as trimethylolpropane tri(meth)acrylate, pentaerythriol (meth)acrylate, ethylene glycol di(meth)acrylate, tetraethyiene glycoldizmeth/acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,5-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, polybutanediol di(meth)acrylate, tripropyleneglycol di(meth)acrylate, glycerol trifmethacnliate, phosphoric acid mono- and di(meth)acrylates, C7-C20 alkyd di(meth)acrylates, trimethyfolpropanetrioxyethyl (meth)acrylate, tris(2-hydroxyethyl)isocyanurate tri(meth)acrylate, tris(2-hydroxyethyl)isocyanurate di(meth)acrylate, pentaerythritot tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol monohydroxy pentacrylate, dipentaerythritol hexacrylate, tricyclodecane diyl dimethyl di(meth)acrylate and alkoxylated versions, preferably ethoxylated and/or propoxylated, of any of the preceding monomers, and also di(meth)acrylate of a diol which is an ethylene oxide or propylene oxide adduct to bisphenol A, di(meth)acrylate of a diol which is an ethylene oxide or propylene oxide adduct to hydrogenated bisphenot A, epoxy (meth)acrylate which is a (meth)acrylate adduct to bisphenol A of diglycidyl ether, diacrylate of polyoxyalkyiated bisphenol A, and triethylene glycol divinyl ether, adduct of hydroxyethyl acrylate, isophorone diisocyanate and hydroxyethy) acrylate (HIH), adduct of hydroxyethyl acrytate, toluene diisocyanate and hydroxyathyl acrylate (HTH), and amide ester acrylate.

**[0045]** Examples of suitable monomers having only one crosslinking group per molecule include monomers containing a vinyl group, such as N-vinyl pyrrolidone, N-vinyl caprolactam, vinyl imidazole, vinyl pyridine; isobornyl (meth)acrylate, bornyl (meth)acrylate, tricyclodecanyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, cyclohexyl (meth)acrylate, benzyl (meth)acrylate, 4-butylcyclohexyl (meth)acrylate, acryloyl morpholine, (meth)acrytic acid, 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)arylate, 2-hydroxybutyl (methiacrylate, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, isopropyl (meth)acrylate, butyl (meth) acrylate, amyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, pentyl (meth)acrylate, caprolactone acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, heptyl (meth)acrylate, octyl (meth)acrylate, isooctyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, isodecyl (meth)acrylate, tridecyl (meth)acrylate, undecyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, butoxyethyl (meth)acrylate, ethoxydiethylene glycol (meth)acrylate, benzyl (meth)acrylate, phenoxyethyl (meth)acryate, polyethylene glycol mono (meth)acrylate, polypropylene glycol mono(meth)acrylate, methoxyethylene glycol (meth)acrylate, ethoxyethyl (meth) acrylate, methoxypolyethylene glycol (meth)acrylate, methoxypolypropylene glycol (meth)acryiate, diacetone (meth) acrylamide, beta-carboxyethyl (meth)acrylate, phthalic acid (meth)acrylate, isobutoxymethyl (meth)acrylamide, N,N-dimethyl (meth)acrylamide, t-octyl (meth)acrylamide, dimethylaminoethyl (meth acrylate, diethylaminoethyl (meth) acrylate, butylcarbamylethyl (meth)acrylate, n-isopropyl (meth)acrylamide fluorinated (meth)acrylate, 7-amino-3,7-dimethyloctyl (methacrylate, N,N-diethyl (meth)acrylamide, N, N-dimethylaminopropyl (meth)acrylamide, hydroxybutyl vinyl ether, lauryl vinyl ether, cetyl vinyl ether, 2-ethylhexyl vinyl ether; and compounds represented by the following formula (I)

$$CH_2{=}C(R^6){-}COO(R^7O)_m{-}R^8 \qquad \text{Formula I}$$

wherein $R^6$ is a hydrogen atom or a methyl group; $R^7$ is an alkylene group containing 2 to 8, preferably 2 to 5 carbon atoms; and m is an integer from 0 to 12, and preferably from 1 to 8; $R^8$ is a hydrogen atom or an alkyl group containing 1 to 12, preferably 1 to 9, carbon atoms; or, RB is a tetrahydrofuran group-comprising alkyl group with 4-20 carbon atoms, optionally substituted with alkyl groups with 1-2 carbon atoms; or $R^8$ is a dioxane group-comprising alkyl group with 4-20 carbon atoms, optionally substituted with methyl groups; or $R^8$ is an aromatic group, optionally substituted with $C_1$-$C_{12}$ alkyl group, preferably a $C_8$-$C_9$ alkyl group, and alkoxylated aliphatic monofunctional monomers, such as ethoxylated isodecyl (meth)acrylate, ethoxylated lauryl (meth)acrylate, and the like.

**[0046]** Oligomers suitable for use as the reactive diluent are for example aromatic or aliphatic urethane acylates or oligomers based on phenolic resins (ex. bisphenol epoxy diacrylates), and any of the above oligomers chain extended with ethoxylates. Urethane oligomers may for example be based on a polyol backbone, for example polyether polyols, polyester polyols, polycarbonate polyols, polycaprolactone polyols, acrylic polyols, and the like. These polyols may be used either individually or in combinations of two or more. There are no specific limitations to the manner of polymerization of the structural units in these polyols. Any of random polymerization, block polymerization, or graft polymerization is acceptable. Examples of suitable polyols, polyisocyanates and hydroxyl group-containing (meth)acrylates for the formation of urethane oligomers are disclosed in WO 00/18696, which is incorporated herein by reference.

