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(54) Title: PALE YELLOW COLOURED AQUEOUS DISPERSION OF SILVER NANOPARTICLES, A PROCESS FOR PREPARATION AND COMPOSITONS THEREOF

(57) Abstract: The present invention provides pale yellow coloured aqueous dispersion of silver nanoparticles and process for preparation thereof. The present invention also provides compositions comprising pale yellow coloured aqueous dispersion of silver nanoparticles for use as antimicrobial finish compositions to be applied on textiles and other substrates. The pale yellow coloured aqueous dispersion comprising silver nanoparticles wherein the dispersion is characterized in - having a single plasmonic peak in the range of 390 to 410 nm in UV-Vis spectrum, - the dispersion having silver nanoparticles of spherical shape with majority of particles (>65%) having equivalent diameter in range of 0.2 to 4 nm, - molar extinction coefficient greater than 12 mM⁻¹ cm⁻¹ preferably in the range of 12 to 21 mM⁻¹ cm⁻¹ at wavelength of maximum absorption in the range of 390-410 nm, - Dispersion stability of at least 15 months, - Minimum Bactericidal Concentration (MBC) lower than 0.3 ppm preferably in the range of 0.03-0.25 ppm.



**“PALE YELLOW COLOURED AQUEOUS DISPERSION OF SILVER
NANOPARTICLES, A PROCESS FOR PREPARATION AND COMPOSITONS
THEREOF”**

5 Field of Invention:

The present invention provides pale yellow coloured aqueous dispersion of silver nanoparticles and process for preparation thereof. The present invention also provides compositions comprising pale yellow coloured aqueous dispersion of silver nanoparticles for use as antimicrobial finish compositions to be applied on textiles and other substrates.

Background of Art:

15 Nanosilver is a highly potent antimicrobial agent. The state-of-the-art antimicrobial finishes based on nano silver are deep yellow to dark brown in colour depending upon the silver concentration. When this yellow silver nanodispersions are applied to textile or polymeric substrates, it often results in poor aesthetics in terms of lower Whiteness Index or higher Yellowness Index, which is undesirable primarily for white and pale shade garments or substrates.

20 The problem of colour is further aggravated as nanosilver dispersions are required to be applied at high concentration in the range of 5 ppm to 100 ppm for effective antimicrobial activity (>80%). The Minimum Bacteriocidal Concentration (MBC) values for dispersions of silver nanoparticles are in the range of 5-1000 ppm (references are given in the text below), which is quite high. The silver is a precious metal and its application at higher concentration is commercially undesirable.

Also the dispersions of nanosilver based finishes available in prior art are non durable. The nanoparticles tend to agglomerate and settle down with time in the dispersion giving poor shelf life. When applied on substrates they lose their efficacy on repeated washing as the silver nano particles or their agglomerate tends to wash off the substrate. If binders are used, the nanosilver loses its high degree of activity against the bacteria.

30 The synthesis techniques of silver nanoparticles are categorized into bottom-up and top-down approaches. Some of the important approaches are listed below:

35 Bottom-up approach can be used with the following methods:

Chemical reduction method: This involves dissolution of silver salt into a solvent (aqueous or non-aqueous) and subsequent addition of a suitable reducing agent e. g. chemical reduction of silver ion in aqueous solutions or non-aqueous solutions (Maribel G. Guzmán, Jean Dille, Stephan Godet, World Academy of Science, Engineering and Technology 43 2008; Zaheer Khan, Shaeel Ahmed Al-Thabaiti, Abdullah Yousif Obaid, A.O. Al-Youbi, Colloids and Surfaces B: Biointerfaces 82 (2011) 513–517; CHEN Yanming Li, CN1994633; Sun, Rong; Zhao, Tao; Yu, Shuhui; Du, Ruxu, CN 102085574).

45 Template method (Shinsuke Ifuku, Manami Tsuji, Minoru Morimoto, Hiroyuki Saimoto, and Hiroyuki Yano *Biomacromolecules* 2009, 10, 2714–2717). This process involves synthesizing a desired material within the pores of a porous membrane.

Electrochemical or ultrasonic-assisted reduction (N. Perkas, G. Amirian, S. Dubinsky, S. Gazit, A. Gedanken, *Journal of Applied Polymer Science*, Vol. 104, 1423–1430 (2007)). The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth, and when solutions are exposed to strong ultrasound irradiation, bubbles in the solution are implosively collapsed by acoustic fields. Cavitation bubble collapse can also induce a shock wave in the solution and drive rapid impact of the liquid to the surface of the particles.

Photoinduced or photocatalytic reduction (C.C. Chang, C.K. Lin, C.C. Chan, C.S. Hsu, C.Y. Chen, *Thin Solid Films* 494 (2006) 274–278; Lizhi Zhang, Jimmy C. Yu, Ho Yin Yip, Quan Li, Kwan Wai Kwong, An-Wu Xu, and Po Keung Wong, *Langmuir* 2003, 19, 10372-10380; Wu Juan, Zhang Hongbin, CN 102198511). It takes very long time (sometimes over 70 hours, R Jin, Y Wei Cao and C A. Mirkin, *SCIENCE* 294 (2001)). The photo process involves surface plasmon excitation, and this feature allows one to tailor the size and shape of the disks by simply varying the irradiation wavelength.

Microwave (MW)-assisted synthesis (K J Sreeram, M Nidhin and B U Nair, *Bull. Mater. Sci.*, Vol. 31, No. 7, Dec 2008, pp. 937–942). MW provides rapid and uniform heating of reagents, solvents, intermediates, and products. Fast heating accelerates the reduction of metal precursors and the nucleation of the metal cluster, resulting in small nanostructures.

Irradiation reduction (S K Mahapatra, K A Bogle, S D Dhole and V N Bhoraskar, *Nanotechnology* 18 (2007) 135602). Electron irradiation (electron energy) is a new method of reduction of precursor in a solution to produce nanoparticles.

Microemulsion method (Zhi Ya Ma, Dosi Dosev and Ian M Kennedy, *Nanotechnology* 20 (2009) 085608). Microemulsion consists of a ternary mixture of water, surfactant and oil or a quaternary mixture of water, surfactant, co-surfactant and oil. Different surfactant, that is, different microemulsion system employed in the fabrication process, silver nanoparticles with different diameters or morphologies are obtained.

Biochemical reduction (M. Sathishkumar, K. Sneha, S.W. Won, C.W. Cho, S. Kim, Y.S. Yun, *Colloids and Surfaces B: Biointerfaces* 73 (2009) 332–338; K. Kalishwaralal, V. Deepak, S.R.K. Pandian, M. Kottaisamy, S. Barath ManiKanth, B. Kartikeyan, S. Gurunathan, *Colloids and Surfaces B: Biointerfaces* 77 (2010) 257–262), and so on.

The top-down techniques use silver metal in its bulk form, then, mechanically reduce its size to the nanoscale via specialized methodologies such as lithography (Xiaoyu Zhang, Alyson V. Whitney, Jing Zhao, Erin M. Hicks, and Richard P. Van Duyne, *Journal of Nanoscience and Nanotechnology* Vol.6, 1–15, 2006,) and laser ablation (A. Pyatenko, K. Shimokawa, M. Yamaguchi, O. Nishimura, M. Suzuki *Appl. Phys. A*, 79, 803–806 (2004)).

Foremost among all of the above processes is the chemical reduction method that allows production of large quantities of nanoparticles in relatively short periods of time. The other processes are complex and/or require expensive controls and/or infrastructure.

It was observed that with time or high storage temperature, the particles tend to grow or aggregate to form large particles. Coalescence of the nanoparticles may lose their characteristic properties. Thus, stability of the nanoparticles in dispersion is a matter of concern for long time use and to achieve the same efficacy. Antonio M. Brito-Silva *et al.*, Journal of Nanomaterials, 2010, Article ID 142897, reported synthesis of silver nanoparticles by laser ablation in preformed colloids in non-aqueous media of methanol, acetone, ethylene glycol etc. The stability could be achieved from 8 days till a maximum of around 5 months with different protective agents in nonaqueous media. Some have tried to see the effect of different protective agents on aggregation behaviour of silver nanoparticles and its antimicrobial activity (L Kvitek, A Panacek and J Soukupova, J. Phys. Chem. C 112 5825 (2008); J Soukupova, L Kvitek *et al.*, J Materials Chemistry and Physics 111 77 (2008)). It was observed that addition of ionic protective agents improved the zeta potential (stability) of the nanoparticle dispersion than without protective agents. However, the use of ionic surfactants, which gave the best results, could improve the stability of nanosilver dispersion to only a limited period and antimicrobial activity (MIC value) to 1 ppm.

