

Nano particles - Application in the Textile finishing

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Abstract

Nanotechnology has opened up, immense possibilities in textile finishing area resulting into innovative new finishes as well as new application techniques which can provide high durability for fabrics, because nano-particles have a large surface area to volume ratio and high surface energy thus presenting better affinity for fabrics and leading to an increase in durability of the function. The properties imparted to textiles using nano technology include water repellency, stain repellency, anti-bacteria, UV protection, flame retardation, improvement in dye ability and so on.

Introduction

Over the past few years, a little word with big potential has been rapidly introducing itself into the world's consciousness. That word is "Nano" and mostly used in nanotechnology. Because of scientific convergence of physics chemistry biology, materials and engineering at Nano scale, it is truly a portal opening on a new world. K Eric Drexler, mentioned word 'Nanotechnology' in 1986 in his famous book 'Engines of Creation: The coming Era of Nanotechnology' to describe what later became known as Molecular Nanotechnology (MNT), following up on visionary ideas presented 27 years earlier by famed physicist, Richard Feynman. As the possibilities of molecular nanotechnology grew and excitement built in the scientific community, many researchers began using the term for their own accomplishments at the Nano-scale, distinct to molecular manufacturing. The first work on nanotechnology in textiles was undertaken by Nano-Tex, a subsidiary of the US-based Burlington Industries. Later, more and more textile companies began to invest in the development of nanotechnologies. Coating is a common technique used to apply Nano-particles onto textiles. The coating compositions that can modify the surface of textiles are usually composed of Nano-particles, a surfactant, ingredients and a carrier medium³. Several methods can apply coating onto fabrics, including spraying, transfer printing, washing, rinsing and padding⁴. Out of these methods, padding method is the most commonly used. The nano-particles are attached to the fabrics with the use of a padder adjusted to suitable pressure and speed, followed by drying and curing. The properties imparted to textiles using nanotechnology include water repellence, soil resistance, wrinkle resistance, anti-bacteria, anti-static and UV-protection, flame retardation, improvement of dye ability and so on⁴. Nanotechnology is all about making products from very small constituents, components or subsystems to gain greatly enhanced material properties and functionality. One area where innovation is proceeding at a very fast pace is miniaturization. High levels of miniaturization is achieved by the emerging field of nanotechnology ability to work in the molecular level atom by atom, to create a large structures with fundamentally new properties and functionalities, with Nano finishing. Nano finishing is concerned with positive control and processing technologies in the sub nanometer range⁴. Nonwoven fabrics composed of electro-spun nanofibres have a large specific surface area, a high porosity and a small pore size in comparison with commercial textiles making them excellent candidates for use in filtration, medical and membrane applications. Nowadays, polymer nanofibres are used in various applications. One of the most widespread applications of nanotechnology is in clothing⁵.

Nanotechnology in Textiles

Nanotechnology has real commercial potential for textile industry. The first commercial application of Nano technology in textile and clothing industry is found in the form of Nano particle (sometimes called Nano bead) through a finishing process, which is generally known as Nano finishing. The aim of Nano finishing is the manipulation of individual atom molecules to create a structure. Nanotechnology can provide high durability to fabrics because Nano particles have large surface area to volume ratio, High surface energy. Thus presenting better affinity towards the fabric without affecting their breathability or feel. Nanotech research efforts in textile have focused on two main areas:

1. Upgrading existing functions and performance of textile materials,
 2. Developing intelligent textiles with completely new characteristics and functions.
- Depending upon the dimensional aspects, there are three main approaches for the application of nanotechnology in textiles are -
- For nanomaterial, which are at Nano scale in one dimension, there appear to be many opportunities for the application of very thin surface coatings.
 - Nanofibres and nanotubes are at Nano scale in two dimensions and their utilization in many forms of composite materials offers opportunities for improving the mechanical properties and altering electrical, optical or biological characteristics.

- The approach involves the use of Nano-particles having Nano scale in three dimensions for incorporation in fibers, coatings, films etc., to provide a number of possibilities such as imparting antimicrobial, flame retardant and chemical softening effects to textiles¹.

SYNTHESIS OF NANOPHASE MATERIALS

There are two ways in synthesis of Nano phase materials they are⁵ Top down approach and Bottom up approach.

Top down approach involving breaking down the bulk materials to Nano sizes (Eg. Mechanical alloying)

Bottom up approach the Nano particles also made by building atom by atom

(Eg. Inert gas condensation).

