1. Introduction

Writing process include ink, writing surface and writer (person or instrument). In this study, the handwriting surface was paper or textile fabrics. The history and development of ink is closely bound to the development of writing, writing instruments and paper.

1.1 Writing inks

Inks are the colored fluid ordinarily employed in writing with a pen on paper, parchment, etc. (writing ink), or the viscous paste used for a similar purpose in printing (printing or printer's ink)."

This part attempts only to cover the major development in the chronology of ink development. It describes when and where they were developed and who was responsible for their conception.

1.1.1 Varnish

Varnish was the earliest vehicle of committing thoughts to writing **[1]**. What the composition and preparation of this ancient varnish was, however, is not known; but it is more than probable that it was a Product obtained from the sap of the lacquer or varnish tree **[2]**.

1.1.2 Carbon Inks

Carbon ink was essentially produced from the smoke of green pine. Lampblack was extracted from the pine and placed in the form of cakes.

The Koreans advanced the cause of ink and conveyed its manufacture to Japanese. According to the Nihongi (Annuals of Japan), the king of Korea sent in A.D. 610 two Buddist priests to Japan. One of these priests, Tam-ch'i was skilled in preparing painters pigments, paper and ink **[2]**. This industry was ardently advocated and promoted by the Japanese royalty.

Carbon ink is one of the oldest forms of writing ink. This class of ink is still widely used in the Far East and by artists worldwide. In the simplest form, carbon ink consists of amorphous carbon shaped into a solid cake with glue. It is converted into a liquid for writing by grinding the cake and suspending the particles in a water – glue medium. The brownish tone of the carbon is generally corrected by the addition of coloring matter. For white colors, the color treated with white lead, black were obtained through various type of charcoal and soot **[3]**. Also available are liquids carbon inks in which the carbon is kept in suspension. Shellac and borax are used in place of animal glue and a wetting agent is added to assist the mixture of the shellac and carbon **[3]**.

Carbon inks are very stable and are not decomposed by light, air, moisture or microbiological organisms. They are insoluble in water and can be removed from paper only by abrasion. Therefore, the ink will endure as long as the paper. This class of ink is usually unsuitable for fountain pens, but is used extensively as drawing inks and printing inks **[3]**.

1.1.3 Iron Gallotannate Inks

Gall ink was invented in the Interior Orient, from the species of oak (chiefly *Quercus lusitanica* var. *infectoria*), on which the gall-wasp deposits its ova that from the excrescence known as galls**[4]**. The utilization of galls for ink is mentioned by Philo of Byzantium in the second century (A.D.), in a description of sympathetic ink, and by Martianus Capella in the fifth century **[5]**.The earliest extant document, written with iron ink is an Egyptian parchment of about the seventh century A.D. **[6]**.

Every nation has nut galls that are indigenous to their respective regions, so there are literally thousands of differing types of galls produced. These galls vary in shape and size and, perhaps most importantly, color. The amount of tannin and gallic acid vary according to these colors **[6]**.

In the fifteenth century there was a strong need for these iron gallotannate inks. The inks of the Renaissance required greater fluidity than those of an earlier period. This could only be obtained by the reduction of the quantity of gummy vehicles blended with an increasing in the use of acids. These new, emerging nation-states required uniformity of these inks formulations. France, in 1626, concluded an arrangement for the manufacture of a gall ink that guaranteed and insured more reproducibility in respect to desirable ink qualities **[6]**. This first step pioneered the European wave of regulation of the industries that were considered vital to the growth of the state **[6]**.

In 1965, the English chemist William Lewis publicly announced that he proposed to investigate the subject of ink chemistry. Doctor Lewis was the first to advocate logwood as a tinctorial agent in connection with iron and gall compositions **[6]**.

The year 1831 witnessed the Academy of Sciences in France designate a committee composed of chemists with instructions to study the subject of a permanent ink. This committee reported that it was in favor of the tanno-gallate of iron inks then in use, but stressed that it was essential to be uniform in its compounds, once again for “the good of the state” **[6]**.

William I. Clark, in 1879, submitted a thesis, to the Edinburg University entitled, An Attempt to Place the Manufacture of Ink on a Scientific Basis." The introduction of blue - black ink as a phase of the development towards modern methods was the essential point he was trying to make **[6]**.

Finally, in 1890, Sehluttig and Newman, in their *Edition Dresden*, discussed the subject of iron and gall inks, which served as the definitive work on the subject of tanno-gallate of iron inks **[6]**.

During those mid to late 1880s, ink classifications became a commercial success. To capture the ever-growing public's eye, ink chemists developed different coloring substances. Previous to the discovery of the soluble anilines, indigo, madder, logwood, and other dyeing components were added to the iron tanno-gallates for basically a twofold purpose: to lower the costs of production and to add to the color selection of inks **[6]**.

Nigrosine was developed as a form of inexpensive ink and became immensely popular due to its blueish color. Another popular favorite was the use of vanadium, which is fairly permanent. These ingredients were utilized in an extremely popular ink utensil known to us as the fountain pen **[6]**.

1.1.4 Fountain Pen Inks

There are two basic types of fountain pen inks — iron-gallotannate type and aqueous solution of synthetic dyes. These iron-gallotannate types are essentially iron salts in combination with gullotannic acid in an aqueous solution. This solution is colorless when first applied to paper, but darkens quickly when oxidized by air. Modern inks of this type contain a synthetic blue dye to provide an immediate blue color to the ink which turns black after oxidation on paper. This explains the origin of the name blue-black fountain pen ink. Blue-black inks are very stable. Unlike carbon ink which remains essentially on the surface of the paper, blue-black inks are absorbed into the fibers of the paper so that the iron compound formed when the ink ages becomes an integral part of the paper. The ink is insoluble in water and cannot be erased effectively by abrasion **[7]**.

The most popular fountain pen ink is the type that consists of an aqueous solution of synthetic dyes. These inks have a bright color and produce attractive writing; however, they are not nearly as stable as the blue-black inks. Synthetic dyes fade and are soluble in water. The most recent inks of this type, however, contain pigmented dyes such as copper phthalocyanate blue which contributes much more permanence to the ink **[7]**.

1.1.5 Ball - Point Pen Inks

In 1888 John Loud, invented and received a patent for what he called a ballpoint pen. Load's invention proved a trifle premature; the country was not ready for a pen with a ball point. Seventeen years after Loud had his invention patented, it entered into the public domain without having been exploited. G.A. Werner and A. W. Askew patented a ball point in 1895 and, for a time, actually produced and sold it commercially, using an ink made from lampblack and castor oil. Another ball-point writing device was patented by Van Vechten Riesberg in 1916; his patent, like Loud's, expired without exploitation. In 1935, a pair of Czechoslovakians named Paul V. Eisner and Wenzel Klimes attempted to market a ball-point pen in Europe. The German war machine rolled over Czechoslovakia in 1937 and flattened out the prospect of any future production **[8]**.

Ladislao Biro, in conduction with his brother George, began to experiment with the ball-point pen. Ladialao Biro moved from Hungary in 1939 to Paris where he developed a ball-point pen that operated on a new ink-feed system based on capillary action instead of gravity flow. The Biro pen differed from the conventional fountain pen in three important respects: first, instead of a nib it had a minature socket that held a ball bearing one millimeter in diameter; second, instead of using ordinary ink, it contained a gelatinous dye with an oil base that, rolled onto a writing surface by the ball bearing both lubricated and dried almost instantly; and, third, it held enough of this unconventional ink to perform for several months without refilling **[8]**.

During the closing months of World Ware II, the United States Air Force showed interest in the idea of the ball-point pen and sent a few of these Biro pens to key American manufacturers. To add some icing to the cake, the Air Force let it be known that they were interested in the purchase of this pen. The big three in pen manufacturing concerns in the United States at that time -Parker, Sheaffer and Eversharp - began looking into the question of patent rights. Although Eberhard Faber, the pencil manufacturing firm, had contracted for those rights, Eversharp won out; and, in the spring of 1945, had matters well in hand, or so they thought **[9]**. While Eversharp's engineers worked on "cleaning up" the Biro pen, a man named Milton Reynolds saw a golden opportunity and seized it. Reynolds and his engineers devised a way of feeding the ink to the ball bearing by the simple and unpatentable law of gravity.

Reynolds, the P. T. Barnum of the ink industry, knew that with the ending of the war with Japan the American public would be ripe for a postwar wonder. Late one rainy evening Reynolds hit upon an idea for the promotion of his pen. While dining one rainy night Reynolds mindlessly began doodling on a damp newspaper. Gradually he became conscious that, soggy as the newspaper was, the lines of his scribbling stood out clearly, Returning to his shop, he put a piece of paper on the bottom of a basin of water, which led to his coining of the phrase, "It writes under water" **[9]**.

The ball-point pens developed shortly after WW II were a far cry from perfection. The Reynolds pen had a number of things that fouled up the mechanism. The pen gooped (or the deposition of large droplets of ink) and was faced with the problems of skipping and directionality as well. Because the parts of the pen often fitted together imperfectly, it plainly leaked, to name but a few of its problems **[8]**.

