Plasma Treatment of Cotton Fabric based on Water Glass using Sol-gel and Silver Nano-particles

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By

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Dedication

Throughout my life two persons have always been there during those difficult and trying times. I would like to dedicate this dissertation and everything I do to my parents.

Acknowledgement

I am indebted to many who contribute to my research. My thanks and appreciation is extended especially to Mr. Haseeb Akram and the hidden support of Allah almighty. I must acknowledge as well the many friends, colleagues and teachers who assisted, advised and supported my research and writing efforts over the year.

Abstract

Much academic and industrial research has been done to develop antimicrobial finishes on cotton fabric. It covers from chemical finishing to coating to plasma. This dissertation explores the influence of the incorporation of plasma in a newly developed Sol-Gel method on antimicrobial finish on cotton fabric. Cotton fabric was first treated with atmospheric pressure plasma. The fabric is then subjected to silica-sol in conjunction with the $AgNO_3$solution. Scanning electron microscopy (SEM) was used to analyze chemical and morphological changes on the surface of fabric. The durability of the Ag+ ion particles on repeated laundered of cotton fabric was proven by antibacterial tests. Maximum resistance from the bacterium can be attained by the process for a long period of time.

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1Introduction:

The textile industry manufactures variety of fabrics through different cellulosic, manmade, regenerated, protein fibers and through their blends in varying proportion [1]. The first step is to prepare the fiber i.e. spun or in case of natural fibers manipulate them to useful fiber. Secondly these fibers are subjected to weaving, knitting and then to dyeing finishing steps. Finally they are fabricated to finished end product.

An industry always looks for new technologies innovations and treatments to reduce cost as well as to increase efficiency and productivity.

Now-a-days people are comparatively very conscious about health, hygiene and cleanliness than they were about a decade or two ago. Hence in the era of IT revolution, even a common person focuses about the harmful effects of the pathogens. Some textiles are also used in medical and healthcare applications. Currently in medical field textile is mostly disposable or non-woven's as durability of antimicrobial is a great issue. Clothing and textile materials are not only the transporter of microorganism such as pathogenic bacteria, odor creating bacteria and mould fungi but also provide a complete environment for their growth such as temperature, moisture pH, humidity etc[2]. So this finish is not only applied to medical usage fabrics but also for public's general use.

1.1Why we use anti-microbial finish:

Thousands of species of microbes exist in surroundings. These microbes are dangerous for both living and non-living things. Insupportable smell from the garment such as socks; spreads diseases. Yellowing or may be discolorations are some of terrible effects by some microbes. Depending upon the end-use we need different types of finishing on textile; antimicrobial is one of them. For example surgical gowns, bandages need to be ensured that they prevent harmful bacteria and other microbes to prevent infections, cross infections and spreading of other diseases. Sometimes the fabric or textile materials that are used for the healing of patients the bacterial attack increase their illness[2].

Natural fibers like wool and cotton are very important as they provide nutrients, oxygen, temperature and required pH to the microbe. So a house is full of the things that provides complete environment for the growth of microbes. In the same way in hospitals people have a great risk of transmission of diseases by microbes. Similarly sport techs need high degree of durability and protection to the skin. Micro-organisms metabolize nutrients, such as sweat and soil present in textile products, producing odor causing intermediates that cause irritation[3]**.**So hi-Tec textiles are globally demanded.

1.2Chemistry of cotton:

Cotton is a natural cellulosic staple fiber. Like other plant cell a cotton molecule has a cuticle, a primary wall, a secondary wall and a lumen. Outer layer or skin of fiber has cuticles which are composed of waxy layers. This wax protects the fiber content inside it against chemicals or other degrading agents[4]. By scouring, or bleaching we actually remove these cuticles. Primary cell wall is made up of fine cellulosic threads called fibrils. Beneath the primary wall there exists the secondary wall that has bulk of fibers in it[1], [5].