There are six widely used methods to produce Nano materials:

1. Plasma arcing
2. Chemical vapor deposition
3. Electro deposition
4. sol-gel synthesis
5. Ball milling
6. Use of nanoparticles.

In the first two methods, molecules and atoms are separated by vaporization and then allowed to deposit in a carefully controlled and orderly manner to form Nano-particle. The electro deposition involves a similar process, since individual species are deposited from solution. The sol-gel synthesis, a colloidal suspension is formed due to hydrolysis and polymerization reactions of the precursors, which on complete polymerization and loss of and loss of solvent leads to the transition from liquid sol into a solid gel phase. In ball milling, macro crystalline structures are broken down into Nano crystalline structure.

Functional Finishing

The application of ultra-fine particles, produced using Nano technology, in textile finishing is fast growing. These application, are imparting multi-functional properties such as ultra violet resistance, anti-bacterial, moisture control to apparel products, made from natural fibers including, cotton, wool, silk and also synthetic fibers such as polyester and nylon. Nano particles can be applied on textiles by two stage process, initially there is the manufacturing of new, stable Nano material, which must be in the first instance be protected against properties defined by the size of the particles. The second step sees the creation of the foils emulsions and dispersions that can be applied to the final textile product, in the most favorable case by means of conventional finishing processes. Nano-particles such as metal oxides and ceramics are also used in textile finishing to alter surface properties and impart textile functions. Unstainable apparels based on Nano technology are becoming widely popular. The Nano technology finish creates care free fabrics that minimize stains, oil repellency and provide wrinkle resistance. These enhanced fabric allow water and oil spills to easily bead and roll off the fabric without penetrating the fibers and maintain in the fabric throughout the life of the garment. Some Naturally available Nano-particles are used for finishing for different functional properties of fabric are as follows⁴.

Nano particles	properties
Silver	Anti-bacterial finishing
Fe	Conductive magnetic properties, remote heating
ZnO and TiO ₂	UV protection, fibre protection, oxidative catalyst
TiO ₂ and MgO	Chemical and biological protective performance provide self-sterilizing function.
SiO ₂ or Al ₂ O ₃ with pp or PE coating	Super water repellent finishing
Ceramic	Increasing resistance to abrasion
Clay	High electrical heat and chemical resistance
Cellulose nano whiskers	Wrinkle resistance, stain resistance, water repellency

In the present paper, following effects or properties achieved by nanotechnology are explained-

- Stain and water repellency property
- Self-cleaning effect
- Antimicrobial property
- UV protection property.

1. Stain and Water Repellency Effect

Repellency: Repellency is a condition of limited wettability.

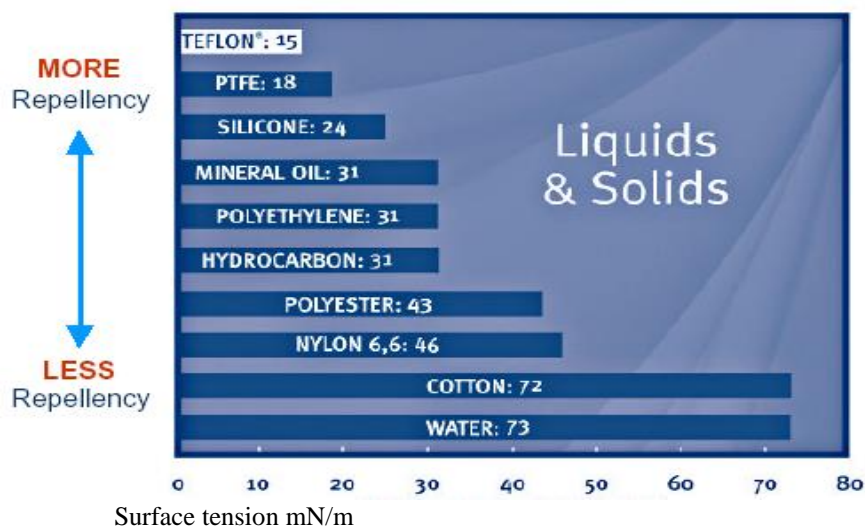
Water & Oil Repellency of a fabric can be defined as, the resistance of a fabric to wetting & penetration of a liquid, such as water or oil, depends on the chemical nature, geometry and roughness of the fiber surfaces and the capillary spacing in the fabric

Theory: Water is having very high surface tension & the attractive force between the molecules of water enable to form droplets when it is forced through a fine hole. When water is placed on a solid, if the attractive force between the water molecules and the molecules of the solid surface is greater than the attractive forces between the water molecules themselves, water will not spread on those surfaces. Thumb rule is that liquids will only spread on surfaces with a higher surface tension than themselves.