**[0047]** Combinations of compounds that together may result in the formation of a crosslinked phase and thus that in combination are suitable to be used as the reactive diluent are for example carboxylic acids and/or carboxylic anhydrides combined with epoxies, acids combined with hydroxy compounds, especially 2-hydroxyalkylamides, amines combined with isocyanates, for example blocked isocyanate, uretdion or carbodilmide, epoxies combined with amines or with dicyandiamides, hydrazinamides combined with isocyanates, hydroxy compounds combined with isocyanates, for example blocked isocyanate, uretdion or carbodiimide, hydroxy compounds combined with anhydrides, hydroxy compounds combined with (etheritied) methylolamide ("amino-resins"), thiols combined with isocyanates, thiols combined with acrylates or other vinylic species (optionally radical initiated), acetoacetate combined with acrylates, and when cationic crosslinking is used epoxy compounds with epoxy or hydroxy compounds.

**[0048]** Further possible compounds that may be used as the reactive diluent are moisture curable isocyanates, alkoxy titanates, alkoxy zirconates, or urea-, urea/melamine-, melamine-formaldehyde or phenol-formaaldehyde (resol, novolac types), or radical curable (peroxide- or photo-initiated) ethylenically unsaturated mono- and polyfunctional monomers and polymers, e.g. acrylates, methacrylates, maleatelvinyl ether), or radical curable (peroxide- or photo-initiated) unsaturated e.g. maleic or fumaric, polyesters in styrene and/or in methacrylates.

Method for Crosslinking or Polymensation

**[0049]** Any cross-linking method that may cause the mixture to crosslink so that a coating is formed is suitable to be used in the process according to the invention, Suitable ways to initiate crosslinking are for example electron beam radiation, electromagnetic radiation (UV, Visible and Near IR), thermally and by adding moisture, in case moisture curable compounds are used. In a preferred embodiment crosslinking is achieved by UV-radiation. The UV-crosslinking may take place through a free radical mechanism or by a cationic mechanism, or a combination thereof. In another preferred embodiment the crosslinking is achieved thermally.

Initiator

**[0050]** An initiator may be present in the mixture to initiate the crosslinking reaction. The amount of initiator may vary between wide ranges. A suitable amount of initiator is for example between above 0 and 5 wt % with respect to total weight of the compounds that take part in the crosslinking reaction.

**[0051]** When UV-crosslinking is used to initiate crosslinking, the mixture preferably comprises a UV-photo-initiator. A photo-initiator is capable of initiating a crosslinking reaction upon absorption of light, thus, UV-photo-initiators absorb light in the Ultra-Violet region of the spectrum. Any known UV-photo-initiators may be used in the process according to the invention.

**[0052]** The coating according to the invention can be prepared in any desired thickness. The coatings according to the invention typically have a thickness ranging between 50 nm to several micrometer. In case of application as an anti-reflective coating the thickness is preferably between 50 and 200 nm, more preferably between 100 and 150 nm.

**[0053]** In a preferred embodiment, the nano-structured and/or nano-porous films or coatings according to the invention increases the optical transmission of a substrate on which they are present for at least a range of visible wavelengths of the electromagnetic spectrum. Therefore the coating shows a reflection of light, at at least one wavelength in the area between 400-800 nm, measured under normal incidence of less than 3%, preferably less than 2%, more preferably less than 1.5%, most preferably less than 1%, per coated side of the substrate in a coating layer thickness between 100-200 nm.

**[0054]** The combination of good mechanical properties as well as anti-reflective performance will allow for the use of these single layer anti-reflective hard-coats in applications were mechanical durability and anti-reflective performance on flat or on non-flat substrates are advantageous. These applications include anti-reflective coatings for automobile and airplane wind screens, displays in general, television tubes, flexible displays and lenses, for example in spectacles. It is possible that the anti-reflective coating is applied to the substrate as a single coating. It is also possible that before the application of the anti-reflection coating, the substrate is coated with a further coating, for example to improve the adhesion between the anti-reflective coating and the substrate. At least an advantage of the anti-reflective coating of the present invention is, that the coating, bringing the anti-reflective properties only needs to be applied in a single layer.

**[0055]** In yet a further embodiment the surface nano-structured and/nano-porous coating according to the invention can be used to affect the wetting properties of the coating.

**[0056]** Generally, a hydrophobic material or coating is characterised by a static contact angle of water of 90° or above.

**[0057]** Hydrophobic polymeric materials such -as poly(tetrafluorethene) (PTFE) or polypropylene (PP) have been available for decades. These materials suffer from a limited hydrophobicity, as well as inferior mechanical properties as compared to engineering materials or highly crosslinked coatings. For instance, PP has a static contact angle of water of roughly 100° whereas PTFE, which is amongst the most hydrophobic polymeric material known, has a static contact angle of water of roughly 112°.

**[0058]** Some hydrophobic coatings are being referred to in the art as superhydrophobic coatings. Superhydrophobic coatings are generally defined by a static water contact angle above 1400 (Nun, Oles & Schleich, Macromole Symp. 187 (2002) 677-682).

**[0059]** Within the framework of the invention, a combination of surface toughness, due to surface nano-structures and/or nano-pores, together with polar surface chemistry achieves static water contact angles below 60°, preferably below 40°. Conversely, the coating may also be affected so that the static water contact angle is above 90° and preferably 120° if the surface chemistry of the nano-structured and/nano-porous coating is apolar, for example via the presence of apolar surface modifying groups on the nano-particles.

**[0060]** Combining the wetting properties with the anti-reflection properties, the surface nano-structured and/or nano-porous films or coatings according to the invention increases the optical transmission of a substrate on which they are present to visible wavelengths of the electromagnetic spectrum while simultaneously exhibiting a static water contact angle of above 90°, preferably 120° and most preferably 140°.

**[0061]** Furthermore due to the surface nano-structures and/or nano pores other properties such as low refractive index, low optical dissipation (low optical loss), low dielectric constant, high relative surface area, low contact area, low adhesion and coating porosity are envisaged. Applications derived from the above properties include the following: anti-reflective coatings for all kinds of display applications, for biological devices and coatings with improved wetting characteristics; easy to clean and self-cleaning coatings; easy to clean and self-cleaning anti-reflective coatings; non-stick coatings, low dielectric coatings for semi-conductors, low dissipation (low optical loss) coatings for optical wave guides; controlled release coatings, hard membranes, biologically active surfaces, anti-fouling and anti-bacterial coatings.