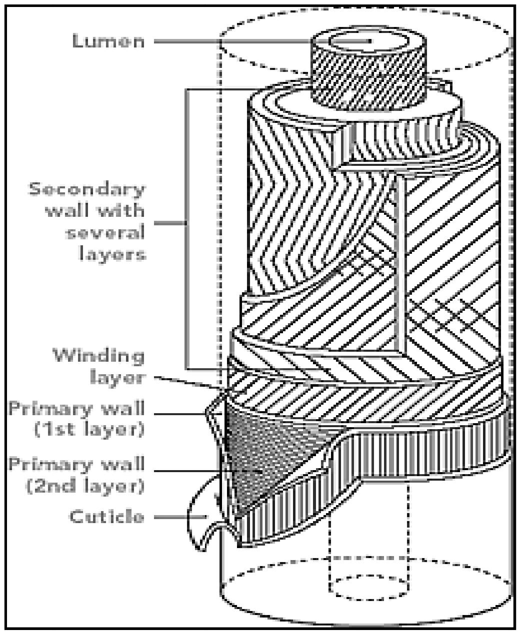

Figure 1 Morphological Structure of Cotton

The hollow tube along the length of the fibers is called a lumen. It is full of cell sap and is responsible for the growth of fibers[5]. It has dilute solution of sugars, proteins, minerals and a cell's waste products. It is also responsible for the color of the fiber that ranges from pure white to grey and yellows[1].

The repeating unit of cotton is cellubiosic that contains two glucose molecules in it. It consists of 5,000 cellubiosic units[1]. The most important functional group is OH which is responsible for bonding. Except this hydrogen bonding, wander wall forces are also dominant. Crystallinity of cotton fiber ranges from 65-70% and the rest is composed of amorphous region[1], [4].

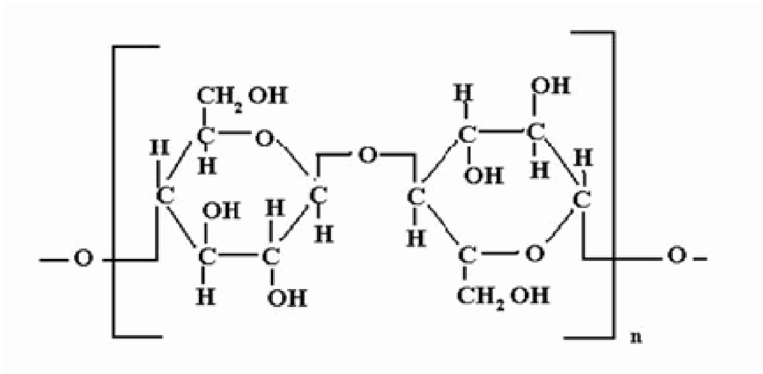

Figure 2 Chemical Structure of Cotton

1.3Need to make cotton microbial resistant:

Cotton is widely used in our daily life for wearing purpose as well as other uses in medical textiles, tissue papers, teabags and in other food industry. Extensive use of cotton is due to its comfort to wear, breathability, softness and elasticity. Some important factors that briefly describe the need to make cotton antimicrobial are explained below[3]:

- While using cotton as bandages, surgical gowns, raw cotton and other medical uses, cotton needs to be resistant to microbes. As in this field compromise to hygiene leads to death. So great care is required.
- Cotton is widely used in food industries. There is also a great need to fulfill hygienic requirements as it also directly related to the health of human being. We widely use cotton in coffee filters, water filters, teabags etc etc... If we ignore the growth of microbes it will cause a severe effect on health.
- Another need of making cotton antimicrobial is the case where some people have sensitive skin. They readily get rashes or other microbial diseases. For such cases customers demands that finish on fabric with durability.
- In some cases, either work ware is sensitive or workers have to deal with some sensitive chemicals e.g. petro chemicals and other hydrocarbon derivatives. These areas are much sensitive to microbes. Care must me needed. Antimicrobial finish treated fabrics must be provided to the workers there.

- In museums we use cotton for the preservation of mummies, animals, insects and other living organism. Without special finishes treated on fabric the preserved item can be rotten.

1.4History of Antimicrobials:

Antimicrobials have been used for many decades. The history of these finishes belongs to the Egyptians who preserve their mummies by different treatments. Due to different human activities and experimentation,an environment gets polluted by different gasses. Hence due to this pollution increase of greenhouse effect, depletion of ozone layer and environmental pollution; the rate of spreading of diseases increases day by day so textiles are extensively demanded with this finish. It is because today in this technological era people are so much aware of the hygienic life style. That’s why we use antimicrobial finishes to stop the growth of bacteria and so prevents many diseases[3].