The antimicrobial activity of silver nanoparticles may be evaluated either in dispersion form to give MBC/MIC values in ppm ($\mu\text{g/ml}$ of dispersion) or after application on substrates in % reduction of microbial growth for a given concentration of silver in ppm ($\mu\text{g/g}$ of fabric) using standard methods such as AATCC100, ASTM E 2149.

The literature reports Minimum Bactericidal Concentration (MBC) for dispersions of silver nanoparticles against pathogenic bacteria to human is in the range of 2-100 ppm for spherical shape. One of the prior art showed 6.7 ppm of 25-50 nm silver nanoparticles against *S. aureus* and 2 ppm against *S. epidermidis* using reducing agent saccharides maltose (Ales Panacek, Libor Kvitek, Robert Prucek, Milan Kolar, Renata Vecerova, Nadezda Pizurova, Virender K. Sharma, Tatjana Nevecna, and Radek Zboril, *J. Phys. Chem. B* 2006, 110, 16248-16253). Another prior art reported an average particle size of 18 nm of spherical nanosilver and MBC values in the range from 10 to 0.15 $\mu\text{g/ml}$ (ppm) against various bacteria that are pathogenic to lower animals such as fish. However, the MBC values were evaluated after 30-90 minutes of incubation time, which is a very short time to see the actual growth of pathogen and is not a standard procedure to evaluate MBC. (Soltani, M., Ghodrattneha, M., Ahari, H., Ebrahimzadeh Mousavi, H. A., Atee, M., Dastmalchi, F., Rahmánya, J., *Int.J.Vet.Res.* 3,2:137-142,2009). In another paper, (Ansari MA, Khan HM, Khan AA, Malik A, Sultan A, Shahid M, Shujatullah F, Azam A, Biology and Medicine, Vol 3 (2) Special Issue: 141-146, 2011).

In another paper, (Ansari MA, Khan HM, Khan AA, Malik A, Sultan A, Shahid M, Shujatullah F, Azam A, Biology and Medicine, Vol 3 (2) Special Issue: 141-146, 2011) MBC value of 12.5 to 100 $\mu\text{g/ml}$ (ppm) have been reported towards *Staphylococcus aureus*, methicillin-sensitive *S. aureus* (MSSA), and methicillin-resistant *S. aureus* (MRSA) were examined against commercially available nanosilver particles (5-10 nm particle size).

Sukdeb Pal *et al.* (Sukdeb Pal, Yu Kyung Tak, 5 Joon Myong Song, *Appl. Environ. Microbiol*, 2007 March; 73(6): 1712–1720) have done comparative study on bactericidal properties of different shaped silver nanoparticles with *E. Coli*. They have shown MIC value for truncated triangular silver nanoparticle to be 1 μg (or 1 ppm), for spherical 50-100 μg (or 50-100 ppm) and for rod shaped particles >100 μg (or >100 ppm).

Antimicrobial activity of silver nanoparticles on textile substrates have also been reported in several studies. For effective antimicrobial activity (> 80%) on textile substrates, finishes based on silver nanoparticles are applied on textiles/substrates in concentrations from 5 ppm (Hee Yeon Ki, Jong Hoon Kim, Soon Chul Kwon, Sung Hoon Jeong, J Mater Sci (2007) 42:8020–8024) to 350 ppm (Kanokwan Saengkiettiyut, Pranee Rattanawaleedirojn and Supin Sangsuk, J. Nat. Sci. Special Issue on Nanotechnology (2008) Vol. 7(1), 75), and even as high as 1000 ppm (Kanokwan Saengkiettiyut, Pranee Rattanawaleedirojn and Supin Sangsuk, J.Nat Sci. Special Issue on Nanotechnology 7 75 (2008).

The silver is a precious metal and its application at higher concentration is commercially undesirable. The result of such a high concentration application eventually gives the fabric yellow to brown tinge depending on concentration. Durability of the silver nanoparticle finish is also a concern. Silver nanoparticles tend to wash off during repeated washing. And if the Ag nanoparticles are used with binders, though wash durability improves to some extent, the maximum efficiency/antimicrobial activity of nanoparticles gets reduced due to hindrance of binder.

Thus, there arises a need to develop antimicrobial finishes based on nano silver that have higher stability, wash durability, antimicrobial activity, and can be applied at very low concentration so that the cost of application is low and unpleasant colour is not imparted to white and pale coloured substrates.

The present invention minimizes the problem of yellowing of fabric and other substrates on application of nanosilver based finishes and solves the problems of stability of the aqueous dispersion of nanosilver during storage, application at low concentrations, and wash durability of nanosilver finish on application. The aqueous dispersion of silver nanoparticles of the present invention is pale yellow in colour, shows 99.9 or better antimicrobial activity towards both gram positive and gram negative bacteria at very low concentrations, is easy to synthesize in aqueous media and is stable at high temperature. The dispersion stability of the particles of present invention is 15 - 24 months. The particles provide wash durability after application on textile, binding with simple heat treatment at temperatures in the range of 120 - 150 degree C or with binders at room temperature. The particles and their dispersions have very high compatibility with binders and surfactants of various types.

Objectives of the invention:

An objective of the present invention is to provide pale yellow coloured aqueous dispersion of silver nanoparticles characterized with a single optical absorption peak in the range of 390-410 nm with molar extinction coefficient greater than $12 \text{ mM}^{-1} \text{ cm}^{-1}$ preferably in the range of $12 - 21 \text{ mM}^{-1} \text{ cm}^{-1}$ in the UV-vis spectrum.

Another object of the present invention is to provide a process for preparation of pale yellow coloured aqueous dispersion of silver nanoparticles.

Yet another object of the present invention is to provide composition comprising pale coloured aqueous dispersion of silver nanoparticles of the present invention for use as anti microbial agents.

Yet another object of the present invention, the pale coloured aqueous dispersion of silver nanoparticles

has >65-% silver particles that are very small in size i.e. in the range of 0.2- 4 nm in diameter, shows 99.9%-100% antimicrobial activity at very low concentrations with MBC value lower than 0.3 ppm, is stable for 15-24 months, when stored at room conditions.

5 Summary of Invention:

The present invention provides pale yellow aqueous dispersion of silver nanoparticles which is stable on storage for at least 15 months and very effective antimicrobial agent having characteristic feature of a single plasmonic peak in the range of 390-410 nm with molar extinction coefficient in the range 12 - 21 $\text{mM}^{-1} \text{cm}^{-1}$ in UV-vis spectrum, the dispersion having silver nanoparticles of isotropic shape with majority of particles 70- 80%) having equivalent diameter in range of 0.2 to 4 nm and Minimum Bacteriocidal Concentration (MBC) lower than 0.3 ppm preferably in the range of 0.03-0.25 ppm. In an embodiment, the present invention also provides process for preparation of said aqueous dispersion.

The process of the present invention comprises steps of adding a protecting agent to silver precursor solution, followed by addition of stabilizer and hydrogen peroxide. The temperature is raised followed by addition of a reducing agent which leads to formation of pale yellow coloured aqueous dispersion of silver nanoparticles.

In an embodiment present invention provides compositions comprising pale yellow coloured aqueous dispersion of silver nanoparticles produced by the method of the present invention.

25 Description of Drawings:

Figure 1: Optical photograph of pale yellow coloured aqueous dispersion of silver nanoparticles.

Figure 2: Small Angle X-ray Diffraction (SAXS) graph of pale yellow coloured aqueous dispersion of silver nanoparticles showing distribution of particle size by volume. SAXS shows actual size of the majority (70-80) of Ag particles to be in the range of 0.2 - 4 nm. Higher sizes are in minority and are likely to be agglomerates of smaller particles.

Figure 3: UV-vis spectroscopy of pale yellow coloured aqueous dispersion of silver nanoparticles as made in Example 1. (a) as-prepared and (b) after 15 months. The graph shows stability of dispersion for over 15 months.