**[0062]** When it is desirable to have patterned coatings, for example, alternating hydrophobic and hydrophilic regions, this can also be achieved by the process according to the invention, by using photolithographic processes. Hence, applications where patterning of nano-structured and/or nano-porous coatings is desired may also result. This could lead to coatings and articles where the optical or wetting properties are patterned as desired.

**[0063]** In a preferred embodiment the mixture according to the invention comprises an adhesion promoter. An adhesion promoter enhances the adhesion between the coating of the present invention and its substrate. In this way the scratch resistance of the coating is also improved.

**[0064]** The skilled artisan knows how to select a suitable adhesion promoter for given groups at the surface of the reactive nano-particles, reactive diluent and substrate.

**[0065]** Examples of suitable adhesion promoters are compounds having at least one reactive group capable of reacting with the groups at the surface of the reactive nano particles and/or with the reactive diluent and further have at least one reactive group capable of reacting or physically interacting, e.g. H bonding with the substrate.

**[0066]** For glass substrates adhesion promoters can include but are not limited to acrylate, methacrylate or thion functional trialkoxy silanes, where the trialkoxy groups of the silane can be propoxy or butoxy but is preferably ethoxy or methoxy. Examples of silane adhesion promoters include: γ-mercaptopropylmethyimonomethoxysilane, γ-mercaptopropylmethyldimethoxysilane, γ-mercaptopropyltrimethoxysilane, γ-mercaptopropylmonoethoxysifane, γ-mercaptopropyldiethoxysilane, γ-mercaptopropyltriethoxysilane, β-mercaptoethylmonoethoxysilane, β-mercaptoethyltdethoxysilane, β-mercaptoethyltriethoxysilane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, γ-aminopropyltriethoxysilane, γ-glycidoxylpropyltrimethoxysilane, γ-glycidoxyl propylmethyidimethoxysiiane, 2-(3,4-epoxycyclohexyl) ethyltrimethoxysilane, γ-chloropropylmethyldimethoxysilane, γ-chloropropyltrimethoxysilane, and γ-methacryloyloxypropyltrlmethoxysilane, Examples of commercially available products of these compounds include SILAACE S310, S311, S320, S321, S330, S510, S520, S530, S610, S620, S710, S810 (manufactured by Chisso Corp.), Siiquest A-174NT (manufactured by OSI Specialties—Crompton Corp.). SH6062, AY43-062, SH6020, SZ6023, S76030, SH6040, SH6076, SZ6083 (manufactured by Toray-Dow Corning Silicone Co., Ltd.), KBM403, KBM503, KBM602, KBM603, KBM803, KBE903 (manufactured by Shin-Etsu Silicone Co., Ltd.), and the like. Also acidic adhesion promoters such as acrylic acid may be used. Phosphate esters such as Eb168 or Eb170 from UCB are feasible adhesion promoters.

**[0067]** For adhesion to polymeric substrates such as, for example polyethylene terephthalate (PET) and or cellulose triacetate(TAC) the above adhesion promoters may be feasible but also good results are obtained with epoxy functional acrylate or methacrylate compounds.

**[0068]** Surprisingly, it has been found that for substrates containing vinylic unsaturation, for example acryiate or methacrylate based substrates, like a crosslinked coating, for example a hard coat, compounds comprising at least one thiol group are very suitable as adhesion promoters. Such thiol compounds may be mono-functional, di-functional, preferably tri-functional and most preferably tetra-functional with respect to the number of thiol groups per molecular species. The thiol compounds may comprise next to the thiol group a further reactive group. In case the thiol compound comprises only one thiol group, it must comprise at least one further reactive group. Examples of thiol compounds may be any of those known in the art. A description of the most common thiol compounds may be found at column 9, lines 1-41 of U.S. Pat. No. 3,661,744, which is incorporated herein by reference. Certain polythiols such as the aliphatic monomeric polythiols e.g. othane dithiol, hexamethylene dithiol, decamethylene dithiol, tolylene-2,4-dithioi, and the like, and some polymeric polythiols such as a thiolterminated ethytcyclohexyl dimercaptan polymer, and the like, and similar polythiols which are conveniently and ordinarily synthesized on a commercial basis are suitable. Examples of the polythiol compounds preferred because of relatively low odor level include but are not limited to esters of thioglycolic acid ($HS—CH_2COOH$), α-mercaptopropionic acid ($HS—CH(CH_3)—COOH$ and β-mercaptopropionic acid ($HS—CH_2CH_2COOH$) with polyhydroxy compounds such as glycols, triols, tetraols, pentaols, hexaols, and the like. Specific examples of the preferred polythiols include but are not limited to ethylene glycol bis(thibglycolate), ethylene glycol bis (β-mercaptopropionate), trimethylolpropane tris(thioglycolate), trimethyloipropane tris (β-mercaptopropionate), pentaerythritol tetrakis (β-mercaptopropionate), ail of which are commercially available. A specific example of a preferred polymeric polythiol is polypropylene ether glycol bis(β-mercaptopropionate) which is prepared from polypropylene-ether glycol (e.g. Pluracol P201, Wyandotte Chemical Corp.) and β-mercaptopropionic acid by esterlication. Poly-α-mercaptoacetate or poly-β-mercaptopropionate esters, particularly the trimethylopropane triesters or pentaerythritol tetra esters are preferred, Other polythiols which can be suitably employed include alkyl thiol functional compounds such as 1,2-dimercapthoethane, 1,6-dimercaptohexane and the like. Thiol terminated polysulfide resins may also be employed.

**[0069]** Suitable examples of aliphatic dithiols include 1,2-ethanedithiol, butanedithiol, 1,3-propanedithiol, 1,5-pentanedithiol, 2,3-dimercapto-1-propanol, dithioerythritol, 3,6-dioxa-1,8-octanedithiol, 1,8-octanedithiol hexanedithiol, dithiodiglycol, pentanedithiol, decanedithiol, 2-methyl 1,4 butanedithiol, bis-mercaptoethylphenyl methane, 1,9-nonanedithio (1,9-dimercaptononane), glycol dimercaptoacetate.