In the beginning of 20thcentury the major causes of death was bacteria known as pathogens [6]. A number of chemicals have been used for this purpose such as salts, iodophors (substance that slowly release iodine), organometallics, phenols, thiophenols, urea, formaldehyde derivatives, amines and other antibiotics[7]. Use of natural antimicrobials such as chitosan and some natural dyes have also been reported. Herbs such as Aloe Vera, tea tree oil, eucalyptus oil, and extract of tulsi leaf and neem are also used for this purpose[3], [7]. So there are many natural occurring antimicrobials but their use on textile or activity on textile is limited. The researchers are continually moving towards eco-friendly antimicrobials for the substitution of toxic ones[8].

Cellulose provides best matrix to microbes so surface modification or the use of nano-particles is supposed to be modern way for preventing them.

1.5Microorganisms and Bacteria:

Microorganisms are the smallest form of life that exists on the Earth. They carry out many chemical reactions that are sometimes beneficial and sometimes detrimental for other organisms. If there were no microorganism, the higher life can never grow, develop or sustain. Moreover recycling of key nutrients i.e. Carbon, Nitrogen, Oxygen cycle and degrading of organic matter also relies on microbial and bacterial activity.

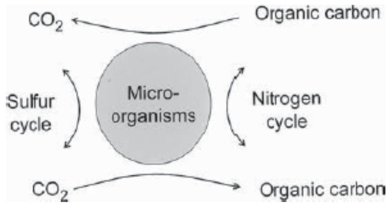

Figure 3

Many industrial processes like food and beverage industry and production of antibiotics or other human protein needs different microbial activity. So we can conclude that microorganisms provide support and maintenance to our life [6]. On the other hand there are some disease causing i.e. pathogenic or harmful microbes exist in environment. Especially when we are talking about the textile industry; the cotton cellulosic fabric gets yellow staining, smell and degradation.

1.6Bacteria:

A bacterium was first discovered by Antony Van Leeuwenhoek in 1676[9]. Bacteria are microscopic organisms. They are prokaryotic that has no nucleus. They are simple and unicellular. Some types of bacteria are harmless or, often are beneficial to human beings. Others are pathogenic, causing diseases and even death. Some species survive themselves by fixing atmospheric nitrogen. Numerous different types exist as single cells or colonies, and they have stiff cell wall that specifies their shape. These shapes can be coccal (spherical), bacillary (rod-shaped), spirochetal (spiral/helical or corkscrew), and vibro (comma-shaped). Bacteria are also classified on the basis of their oxygen requirement (aerobic vs. anaerobic) to tissues. All types play a foremost role in the cycling of nutrients in ecological unit via aerobic and anaerobic disintegration[6].

1.7. Chemistry of Bacteria:

Cell is the fundamental unit of a life. Its outer wall gives it a structural shape and inside there is membrane that is semi permeable; it prevents leakage and maintains the correct consistency of nutrients or other internal components. The cell can move, transport material to environment[9].

Cell performs metabolism that is they import material from the environment and convert them to cell nutrients with waste products. Metabolism process called catalytic reaction. In microorganisms we generally use the word growth instead of reproduction for the division of cells by metabolism. Madigan et al suggests that cell performs another important process i.e. replicates DNA to give RNA and other cell proteins.

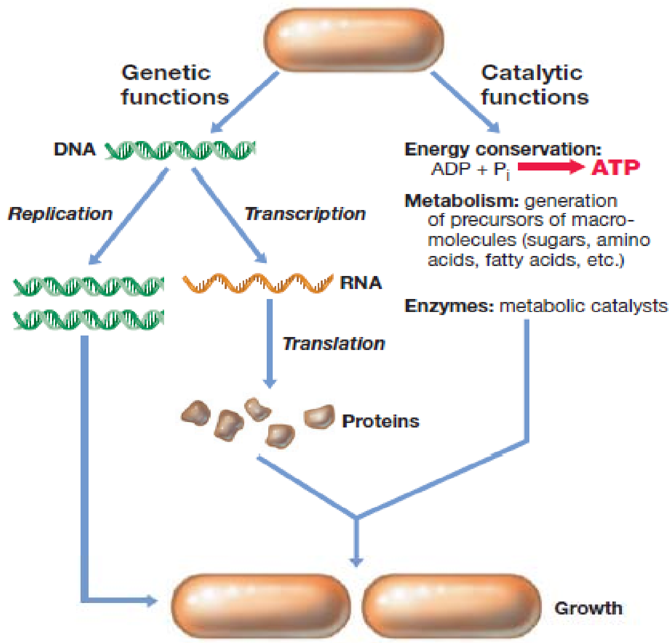

Figure 4 Cell division in Bacteria

Naturally the microbial cell lives in populations. Basically a population is a group of cells that originates from single parental cell by cell division process. The environment in which a microbial cell lives in called habitat[6].