Figure 4: Pale yellow coloured aqueous dispersion of silver nanoparticles(just prepared) a) Particle size distribution by volume using Dynamic Light Scattering (DLS) (b) Zeta potential. DLS shows composite hydrodynamic diameter of Ag particle and the protective agent.

Figure 5: Pale yellow coloured aqueous dispersion of silver nanoparticles (after 15 months) a) Particle size distribution by volume using DLS (b) Zeta potential. DLS shows composite hydrodynamic diameter of Ag particle and the protective agent.

Figure 6: UV-vis spectroscopy of composition of pale yellow coloured aqueous dispersion of silver nanoparticles with 0.30 wt% SDS (surfactant).

List of definitions:

Molar extinction coefficient (ϵ): It is the measure of how strongly a substance absorbs light at a particular wavelength. It is given by $\epsilon = A/cL$, where A is absorption recorded in a UV-vis, c is concentration of dispersion in mMoles and L is pathlength of the sample measuring cell. Its units are $\text{mM}^{-1} \text{cm}^{-1}$; SI units are $\text{M}^{-1} \text{m}^{-1}$.

Antimicrobial activity: Percentage reduction of microbes of an antimicrobial agent at a particular concentration. It can be evaluated by different standard testing methods either qualitatively or quantitatively. For non leaching type of testing more preferred method is colony counting method e. g. AATCC 100, ASTM E-2149. For leaching type of testing more preferred method is zone of inhibition e.g. AATCC 47, AATCC 90 etc.

Minimum Bactericidal concentration (MBC): It is the lowest concentration of antimicrobial agent required to kill the germ.

Procedure to evaluate MBC of aqueous dispersion of pale yellow Ag nanoparticle: It is done by AATCC 100 (colony counting method). The silver dispersions were diluted 50-1000 times with Luria broth solution, inoculated with the tested bacteria at a concentration of 10^5 to 10^6 CFU/mL. The minimum bactericidal concentration (MBC) was evaluated after 24 h of incubation at 37 °C. After 24 hours of incubation, the minimum particular Ag concentration was determined at which more than or equal to 99.9% bacteria were killed.

Protective agent/stabilizer: It is a material that prevents the nanoparticles in aggregating in dispersion (liquid media).

Dynamic light scattering (DLS): It sometimes referred to as **Photon Correlation Spectroscopy (PCS)** or **Quasi-Elastic Light Scattering (QELS)**, is a well-established technique for measuring the size of macromolecules and particles typically in the submicron region. Particles, emulsions and macromolecules in suspension undergo Brownian motion. This is the motion induced by the bombardment by solvent molecules that themselves are moving due to their thermal energy. If the particles or molecules are illuminated with a laser, the intensity of the scattered light fluctuates at a rate that is dependent upon the size of the particles. Analysis of these intensity fluctuations yields the velocity of the Brownian motion and hence the particle size using the Stokes-Einstein relationship (Malvern Instruments, technical note). The fundamental size distribution generated by DLS is an intensity distribution, and then, it is converted, using Mie theory (Malvern Instruments, technical note; Chem. Rev. **2007**, 107, 4797-4862), to a volume distribution. Intensity graph is not a true representation of amount of particles, as scattering intensity of signal is proportional to $\sim(\text{diameter of particle})^6$. Volume distribution describes the volume of material present in the mixture having a particular diameter.

Hydrodynamic diameter: It is the composite diameter of a particle (surrounded by different ions and protective agents) in liquid media. In general, true diameter of the particle is less than its hydrodynamic diameter.

Zeta Potential: It is the potential difference between the dispersion medium (here water) and the stationary layer of fluid attached to the dispersed particle. It indicates the degree of repulsion between adjacent, similarly charged particles in a dispersion. Its units are mV.

Stability: Stability of a dispersion is related to the time taken by the dispersed particles in a dispersing medium to agglomerate and settle down under gravity. This makes the dispersion inhomogeneous and can not be used for applications. Dispersion with higher stability takes longer time to settle down.

Washing using method AATCC- 61 –IIA :

Temperature used: 49 degree C, Time: 45 minutes, Steel ball: 50 steel balls, Soap used: Non-ionic detergent (0.15wt%). This washing technique simulates actual conditions equivalent to 5 home laundry washings.

Detailed description:

The present invention provides pale yellow coloured aqueous dispersion of silver nanoparticles which are spherical in shape.

Pale yellow coloured aqueous dispersion of silver nanoparticles having higher activity, in comparison to other spherical silver nanoparticles/dispersions reported in the literature, has been developed using a new method of preparation and using different concentration of additives. This pale yellow coloured aqueous dispersion of Ag nanoparticles has overcome the above mentioned shortcomings of the existing antimicrobial nanofinishes. The combination of characteristic features of the pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention, which distinguishes it from the prior art, are (a) the smaller size of the particle (measured by SAXS to be 0.2 to 4 nm diameter for 70-80% of the particles in the dispersion, and (b) purity of composition having Ag particles of only spherical shape (as evidenced by single plasmonic peak in the region of 390- 410 nm.(c) molar extinction coefficient in the range of 12 - 21 $\text{mM}^{-1} \text{cm}^{-1}$ at wavelength of maximum absorption in the range 390-410 nm, (d) minimum bactericidal concentration (MBC) in the range of 0.03 - 0.25 ppm, and (e) dispersion stability in the range of 15 - 24 months.

The dispersion of pale yellow colored particles obtained by the process of the present invention is optionally mixed with surfactants and binders or in situ synthesized with surfactants to yield even more effective compositions for antimicrobial finishing of textiles as evidenced by increase in molar extinction coefficient in the range of 18 - 25 $\text{mM}^{-1} \text{cm}^{-1}$ and minimum bactericidal concentration (MBC) values lower than 0.1 ppm preferably in the range 0.01 to 0.099 ppm, more preferably in the range of 0.01- 0.05 ppm, for control of the growth of microbes and perspiration odors, for a variety of substrates including textile materials such as cellulose such as cotton, wool, silk, polyester, viscose, polypropylene, nylons, Lycra, acrylic etc, and blends thereof.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be applied during textiles manufacture, processing, finishing and printing of various forms of fibers, filaments, yarns, sewing threads, towels, knits & woven & non woven textile and apparel.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be applied along with durable press and wrinkle free finishing systems. The wrinkle free systems include thermosetting resins such as dimethylol dihydroxy ethylene urea (DMDHEU) resins; Dimethyl dihydroxy ethylene urea (DMeDHEU) certain transition-metal complexes, along with catalysts used for resin curing, polyethylene emulsions, softeners etc. This cross linking of yellow silver with resin system provides durability on apparel up to 50 washes at an application dosage level of 2% of the

fabric weight.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention also finds antimicrobial applications in many different textiles for the home, apparel, medical, military and industrial use. Non-limiting examples of such textiles are shape-wear, socks, mattress ticking, roller hand towels, dish towels, bed linen, upholstery, soft furnishings, curtains, boot and shoe linings, carpets and mats, innerwear, intimate apparel and underwear briefs, T-shirts, active and athletic wear, leisure wear, sleepwear, swimwear, suits, uniform fabric & work wear, knitwear, denims, trousers, women's knee-highs, hosiery and leg wear.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be incorporated into articles of clothing for antimicrobial applications in jackets, vests, headwear, footwear (toe caps, heels, insoles, uppers, etc.), gloves, scarves, socks and leggings, neck gaiters, tents, sheeting & bedding, coated fabrics (PV, Polyurethanes, Silicone & PVC), sportswear, bath rugs, luggage fabrics, sleeping bags & duvets, and hats.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention is compatible for use along with Textile processing chemicals and chemical auxiliaries. Textile auxiliaries include but are not limited to Textile finishing agents, fabric conditioners, Moisture management finishes, antistatic agents, nucleating agents, soil release agents, optical brightening agents, antioxidants, UV stabilizers, fillers, softeners, lubricants, curing accelerators, encapsulated fragrances, textile detergents, and the like for providing malodor control and antimicrobial properties. All of such additional materials are well known to those skilled in the art and are commercially available.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be used in textile composite materials including but not limited to textile foot mattress composites. Textile accessories including but not limited to textile collar linings, shirt buttons jacket fiber fillers and jacket insulating materials. All of these benefit from the antimicrobial protection provided by yellow coloured silver nanoparticles of present invention.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be used for textile recycling and waste recycling to avoid the mildews generated during recycling and to help avoid the spread of diseases which may arise during the recycling process. Pale yellow coloured silver nanoparticles of present invention can be used in textile preservation, including protection from dampness of apparel in all textile fabrics including canvass fabrics. Pale yellow coloured silver nanoparticles of present invention can be incorporated into non-woven fabrics and usually added along with latex binders for various applications including but not limited to non woven air filters.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be incorporated into a wide range of consumer goods products, for the purpose of bringing an additional antimicrobial effect, or a boosted freshness effect. Examples of such products include but are not limited to washing detergents, whether in liquid, powder, tablet or gel form, or rinse conditioners or rinse additives whether dilute or concentrate in nature. Also included are laundry wash additives such as stain removal enhancement products. Pale yellow coloured silver nanoparticles can also be incorporated into tumble drier sheets. Additionally, pale yellow coloured silver nanoparticles can be incorporated into fabric sprays, both with and without additional fragrance.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be incorporated into many household products to bring an additional antimicrobial benefit or a freshness enhancement. This includes but is not limited to cat litter, air fresheners, hard surface cleaners and sprays, and floor cleaners. Pale Yellow coloured aqueous dispersion of silver nanoparticles can also be used to treat mops, wipes and cloths to prevent bacterial growth and to keep such substrates fresh.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be used to enhance the antimicrobial properties of a broad range of paper based products, such as diapers, incontinence products, facial tissues, toilet tissues, wipes and kitchen towels.