Within a few short years, the majority of the imperfections of the ball-point pen had been worked out. By 1950, excluding the Reynolds pens, the ballpoint pen had arrived as an acceptable writing instrument. Around 1950, a new type of ball-point ink had been developed by a Hungarian chemist named Fran Seec. Seec's ink was instant drying and nontransferable. He sold his formulations to Patrick Frawley, Jr., who owned the Frawley Pen Company located in Los Angeles, California. Frawley turned around and introduced the Paper Mate ball pen, using the ink developed by Seec. Eventually Frawley sold his concerns to Gillette Company **[10]**.

1.1.5.1 Composition

Ball-point inks consist of synthetic dyes in various solvents. The dyes are soluble in the solvents, but the inks also may contain insoluble pigments in suspension. The dyes in ball-point inks can contain as much as 50 percent of the total ink formulation that produces a very viscous ink with a consistency similar to honey or molasses **[7]**.

A number of additional ingredients usually are included in the ink to impart specific characteristics, and these materials generally are kept secretive by ink manufacturers. Basically, these secret ingredients are acidic materials, resins, surface active agents, and viscosity adjusters. The acid materials are normally fatty acids that act as a lubricant for the ball of the pen, help the starting characteristics of the ball-point, and neutralize dyes. Resinous materials consist of natural resins or synthetic polymers and are used primarily to adjust the viscosity of the inks and to reduce the cost. These polymeric materials affect properties such as adhesiveness, tackiness, and elasticity. Some resins also serve to lubricate the ball in the socket of the pen. Surface active agents promote and adjust the wetting characteristics of the ink. Other organic additives serve as corrosion inhibitors or improve the solubility of the dyes in the various possible solvents.

Ball-point ink made prior to about 1950 used oil-based solvents such as mineral oil, linseed oil, recinoleic acid, methyl and ethyl esters of recinoleic acid, glycerin monoricinoleate, coconut fatty acids, sorbital derivatives, and plasticizers such as tricresylphosphate. Modern ball-point inks (those made after 1950) are referred to as glycol-based inks because of the common use of ethylene glycol as a solvent for the dyes. The following are commonly used solvents:

ethylene glycol, 1, 2-propylene glycol, 1, 3-hutylene glycol, hexylene glycol, octylene glycol, di and tri ethylene glycol, di propylene glycol, glycerin, phenoxyethylene glycols, benzyl alcohol, ethylene glycol monomethylether and diethylene glycol monomethylether

The dyes used in the early oil-based inks were primarily basic dyes for the colored inks and nigrosine for the black inks. The colors, which faded quickly, consisted primarily of methyl violet, victoria blue, rehodamine red, victoria green and ausamine. Some of these early inks also contained carbon or graphite to provide permanence. Modern glycol-based inks contain chelated metalized dyes that are specially treated to effect solubility in glycol or similar solvent. The most popular dyes are the blues based on the compound copper phthalocyanine.

These dyes are prepared by sulfonating or chlorosulfonating copper phthalocyanine pigment and reacting the sulfonic acid salts or sulfonamides. The resulting dyes are durable to light and have excellent solubility properties. Other premetalized dyes (reds, green, yellow, etc.) are similarly made to produce a variety of colored inks. Other commercial names for the metalized dyes are Azosol, Luxorl Fast, and Spirit Soluble. However, nonmetalized basic dyes utilized in the oil-based inks are still extensively used provided they are first made into organic salts soluble in glycols by mixing (dissolving) in organic acids (oleic, etc.). Some dyes used in glycol-based inks are referred to as "Spirits Soluble" instead of "Oil Soluble" because they are soluble in spirits (alcohol) **[7]**.

Pressurized ball-point pen inks were developed about 1968. In 1969, Paul Fisher developed the pressurized cartridge using ink that was very heavy, with the consistency of chewing gum. Fisher used nitrogen pressure to force the ink forward; and, when applied to a surface, the ink liquifies and flows smoothly. The physical characteristics of these inks are quite different from standard ball-point pen inks. Compositional they are similar except the ink is a thixotropic material that is essentially nonfluid until disturbed by rotation of the ball-point in the socket. Cartridges containing these inks are usually under the pressure of nitrogen or some other inert gas. The positive pressure on the ink allows the pen to write in all positions and in a vacuum: these pens were used by American astronauts during space travel **[7]**.

1.1.6 Fiber or Porous Tip Pen Inks

The fiber tip pen entered the marketplace in 1963 when Japan Stationery Companies' Pentel introduced its 49-cent model **[11]**. This soft tipped pen became very popular in the United States during the 1960s, and the number of units of these instruments sold had surpassed the number of ball-point pens during that time period.

As far back as 1500 BC the Chinese were using soft tip pens made from line animal hairs. The early Egyptians used a kind of porous point pen made from rushes, and both the Greeks and Romans used writing instruments that employed similar principles **[12]**.

The market for modern markers had its beginning in the early 1940s. At that time, only a little of manufactures in the United States were making a complicated instrument called the "brush pen" It was sold primarily to industrial users for factories, warehouses, and shipping rooms. It also became a favorite of artists and art studios. Those first markers were blunt instrument. Their felt points (called nibs) were too thick for fine writing. The "brush pen" came with a kitful component that included the pen itself, several chisel or bullet-shaped felt tips and washers, cans of ink and ink cleaner, and several fine-line tips with an adapter. Selling for around three dollars per unit, it was the genesis of our modern marker **[13]**.

In 1951, the first canister type marker was introduced. The newly-designed marker was a firm, wedge-shaped fell nib or tip attached to an ink-saturated wick that was housed in an airtight, leak-proof, metal or plastic barrel. By the mid 1950s Carter's inks Company produced a device that was actually called a "marker," but you practically had to be an engineer to assemble and operate the device.

Redeveloped in 1962 in Japan, in this type of pens. These pens produce very attractive, smooth, and bold writing strokes and are commonly used for writing signatures. The major disadvantage of many of these pens is that the fiber tip wears quickly, and the writing stroke becomes wider and wider until it has the appearance of a marker pen **[7]**.

1.1.6.1 Composition

Fiber tip inks are usually water - or xylene - based and contain dyes and additives similar to those used in fluid inks (fountain and rolling ball marker inks). The early pens of this type had problems with the tip drying out. New formulations contain formamide, and/or glycol additives which adjust the surface tension to allow the tip to remain wet even when uncapped. The water based fiber tip inks are water soluble and are, therefore, nondurable. The xylene based inks, however are water resistant and are quite permanent on paper. The inks that contain metalized chelated dyes are relatively light fast **[7]**.

1.1.7 Rolling Ball Marker Inks

Rolling marker pens first appeared at the marketplace in 1968. Consumers had two models from which to choose: the Uni-Pen, manufactured by Mitsubshi Pencil Company and distributed in the United States by Yasutomo & Company; and the Pentel Rolling Writer, manufactured by Pentel of Japan (a subsidiary of the Japan Stationery Company) and distributed by Pentel of America **[14]**.

There had been previous attempts to produce and market writing instruments of a similar disposition. Harrison makes note of a ball-point pen using ordinary writing ink. "One such pen has been marketed in which the ball consists of a tiny sphere of sapphire working in a housing of platinum". The instrument mentioned aboved lacked popularity with the writing public and drifted into obscurity **[14]**.

Autoball Pen Company, in 1965, attempted to market a rolling ball marker type of instrument. Autoball found it more profitable to sell their idea to Pentel of Japan, who further developed the pen prior to its introduction on the market **[7]**.

1.1.7.1. Composition

The rolling ball marker inks are water based and usually contain organic liquids such as glycols and formamide to retard the drying of the ball-point. The dyes in these inks are water soluble or acidic dye salts. Since these dyes are the type used in the textile industry, there are a large number available for use in ink compared to the standard ball-point inks. The light fastness of these dyes range from good for the metalized acid dyes to poor for some of the basic dye salts. Water fastness is usually poor, but some of the dyes have an affinity for cellulose paper fibers, which produce a certain degree of water fastness. The writing produced by these fluid rolling ball marker inks resembles the writing of a fountain pen ink more than standard ball-point ink because the fluid nature of the ink causes it to flow into the capillary surface of the paper. The concentration of dyes in fluid rolling marker inks is substantially less than in standard ball-point inks, but is higher than the amount of dyes in fountain pen inks. Rolling ball marker pens are very comfortable to write with, but the ink is consumed more rapidly than standard ink in the ball-point pens **[7]**.

1.1.8 Disappearing Inks

Disappearing inks are used in textile industry such as dressmaking crafts **[15]** , and as kinds of teaching material in it the question printed as visible parts and the spaces for answers are printed as the invisible printed parts (faded disappearing ink). The answers only become visible using a coloring assistant [16].

Disappearing inks are also used in paints for example, when applying a new paint of a similar shade over an existing coating of white paint when the lighting is poor it is difficult to determine the areas which not paints but the using of the disappearing ink solve the problem **[17, 18]**.