Natural cellulosic cotton fabric provides excellent habitat for the growth of microbes. There exists a wide diversity among the required parameters for the microbial growth for example some microbes requires simple ammonia and carbon dioxide while some needs complete organic environment to grow. These required parameters reflect the way they react and reproduce. The important requirements of their growth that are almost same for all kinds of bacteria and microbes are explained below[9]:

1.7.1 Water:

The bacterial growth and multiplication needs a high concentration of water in their environment. Water is the basic medium that transfers all nutrients to the cell and taken away the waste products. Organism’s protoplasm has water content in it as well as water is also a reactant in metabolic reactions.

1.7.2 Inorganic Salts:

Like all organisms bacteria also entails some salts that are necessary for

- **i)** Maintenance of osmotic pressure
- **ii)** Maintenance of acid-base balance within the cell and
- **iii)** As activators of enzymatic reactions

Iron, sulphur, magnesium and phosphorous are commonly required minerals. For some types of microbes; calcium, manganese, zinc, copper or cobalt are necessary.

1.7.3 Carbon dioxide:

Bacteria will not grow when it is deprived of carbon dioxide.

1.7.4 Oxygen:

Oxygen (O_2) is avital nutrient for some microorganisms but a poison to others. That’s why we categorize them into aerobic and anaerobic. Aerobic are those that require oxygen for respiration while anaerobic doesn’t require oxygen. If aerobic (oxygen-consuming) microorganisms removes $O_2$from a habitat, rendering it anoxic (O_2 free); the changed conditionsmay favor the growth of anaerobic microorganisms thatwere formerly present in the habitat but unable to grow.

1.7.5 pH:

pH is the negative logarithm of the hydrogen ion (H+) concentration of a solution[10]. Optimum range of pH for the bacterial growth is 6.5-8.0. There are very few types that can grow at extreme levels of pH [11].

1.7.6 Temperature:

Bacterial growth requires a specific range of temperature. The temperature at which almost all types of bacteria grow rapidly is known as optimum temperature. The optimum range can vary for some kinds of bacteria and it depends upon the environment in which they are habituated. Optimum temperature is 37 and its range lies from 18 - 42 C [11].

1.8Classification of Bacteria:

Dyes are organic in nature and different dyes are used to stain the cell so that they can be easily seen under microscope. Different types of bacteria show different stains by absorbing dyes. Usually basic dyes are used for microbes because these dyes have positive charges and microbes have negative charge on the surface of cell. So they have more affinity to absorb basic dye than any other class of dyes. When Bacteria absorb dye they exhibit different colors and particular color is for one type of bacteria. Gram positive bacteria has much thicker cell wall and having single types of layer on it while gram negative bacteria has thin wall and two types of complex molecules makes a layer on it [6], [12].

1.8.1 Gram Positive and Gram Negative Bacteria:

In the laboratory, bacteria are classified as Gram positive (blue) or Gram-negative (pink) bacteria. Both show variance in color because of the structure of cell wall. The dye reacts with ethanol group present in cell and show color. Gram-negative bacteria are those that spread the plague, cholera, typhoid fever, and salmonella. They have two outer membranes, which make them more resistant to conventional treatment. They can also easily mutate and transfer these genetic changes to other strains, making them more resistant to antibiotics[12]. Gram-positive bacteria are those that cause anthrax and listeriosis, are more rare and treatable with penicillin, but they can cause severe damage either by releasing toxic chemicals (e.g., clostridium botulinum) or by penetrating deep into tissue (e.g., streptococci). Bacteria are often called germs. Different types of bacteria attacks on cotton. Some of them are explained below[6]:

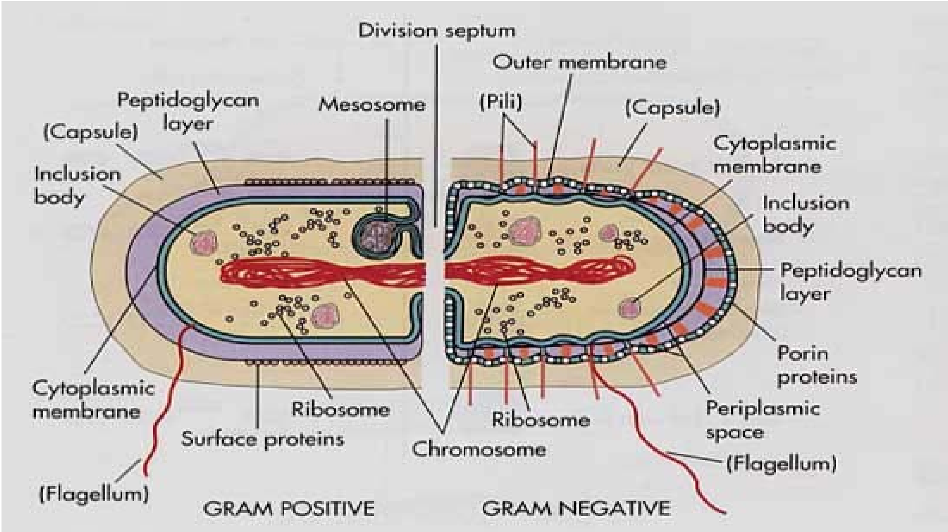

Figure 5a Bacterium

- **Escherichia coli:**

  Escherichia coli are gram negative bacteria. They use H_2S for their metabolism[6].

- **Bacillus:**

  Bacillus is gram positive bacteria. They have lack of cell wall and very few Genomes. They have lactic acid in them. They require O_2 for respiration hence they are aerobic[6],[12].

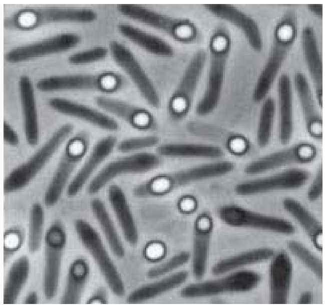

Figure 6 Electron microscopic view of Bacillus

- **Staphylococcus aureus:**

  It is also gram positive bacteria. They don’t need oxygen to breath. They spread wide range of infections in human body as well as food poisoning. Lactic acid fermentation takes place in them[6].

1.9Types of antimicrobials:

a. Leaching type

b. Non-leaching type

1.9.1 Leaching type:

This type of antimicrobial diffuses from the fabric to get contact with the microorganism. This type gets off from the fabric and with the passage of time it is completely consumed by the microbe and thus lost its effectiveness[2], [3], [7].

1.9.2 Non-Leaching type:

This type of antimicrobial bounds to the substrate and controls the microbes. This type of finishing will remain on the surface and doesn't consume by the bacteria[2]. It has more life then leaching type has. It can withstand up to 40 washes with the substrate[13].

There are different methods to apply these finishing on the substrate. Some of them are[3], [7]:

- Insolubilization of chemical reagents into the fabric or on to it
- Fiber treatment with resins, condensates or cross-linking agents
- Micro-encapsulation of the antimicrobial agent with the fiber in a matrix
- Coating of the fiber surface
- Chemical modification of the fiber by covalent bond formation
- Use of graft polymers and/or co-polymerization onto the fiber

1.10Properties of antimicrobials:

The term antimicrobial indicates a protection to textile. Their purpose is to prevent the action and growth of different microorganism on the surface of textile. Ideal antimicrobial finish must possess some specific qualities so that maximum objective can be achieved. So it must have following characteristics[2], [3], [7]:

- Colorless
- Odorless
- Good fastness to washing, drying, pressing rubbing etc
- Nontoxic to consumer, manufacture and environment
- Non allergic

- Non carcinogenic
- Non irritating to skin
- Antistatic
- Cheap or economical
- Easily available in the market
- Easily applicable
- Resistant to body excretions
- Compatible with chemical process
- Must not deteriorate the quality of fabric

1.11Mode of Action:

Different agents behave differently because all have dissimilar chemistry so their mechanism varies from one to another. Their mode of action is also dependent upon the concentration of that applied finish and the type of substrate. Generally they prevent their growth by attacking on their cell wall, denature protein and destroy enzymes thus making impossible the survival of organism[13]. So in general all the finishes possess these six common steps and they are as follow[2], [3], [7]:

1. Adsorption onto the microbial cell surface
2. Diffusion through the cell wall
3. Binding to the cytoplasm membrane
4. Disruption of the cytoplasm membrane
5. Release of cytoplasmic constituents such as K+ ion, DNA and RNA
6. Death of the cell

1.12Benefits of Antimicrobial Finishes:

These finishes add worth to the product for both the producer and the customer in the following ways[3], [2]:

- Protect the raw material from decomposition or degradation
- Controls the staining of microbial growth

- Add originality and freshness to the fabrics
- Eradication of odors produced by microorganisms
- Increase life period of the fabric as it prevents the growth of microbes
- Improve handle and feel for most of the fabrics

These finishes are also important for industrial fabrics that are out in the open weather e.g. fabrics used for sun shelter, partitions, tents, tarpaulins, ropes and such others need protection from rotting and mildew[7]. Similarly in home furnishings such as carpeting, shower curtains, mattress ticking and upholstery also normally subjected to antimicrobial finishes[3].

1.13What Finishes have been applied to cotton?

Bacterial and microbial infections cause serious diseases and textiles are excellent substrate for their growth. To minimize this threat different finishes have been applied on textiles by different periods of time. However any chemical that is being applied to the substrate must be registered as non-toxic, bio-degradable, non-allergic and safe to skin. So eco-friendly chemicals are being applied to make textiles resistant to microbes[8].

Aloevera is a natural plant that has aloe gel in its leaves. It has the ability to resist as well as inhibit the growth of bacteria.

Chitosin is also naturally occurring biopolymer which is used as antimicrobial on textiles. It is non-toxic, biodegradable and resistant to microbes. It has positive charge until the $pH<6.5$ so it interacts with the negatively charged molecules of microbe i.e. cell wall and hence inhibit the growth of bacteria[2], [8].

Curcumin is tuber of Curcuma plant that has methoxyl and hydroxyl groups on it. These groups are considered as responsible of antimicrobial activity.

Citric acid was used for hygienic and disinfectional chemical in past. Its application on textile was cheap, environmental friendly and non-toxic. It is one of the active substances that easily crosslinks with cellulosic chain and produces the ester linkages. Its effectiveness can be observed till 10 washes if it is exhausted well to the substrate.

Neem is another naturally present chemical that is used as antimicrobial agent. This ever green tree is also used in medicines and in pesticides. Active chemicals can be extracted from root, stem leaves etc

1.14 Application methods of Antimicrobial Finishes on Textiles:

We can apply finish on substrate by different techniques such as surface application, chemical bonding, internal antimicrobial release, and micro-encapsulation.

1.14.1 Coating:

This method has the following characteristics:

- It is appropriate to all fibers
- Affinity of antimicrobials will determine its life or durability after wash
- For certain fibers like PAN, ionic charge must be considered

1.14.2 Chemical bonding:

This method has the following characteristics:

- This process is applicable only to those fibers that can be dyed by reactive group e.g. cellulose, wool and polyamide.
- strength of the chemical bond between the antimicrobial agent and the fiber will determine the washing durability
- It is theoretically the best way to achieve durable antimicrobial finish. As; the bond remains stronger the more durable will be the finish.

1.14.3 Internal antimicrobial release:

This method has the following characteristics:

- During spinning the antimicrobials are incorporated in fibers
- It is a feasible process for synthetic fibers.
- It does not work well on cotton.

1.14.4 Micro-encapsulation:

This method has the following characteristics:

- It is a mixture of “chemical bonding and controlled internal release”.
- In this method, not the antimicrobials making the chemical bond with fibers but micro-capsules that contain the antimicrobials are covalently fixed on the fibers.

Effective antimicrobial effect depends on the particular capsule system to regulate the release of antimicrobials in a sustained way[14].

1.15 Plasma:

It is the fourth state of matter. It comprises of ions, radicals, neutral particles, electrons and protons. Due to the presence of such matter it is highly reactive and in textile industry we use it to modify surface of textiles. The advantage of using this technique is that the bulk properties of substrate will become unaffected after application of plasma rays.