Pale yellow coloured aqueous dispersion of silver nanoparticles of present invention can be incorporated into numerous personal care products, including but not limited to such products as deodorants, anti-perspirants, talcum powders, body lotions, hair shampoos, hair conditioners, shower gels, bar soaps, body lotions and moisturizers and shaving gels.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be incorporated into air filters, which can be vehicle and aircraft cabin air filters, or room and building based air filters in homes, offices and hotels. Yellow coloured silver nanoparticles incorporation ensures filter materials are resistant to bacterial and fungal growth.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be incorporated into medical dressings such as wound care materials and burn dressings to suppress bacterial and fungal growth, and the related risk of infection, in materials used for wound care dressings and burn dressings. In addition, pale yellow coloured silver nanoparticles of present invention can be utilized in medical-healthcare products such as medical/healthcare wipes possessing anti-microbial properties.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can additionally be used in paints, coatings and wood preservative products, where it acts as a preservative and also delivers antimicrobial properties to the products.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be incorporated into products designed to repel or eradicate bedbugs, such as textile coverings and sprays. The textile coverings include but are not limited to mattress ticking, sheets and bed coverings, and mattress coverings.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can be incorporated into products designed to kill or repel lice. This can be incorporated into textiles, covering and sprays or gels. Non-limiting examples are hats, hair netting and caps, hair spray, hair gels and creams.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention can provide residual protection against pests like microorganisms or insects, prevents the growth of bacteria and can kill existing bacteria on various surfaces.

Pale yellow coloured aqueous dispersion of silver nanoparticles of the present invention is effective against formation of Bio films on various surfaces.

The present invention provides pale yellow coloured aqueous dispersion of silver nanoparticles wherein the dispersion is characterized by a single plasmonic peak in the range of 390 to 410 nm in UV-vis spectra with molar extinction coefficient greater than $12 \text{ mM}^{-1} \text{ cm}^{-1}$ preferably in the range of $12 - 21 \text{ mM}^{-1} \text{ cm}^{-1}$ and having 70-80% particle of size in the range of 0.2 - 4 nm, dispersion stability of at least 15 months and Minimum Bactericidal Concentration (MBC) lower than 0.3 ppm preferably in the range of 0.03-0.25 ppm.

The invention also provides a process for preparation of pale yellow coloured aqueous dispersion of silver nanoparticles, the process comprising the steps of

- (i) adding a protective agent to silver precursor solution;
- (ii) adding a stabilizer and hydrogen peroxide to the solution of step (i);
- (iii) heating solution of step (ii) to a temperature in the range of 55 to 100 °C;
- (iv) reducing the solution of step (iii) with a reducing agent to obtain pale yellow coloured aqueous dispersion of silver nanoparticles.

wherein the mole ratio of silver salt to reducing agent is in the range of 1:55 to 1:200 to obtain pale yellow coloured aqueous dispersion of silver nanoparticles.

The present invention also provides compositions comprising pale yellow coloured aqueous dispersion of silver nanoparticles.

In an embodiment, the silver precursor is selected from a group consisting of silver nitrate, silver perchlorate, silver acetate, silver sulphate and silver tetraoxochlorate.

In an embodiment, the silver precursor is silver nitrate.

In another embodiment, the protecting agent is selected from a group consisting of poly(ethylene-diamine), sodium acetate, bis(p-sulfonatophenyl)phenyl phosphine dipotassium dihydrate, polyethylene glycol, polyvinyl alcohol and polyvinyl pyrrolidone.

In another embodiment, the protecting agent is polyvinyl pyrrolidone.

In yet another embodiment, a stabilizer is selected from the group consisting of ethylenediamine tetra acetate salt, nitrilo acetic acid salt and trisodium citrate.

In yet another embodiment, a stabilizer is trisodium citrate.

In another embodiment, a surfactant is optionally added before step (iv).

In still another embodiment, the surfactant is selected from the group consisting of anionic and non ionic surfactants including sodium dodecyl sulfate(SDS), polysorbates, sodium salts of polyacrylic acids, and salts of alkylbenzo sulphonates and its condensates.

In still another embodiment, the surfactant is sodium dodecyl sulfate(SDS).

In yet another embodiment, the reducing agent is selected from the group consisting of ascorbic acid,

sodium tri-sec-butylborohydrate, lithium aluminium hydride, potassium tri-sec-butyl borohydride, potassium triethylborohydride, sodium triacetoxy borohydride and sodium borohydride.

In yet another embodiment, the reducing agent is sodium borohydride.

Different temperature and concentration of the reducing agent gives different colour.

In still another embodiment, the reaction mixture is heated in the range of 55 to 100°C preferably in the range of 70 - 90 °C.

In another embodiment, the mole ratio of silver precursor to protecting agent ranges from 1:0.1 – 1:100, preferably 1:1 to 1:10, more preferably 1:1 to 1:5.

In yet another embodiment, the mole ratio of silver precursor to stabilizer ranges from 1:1 to 1:100, preferably 1:1 to 1:50, more preferably 1: 5 to 1:15.

In yet another embodiment, the mole ratio of silver precursor to reducing agent is in the range of 1: 55 to 1:200 preferably 1:60 to 1:100.

In still another embodiment the mole ratio of silver precursor to hydrogen peroxide ranges from 1:50 to 1:500, preferably 1:100 to 1:300.

In still another embodiment, the mole ratio of silver precursor to surfactant is in the range of 1:0.5 to 1:350, preferably in the range of 1:5 to 1:150.

The pale yellow coloured aqueous dispersion of silver nanoparticles obtained by the process of present invention is optionally mixed with surfactants and/or binders to yield effective compositions for antimicrobial finish for variety of substrates including textile materials such as cellulose, cotton, wool, silk, polyester, viscose, polypropylene, nylons, Lycra etc., and blends thereof.

In still another embodiment, a composition made in water comprising 1 – 99 wt% of pale yellow coloured aqueous dispersion of silver nanoparticles, 0.001 to 10 wt% preferably 0.01 to 3.0 wt% of a surfactant optionally with 0.1 to 10 wt% of a binder of the final composition.

In yet another embodiment, the composition in water comprises 1- 99 wt% of pale yellow coloured aqueous dispersion of silver nanoparticles and a binder, wherein the binder is in the range of 0.1 to 10 weight% of the final composition.

In still another embodiment, the surfactant is selected from the group consisting of anionic and non ionic surfactants including sodium dodecyl sulfate (SDS), polysorbates, sodium salts of polyacrylic acids, and salts of alkylbenzo sulphonates, its condensates or a mixture of any two or more selected from the group.

In still another embodiment, the surfactant is sodium dodecyl sulfate(SDS).

In still another embodiment, the binder is selected from the group consisting of acrylic based binder,

epichlorohydrin-bis-hexamethylenetriamine based binder, copolymer binder with maleic acid, epoxy based binders, polyurethane and polyester resin based binders.