They can also be used as a marking system for dance lessons, sports, training of any other activities that require the proper placement of feet (a sole contain marking system) **[19]**.

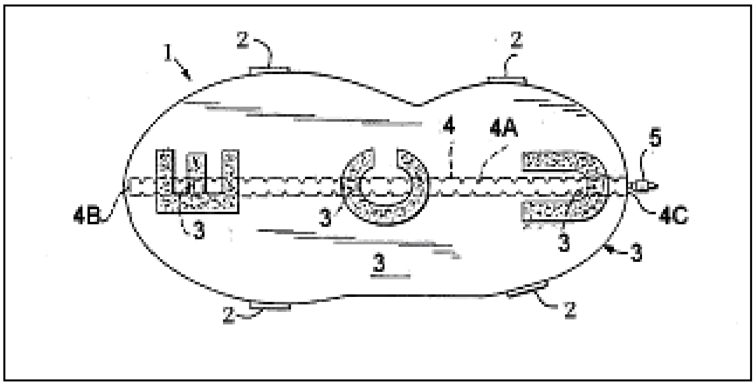

Figure 1: A sole of disappearing ink marking system

1- a sole of disappearing ink marking system

2- easily adaptable retaining straps

3- lower layer surface 4- reservoir tube

4A- plurality of reservoir tube apertures

4B- reservoir tube fixed end 4C- reservoir tube free end

5- injection port nozzle

Disappearing ink marking system adaptable to a sole of a user that includes the upper layer, the lower layer and intermediate layer, this intermediate layer is fixed between the upper layer and the lower layer. A reservoir tube passing into the intermediate layer and communicate it with disappearing ink fluid. The image block is affixed to the lower layer and in fluid communication with the intermediate layer. When pressure is applied to the intermediate layer, disappearing ink flowing through the reservoir tube escapes through the plurality of reservoir tube apertures and enters the intermediate layer and is absorbed therein. The disappearing ink is forced from the intermediate layer through the lower layer aperture and into the image block which in turn causes the image block to disperse the disappearing ink and leave a temporary image.

Disappearing inks have also been abused, it may be abused in forgery or counterfeiting crimes, as happened in a case, when a personal check was cashed by a local merchant in the amount of $ 200.00 but when the check was processed by the bank, it reflected only $2.00 the subsequent investigation and research verified the use of accessible disappearing ink was used when the check was written **[20]**.

Acid-base indicators can be used as disappearing inks; this can be explained from studying the behavior of acid-base indicators.

1.1.8.1 The Behaviors of Indicators

Indicator is weak acid (or base) whose acidic and basic forms have different colors. The earliest known acid base indicators in the history of chemistry were plant extracts such as syrup of violets or lilacs. These indicators were later absorbed onto paper and dried to yield indicator papers. Among the most common of modern indicator papers are red and blue litmus paper. Red litmus turns blue in basic solution and blue litmus turns red in acidic solution **[21]**.

Detailed examination of the behavior and constitution of indicator dyes shows that the structural changes which accompany or bring about the change of color. For example, most phthaleins apparently exist largely in a colorless lactone form in moderately acidic media, whereas the colored alkaline form has a quinone-phenolate structure.

Indicators may have two color transformation, for example methyl orange indicator have two color acidic color (orange) and basic color (yellow) but there are many "one-color" indicators, only one form of which (usually the alkaline species) absorbs light in the visible region of the spectrum. The same equations hold for one colour and two colour indicators **[22]**.

Table 1: lists of a number of commonly acid-base indicators and their pH ranges [23]

Indicator Name	Acid Color	pH Range	Base Color	pK_{In}
Thymol blue	Red	1.2 – 2.8	Yellow	1.51
Bromophenol blue	Yellow	3.0 – 4.6	Blue-violet	3.98
Chlorophenol blue	Yellow	4.8 – 6.4	Red	5.98
Bromothymol blue	Yellow	6.0 – 7.6	Blue	7.0
Cresol red	Yellow	7.0 – 8.0	Red	8.3
Methyl orange	Orange	3.2 – 4.4	Yellow	3.7
Methyl red	Red	4.3 – 6.0	Yellow	5.1

Thymolphthalein and phenolphthalein indicators can be used as disappearing inks. When using thymolphthalein and phenolphthalein as handwriting ink, pH of them will be decreased and the handwriting will be faded (Section 3.1).

Thymolphthalein Chemical formula is is $C_{28}H_{30}O_4$. And its chemical name is 3,3-bis (4-hydroxy-5-isopropyl-o-tolyl) phthalide

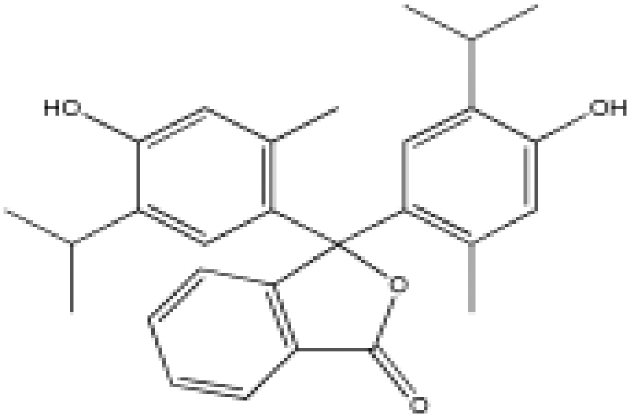

Figure 2: Chemical structure of thymolphthalein

Phenolphthalein Chemical formula is is $C_{20}H_{14}O_4$. And its chemical name is 3,3-bis(4-hydoxyphenyl)-1-(3h) isobenzofuranone

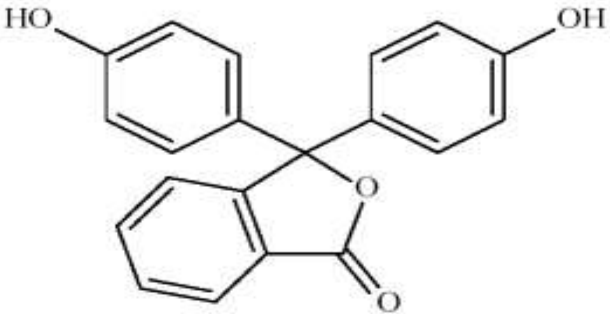

Figure 3: Chemical structure of phenolphthalein

1.2 Paper

Paper is the basic means for the communication and dissemination of the information. Paper records economical, political and social transactions. It carries the symbol of value in the form of money and certificates. It serves the needs of art, literature and science, as well as preserving the great legacy of human Knowledge for the future.

1.2.1 Historical Development of Paper and the Paper Manufacture Process

The world "paper" is derived from the name of the reedy plant, papyrus, which grows abundantly along the Nile River in Egypt. In ancient times, the fibrous layers within the stem of this plant were removed, placed side by side, and crossed at right angles with another set of layers similarly arranged. The sheet so formed was dampened and pressed. Upon drying, the sugary sap of the plant served as an adhesive to cement the layers together. Complete defibering, which is an indispensable element in modern paper making, was not a part of making papyrus sheets. Papyrus was the most widely used of writing materials of ancient times. Many of these records still survive.

The material that we know as paper, however, originated in China about 100 A.D. by the discovery that a mat or layer of fibers could be formed by filtering a water suspension of the beaten and macerated fibers through a fine screen. The fibers first used were those composing the inner bark (bast) of certain plants such as bamboo and mulberry. The mat so formed, upon drying, became a strong, coherent sheet suitable for writing and drawing pictures. It is the property of natural cellulosic fibers, after being beaten in water, to bond or adhere to each other upon pressing and drying, that has furnished the basis for paper technology.

Paper making developed into a highly skilled art in China. Many beautiful examples of ancient Chinese illustration on paper are still in existence. Over a period of many centuries, the art of paper making spread westward to the Arabic countries and then to Europe. During the period, the use of cotton and linen rags supplanted the Original bast fibers of plants and became the principal raw material for paper. The first paper mill in America was established in 1690 on Wissahickon Creek near Philadelphia by one William Rittenhouse who had learned the art in Germany. The Rittenhouse mill used linen rags as the source of paper and is supposed to have turned out 100 pounds of paper per day **[7, 24]**.

As Doctor Dard Hunter pointed out, the first attempt which possessing sufficient vision and foresight to record the happening in the field of paper making progress at such a chronology of the origin and progress of paper was accomplished by Joel Munsell's book " A chronology of the Origin paper and Progress of Paper and Paper-Making" was first printed in 1856. Also much of this chronology belongs to the efforts of Doctor Dard Hunter **[25, 26]** whose name is widely Known throughout the papermaking industry.

Chronology of Paper and Paper Making

B.C. (Before Christ) [25, 26]

2700 B.C., Chinese characters conceived; Ts' ain Chieh credited with the invention.

2200 B.C., Prisse manuscript on papyrus, probably the oldest Egyptian document. The Great Harris Papyrus, in British Museum, measuring 133 feet in length and 16.75 inch in breadth, is one of the largest in the world. It is dated in the 32nd year of Ramses III.