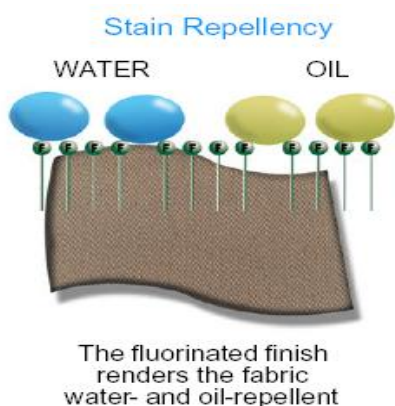
Contact angle: Contact angle between liquid & solid is less than 90°, the liquid will wet the solid

Contact angle between liquid & solid is greater than 90°, the liquid will not wet the solid and the surface is termed non-wetting or repellent

Surface tension of some common materials

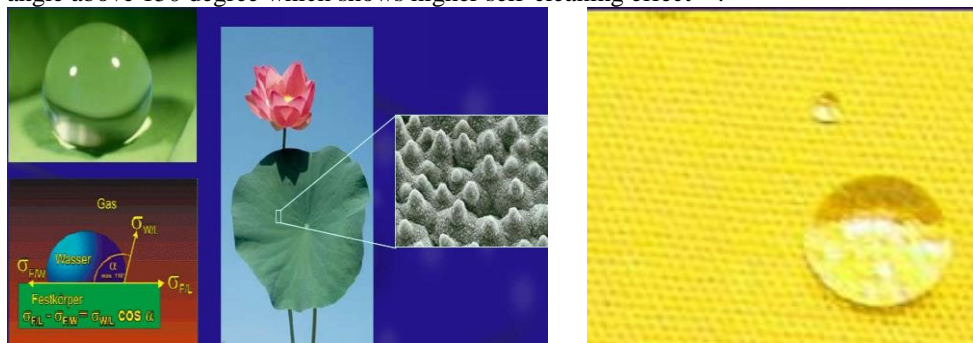


Fluorocarbons are organic compounds consisting of per fluorinated carbon atom. Reduces the critical surface tension of the fabric by forming a thin film coating around the fiber which gives durable Oil and Water repellent, Stain and Soil repellent finishing on all types of fibers & doesn't affect breathability as it leaves the spaces between each fiber open.



Hydrophobic fluorocarbon shows better adhere to synthetic surface than cotton also hydrophobic fluorocarbon by simple coating can give minimum water angle of 120 degree, so to solve this problem nanotechnology have been developed new methods using nanotechnology known as Lotus effect . The self-cleaning of super hydrophobic micro to Nano structured surfaces was observed to be a property of lotus plant leave Through micro to Nano surface structure repel dirt this is not only due to chemistry of hydrophobic surface but due to bulky micro structure (5-10 m in diameter) and a fine Nano structure (10nm to 5nm) layered on top surface, oil or dirt touch minimal top surface only, they are washed away by water droplet so surface stay dry even in heavy shower. This keeps lotus leaf clean under light rain. This effect is known as Lotus effect and trade name was introduced to commercial product was introduced in mid 1990s. Nano -Tex water repellent coating improves water repellency by creating Nano whiskers, which are made of hydrocarbons and have about 1/1000 of size of a typical cotton fibre. They are added to the fabric to create a peach fuzz effect .The spaces between the whiskers

on the fabric are smaller than the typical drop of water, but still larger than water molecules water thus remains on top of the whiskers and above surface of the fabric. This concept is based on Lotus plant, and can give contact angle above 150 degree which shows higher self-cleaning effect^{8,9}.



Lotus Leaf and a SEM image of its surface

A) Water drop on the surface of a lotus leaf B) A drop on treated textile as compared with fig. (A).