In still another embodiment, the binder is epichlorohydrin-bis-hexamethylenetriamine based binder.

In yet another embodiment, the minimum bactericidal concentration (MBC) of the composition is in the range of 0.01-0.099 ppm more preferably lower than 0.01 – 0.05 ppm.

In still another embodiment, the molar extinction coefficient of the composition is above $18 \text{ mM}^{-1} \text{ cm}^{-1}$ preferably in the range of $18 - 25 \text{ mM}^{-1} \text{ cm}^{-1}$.

The process of the present invention provides pale yellow coloured aqueous dispersion of silver nanoparticles with quantitative yield, smaller size, high purity with respect to particle shape and size and high molar extinction coefficient with significantly better properties, such as higher dispersion stability with storage time and better compatibility with various additives, higher antimicrobial activity at lower concentrations and higher fixation to polymeric substrates as compared to the processes and products of the prior art.

The present invention also provides composition of pale yellow coloured aqueous dispersion of silver nanoparticles. In a preferred embodiment the aqueous composition comprises the pale yellow coloured aqueous dispersions of silver nanoparticles as obtained above with a surfactant optionally with a binder, which gives even higher molar extinction coefficient, better dispersion stability, antimicrobial activity and fixation on substrate than the above mentioned composition without surfactant.

The amount of pale yellow coloured aqueous dispersion of silver nanoparticles in the composition may vary in the range of 1 – 99 wt%, surfactants in the composition may vary in the range from 0.001 to 10 weight%, preferably 0.01 to 3 wt% and binder in the range 0.1 wt% to 10 wt% of the final composition.

Example 1:

Synthesis of pale yellow coloured aqueous dispersion of silver nanoparticles :

In 100 ml of deionized water, 0.01 mMole of AgNO_3 was added. To this, 0.035 moles of Poly(vinyl pyrrolidone) of number average molecular weight of 40,000 was mixed. Then 0.092 mmoles of trisodium citrate and 2.0 mmoles of H_2O_2 were added stepwise and mixed at the room temperature in the range of 20°C . Then the temperature of the mixture was raised to 70°C and then 0.75 mmoles of sodium borohydride was added to produce pale yellow coloured aqueous dispersion of Ag nanoparticles.

Example 2.

In 100 ml of deionized water, 0.01 mMole of AgNO_3 was added. To this, 0.05 moles of Poly(vinyl pyrrolidone) of number average molecular weight of 40,000 was mixed. Then 0.1 mmoles of trisodium citrate and 2.5 mmoles of H_2O_2 were added stepwise and mixed at the room temperature in the range of 40°C . Then the temperature of the mixture was raised to 82°C and then 0.90 mmoles of sodium

borohydride was added to produce pale yellow coloured aqueous dispersion of Ag nanoparticles.

Example 3:

Application of yellow coloured aqueous dispersion of silver nanodispersion on textile substrate

1 wt% of yellow coloured aqueous dispersion produced in Example 1 was taken in DI water. To this 1.0 wt% SDS was added and stirred well. Fabric dipped and padded with 80-100% expression (% weight of pale yellow coloured aqueous dispersion based on the dry weight of fabric). Fabric was dried at 80 degree C for 5 min and cured at 150 degree C for 3 min to get durable antimicrobial finish with out binder.

Example 4

A composition of the yellow coloured aqueous dispersion of silver nanodispersion

1 wt% of yellow coloured aqueous dispersion produced in Example 1 was taken in water. To this 3.0 wt% of SDS was added and mixed well. To this 1 wt% of Epichlorohydrin-bis-hexamethylenetriamine polymer based binder was added and mixed well by stirring at room temperature.

Example 5

The Fabric was dipped and padded using the mixture of Example 4 at an expression of 80-100%. The treated fabric was dried at room temperature to get durable antimicrobial finish.

Product properties

Size and shape of the pale yellow coloured aqueous dispersion of silver nanoparticles

1. Small angle X-ray diffraction measurement for precise particle size analysis

The size of pale yellow coloured aqueous dispersion of silver nanoparticles was determined by small angle x-ray diffraction is shown in Figure 2. This clearly shows 2 major peaks with more than 70% of particles, 1st peak value at around 1.25 nm diameter (0.625 nm radius), and 2nd major peak at 3.75 nm diameter (1.85 nm radius). There are a few other peaks (minor peaks) with diameter of about 10-20 nm. All these large size peaks are likely to be agglomerates of the actual particle size.

2. UV absorption spectroscopy analysis

The UV-Vis measurements of the as-prepared pale yellow coloured aqueous dispersion of Ag nanoparticles exhibited a single plasmonic peak at ~398 nm (Figure 3 (a)) which clearly reflects their isotropic shape. Molar extinction coefficient of the dispersion is $13.2 \text{ (mM-cm)}^{-1}$, which is much higher than that reported in prior art.

The UV-Vis measurements of the pale yellow coloured aqueous dispersion of silver

nanoparticles after 15 months of storage (Figure 3(b)). The graph gives a characteristic UV vis spectrum which clearly reflects their isotropic shape is preserved with time. There is only a slight shift of maximum absorption wavelength to 406 nm. Molar extinction coefficient of pale yellow coloured aqueous dispersion of Ag nanoparticles remains high at $14.0 \text{ (mM-cm)}^{-1}$

3. Particle size/Zeta analysis

- a) Particle size analysis of pale yellow Ag nanodispersion (Figure 4 (a)) (just prepared) shows particle diameter by volume distribution = 1.7 nm (92%) and 7.3 nm, 7%, Zeta potential (Figure 4 (b)) is = -7.11mV with 59.3% area and -33.0 mV with 40.7% area. The majority of particles have hydrodynamic diameter less than 3 nm, peak value of 1.7 nm (92%).
- b) Particle size analysis of pale yellow Ag nanodispersion (Figure 5 (a)) (After 15 months) shows particle diameter by volume distribution = 3.8 nm, 99%, Zeta potential (Figure 5 (b)) is = -6.43 mV, 100%. The slightly larger particle size after 15 months indicates a slight aggregation of nanoparticles with time.

Hydrodynamic diameter determined by DLS technique is a composite diameter of particle and protective/dispersing agent molecules surrounding the particles, and therefore, is usually greater than the actual particle diameter. The aqueous dispersion of pale yellow nanosilver has silver nanoparticles of size much smaller than known in the prior art.

4. Antimicrobial properties

The Minimum bacteriocidal concentration (MBC) value for aqueous dispersion of pale yellow Ag nanoparticles is less than 0.3 ppm preferably in the range of 0.03 - 0.25 ppm, which is significantly lower than the values reported in prior art.

5. Stability of the aqueous dispersion of pale yellow Ag nanoparticles

The product is highly stable even after 15 months of storage under standard room conditions (30-40 deg C) of tropical weather. The UV vis data shows only slight shift in maximum wavelength value with storage time while the optical absorption values remain nearly same. Also DLS measurement at 15 months shows that the dispersion properties have not changed significantly with time. This implies that pale yellow coloured aqueous dispersion of silver nanoparticles has stable properties with storage time. There is no settlement of nanosilver particles or change in colour or appearance. The stability of the current product is significantly higher than reported in the prior art.

6. Stability under different conditions

- a) **pH stability:** pH stability range of pale yellow silver nano dispersion is 7 to 14. Pale Yellow coloured aqueous dispersion of Ag nanoparticles becomes even lighter yellow in the acidic pH range from 1 to 6.
- b) **Stability under accelerated g conditions:** Centrifugation at high rpm such as 6000 rpm or more for 15 minutes does not give precipitation or colour change.

- c) **Stability on dilution to tap water:** Pale yellow coloured dispersion of silver nanoparticles (the above composition based on 0.01 mmoles silver in 100 ml) when **diluted to 1 to 2%** with tap water (hardness of tap water: 200 to 1000 ppm) does not precipitate or undergo colour change.

d) **Compatibility with different agents:**

- i) Compatible with non-ionic, cationic and anionic surfactants. Antimicrobial activity tends to improve significantly with the use of surfactants. The samples show higher antimicrobial activity with MBC value in the range of 0.01-0.099 ppm, more preferably in the range of 0.01-0.05 ppm. Also the molar extinction coefficient increases to a value in the range of 18 – 25 (mM-cm)⁻¹ (Figure 6) when composition is made with addition of 3 wt% sodium dodecyl sulphate (SDS).