900 B.C., True felt made by Greeks, but not used as a "couching" material by papermaking until the introduction of paper making in Europe.

A.D. (Anno Domini) (After the birth of Christ) [25, 26]

105 A.D., Traditional date of the invention of paper making by Ts' ai Lun, an official attached to the Imperial Court of China. The sources of fiber included mulberry and other bast fibers as well as fish nets, rags and hemp.

751 A.D. In this year paper was mad in Samarkand in Central Asia, the first place outside China to understand the secrets of the craft, revealed by Chinese prisoners of war.

793 A.D. First paper made in Baghdad in the time of Harun Al-Raschid, who acquired skilled artisans from China for the purpose. This coincided with golden age of Arabic power and culture which brought paper making to the frontiers of Europe **[25, 26]**.

1390 A.D. By this date a number of paper mills existed in Europe, particularly in Spain, Italy, France and Germany.

1455 A.D. The Gutenberg Bible, which marked the beginning of book printing in Europe and the consequent increased demand for paper.

1495 A.D. First paper mill in England established in Hertfordshire by John Tate **[25, 26]**.

1680 A.D. Invention of the "Hollander" or beater for maceration of paper stock in preparation for sheet making, invented in Netherlands. Previously beating had been performed by "stamping mills".

1690 A.D. First paper mill in America established by William Pattenhouse near Germantown, Philadelphia, Pennsylvania.

1765 A.D. Publication of treatises by Jacob Christian Schaffer on the use of various plant materials for making paper **[25, 26]**.

1774 A.D. Discovery of chlorine by Karl Wilhelm Scheele (a Swedish chemist).The bleaching ability of chlorine was quickly recognized and it was soon used for bleaching paper stock. Unfortunately, lack of chemical knowledge at the time resulted in producing inferior paper by this method which brought much discredit upon chlorine bleaching. Eventually, chlorine bleaching became a valuable part of paper making **[25, 26]**.

1798 A.D. The invention of the paper machine by Nicholas-Louis Robert in France. The small, undeveloped machine was set up in Essonnes paper mill. The French Government granted Robert A fifteen-year patent and advanced money for the perfection of the machine. However, the paper machine did not become a practical reality until the work of John Gamble and Bryan Donkin some years later in England.

1800 A.D. The discovery of vat sizing with rosin and alum by Moritz Friedrich Ellig, in Germany. Previous to this time paper sheets were sized by the expensive and tedious process of impregnating the sheets with animal glue or vegetable gums. Illig published his discovery in 1807, but not until about 1830 did the method become widely used in paper making **[25, 26]**.

1801 A.D. Publication of book by Mathias Koops suggesting new materials that might-be used for paper making. The work of Schaffer and Koops foreshadowed the development of practical methods for the manufacture of wood pulp and other vegetable pulps.

1807 A.D. Patent issued to Henry and Sealy Fourdrinier for an improved paper machine. Also active in this development were John Gamble, who was familiar with the work of Robert in France and brought the idea of a paper machine to England.

1809 A.D. Invention of the cylinder paper machine by an English paper maker, John Dickinson **[25, 26]**.

1817 A.D. First paper machine in America installed in the paper mill of Thomas Gilpin on the Brandywine near Wilmington, Delaware. This machine was the Dickinson cylinder type **[25, 26]**.

1827 A.D. First Fourdrinier type paper machine built in America. The machine was built by Bryan Donkin in England and installed in a paper mill at Saugerties, New York, in the mill of Henry Barclay.

1840 A.D. Groundwood pulp made in Germany by Friedrich Gottlob Keller. Process did not come into commercial use until about 1870 **[25, 26]**.

1854 A.D. First manufacture of soda pulp from wood, by Watt and Burgess in England.

1867 A.D. Patent issued to Benjamin C.Tilghman of Philadelphia disclosing the basic principles of the sulfite pulping process.

1874 A.D. Sulfite pulp manufactured in Sweden by Carl Daniel Ekman and in Germany by Alexander Mistcherlich.

1875 A.D. By this time paper coated by machinery was being made for use in printing of halftones by the new photo engraving process.

1884. Invention of sulfate (kraft) pulp by Carl F. Dahl in Danzig, Germany.

1897 A.D. Paper machine speeds had reached 500 feet per minute by this time.

1909 A.D. First kraft pulp and paper made in the United States.

1920 A.D. Paper machines attain speeds of 1000 feet per minute.

Since 1920 A.D., there has been a rapid pace of technical progress in the paper industry. These advances are generally the result of team work by a number of people working together in large organizations. Hence, it is difficult to assign credit to individuals or to be exact about dates and places. Some of the more important developments in recent decades are listed on the following points **[25, 26]**.

(1) Multistage bleaching of kraft pulp, leading to availability of fully bleached kraft pulp.

(2) Use of chlorine dioxide for pulp bleaching permitting higher brightness with retention of strength.

(3) Coating of paper while passing through paper machine dryer section, greatly expanding use of coated paper for printing.

(4) Use of soluble bases for sulfite pulping permitting pulping of more species of wood by the sulfite process.

(5) Bleaching of high yield pulps, groundwood and semichemical, with peroxide and hydrosulfite.

(6) Wet strength paper: use of synthetic resins for economic production of wide variety of papers that are strong when wet.

(7) Multi-stage sulfite pulping permitting greater variety of pulp properties.

(8) Continuous cooking of kraft and semichemical pulps making possible reduction in capital and operating cost.

(9) High-yield pulping: combined chemical and mechanical action to produce pulp from wood in high yield, particularly advantageous with hardwoods.

(10) The use of synthetic fibers admixed with wool or in the form synthetic fabric as the sheet carrying and water removal felt of the paper machine press section **[25, 26]**.

1.2.2 Additives in Paper Manufacture

The writing and printing paper consists of two main components, namely the fibrous and non-fibrous component. A part from newsprint and magazine paper, the fibrous component is bleached chemical or semichemical pulp obtained from softwood or hardwood. Beside wood, agricultural residues are used -but to lesser extent -for manufacture of paper pulps. In Egypt rice straw and sugar cane bagasse are the main fibrous component source of writing and printing paper. The non-fibrous portion of paper is added to the pulp during papermaking operation; therefore, is called "additive". Additives are added either in beater or after beating the pulp in the stock preparation process. For this reason they are called beater additives when added to the beater or wet end additives when they added in latter case. These additives modify sheet properties in order that paper meets the specific requirements for its intended use **[27-29]**. Some additives are used for special purposes. Antifoam materials prohibit foaming of the pulp slurries. Other additives increase wet strength of paper. A further class of additives is used to colour paper.

The most common additives can be classified in three main types: sizing agents, binders or adhesives and filling materials. The objective of sizing is to retard the penetration of water or ink into the pores of paper and their spreading on the paper surfaces **[30, 31]**.

The binders or adhesives represent the second main class of additives used in papermaking. Their main function as can be anticipated from their name: is to promotion of fiber bonding i.e. to increase the number of interfiber bonding and hence paper strength. These substances are usually hydrophilic compounds such as starches, vegetable gums, synthetic hydrophilic or water-soluble materials and resin emulsions or lattices.

The third main class of additives is represented by the filling and loading is to increase the opacity and brightness of the paper, and to some extent the smoothness and finish of the paper which are important properties especially in printing papers.

Additives may be inorganic pigments (fillers) which, because of their small particle size and high light scattering power, are used as opacifying agents. Fillers are highly desirable in printing papers where they increase the opacity, raise the brightness, and generally improve the printing properties. The principal fillers used are clay, calcium carbonate, talc and titanium dioxide. The clay and calcium carbonate are the most widely used. In recent years new synthetic pigments have been developed both of an inorganic and organic type. The inorganic types are most frequently precipitated silicates with very fine particle size, the organic fillers are high molecular weight polymers. It is desirable that the filler should be chemically inert to avoid unfavorable reactions with other components in the sheet and in the papermaking system.

1.2.3 Fibrous Raw Materials for Paper Manufacture

Most of the newly introduced fiber will also probably continue to be derived from wood, although annual crops can be expected to play an increasingly important role.

Approximately 30% of the earth's land surface is forested, and around half of this is harvested commercially. Over 80% of the wood for all industrial uses comes from the forests of North America, Europe and what was formerly the Soviet Union. Approximately two thirds of this is either sawn or peeled. Paper is generally made either from logs that are unsuitable for sawing or peeling or from residues arising from these processes **[32]**.

Both hardwoods and softwoods are used for making paper and they have very different fiber morphologies and thus very different paper-making properties. The fibers of softwoods are longer and stronger than those of hardwoods and they make up the bulk of paper-making fiber world-wide (Table 2). However, because they easily form macroscopic flocs of entangled fibers during the sheet forming process, they tend to produce a sheet with a relatively non-uniform mass distribution and hence a poorer quality of appearance (this is known by paper technologists as formation). It is common therefore to use blends of softwood and hardwood fibers to give an appropriate compromise between strength and formation **[32]**.