**[0070]** Suitable examples of aromatic dithiols include 1,2-benzenedithiol, 1,3-benzenedithiol, 1,4-benzenedithiol, 2,4,6-trimethyl-1,3-benzenedimethanethiol, durene-α1, α2-dithiol, 3,4-dimercaptotoluene, 4-methyl-1,2-benzenedithiol, 2,5-dimercapto-1,3,4-thiadiazole, 4,4'-thiobisbezenedithiol, bis(4-mercaptophenyl)-2,2'-propane(bisphenol dithiol) (made according to the method of Meng Y. Z., Hay. A. S., J. of App. Polym. Sci., V74, 3069-3077(1999).

**[0071]** Suitable examples of oligomeric dithiols include difunctional mercapto functional urethane oligomers derived from end capping moieties of hydroxyethyl mercaptan, hydroxypropyl mercaptan, dimercaptopropane, dimercapto ethane as described in patent by Shustack U.S. Pat. No. 5,744,514.

**[0072]** Examples of suitable trithiol functional compounds include, trimethylolethane tris-mercaptopropionate, trimethylolpropane tris-mercaptopropionate (TMPTSH), trimethylolethane tris-mercaptoacetate, and trimethylolpropane tris-mercaptoaacetate glycerol tri(11-mercaptoundecanoate), trimethyloi propane tri (11-mercaptoundecate). A preferred trithiol is trimethylolpropane tris(2-mercapto-propionate) TMPTSH.

**[0073]** Examples of suitable tetrafunctional thiols include pentaerythritol tetramercapto propionate, pentaerythritol tetramercapto acetate, and pentathritoltetra(11-mercaptoundecate)

**[0074]** Examples of multifunctional thiols having functionality greater than 4, include polythiols as described on page 7 of WO 88102902.

**[0075]** Multi functional thiols can be obtained by reacting thioalkyl carboxylic acids e.g. thioglycolic acid, mercapto propionic acid with high functional alcohols, mines and thiols. Furthermore, multifunctional thiols can be obtained by reacting mercapto alkyl trialkoxy silanes with silanois that may be polymeric or silica based sifanols.

**[0076]** Other preferred multifunctional thiols are obtained using thiol carboxylic acids (HS—R—COOH) where R=alkyl, or aryl groups eg thioundecanoic acid of which the COOH groups are reacted with reactive enes, alcohols, thiols or amines that are multifunctional.

**[0077]** The adhesion promoters may be used in an amount of 0.1-10 wt-% of the total solids in the mixture, after evaporation of the solvent. Preferably the adhesion promoter is used in an amount of 5-10 wt-%.

**[0078]** A further improvement of the scratch resistance is obtained if the mixture according to the invention comprises a compound having a surface energy of less than 25 mili Joules per square meter ($mJ/m^2$). The surface energy is preferably measured of the pure compound according to ASTM D2578, preferably using a ACCU DYNE TEST™ marker pen, An example of such compounds are reactive polydimetylsiloxane compounds. Preferred are reactive fluoro compounds. Reactive fluoro compounds are for example described in U.S. Pat. No. 6,391,459. The fluoro compounds further have the advantage that they don't disturb the antireflective properties very much.

**[0079]** In a further improved embodiment the substrate is in a first step coated with a first coating, preferably a highly crosslinked coating or a hard coat, and in a second step the mixture according to the present invention is applied on top of the first coating. In this way the first coating acts as the substrate for the mixture of the present invention. In this case the first coating preferably comprises vinylic unsaturations and thiol compounds are preferably used as adhesion promoters. In this way a still better scratch resistance of the coating of the present invention is obtained.

**[0080]** Suitable examples for the first coating are the coatings described in EP-A-1276810.

**[0081]** Preferably in the first step of application of the first coating, the first coating is partly cured at least at the surface, in case that in the hard coat, a radical curing resin system is used, like for example an acrylate based resin system, partly surface curing is preferably obtained by curing in the presence of oxygen, for example curing in an air atmosphere. In this way a still further improved adhesion between the hard coating and the antireflective coating is obtained, resulting in a still further improvement of the scratch resistance of the coating according to the present invention.

**[0082]** The scratch resistance can be still further improved by thermally treating the first coating and the coating according to the invention, by for example Infra red lamps or thermal ovens. Good results are obtained if the coating according to the invention and preferably also the first coating comprise a thermal initiator for subsequent cross-linking during thermal post-treatment, especially if the cure of hard coat and nano-structured coatings has been induced photo-chemically. The skilled artisan knows how to select such a thermal initiator.

**[0083]** It is also possible to produce a film out of the composition according to the invention, and to use the film as a membrane.

**[0084]** It is also possible to use the coating according to the invention in a process of reverse sorption of at least one non-cross-linkable species.

## EXAMPLES

Nano-Silicate Particles.

**[0085]** Nano-silicate particles MT-ST (spherical particles) and IPA-ST-UP (elongated particles) were obtained from Nissan Chemical American Corporation. These particles were used in illustration of the invention. Their properties and properties of their supensions are listed in table 1 below,

TABLE 1

Types and properties of nano-silica particles.

| Nano-particle | Particle Size (nm) | $SiO_2$ (wt %) | $H_2O$ (%) | Viscosity (mPa · s.) | Specific Gravity | pH | Particle Shape | Solvent |
|---|---|---|---|---|---|---|---|---|
| MT-ST | 10-15 | 30-31 | <2.0 | <5 | 0.98-1.02 | 2-4 | Spherical | Methanol |
| IPA-ST-UP | 9-15 Elongated* | 15-16 | <1.0 | <20 | 0.85-0.90 | 2-4 | Elongated* | Isopropanol |

*Elongated particles have a diameter of 9-15 nm with a length of 40-300 nm. (Information source www.s-nowtex.com).