The effectiveness of compositions of pale yellow aqueous dispersions of silver nanoparticles with various binders for improving antimicrobial activity on cotton is shown in Table 1.

- ii) **Compatibility with binders:** The pale yellow nano silver dispersion is compatible with several types of binders and shows better properties such as higher fixation and activity in the presence of binders on application to various substrates. The types of binders tested are:

- acrylic based binder
- Epichlorohydrin-bisexamethylenetriamine based binder
- Copolymer binder with maleic acid
- polyester resin

The effectiveness of compositions of pale yellow aqueous dispersions of silver nanoparticles with various binders for improving antimicrobial activity and durability on cotton is shown in Table 1.

e) **Antibacterial Testing of pale yellow silver dispersion with different agents: Applied by pad-dry method.**

Method used – ASTM E-2149

Bacterium Used – E-Coli

Table 1. Application of pale yellow nanosilver dispersion on polyester fabric

S. No.	% of Pale Yellow Silver product of example 1 in aqueous medium (ppm application)	Additive	Un washed	10 washes	20 washes	30 washes
1	1% (0.1 ppm)	-	99.9%	75%	50%	30%

2	1% (0.1 ppm)	wetting agent, a mixture of alcohol ethoxylates (0.1 to 1% w/w)	99.9%	95%	60%	40%
3	1% (0.1 ppm)	Cationic Surfactant dosage of (0.1 to 1% w/w)	99.9%	99.9%	99.9%	85%
4	1% (0.1 ppm)	Epichlorohydrin - bishexamethylenetriamine polymer based binder dosage of (0.1 to 1.0% w/w)	99.9%	99.9%	99.9%	85%
5	1% (0.1 ppm)	Acrylic Copolymer binder dosage of (0.1 to 1% w/w)	99.9%	99.9%	98%	80%
6	1% (0.1 ppm)	Polyester resin dosage of (0.1 to 1% w/w)	99.9%	99.9%	95%	80%

(Bactericidal effect with zone of inhibition of < 1 mm)

The product even when diluted to 1-2% (i.e. dilution of up to two orders of magnitude) gives high antimicrobial activity than shown by nanosilver of prior art.

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Prior art showed, **1000 ppm** of nanosilver (average particle size 100 nm) is required to be applied on cotton fabric, for obtaining washing durability of upto 20 washes with 99.9% activity. (Pranee Rattanawaleedirojn Kanokwan Saengkiattiyut, and Supin Sangsuk, J.Nat.Sci. Special Issue on Nanotechnology (2008) Vol. 7(1)) One of the other prior art showed **60 ppm** of nanosilver (size 10-35 nm) application on silk fabric at 40 degree C by exhaust method. It was found that after 10 washing cycles antimicrobial activity came down to 78% from 100% (before wash)(M. L. Gulrajani, Deepti Gupta, S. Periyasamy, S. G. Muthu, Journal of Applied Polymer Science, Vol. 108, 614-623 (2008))

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Another study of the prior art showed **50 ppm** of nanosilver application was necessary on woven cotton fabric to give 99.9% antimicrobial activity. The activity reduced to 90.1% after 20 mild washing cycles (AATCC 61-IA) and for polyester 50 ppm gave antimicrobial activity of only 91.6% (without wash) to 84.3% (after 20 washes) (H. J. LEE, S. Y. YEO, S. H. JEONG, JOURNAL OF MATERIALS SCIENCE **38** (2003) 2199 – 2204).

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The material of present invention with surfactant gives antimicrobial activity up to 99.9% at an application of 0.1 ppm and a durability with up to 99.9% activity for 20 harsher washes (AATCC 61 II A).

8. Colour change of the substrates

The product is pale yellow in colour and highly effective at very low concentrations. Therefore, when applied at above concentrations (MBC values are just 0.01-0.05 ppm, if applied at these concentration, there is hardly any colour that can be visually seen on the fabric), gives no perceptible colour changes to even lightly coloured substrates such as white textiles or pale shade dyed textiles.

9. Fixation without binder by pad-dry and cure method:

The above composition may be fixed without the use of binder by heat treating the padded fabric at temperatures >120 deg C to give significantly higher wash fastness.

Table 2: Antibacterial activity of pale Yellow coloured aqueous dispersion of silver nanoparticles when applied on cotton fabric by dip-pad method and cured at 150 deg C for 3 min

Concentration of Bacterial culture (<i>S. aureus</i>)	Material Treated with pale yellow coloured aqueous dispersion of silver nanoparticles of Example 1 of the present invention	Antibacterial activity (%)	
		Without wash	After 20 washes
10 ⁵ CFU/ml	Treated cotton only dried at 80°C for 5 min	95.9%	89.5%
	Treated cotton dried at 80°C for 5 min & cured at 120°C for 5 min)	97.15%	90.3%
	Treated cotton dried at 80°C for 5 min & cured at 150°C for 5 min)	99.7%	99.47%

The results show that the heat treatment at 120-150 degree C to the treated fabrics with the pale yellow aqueous dispersion of silver nanoparticles of the present invention provides better durability to the applied silver nanoparticle finish.

ADVANTAGES OF THE INVENTION

1. The aqueous dispersion of silver nanoparticles of the present invention is pale yellow in colour, has 80% - 100% of silver particles that are very small in size (in the range 0.2- 4 nm), and can be applied on white and pale coloured substrates.
2. It shows 99.99% antimicrobial activity at very low concentrations of less than 0.3 ppm, preferably in the range 0.03 – 0.25 ppm, and with surfactant in the range 0.01-0.099, more preferably in the range of 0.01 – 0.05 ppm.
3. It is easy to synthesize directly in aqueous media and is stable at high temperature.
4. The dispersion stability of the silver nanoparticles of present invention is 15-24 months at normal room conditions.
5. The silver particles provide wash durability after application on textile, binding with simple heat treatment at temperatures of 120 – 150 degree C or with binders at room temperature.
6. The dispersion has very high compatibility with binders and surfactants of various types.
7. The silver particles have higher fixation to polymeric substrates as compared to the processes and products of the prior art.
8. It is expected that the dispersion of present invention would give very low degree of yellowing of substrates when applied on different construction of fabrics and dried at 120 - 150 deg C. This is because the colour of the dispersion is pale yellow and is needed to be applied at very low concentrations (0.1 ppm) for effective antimicrobial activity.

We Claim:

1. A pale yellow coloured aqueous dispersion comprising silver nanoparticles wherein the dispersion is characterized in
 - having a single plasmonic peak in the range of 390 to 410 nm in UV-Vis spectrum,
 - the dispersion having silver nanoparticles of spherical shape with majority of particles (>65%) having equivalent diameter in range of 0.2 to 4 nm,
 - Molar extinction coefficient greater than $12 \text{ mM}^{-1} \text{ cm}^{-1}$ preferably in the range of 12 to $21 \text{ mM}^{-1} \text{ cm}^{-1}$ at wavelength of maximum absorption in the range of 390-410 nm,
 - Dispersion stability of at least 15 months,
 - Minimum Bactericidal Concentration (MBC) lower than 0.3 ppm preferably in the range of 0.03-0.25 ppm.
2. A process for preparation of pale yellow coloured aqueous dispersion of silver nanoparticles, the process comprising the steps:
 - (i) adding a protecting agent to a silver precursor solution;
 - (ii) adding a stabilizer and hydrogen peroxide to the solution of step (i) ;
 - (iii) heating solution of step (ii) to a temperature in the range 55 to 100 degree C;
 - (iv) reducing the solution of step (iii) with a reducing agent wherein the mole ratio of silver salt to reducing agent is in the range of 1:55 to 1:200 to obtain pale yellow coloured aqueous dispersion of silver nanoparticles.
3. The process as claimed in claim 2, wherein a surfactant is optionally added at any step before step (iv).
4. The process as claimed in step (iii) of claim 2, wherein the the reaction mixture is heated in the range of 55 to 100°C preferably in the range of $70\text{-}90^{\circ}\text{C}$.
5. The process as claimed in claim 2, wherein the silver precursor is selected from the group consisting of silver nitrate, silver perchlorate, silver acetate, silver sulphate and silvertetraoxychlorate.
6. The process as claimed in claim 2, wherein the silver precursor is silver nitrate.
7. The process as claimed in claim 2, wherein the protecting agent is selected from the group consisting of poly(ethylenediamine), sodium acetate, bis(p-sulfonatophenyl)phenyl phosphine dipotassium dihydrate, polythene glycol, polyvinyl alcohol and polyvinyl pyrrolidone.
8. The process as claimed in claim 2, wherein the protecting agent is polyvinyl pyrrolidone.
9. The process as claimed in claim 2, wherein the stabilizer is selected from the group consisting of ethylenediammine tetra acetate salt, nitriloacetic acid salt and trisodium citrate.
10. The process as claimed in claim 2, wherein the stabilizer is trisodium citrate.