Table 2: World-wide hardwood, softwood and non- wood Pulp production (in 1988) [33].

World wood pulp production	Million tonnes	%
Softwood pulp	99.2	62
Hardwood pulp	41.6	26
Non-wood pulp	19.2	12
Total	160	100

Non-woody fiber, although relatively small in volume is nevertheless important, particularly in the developing world where the use of indigenous raw materials can substantially reduce the amount of foreign exchange spent on importing costly wood pulp. The main sources of these fibers are bagasse, bamboo, jute, ramie, hemp, flax and cotton, and also various grasses and straws, such as esparto, wheat, barley or rice. Their main advantage over wood is that they can frequently be grown in areas which will not support trees, and in limited rainfall in low quality soil. In general, they produce an annual crop with a higher yield than wood. For example, straw can be produced at yields as high as 20 metric tonnes per hectare, which is considerably greater than the annual growth of most tree species. Non-woody plants can also be harvested relatively quickly- usually one or two years after planting-whereas trees require ten to twenty years to reach sufficient maturity.

The paper-making properties of all of these fibers are quite different from each other and also from wood. This is mostly due to the differing morphology and to some extent the differing chemistry of the fiber cells.

There are different paper product types. Just over 40% of all the paper which is produced throughout the world is used for communication purposes (newsprint and printing and writing), and over 50% is used for packaging and tissue (Figure 4). The remainder is used in rather specialised applications such as filtration media, tea bags and electrical insulation in transformers. Paper is classified in terms of its weight per unit area (basis weight or gram). Tissue grades are generally in the range 10-40 g m^{-2}, newsprint around 40-50 g m^{-2}, printing and writing grades around 60-90 gm^{-2} and boards are usually in excess of 100 gm^{-2}. Because of the need to obtain specific characteristics in the final product, for example water absorbency or wet strength, there is a great difference in the chemistry and method of production of these grades **[32]**.

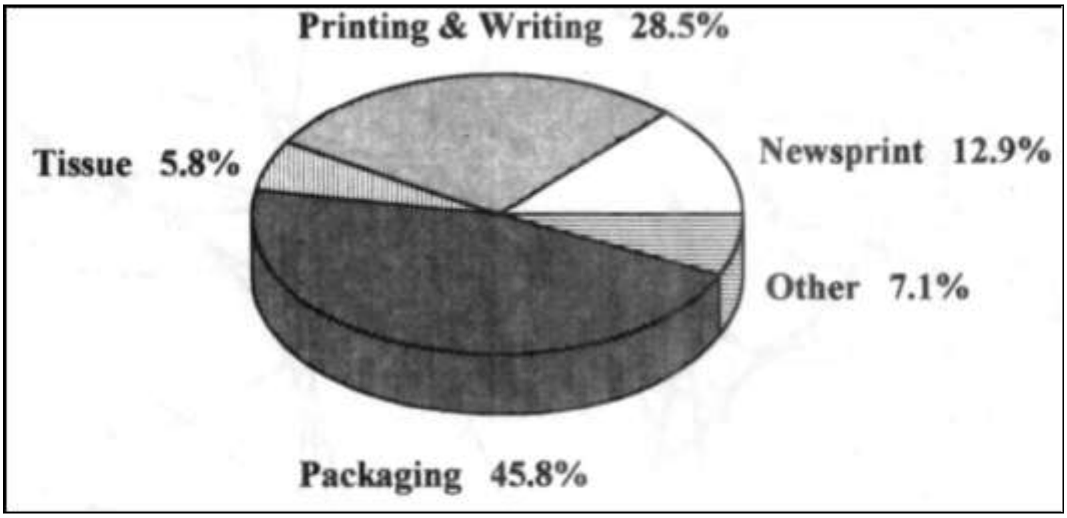

Figure 4: World-wide distribution of paper and board product types (1992).

1.2.3.1 Paper from Non-Wood Sources

Increasing concerns for future fiber supplies and potential increase in wood costs have strengthened the pulp and paper industry's interest in alternative pulp fiber sources **[34]**.

For most of its history, paper was made from non-wood fibers. Traditional fiber sources for paper were old rags and other textile wastes. Wood became the major fiber source for paper in the mid 1800s. **[35]** Hemp is probably one of the oldest plants cultivated for fiber; a work of the Sung Dynasty (A.D. 500) contains a statement that the Emperor Shen Meng in 2800 B.C. first taught the people of China to cultivate hemp for making cloth **[36]**. The use of hemp fiber for paper dates back more than 2,000 years. The oldest surviving piece of hemp fiber paper in the world was discovered by archeologists in a tomb near Sian in Shensi Province, China. Scientists believe it was produced between the years 140 and 87 B.C. **[37]**.

Non-woods are a major fiber source in developing countries with limited access to forest resources. Worldwide, non-woods made up 16.5 million metric tons of the worldwide fiber supply for paper production in 1991, corresponding to 10% of the virgin fiber supply and 6% of the total fiber supply (including recovered fiber). The main producing countries were China (12 million metric tons), India (1.8 million metric tons) and Latin America (0.7 million metric tons) **[38]**. In the United States, the non-wood capacity currently is approximately 400,000 metric tons, corresponding to less than one percent of the virgin fiber supply **[39]**. Most mills in developing countries use chemical pulping processes and are very small. They produce less than 20,000 tons of pulp per year **[40]**. Most of these mills do not employ chemical recovery or wastewater treatment. Chemical recovery systems reduce chemical costs and environmental releases. However, conventional recovery systems, such as the one used in the kraft process, have high economies of scale and generally are too expensive to install at these small mills. Lack of wastewater treatment makes the situation more severe. Often, untreated effluent is discharged into the local surface waters **[41]**.

In the U.S., paper was traditionally made from non-woods, mainly waste products from the textile industry. During World War II, there were 25 mills in the midwest producing corrugating medium from wheat straw **[35]**.

Non-wood pulp production has survived in the U.S. because of the characteristics of particular non-wood fibers for specialty papers. The main fibers pulped are flax, cotton and abaca. In contrast, on a worldwide scale, the major non-wood fibers used for the production of commodity papers are straw, bagasse and bamboo. Because of its odor and taste, flax fiber from oilseed flax crops is the primary raw material used for cigarette paper in the U.S. Byproducts of textile flax crops are imported to enhance the properties of cigarette paper and are also used in currency paper. Standard U.S. currency paper is 80% cotton and 20% flax. Abaca is used for tea bags because of its combination of high tear strength, wet strength and porosity. Other specialty grades made from non-woods include filtration bags, sausage casings, and premium quality letterhead papers **[42]**.

In Egypt, bagasse and rice straw are the main sources of fibrous raw materials for pulping and paper manufacture. About 1,200,000 tons of dry bagasse is produced through 1999 however only 40,000 tons are used for the production of paper pulp at Edfo sugar and paper pulp mills **[43]**.

1.2.3.1.1 Bagasse as Non-Wood Source for Paper Manufacture

In tropical regions of the world sugar cane represents a major crop. Because of the increasing demand for sugar in the last century, large areas in the tropical and subtropical countries all around the world were allotted for sugar cane crops. Low level of maintenance and good productivity made sugar cane an attractive crop for farmers in these regions.

In the US the sugar cane industry started to develop in the second half of the 19th century once steam power was available for agriculture machinery. Today, Louisiana is the second largest producer of sugar cane in the US, only behind Florida. Besides the main product, sugar juice, several by-products are available in the sugar cane extraction process. The most important is considered to be bagasse **[44]**.

As it can be seen in Figure 5, cane is crushed in a series of mills, each consisting of at least three heavy rollers. Due to the crushing, the cane stalk will break in small pieces, and subsequent milling will squeeze the juice out. The juice is collected and processed for production of sugar. The resulting crushed and squeezed cane stalk, named bagasse, is considered to be a by-product of the milling process **[45]**. Bagasse is essentially a waste product that causes mills to incur additional disposal costs.

Current research in the US agricultural and forestry industry is concerned with the development of new uses and added value to farm and forestry products for greater economic benefits. Processing and recycling of the natural products is done in an environmentally responsible manner, using these resources efficiently. Utilization of the agricultural crops as alternate raw materials for many industries is more than an option. Sugar cane bagasse is established as the future fiber in tropical and subtropical regions for pulp and paper making.