A. Grafting of Spherical or Elongated Silica Nano-Particles:

**[0086]** Reactive organic groups were grafted onto the silica nano-oxide particles by adding a trimethoxy-silane compound comprising an acrylate group (e.g., a compound according to formula II) together with p-mehoxy-phenol, a compound that inhibits polymerization of the acrylate groups, to a suspension of the oxide particles in methyl ethyl ketone. Table 2 shows the exact amounts of chemicals used. After stirring, a catalytic amount of water was added to the mixture and the mixture was refluxed at 80° C. for at least 3 hours. Subsequently as a dehydrating agent trimethyl orthotormate was added to remove any traces of water, and the resultant mixture stirred at 60° C. for at least one hour. Another method for preparing the grafted particles was to add a methoxy-silane compound comprising an acrylate group together with p-methoxy-phenol, to a suspension of the oxide particles in methanol. After stirring, the mixture was refluxed at 60° C. for at least 1.5 hours for MT-ST nano-silicates particles or at least 3 hours for IPA-ST-UP nano-silicate particles, and subsequently a trialkoxy silane compound, was added. As subsequent trialkoxy silane methyl trimethoxy silane, or in case hydrophobic apolar surface characteristics are required a peefluoroalkyl trialkoxy siane was used. After refluxing for at least one more hour at 60° C., a dehydrating agent was added and the resultant mixture was stirred at 60° C. for at least one hour,

B: Preparation of a Coating or Film on a Substrate

**[0087]** Thin films of various mixtures were prepared on microscope glass slides or polyethyleneteraphthalate (PET) films (for transmission measurements) and/or silicon wafers (for measurements of wetting properties and thickness determination) by the following procedure.

**[0088]** A drop of a mixture (see table 3 and 4 for the mixtures) was applied to the substrate by spin-coating at a rate of 4800 r.p.m. Thin films (100-200nm) were spin coated from mixtures containing less than 10 wt-% solids white thicker (1-5 μm) coatings were spin coated from formulations with ca 35-50 wt-% solids, see table 3, 4 and 5. The resultant wet film was crosslinked with UV radiation using a D-bulb under nitrogen at a dose of 1.7 J/cm2. The thickness of the crosslinked transparent coating was measured with a multi-spectral reflectometer (F20, AG Electro Optics), Samples for contact angle determination were post baked (i.e heated) for 1 hour at 70° C., prior to contact angle determination.

C: Optical Properties of Surface Nano-Structured and/or Nano-Porous Coatings

**[0089]** Nano-structured and/or nano-porous films or coatings were prepared as described under "B. Preparation of a coating on a substrate", on one side or both sides of either glass microscope slides or polyethyleneteraphthalate (PET) films from various formulations as listed in Table 3, 4 and 5. Spectral transmission in the visible region of the spectrum was measured with a Perkin-Elmer Lambda-20 UV-Vis spectrometer.

D: Measurement of Water Contact Angle

**[0090]** Static contact angles were measured using a FTA (First Ten Angstroms) 200 apparatus. This piece of equipment consisted of a motorised syringe pump, a sample stage and a video camera. The software used with the system was PTA Video drop shape analysis version 1.98 Build B.

**[0091]** Before the measurements were carried out the surface tension of the water in the syringe was measured. This was done by dispensing a droplet from the syringe, and then recording an image whilst the droplet was still attached to the syringe. The droplet was lit from behind, so it appeared black on a white background. The software measured the dimensions of the droplet and used them to calculate the surface tension.

**[0092]** The static contact angle of a coating was measured by dispensing a 12Al droplet of distilled water onto the surface of a coated substrate. 65 images of the droplet were taken over a 130 second period. From the images the software determined the baseline (the surface) and the edges of the droplet, the contact angle was calculated where these lines intercept. The contact angles were determined for at least two droplets on different areas of the surface, the average of these measurements was quoted as the contact angle. Results of static contact angles for various coatings are given in table 6. Contact angle measurements were carried out either directly or after post-baking (t=0) or 2.5 days after post-baking (t=2.5 days). The values in table 6 are the contact angles 100 seconds after the drop had been deposited onto the surface of the samples of various ages.

E. Measurement of Hardness and Reduced Modulus of Coatings

**[0093]** To determine the hardness and reduced modulus of the spincoated coatings, three coatings were prepared as described above in B. The hardness measurements were performed with a Hysitron TriboScope, using a calibrated Berkovich diamond tip as indenter. The tip was inserted into the coatings with a known load, and the penetration depth in the coating was recorded. A typical load function used is shown in FIG. **8**, this results in a graph of force versus displacement. The hardness was calculated via the relationship $H$ (in GPa) $=F_{max}/24.5\ d^2$, where $F_{max}$ is the highest load applied and $d$ is the penetration depth, The reduced modulus was calculated from the force—displacement curve using $E_r=0.5\ (\pi/24.5\ d^2)^{1/2}\ (\delta F/\delta d)$. More details concerning nano-indentation experiments may be found in F. J. Balta Calleja & S. Fakirov, Microhardness of Polymer, Cambridge Un. Press, 2000.

**[0094]** It should be noted the results from nano-indentation with respect to hardness and reduced modulus are dependant on the geometry of the tip of the indenter used. Therefore, direct comparison can only be made by using an experimental set up with a tip of similar geometry.