11. The process as claimed in claim 2, wherein the reducing agent is selected from the group consisting of ascorbic acid, sodium tri-sec-butylborohydrate, lithium aluminium hydride, potassium tri-sec-butyl borohydride, potassium triethylborohydride, sodium triacetoxo borohydride and sodium borohydride.
12. The process as claimed in claim 2, wherein the reducing agent is sodium borohydride.
13. The process as claimed in claim 3, wherein the surfactant is selected from the group consisting of anionic and non ionic surfactants including sodium dodecyl sulfate(SDS), polysorbates, sodium salts of polyacrylic acids, salts of alkylbenzo sulphonates and its condensates.
14. The process as claimed in claim 2, wherein the mole ratio of silver precursor to protective agent is in the range of 1:0.1-1:100, preferably 1:1 to 1:10, more preferably 1:1 to 1:5.
15. The process as claimed in claim 2, wherein the mole ratio of silver precursor to stabilizer ranges from 1:1 to 1:100, preferably 1:1 to 1:50, more preferably 1:5 to 1:15.
16. The process as claimed in claim 2, wherein the mole ratio of silver precursor to reducing agent is 1:55 to 1:200, preferably in the range of 1:60 to 1:100.
17. The process as claimed in claim 2, wherein the mole ratio of silver precursor to hydrogen peroxide is in the range of 1:50 to 1:500, preferably 1:100 to 1:300.
18. The process as claimed in claim 3, wherein the mole ratio of silver precursor to surfactant is in the range of 1:0.5 to 1:350, preferably in the range of 1:5 to 1:150.
19. The process as claimed in claim 2, wherein optionally a binder or a surfactant or both are added to the nanosilver dispersion.
20. A aqueous composition comprising 1 – 99 wt% of pale yellow coloured aqueous dispersion of silver nanoparticles as claimed in claim1, 0.001 to 10 wt% preferably 0.01 to 3.0 wt% of a surfactant and optionally with 0.1 to 10 wt% of a binder of the final composition.
21. A composition comprising 1 – 99 wt% of pale yellow coloured aqueous dispersion of silver nanoparticles as claimed in claim 1 and a binder, wherein a binder is in the range of 0.1 to 10 weight% of the final composition.
22. The composition as claimed in claim 20, wherein the surfactant is selected from the group consisting of anionic and non ionic surfactants including sodium dodecyl sulfate (SDS), polysorbates, sodium salts of polyacrylic acids, salts of alkylbenzo sulphonates and its condensates or a mixture of any two or more selected from the group.
23. The composition as claimed in claim 20, wherein the surfactant is sodium dodecyl sulfate (SDS).
24. The composition as claimed in claims 20 or 21, wherein the binder is selected from the group consisting of acrylic based binder, epichlorohydrin-bis-hexamethylenetriamine based binder,

copolymer binder with maleic acid, epoxy based binders, polyurethane and polyester resins.

25. The composition as claimed in claims 20 or 21, wherein the binder is Epichlorohydrin-bis-hexamethylenetriamine polymer based binder.

26. The composition as claimed in claim 20 or 21, wherein the minimum bacteriocidal concentration (MBC) is lower than 0.01 to 0.099 ppm preferably in the range of 0.01- 0.05 ppm.

27. The composition as claimed in claim 20 or 21, wherein the molar extinction coefficient is above 18 mM^{-1} preferably in the range of $18\text{-}25 \text{ mM}^{-1}\text{cm}^{-1}$.

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Figure-1

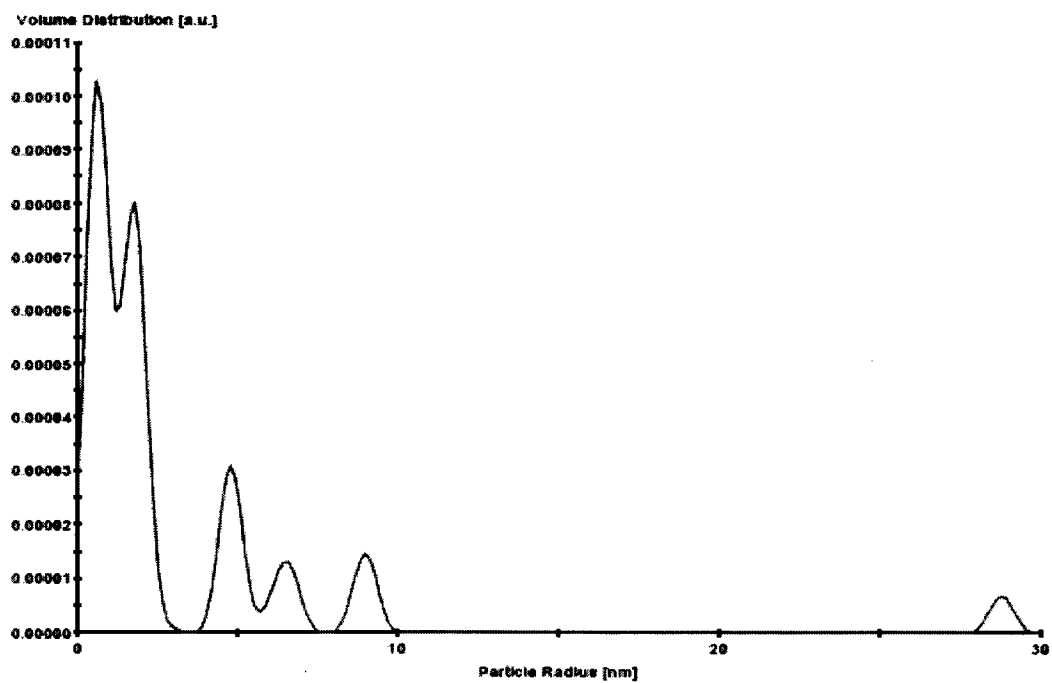


Figure 2

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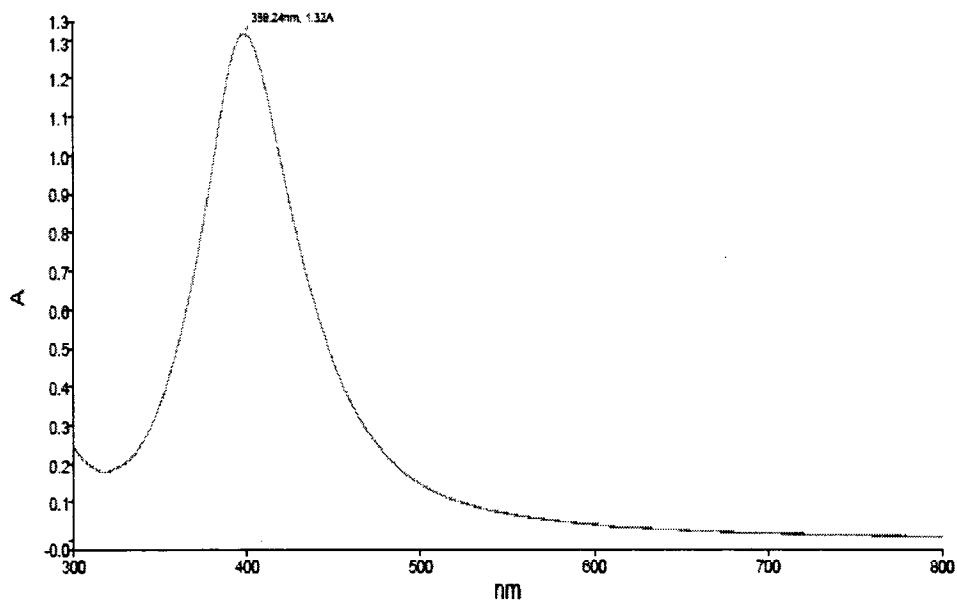