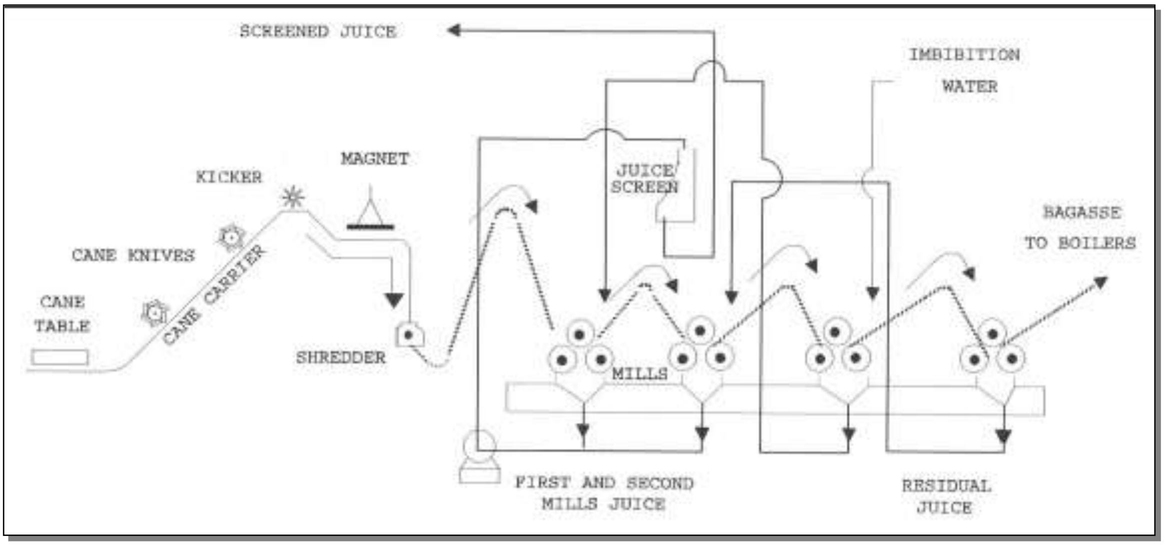

Figure 5: **Current technological process for extraction of sugar juice from cane in a sugar cane mill [45].**

Bagasse will be ahead of other crops as a source for the pulp in paper industry. It is estimated that the amount of bagasse produced annually is about 80,000,000 metric tons (MT), from which 25,000,000 metric tons will be used for pulping (equal to 13% of the total paper-making pulp capacity)**[45]**.

Fibers in bagasse consist mainly of cellulose, pentosans, and lignin. Cellulose is a natural linear polymer and has polymer chains of 2000 to 3000 units **[44]** and a specific gravity about 1.55 **[45]**. Cellulose is highly crystalline regardless of the source. The ordered chains are tightly packed and have strong intermolecular hydrogen bonding because of the preponderance of hydroxyl groups **[46]**. The cellulose is present in three types: α, β, and γ. The α cellulose is known as pure cellulose, whereas β and γ cellulose combined are called hemicellulose **[47]**. The hemicelluloses are chemically linked with cellulose molecules. The other main compound in sugar cane fiber bundles is lignin which is a high molecular weight substance. Because it is not possible to isolate lignin quantitatively from plant materials without chemical or mechanical degradation, its true molecular weight is not known. The amount of lignin that naturally occurs in sugar cane depends to a great extent on the variety and age of the cane.

In Egypt, agricultural residues are the main lignocellulosic source for paper manufacturing. Egyptian bagasse represents one of the most important sources presently being used for paper industry **[48]**. As the quality of paper produced from bagasse pulp is inferior in strength properties to that obtained from wood pulp due to the longer fiber length of wood pulp, numerous methods have been used to improve paper properties. Starch and modified starches have been used as strength improvement additive **[49]**. Bagasse contains about 65% fiber, 25% pith cells and 10% water-soluble and foreign materials. Bagasse fiber averages 1.5 to 2.0 mm and fibers are relatively fine as compared with wood pulp **[24]**.

In practice, the fibers are often suffer a considerable shortening and damage of the cell wall during the sugar extraction process, and the average fiber length is usually lowered by the presence of non-fibrous materials. The epidermis and pith materials don not contribute to the strength properties of the pulp in the pulping process and they cause drainage problems in the paper machine and give rise to a low paper opacity. A depthing step is, therefore, usually applied prior to the pulping process, in order to eliminate these "non-fibrous" material. The operation can be performed in the 'dry" or "wet" state using different techniques **[50]**.

The economical reason for choice of bagasse over the other potential raw materials can be summarized in the following; bagasse is a by-product of sugar industry, and therefore, bagasse can be located in large amounts near the sugar cane mills. This gives bagasse an advantage over the agricultural residues, namely, that harvest and transport problem from scattered fields have already been solved. The disadvantage of bagasse over wood as cheap raw materials is thus apparent, since for this latter it must be planted, cultivated, cut, transported, barked and chipped.

The bagasse has much greater economic value as a raw material for pulp and paper production. An important advantage with bagasse is that there is usually very little problem associated with collection of the fibrous resource; the coasts collection, processing, and washing are born by the sugar mill. However, the bagasse must be properly depithed and stored to produce high quality pulps.

Although a large volume of work has been done on the manufacture of paper from bagasse, it still has a lake of commercial acceptance, this is due, in apart to the presence in bagasse in an appreciable quantity of parenchyma or pith, which not only increases the consumption of chemicals in pulping, but also influence papermaking properties adversely, the pith tends to slow the rate of water drainage in the paper machine "wire" and to render sheets stiffer and more brittle. The possibility of using bagasse in manufacture of paper has been increased by the development of satisfactory mechanical methods for affecting substantially complete separation of the fibers and pith **[51]**.

1.2.3.1.2 Straw as Non-Wood Source for Paper Manufacture

The Agricultural Research Service of the U.S. Department of Agriculture (USDA) conducted an extensive study of 500 plant fibers as alternatives to wood in pulp and papermaking in the late 1950s and found kenaf to be the most promising annual fiber crop . Hemp as a fiber source for papermaking is of interest to many members of the environmental community. In Europe, hemp is being explored as an alternative fiber source for paper, while in the United States, it has been illegal to grow hemp since 1937 **[52]**.

Wheat straw is the second highest-volume agricultural residue available for papermaking in the United States and one of the most researched agricultural residues for that purpose. Rye seed grass straw has similar properties to wheat straw and is currently being explored as a fiber source for corrugated packaging by Weyerhaeuser in the Willamette Valley of Oregon. Rice straw is currently being investigated as a fiber source for newsprint.

Agricultural Residues: Cereal Straw

- Large quantities of this additional source of short fiber are currently available.

Advantages:

- Good source of short fiber. • Readily available in large quantities.
- Beneficial use of waste material.
- Fiber acquisition and pulping costs are similar to those for wood.
- Chemical pulping processes do not require sulfur.

Disadvantages:

- Requires a dedicated pulping process with a digester designed to pulp straw.
- High silica and hemicellulose content of straw makes black liquor difficult to recover.
- Must produce pulp at an integrated paper mill because the properties of the straw pulp deteriorate if the pulp is dried before use **[53]**.

1.3 Textile Fabrics

Fibers have been defined by the textile institute as units of matter characterized by flexibility, fineness, and a high ratio of length to thickness **[54].** Fibers are the basic units from which all textile materials are made **[55]** .Textile goods are manufactured from fibrous material which may be either of natural or man-made origin **[56].**

Natural fibers are divided in three groups: vegetable fibers (cotton, flax, hemp, kenaf, sisal and other); animal or proteinic fibers (wool, silk); and non-organic or mineral fibers (asbestos) **[57].** Figure 6 illustrates the classification for natural fibers **[58].**

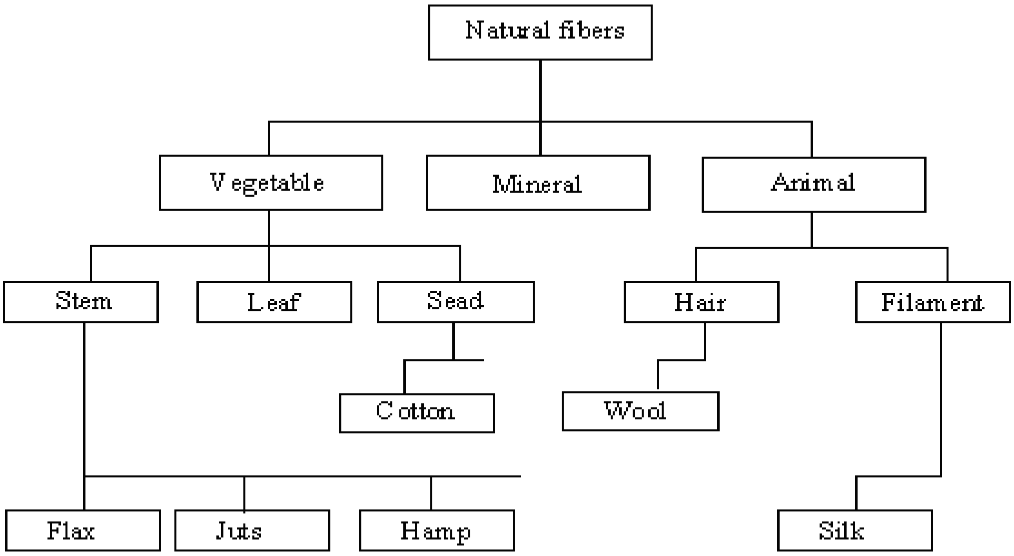

Figure 6: Natural fibers-partial classification

Man made fibers are those, which are produced in industrial conditions and mainly, consist of organic heterochain and carbochain compounds; only a small part, of natural non-organic compounds **[57].**Figure 7 illustrates the classification for Man-made fibers **[58].**