Self-cleaning effect can be achieved through self-catalytic property of some of the metal oxides nano particles. Nano sized silver; titanium dioxide and zinc oxide are used for imparting self-cleaning and antibacterial properties. Metallic ions and metallic compounds display a certain degree of sterilizing effect. It is considered that part of oxygen in the air wind water is turned into active oxygen by a catalyst containing metallic ion, thereby destroying the organic substance to create a sterilizing effect¹¹. Titanium dioxide is a photo catalyst, when it is illuminated by light of energy higher than its band gap electrons in TiO_2 will jump from the valence band to conduction band and electron and electric hole pairs form on the surface of photo catalyst. electron and oxygen will combine to form O_2 radical ions, whereas the positive electric holes and water will generates hydroxyl radicals OH . Since both products are unstable chemical entities, when organic compound fall on the surface of photo catalyst it will combine with O_2 and OH radicals and turn into CO and H_2O . This reaction belongs to oxidation reaction¹². During reaction, photo catalyst is able to decompose common organic matter in the air, such as molecules causing odour bacteria and viruses or organic stain and dirt. Hence, Nano TiO_2 provide effective protection against discoloration of stain and bacteria. Zinc oxide is also a photo catalyst and photo catalysis mechanism is similar to titanium dioxide. Photo catalytic property of zinc oxide (3.37eV band gap) is higher than titanium dioxide (3.2eV band gap) as its band gap is higher than titanium dioxide.

Antimicrobial Effect

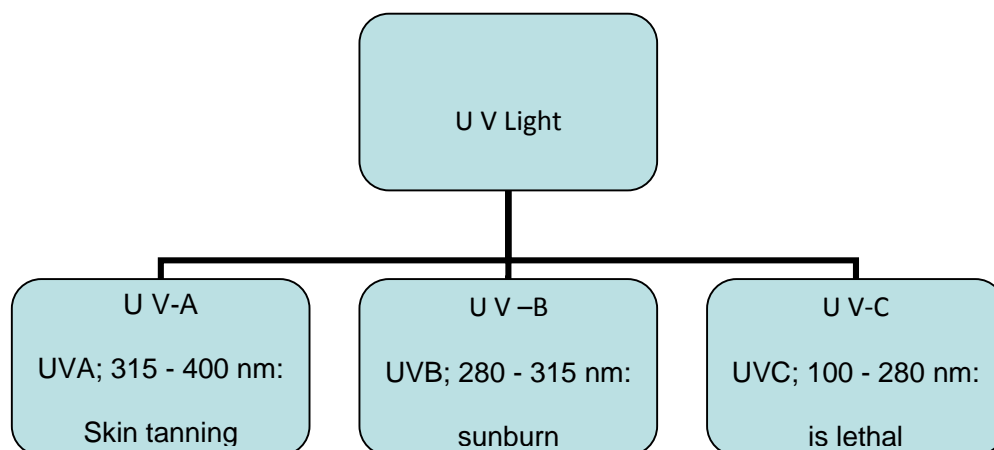
Due to direct skin contact, textiles are also permeated with microorganisms even after only a short period of body wear. Textile-relevant bacteria are mainly those present on the skin, as well as those found in faces. The favorable conditions prevalent on the skin and in close-fitting textiles, such as humidity, warmth and nutrients (perspiration, urine) enable the bacteria to increase their number very rapidly²².

Common microorganisms	Effects on textiles
Bacillus subtilis, Corynebacterium acnes, Listeria monocytogenes, Staphylococcus aureus, Streptococcus saprophyticus, Escherichia coli, Klebsiella pneumoniae, Proteus vulgaris, Salmonella enteritidis, Candida albicans, Epidermophyton floccosum and Trichophyton mentagrophytes	Pathogenic, Body odor, Foot odor, Urine odor, Color change and Stains

Nano-particles which shows antibacterial effect given in table no.1. For antibacterial finishing, ZnO Nano-particles scores over Nano-silver in cost-effectiveness, whiteness but Nano silver, particles have extremely large surface area thus increasing their contact with bacteria and fungi and shows higher antibacterial property than zinc oxide, in addition, Nano-silver can be applied to a range of other healthcare products such as dressing for burns and so on. Nano ZnO particle size 38 ± 3 nm has demonstrated excellent antibacterial activity against S.aureus and Pneumonia bacterium.

UV Protection Property

Sunlight reaches the surface of the earth at a wavelength between 290 and 3000nm. Radiation between 290 and 400 nm, called as ultraviolet or UV radiation (UVR) consists of the shorter, high-energy UV-B rays (280-320nm), and the longer energy UV-A rays wavelength (320-400 nm). UVC is not present in the solar spectrum at the earth's surface, due to the absorption by the ozone layer in the upper atmosphere.