“Plasma polymer doesn’t contain regularly repeating units; the chains are branched and are regularly terminated as high degree of cross linking. They adhere well to solid surfaces. Thus plasma polymerization is thought of as a tool box of technologies which can provide surface solutions for the deposition of solid polymer films to a wide range of materials and applications.” [15] Four main effects can be achieve by plasma treatment on textiles i.e. cleaning, surface modification, ablation and cross linking[15].

1.16 Reason to eradicate conventional processes:

Plasma technology is becoming an issue of great interest in Textiles as it can be used in wide ranges of modification especially in chemical processing of textiles. Conventional processes used for different processing’s don’t provides permanent effects. The durability will be lessened after repeated laundering or with the passage of time[15]. Conventional processes also use large amount of water and energy and other effluents. Therefore to acquire permanent modifications of textile substrate and less use of resources and material we move towards plasma technology. Undoubtedly the tremendous functionalities can be achieved in processing of woven and non-woven textiles[16].

Plasmas are accredited to be distinctively useful surface engineering tools due to the following characteristics:

- Its unequaled physical, chemical and thermal range allows the tailoring of surface properties of substrate to unexpected accuracy.
- Low temperature leads to prevention of substrate's surface destruction.
- Permanent results of modifications provoke new areas of research.
- It is environmental friendly process as its completely dry process.

1.17 Plasma generation:

Plasma can be generated by different types of power supplies and they are:

1. Low-frequency (LF, 50–450 kHz)
2. Radio-frequency (RF, 13.56 or 27.12 MHz)
3. Microwave (MW, 915 MHz or 2.45 GHz)

We can create plasma at low pressure and at atmospheric pressure. Atmospheric pressure is further divided into corona treatment, dielectric barrier discharge and glow discharge.

Use of plasma treatments of fibers, yarns and fabrics is for the following types of fictionalization[16]**:**

- Anti-felting/shrink-resistance of woolen fabrics.
- Hydrophilic enhancement for improving wetting and dyeing
- Hydrophilic enhancement for improving adhesive bonding.
- Hydrophobic enhancement of water and oil-repellent textiles.
- Removal of sizing agents.
- Removing the surface hairiness in yarn.
- Scouring of cotton, viscose, polyester and nylon fabrics.
- Anti-bacterial fabrics by deposition of silver particles in the presence of plasma.
- Room-temperature sterilization of medical textiles.
- Improved adhesion between textiles and rubber.
- Plasma-treated fabrics with high hydrophilic stability when stored in alkaline media.

- Graft plasma polymerization for producing fabrics with laundry-durable oleo phobic, hydrophobic and stain-resistant finishes.
- Atmospheric plasma-based graft polymerization of textiles and non-woven's having different surface functional properties on the face and backside of the fabric.
- A fabric which is coated with sizing agent inactive to plasma on one side and on the other side left as hydrophobic or hydrophilic after size removal, the resultant fabric having different functionality on its two sides.
- Flame-retardant coating using monomer vapors (halogen and/or phosphorus) in combination with nitrogen and/or silicone.
- Silicone coating of air-bag fabrics using cross-linked silicone (polyorganosiloxanes).
- Scouring of cotton, rayon, polyester fabrics using a non-polymerizable gas (nitrogen, argon, ammonia, helium), followed by wet treatment for removing the impurities.
- Prevention of readily-occurring color variation in textiles.
- Durable antistatic properties using PU-resin and plasma processing.
- Shrink resistance of animal hair textiles using urethane-based resin and plasma processing.
- Electro-conductivity of textile yarns by surface plasma deposition.

1.18 Plasma-surface interactions:

Plasma induces various modifications on the substrate. Some commonly used processes are plasma cleaning or etching, plasma activation, plasma-assisted grafting and plasma polymerization.

1.18.1 Plasma cleaning and etching:

Plasma cleaning and etching means a removal of material or impurities from the surface.

1.18.2 Plasma activation:

Plasma activation means the opening of new functional groups onto the treated surface. The applied chemical may change the properties of substrate.

1.18.3 Plasma-assisted grafting:

This process has two steps. At first the plasma activation is followed by the exposure to a liquid or gaseous precursor, e.g. a monomer. This monomer then suffers a conventional free radical polymerization on the activated surface.

In this technique monomers are exposed onto the surface and polymerization occurs afterwards.