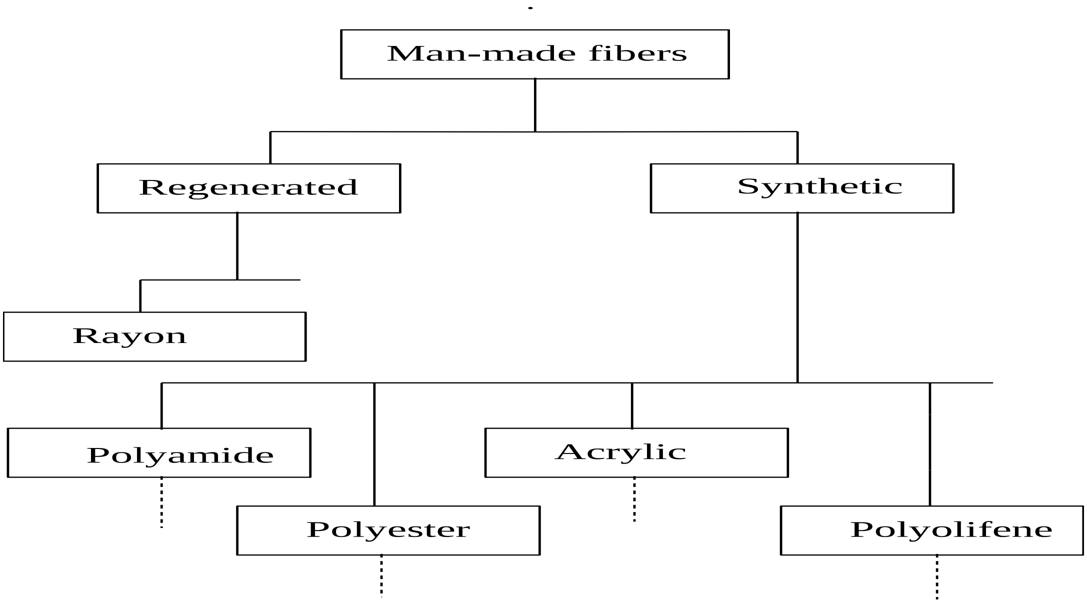

Figure7: Man-made fibers – partial classification

Cotton, polyester as well as polyamide fibers are the widely used fibers in textile manufacture. In the following, a brief account about their structures and properties is reported **[56].**

1.3.1 Cotton

Cotton is the oldest and most important of textile fibers. It has been used for thousands of years **[59]**. Cotton fiber has the shape of a tube with one breaking when the fiber is torn away from the seeds. The fiber properties are determined by its chemical composition and structure **[**57**]**.

Cotton fiber contains, %

Cellulose	97
Pectin substances and pentodes	1.5
Nitrogen and protein substances	0.3
Fats and wax	1.0
Ash	0.2

1.3.1.1 Chemical Structure

The molecules of cellulose, which is the main substance of the cotton fiber, together with admixtures join into macromolecules fibrils of elongated shape **[57]**.Like all cellulose fibers, cotton contains carbon, hydrogen, and oxygen with reactive hydroxyl (OH) groups. The basic unit of the cellulose molecule is glucose which is the same for both natural and regenerated fibers. Cotton may have as many as 10,000 glucose units per molecule. The molecular chains are arranged in spiral form **[**60**]**.

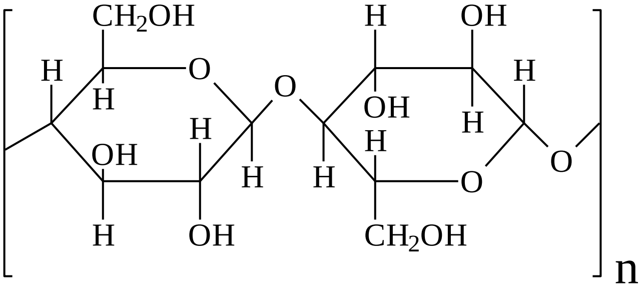

Figure 8: Chemical Structure of Cellulose

The chemical reactivity of cellulose is related to the hydroxyl groups (OH groups) of the glucose unit. These groups react readily with moisture, dyes, and many finishes. Chemicals such as chlorine bleaches break the molecular chain of the cellulose by attacking the oxygen atom between the two ring units or within the ring, rupturing the chain or ring. The cellulose molecule is a long, linear chain of glucose units. The length of the chain is a factor in fiber strength **[60]**.

1.3.1.2 Fiber Properties

- **Microscopic**

The longitudinal view of the fiber shows a ribbon like shape with twist, called convolutions, at irregular intervals (Figure 9). The diameter of the fiber narrows at the tip. The lumen may appear as a shaded area or as striation; this is more obvious in immature fibers.

The cross section of the fiber usually shows three areas: the outer skin, or cuticle; the secondary wall; and the lumen (Figure 10). The contour varies considerably; some fibers are nearly circular, some are elliptical, and some are kidney shaped. Immature fibers are more irregular in contour than mature fibers **[61]**.

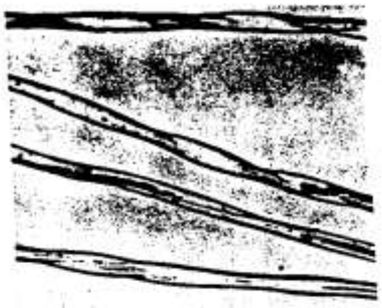

Figure 9: Photomicrograph of regular cotton, view.

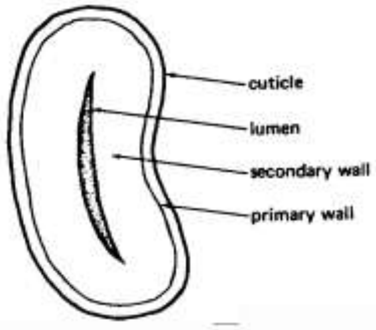

Figure 10: Diagram of the cross section of cotton fiber

●Physical

- Color

Cotton is available in a range of colors. Naturally creamy white is highly desirable because it can be dyed or printed to meet fashion and consumer needs. These fibers may yellow or become more beige as they age. If it rains just before harvest, these fibers become grayer **[60]**.

-Tensile strength

Fiber strength is typically normalized by reporting tensile strength as “tenacity.” Tenacity is the breaking load in grams divided by the linear density. Linear density, the mass or weight of a unit length of fiber, is given as grams per 1000m and called "tex," or as grams per 9000m and called "denier". Cotton fiber is relatively strong due to the intrinsic structure of layers of crisscrossed, minute, spiraled fibrils that compose the fiber cell **[62]**.

-Heat Conductivity

Heat conductivity of cotton fiber is low and the looser the cotton fiber mass, the lower the conductivity. This property is used for manufacturing cotton wadding. Cotton fiber in dry condition presents low electrical conduction owing to which cotton fabrics may be used as insulation. This electrical conduction increases with humidity **[57]**.

-Absorbency

The ease and extent to which moisture can penetrate into a fiber determines its absorbency. Once the outer protective cuticle of the cotton fiber is broken down by finishing processes, such as kiering and mercerizing, the fiber becomes very absorbent **[63]**.

●Chemical

-The action of acids on cotton

Boiling with dilute acids will ultimately hydrolyze the cellulose to glucose. Milder action by acids at lower temperatures gives rise to tendering with the formation of hydrocellulose. Nitric acids on account of its oxidizing action, differs from other acids in its behavior towards cellulose. Immersion for a short time in concentrated nitric acid causes some shrinkage accompanied by a degree of increase in tensile strength and affinity for dyestuffs. Prolonged action of cold nitric acid oxidizes the cellulose to oxy cellulose and finally breaks it down to oxalic acid, the reaction being accelerated at higher temperature **[64].**

-The action of alkalis on cotton

Mild alkalis, such as sodium carbonate, have no action on cellulose at low or at higher temperatures in the absence of air. In the presence of oxygen, however, oxycellulose is produced gradually with consequent tendering. A solution of 20 percent sodium hydroxide is used to mercerize cotton, making it stronger, smoother, and had acquired a greater affinity for dyes **[65]**.

- Effect of organic solvents

Cotton fiber is insoluble in most organic solvent; it dissolves in few complex solutions, such as cuprammoniom. Dry cleaning solvents do not have any deleterious effect **[66]**.

-Effect of light

Cotton fiber oxidizes, turning yellow and losing strength from exposure to sunlight over a prolonged period of time. Cotton fabric should therefore be shaded from direct sun light **[67]**.

-Affinity for dyes

Cotton has a good affinity for dyes. It is dyed best with vat dyes, but azoic and reactive dyes may also be effectively used. Color fastness is generally good, but specific condition should be considered **[68]**.