TABLE 2

| | Compounds in weight percentage used for acrylation and surface modification of silica nano particles | | |
|---|---|---|---|
| Material | Modified nano-parficle A (Acry-MT-ST) | Modified nano-particle B (Acry-IPA-ST-UP) | Modified nano-particle C (Acry-F-MT-ST) |
| MT-ST nano-silica<br>Particle size 10-15 nm | 24.75 wt-% | | 23.81 wt-% |
| IPA-ST-UP elongate nano-silica<br>Particle diameter 9-15 nm<br>Particle length 40-300 nm | | 13.85 wt-% | |
| Int-12A (coupling agent)<br>(See formula II) | 7.84 wt-% | 4.55 wt-% | 7.71 wt-% |
| Hydroquinnone mono-methylether<br>(HQMME polymerization inhibitor) | 0.14 wt-% | 0.87 wt-% | 0.14 wt-% |

TABLE 2-continued

Compounds in weight percentage used for acrylation and surface modification of silica nano particles

| Material | Modified nano-parficle A (Acry-MT-ST) | Modified nano-particle B (Acry-IPA-ST-UP) | Modified nano-particle C (Acry-F-MT-ST) |
|---|---|---|---|
| Methyltrimethoxysilane (MTMS surface derivatisation agent) | 1.23% wt-% | 0.72 wt-% | |
| 1H,1H,2H,2H-(Perfluorooctyl)triethoxysilane (apolar surface derivatisation agent) | | | 4.63 wt-% |
| Methanol (solvent) | 57.75 wt-% | | 55.54 |
| isopropanol (solvent) | | 75.31 wt-% | |
| Trimethyl orthoformate OFM (dehydrating agent) | 8.29 wt-% | 4.70 wt-% | 8.17 wt-% |
| Total | 100 wt-% | 100 wt-% | 100 wt-% |

TABLE 3

Formulations for examples and comparative experiments.

| | Comparative experiment 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 |
|---|---|---|---|---|---|---|
| Material | mg | mg | mg | mg | mg | mg |
| Modified nano-particle A (Acry-MT-ST) (without solvent) | 41.5 | 30.5 | — | — | — | — |
| Modified nano-particle C (Acry-F-MT-ST) (without solvent) | — | — | 84.0 | 1556.2 | — | 236.1 |
| Modified nano-particle B (Acry-IPA-ST-UP) (without solvent) | — | — | — | — | 23.52 | — |
| Dipentaerythritol pentaacrylate (reactive diluent) | 22.1 | — | — | — | | — |
| Ethoxylated (9) trimethylolpropane triacrylate (reactive diluent) | 14.6 | — | — | — | | — |
| Methanol (solvent) | 1379.4 | 1016 | 1588.9 | 2621.7 | 460.75 | 498.9 |
| Isopropanol (solvent) | — | — | — | — | 99.57 | — |
| Photoinitiator (Irgacure184 trademark by Ciba) | 0.39 | 0.31 | 0.21 | 3.9 | 0.15 | 10 |
| 1H,1H,6H,6H-Perfluoro-1,6-hexyl diacrylate. (reactive diluent) | — | — | — | — | — | 248 |

TABLE 4

Formulations for examples and and values for transmission, effect of increasing amount of reactive diluent on anti-reflective properties.

| wt-% Dipentaerythritol pentaacrylate w.r.t total weight of modified particle B and diluent | Example 7 (0%) | Example 8 (2.7%) | Example 9 (5.8%) | Example 10 (11.2%) | Example 11 (15.6%) |
|---|---|---|---|---|---|
| Material | Mg | mg | mg | mg | mg |
| Modified nano particle B (Acry-IPA-ST-UP) | 21.7 | 22.1 | 28.0 | 26.5 | 23.3 |

TABLE 4-continued

Formulations for examples and and values for transmission, effect of increasing amount of reactive diluent on anti-reflective properties.

| wt-% Dipentaerythritol pentaacrylate w.r.t total weight of modified particle B and diluent | Example 7 (0%) | Example 8 (2.7%) | Example 9 (5.8%) | Example 10 (11.2%) | Example 11 (15.6%) |
|---|---|---|---|---|---|
| Dipentaerythritol pentaacrylate (reactive diluent) | 0 | 0.62 | 1.72 | 3.36 | 4.29 |
| Methanol (solvent) | 531.0 | 530.9 | 680.2 | 639.8 | 561.8 |
| Isopropanol (solvent) | 92.0 | 94.7 | 118.6 | 112.2 | 98.4 |
| Photo initiator (Irgacure 184 trademark by Ciba) | 0.13 | 0.14 | 0.19 | 0.18 | 0.16 |
| Maximum Transmission (%) | 97.40 | 97.40 | 97.25 | 97.20 | 96.80 |

**[0095]** The data from table 4, examples 7-11 show the effect of increasing amount (wt-%) of reactive diluent (Dipentaerythritol pentaacrylate) on the anti-reflective properties of surface nano-structured and nano-porous coating comprising elongated acrylated nano-particles (modified particle B (Acry-IPA-ST-UP)). It can be seen that increasing the relative weight percentage of reactive diluent with respect to nano-particles reduces the anti-reflective performance of the coatings as the maximum percentage of transmission decreases.

**[0096]** Transmission spectra from this series of examples can be found in FIG. **7**. If the relative amount of reactive diluent is increased to the point that all nanoparticles are embedded, a non surface nano-structured and/or nano-porous coating will result. Such coatings will display no or extremely little anti-reflective performance. This can be seen illustrated by the comparative experiment, a conventional hard coat sample (thickness 100-200 nm) the transmission spectra of which can be seen as spectrum 4 in FIG. **3**. Here there is almost no improvement in the maximum transmission (95%) and in hence anti-reflective performance with respect to the transmission of the glass microscope slide substrate, spectrum 5 in FIG. **7** (94.8%).

TABLE 5

Influence photo initiator concentration on Anti-reflective properties

| % Irgacure184 w.r.t modified particle B | Example 12 (0.10%) | Example 13 (0.51%) | Example 14 (0.93%) | Example 15 (2.09%) |
|---|---|---|---|---|
| Material | mg | Mg | mg | mg |
| Modified nano particle B (Acry-IPA-ST-UP) | 27.4 | 28.7 | 35.2 | 23.5 |
| Methanol (solvent) | 664.1 | 672.5 | 855.8 | 570.6 |
| Isopropanol (solvent) | 119.5 | 139.8 | 150.0 | 100.0 |
| Photo initiator (Irgacure 184 trademark by Ciba) | 0.026 | 0.148 | 0.327 | 0.490 |
| Transmission Maximum | 97.2 | 97.2 | 97.3 | 97.2 |

**[0097]** As is shown in the results of table 5, there is no influence on the anti-reflective properties by the coatings according to the invention of the concentration of the photo initiator system. This is very favourable, and it shows the robustness of the process and the coatings according to our invention, while known systems suffer with respect to this aspect.