Figure 3 (a)

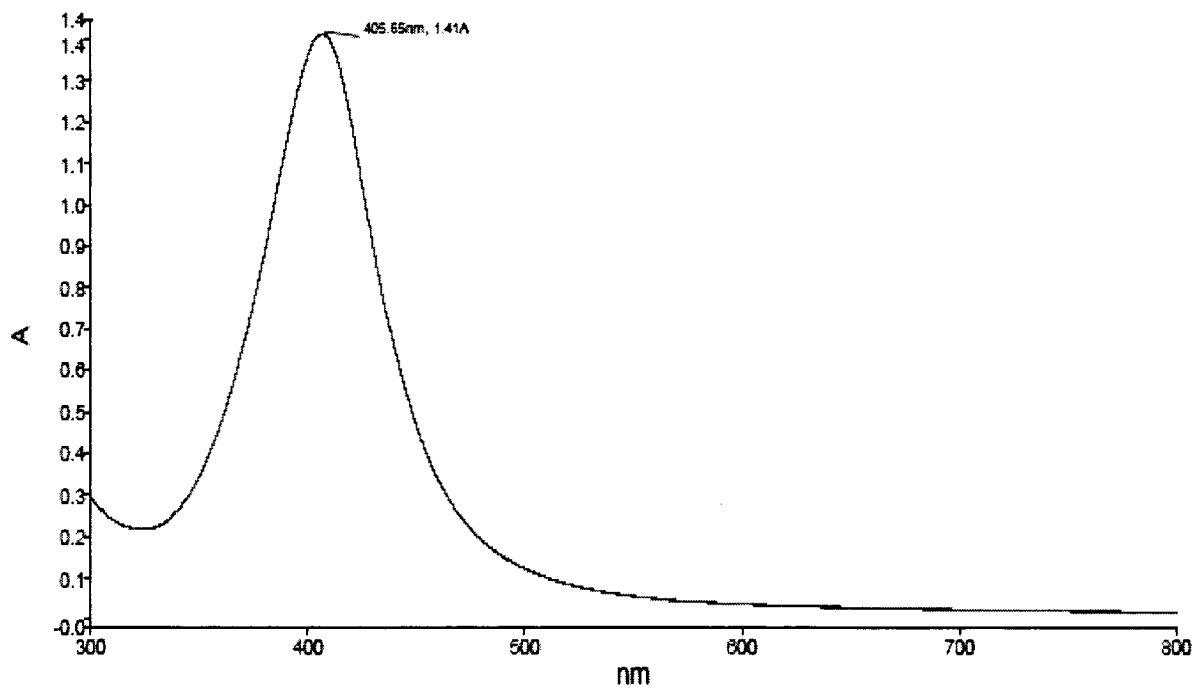


Figure 3 (b)

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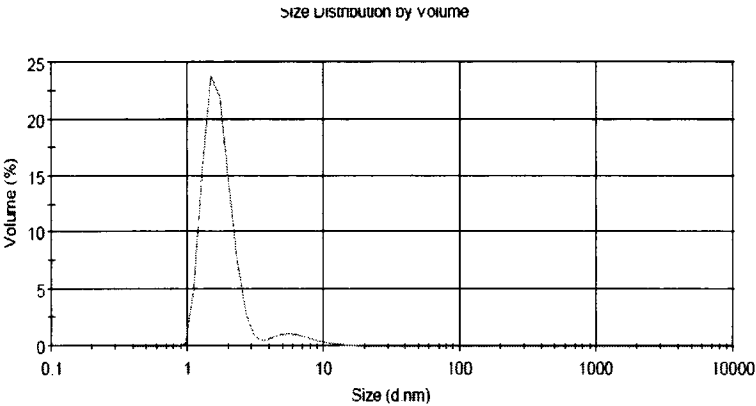


Figure 4 (a)

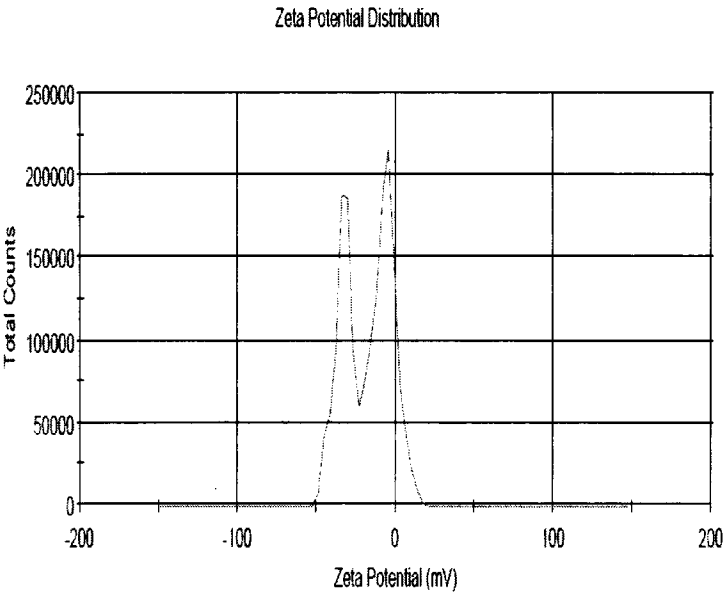


Figure 4 (b)

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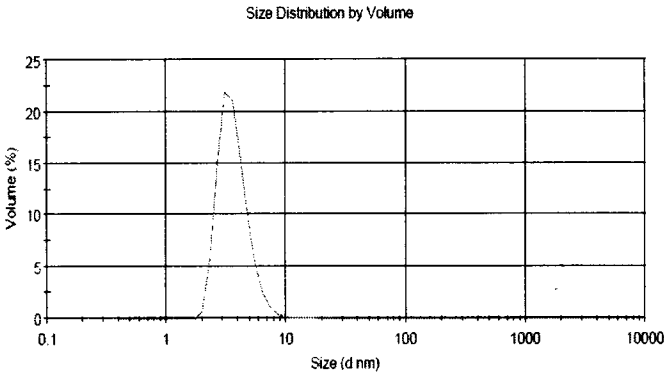


Figure 5 (a)

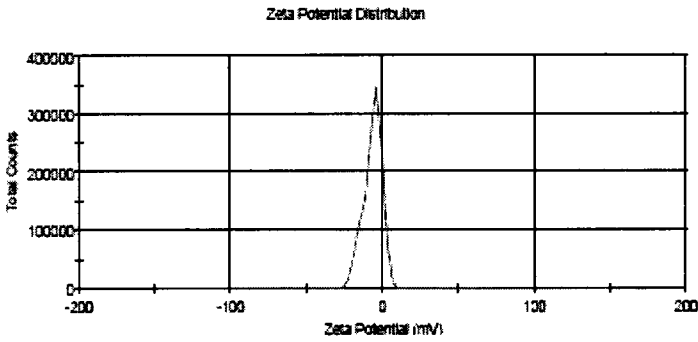


Figure 5(b)

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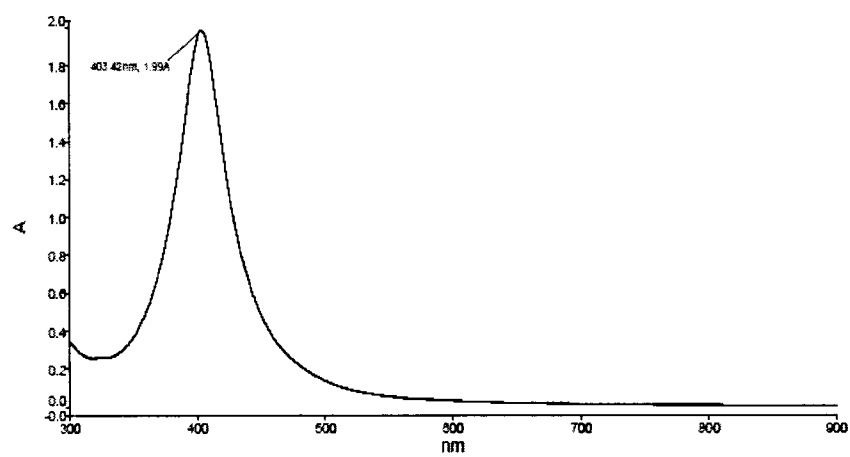


Figure 6