Medical research has shown that the connection between UV radiation and health risks must not be underestimated. UV-light leads to cellular damage and causes inflammation of the skin. The most obvious result of the inflammation is the formation of erythema, commonly known as sunburn. It is especially dangerous for people whose skin burns easily or moderately. Technology, progress, and emigration have led people to move, not only within their own country or continent, but also to areas where their skin was not adapted to change in environment. Change in leisure activities, such as outdoor sports (tennis, golf, swimming etc.) or holiday in sun-intensive zones²². The reduction of the ozone layer increases the intensity of UV radiation. UV protection depends on the extent to which a woven or a knitted fabric transmits, absorbs, or reflects UV radiation determines its sun protection properties. The transmission, absorption, and reflection are in turn dependent on the fiber, fabric construction (thickness and porosity) and finish. To differentiate clothing and other textiles from sunscreens, the term Sun Protection Factor (SPF) is normally used for sunscreens and the term Ultraviolet Protection Factor (UPF) for textiles.

UPF classification & Protection in Textiles

UPF Range	UVR protection category
15-24	Good protection
25-39	Very good protection
40-50,50+	Excellent protection

Transmission through the fibers can be effectively reduced by use of selected dyes, fluorescent-whitening agents and by means of UV absorbers. These products have chromophoric systems that absorb very effectively in the UV region, enabling them to maximize the absorption of UV radiation on textiles¹². Inorganic UV blockers are more preferable to organic UV blockers as they are non-toxic and chemically stable under exposure to both high temperatures and UV. Inorganic UV blockers are usually certain semiconductor oxides, such as TiO₂, ZnO, SiO₂, and Al₂O₃. Nano Titanium dioxide and zinc oxide were more efficient at absorbing and scattering UV radiation due to fact that nanoparticles have larger surface area per unit mass and volume than conventional materials. For small particles, light scattering predominates at approximately one tenth of wavelength of the scattered light. Raleigh's scattering theory suggests that scattering was strongly dependent upon the wavelength, where the scattering was inversely proportional to wavelength to the fourth power. This means in order to scatter UV radiation between 200 and 400 nm, the optimum size of particle will be 20 to 40nm^{13, 14}.

Coating Methods present and future:

Coating is a common technique used to apply nanoparticles onto textiles. The coating composition that can modify the surface of textiles are usually composed of nano particles, a surfactant, ingredients and a carrier medium⁷. Spraying, the coating composition is sprayed on to textiles, with the control of the depth and targeting to specific areas. Transfer printing such as rotary, flexography and inkjet printing. Washing, accomplished by using a washing solution coating nanoparticles during wash or rinse cycles in a washing machine. Padding, where Nano particles are attached to the fabrics with the use of padder applied under pressure. Nano matrix by which a functional material Nano scale coating on each of monofilaments that forms a woven or knitted fabric is possible. Plasma assisted coating by which uniform coating of Nano-particles without dispersion of nanoparticles in liquid is possible which avoids problem of nanoparticles agglomeration during dispersion.

Some market place examples of Nano products for textiles:

- Degussa Japan based Company produces nanoparticles which gives hydrophobic self-cleaning surfaces to textile.

- Schoeller Textiles –AG, Switzerland base company developed water repellent fabrics using nanosphere technology.
- A self-cleaning cotton fabric known as Nano-care was developed and is marketed by an American Company Nanotex, and stain resistant Jeans and khakis also produces water repellent cotton surfaces by modifying the cylindrical structure of the cotton fabrics then by applying Nano-particles on fabric (nanosphere technology) which creates Nano whiskers .
- Ciba specialty chemicals developed microcapsules of Nano-particles which releases antimicrobials during dyeing or finishing processes.
- Hyosung R &D private institute developed a Nano silver containing nylon fibers which can use for sports and military applications.
- NanoHorizons (Us) produces nanosilver coated sports clothings.
- BASF is developing Minicor TX, TT finishes for self-cleaning effect to technical textiles where soft handle and high wash fastness are not requirement.
- Kanebo spinning, Japan produces polyester yarn with 20 layers (50 nanometers) to absorb moisture.
- Also Toray Industries INC, Japan developed ultra-fine nanometer nylon threads with superior moisture absorption properties.

Conclusion

Nanotechnology holds an enormously promising future for textiles. It is estimated that nanotechnology will bring about hundreds of billion dollars of market impact on new materials within a decade to textile certainly. Therefore, advances in the customer-oriented products should be focus for the future nanotechnology applications. The future research should be concentrate on developing self cleaning, crease and shrink resistance properties in apparel fabrics, sports clothing and in developing odorless undergarments.

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