TABLE 6

Contact angles of various hydrophobic and hydrophilic nano-structured and/or nano-porous coatings.

| Formulation | Rmax | Contact angle t = 0 days | Contact angle t = 2.5 days |
|---|---|---|---|
| comp. exp.(Hard coat) | 6 nm | | 62.1° |
| Example 2 (Acry-MT-ST) | 119 nm | | 50.3° |
| Example 3 (Acry-F-MT-ST) (thickness 100-200 nm) | 133.5 nm | 97.3° | 120.7° |
| Example 4 (Acry-F-MT-ST) (thickness 1-5 μm) | 65.5 nm | 95.9° | 114.1° |
| Example 5 (Acry-IPA-ST-UP) | 108 nm | | 28.2° |
| Example 6 (Example 3 + Fluorodiacrylate) | 27 nm | | 108.5° |

**[0098]** The static water contact angle of Example 1 as shown in Table 6 is typical that of a polar acrylate hard coating. If the surface is surface nano-structured and/or nano-porous, the static water contact angle drops significantly. This is the case for Example 2 (Acry-MT-ST) where the value of the contact angle was 50.3° and for Example 5 (Acry-IPA-ST-UP) where the value is 28.2°. Similarly, the static water contact angle of Example 6, a coating of a formulation comprising hydrophobically modified reactive nano-particles (Acry-F-MT-ST) with hydrophobic reactive diluents (Fluorodiacrylate), was 108.5° and its roughness was relatively low, 27 nm. In the case of Example 4 (Acry-F-MT-ST) (thickness 1-5 μm) and 3 (Acry-F-MT-ST) (thickness 100-200 nm) the value of the roughness increased and therefore the static contact angle increased respectively as well. This demonstrates that by controlling both the surface chemistry in terms of polarity of the nanoparticles and the roughness of the resultant coating through the process according to the invention, the wetting properties can be varied greatly as well.

TABLE 7

Hardness, Reduced Modulus and Scratch results of example 2, 3 and 7

| Formulation | Hardness (Gpa) | Reduced Modulus (Gpa) |
|---|---|---|
| Example 2 Acr MT-ST | 1.2 +/− 0.1 | 22 +/− 2 |
| Example 3 Acr FI MT-ST | 0.5 +/− 0.05 | 14 +/− 1 |
| Example 7 Acry-IPA-ST-UP | 2.5 +/− 0.2 | 45 +/− 5 |

**[0099]** FIG. **1** depicts the three dimensional (3D) topography of the coatings obtained in various examples and the comparative experiments acquired by atomic force microscopy (AFM). The maximum height of the features (Rmax) in these images is given as the maximum height difference over the whole area of the image. FIG. **1***a* shows the surface roughness of the coating according to the comparative experiment, the conventional hard coat sample, the components of which can be found in table 3, example 1. As can be deduced form this AFM image the surface roughness of the coating is very small and only in the range of ca 6nm, which is well below the smallest dimension of the nanoparticles used in the coating. Therefore this is a not a nano-structured and/or nano-porous coating as described within the framework of the invention. For this hard coat the relative volume of reactive diluent is so large that all nanoparticles are embedded and do not contribute to the formation of a nano-structured and/or nano-porous coating. This roughness however is typical for acrylate coatings, irrespective of the presence of nanoparticles. FIG. **1***b* and FIG. **1***c* show the surface topography of coatings of fluorinated acrylated spherical nano-silicates (modified nano-particle C) (Table 3, Example 3) and a coating of acrylated spherical nano-silicates (modified nano-particle A) (Table 3, Example 2), respectively. For both of these coating the lack of any reactive diluent leads to the formation of nano-structured and nano-porous coatings as described within the framework of the invention. Similarly FIG. **1***d* shows a coating with a surface roughness of ca 140 nm, which is formed by the crosslinking of elongated acrylated nano-silicate particle (modified nano-particle B) (table 4, example7) without any reactive diluent. Here again the absence of any reactive diluent leads to the formation of nano-structured and nano-porous coatings. FIG. **1***e* (table 4, example 8) shows the effect of small amount of reactive diluents (2.7 wt-% of total solids) on the surface topography of coatings comprising elongated acrylated nano-silicates (modified nano-particle B). It can be seen that the addition of small volumes of reactive diluents lead to a decrease of the maximum feature height (Rmax). However again the relative volumes of reactive diluent are so low that the content is below 1-the random close volume packing of the nanoparticles and thus form nano-structured and nano-porous coatings.

**[0100]** FIG. **2** shows the cross-sectional topography as acquired by Atomic force microscopy. For these cross-sections, the Rmax given in FIG. **2** is the maximum height difference across the cross-section. FIG. **2***a* shows the cross-sectional topography of a coating of acrylated spherical nano-silicates (modified nano-particle A) (Table 3, Example 2). Here a surface nano-structure (roughness on the surface) as well as nano-pores (deeper features) can be seen. Similarly FIG. **2***b* shows the cross-sectional topography of a coating of elongated acrylated nano-silicates (modified nano-particle B) (Table 4, Example 7). Again here the roughness on the surface is the surface nano-structure while the deepest features can be regarded as nano-pores. It is also expected that small voids of air will exist in the bulk of the coating between individual nano-particles or clusters thereof however, these nano-pores cannot be visualized by AFM.

**[0101]** FIG. **3** shows the visible transmission spectra of a number of example and comparative coatings on one side of a glass microscope slide substrate. Spectrum 5 is of an uncoated glass microscope slide. Spectrum 1 is of unmodified MT-ST nano-particles, which were spin-coated at 4800 rpm from a suspension of 3 wt-% solids, giving a coating thickness in the range of 100-200 nm, This spectrum shows that unmodified MT-ST nano-silicates display anti-reflective properties as the maximum transmission increases to ca 96.8% with respect to the maximum that of the uncoated glass microscope slides (94.8%). Obviously such a coating would have no mechanical durability as the unmodified MT-ST nano-particles are not surface modified with reactive groups and therefore are incapable of crosslinking. In this coating there is a maximum space between nano-particles, as the surface of the MT-ST nano-particles is not modified. Once the surface of these particles is grafted, the space between the nano-particles is partially filled by the polymerisable organic groups and spectrum 2 results.

**[0102]** This effect can be seen again when the surface modifying agent methyltrimethoxysilane groups are replaced with even bulkier groups such as 1H,1H,2H,2H-(Perfluorooctyl) triethoxysilane (apolar surface derivatisation agent), see spectrum 3. In the case of spectrum 4 the space between the nano-particle is completely filled with reactive diluent and thus this conventional hard coat has a maximum transmission (95.0%), which differs very slightly from that of the uncoated glass microscope slide (94.8%).

**[0103]** FIG. **4** shows the visible transmission spectra of of the coatings of example 7 (spherical particles, spectrum 2) and example 7(elongated particles, spectrum 1) Spectrum 3 is the uncoated glass microscope slide. It is clearly shown that the coating comprising elongated particles shows even further improved anti-reflective properties compared to the coating comprising the spherical particles.

**[0104]** FIGS. **5** and **6** show the effect of coating both sides of reflective substrate, glass microscope slides in the case of FIG. **5** and PET films in case of FIG. **6**, with a coating of crosslinked acrylated elongated nano-particles (Acry-IPA-ST-UP, modified particle B). As both the top and bottom surface of the untreated substrates cause reflection transmission greater than 98% are usually only possible if both sides of the substrate have been coated. In the case of both of these examples the coating on both sides of the substrates results in objects, which are almost invisible to the naked eye and where surface reflections are only observable, by direct reflection of bright light sources.

**[0105]** FIG. **7** shows that in case of elongated particles there is only a small decrease in anti-reflective properties if a reactive diluent is used.

## Example 16

### Preparation of Durable Anti-Reflective Coating System on Top of Hard Coat

**[0106]** In the first step a hard coat according to comparative experiment 1 is applied to the substrate to a thickness of ca 3-5 pm and cured in Air at a total UV dose of 0.75 Jcm$^{-2}$. The surface of the resulting hard coat was partially cured. In the second step a coating according to the invention is applied on top of the Hard coat to a thickness of 100-200 nm by spin coating as described previously.

**[0107]** The said coating according to the invention consists of the following components; 0.376 g (dry weight) reactive nano-particle (modified Particle B, Table 2), 0.061 g of Dipentaerythritol penta-acrylate (reactive diluent), 0.013 g tri-methylolpropane tri-(3-mercaptopropionate) (reactive diluent and adhesion promoter), 0.8 mg of propyl gallate (polymerisation inhibitor), 5.1 mg of Irgacure 907 (photo-initiator), 12.902 g of methyl ethyl ketone (solvent) and 1.642 g of isopropanol (solvent).

**[0108]** The said coating according to the invention is then fully cured with a total of 2×1 $Jcm^{-2}$ and subsequently heated to 120° for ca 1 minute using an infra red lamp. The resultant nano-structured coating has a pencil hardness of 2-3H according to ASTM D3363-00, while retaining anti-reflective properties.

**[0109]** The use of hard coat which is partially cured at the surface, addition of multi-functional thiols and subsequent thermal post-backing, after fully UV curing the combined system, as described above, improves the mechanical durability of all coatings with respect to the coatings where these steps are not taken.

**1**. A coated substrate which comprises a transparent substrate and an anti-reflective coating on the substrate, wherein the anti-reflective coating consists of a single layer which is the polymerized product of a mixture comprising:
 i) reactive nano-particles, having reactive organic groups on their surface,
 ii) at least one solvent
 iii) optionally a compound having at least one polymerisable group in an amount small enough to allow the formation of a nano-structures and/of nano-porous surface after polymerisation of the mixture, and wherein
the single layer anti-reflective coating exhibits an increased transmission by at least 0.5% for at least part of the electromagnetic spectrum between 400 and 800 nm when the coating is present on a transparent substrate in comparison with the same substrate without the coating.

**2**. A coated substrate according to claim **1**, wherein the coating contains an amount of reactive nano-particles between 70-100 wt %, relative to the weight of the coating.

**3**. A coated substrate according to claim **1** wherein the coating has a thickness of between 50-200 nm.

**4**. A coated substrate according to claim **1**, wherein the coating increases the transmission by at least 1% for at least part of the electromagnetic spectrum between 400 and 800 nm if the coating is present on a transparent substrate in comparison with the same substrate without a coating.

**5**. A coated substrate according to claim **1**, wherein the coating increases the transmission by at least 3%.

**6**. A coated substrate according to claim **1**, wherein the coating exhibits a static water contact angle of less than 60°.

**7**. A coated substrate according to claim **1**, wherein the coating exhibits a static water contact angle of less than 40°.

**8**. A coated substrate according to claim **1**, wherein the coating exhibits a static water contact angle of more than 90°.

**9**. A coated substrate according to claim **1**, wherein the coating exhibits a contact angle of more than 140°.

**10**. A process for making an antireflective transparent substrate comprising:
 (a) coating a transparent substrate with an anti-reflective coating, wherein the anti-reflective coating consists of a single layer which is a mixture comprising:
  i) reactive nano-particles, having reactive organic groups on their surface,
  ii) at least one solvent
  iii) optionally a compound having at least one polymerisable group in an amount small enough to allow the formation of a nano-structures and/of nano-porous surface after polymerisation of the mixture, and wherein
 (b) polymerizing the mixture on the substrate to obtain a polymerized single layer anti-reflective coating on the substrate which exhibits an increased transmission by at least 0.5% for at least part of the electromagnetic spectrum between 400 and 800 nm when the coating is present on the transparent substrate in comparison with the same substrate without the coating.

**11**. The process of claim **10**, wherein step (b) includes exposing the mixture on the substrate to UV radiation.

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