1.3.2 Polyester

Polyester fibers is defined as " a manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85 percent by weight of an ester of a substituted aromatic carboxylic acid, including but not restricted to substituted terephthalate units $P(—R—O—CO—C_6H_5—C—O—)$ and parasubstituted hydroxybenzoate units $P(—R—O—C_6H_4—CO—O—)$ "**[61]**.

Polyester, polyethylene terephthalate are the most important synthetic textile fibers. These are manufactured under different names such as, Terylene(ICI),Terene(CAFI, India), Dacron(Du Pont), Lavsan(USSR). Tergal (Sociate Rhodiaceta, France), Terital (Societ Rhodiatoce, Italy), Tetoron (Teijin Ltd), Trevira (Hoechst) etc. certain modified polyester is also manufactured. These include kodel (derived from 1:4 dihydroxycyclohexane) of Eastman Kodak, U.S.A, and Vycorn (derived from isophthalic acid) of Goodvear Beaunit Mills, U.S.A **[69]**.

1.3.2.1 Chemical Structure

Polyester fibers are synthetic textile fibers of high polymers (condensation products) which are obtained by esterification, especially of dicarboxylic acids, with glycols or glycol derivatives or by ester exchange reaction between dicarboxylic acid ester and glycols. Terylene is made by polymerizing, using ester exchange reaction between dimethyl terephthlate and ethylene glycol **[69].**

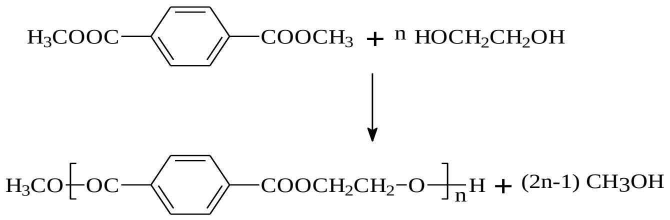

Figure 11: Preparation of Terylene

Dacron is made by polycondensation reaction using terephthalic acid and ethylene glycol.

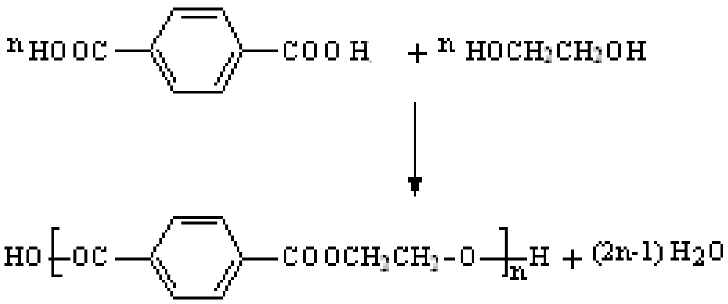

Figure 12: Preparation of Dacron

It is clearly seen from the above reactions that both Terylene and Dacron are essentially the same and that they differ in that whereas the former contains a methyl ester group at one of the macromolecule. The latter contains an acid group instead **[69]**.

1.3.2.2 Fiber Properties

- **Microscopic**

A longitudinal view of polyester fiber exhibits uniform diameter, smooth surface, and a rodlike appearance (Figure 13). The cross section may be perfectly round (Figure 14) or lobal in shape. The modifications in which trilobal- and pentalobal – shaped filaments are formed are the most popular **[61].**

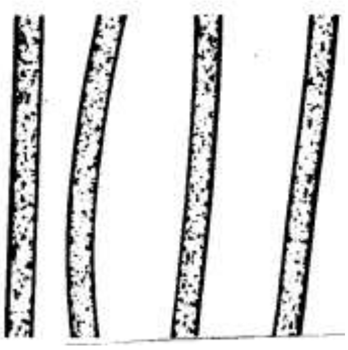

Figure 13: Photomicrograph of regular polyester fiber longitudinal view

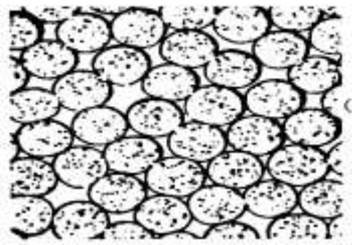

Figure 14: Photomicrograph of regular polyester fiber, cross section.

.

- **Physical**

- Color

Polyester can be made in any length or diameter required for potential end uses. The fiber is partially transparent and white or slightly off-white in color. Pigment can be combined with the spinning solution, which permits control of the degree of luster- not color. Optical brighteners are frequently added to produce clear, bright fibers **[61].**

-Tensile strength

The strength, or tenacity, of polyester varies with the type of fiber; however, as a general category, polyester would be considered a relatively strong fiber. Its strength is not affected by moisture. Regular filaments have a breaking tenacity of 4-7 g/denier; high-tenacity filaments are rated at 6.3-9.5 g/denier **[61]**.

The strength of polyester varies widely; it depended on the end use and is controlled by the manufacturer. Polyester has a very high dry and wet tensile strength **[68]**.

- Heat conductivity

Fabrics of polyester fiber are good conductors of heat; it would be warmer than if made of cotton. One of the reasons for the apparent warmth of polyester is its low absorbency **[70]**.

- Absorbency

Although polyester is nonabsorbent, they do have wicking ability. This quality makes polyester relatively comfortable to wear in warm weather, as perspiration is carried to the surface of the fiber and evaporated. Multilobal fiber cross sections improve the wicking qualities of polyester. Special finishes can be applied to polyester to make it more hydrophilic **[61]**.

- **Chemical**

- The action of acids

Polyester fibers have excellent to good resistance to mineral and organic acids. Highly concentrated solution of mineral acids, such as sulfuric acid, at high temperatures will result in degradation **[70]**.

- The action of alkalis

At room temperature, polyester has good resistance to weak alkalis and fair resistance to strong alkalis. This resistance is reduced with increased temperature **[71]**.

- Effect of organic solvents

Polyester fiber shows high resistance to most of the common organic solvents, example acetone, dioxin, ether, methyl alcohol and carbon tetrachloride. The range of chemicals will dissolve polyester fiber at normal or moderate temperatures are limited, and the only chemicals - which as a class - will do this are phenols. Most phenols will swell or dissolve polyester fiber depending on the temperature and concentration used. Hot m-cresol destroys the fiber and mixtures of phenol in trichloroethane dissolve the fibers **[71]**.

- Effect of light

Polyester has good resistance to degradation by sunlight, fabrics of polyester are therefore well suited for outdoor use. Over a prolonged period of exposure to direct sunlight however, there will be a gradual deterioration of the fibers **[72]**.

- Affinity for dyes

Polyester fiber is difficult to dye, since there are no chemical groups in the polyester molecule that will unite with dyestuffs and the molecules are packed so, there is no space to wedge in dye molecules. Also, the interchain forces are so strong that high temperatures are required to loose them so dye molecules can enter. In darker shades, expansive dye assistants or carriers are needed and these must be removed from the fiber after dyeing preserve light fastness. Only by use of disperse, azoic and pigment dyes at high temperature. Some polyester is modified to take basic dye. Also the enzyme treatment could result in enhancing hydrophilicity and increased cationic dye binding. For example, using polyester, enzymatic improvement of many undesirable properties of polyester under mild condition has been demonstrated **[73,74].**

1.3.3 Polyamide

Polyamides are one of the most important synthetic fabrics. The name nylon was chosen for polyamide, but the reason for the choice is not known. Nylon was the first synthetic fiber **[60]**. Any nylon must contain atoms of carbon, hydrogen, oxygen and nitrogen. The number after the word nylon indicates the number of carbon atoms in the molecule of starting materials. Nylon 6,6 is made from hexamethylene diamine, which has six carbon atoms, and adipic acid HOOC-$(CH_2)_4$-COOH , which also has six carbon atom. Nylon 6 is made from Amino-caproic acid H_2N-$(CH_2)_5$-COOH which has six carbon atom **[60]**.

1.3.3.1 Chemical structure

The most wide-speared polyamides in use and production are nylon 6 and 6,6. The essential structural similarities and differences between nylon 6 and 6,6 are illustrated in below**.**

Nylons differ in their chemical arrangements and this accounts for sight differences in some properties. The molecular chains of nylon are long, straight chains of variable length with no side chains or crosslinkages. Cold drawing aligns the chains so that they are oriented with the lengthwise direction and are highly crystalline.

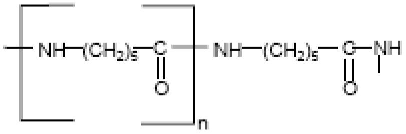

Figure 15: Chemical structure of nylon 6

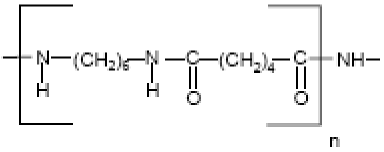

Figure 16: Chemical structure of nylon 6,6

1.3.3.2 Fiber properties

- **Microscopic**

Nylon is available in wide range of shapes. Regular nylon has a round cross section and is perfectly uniform throughout the filaments. Microscopically, the fibers look like fine glass rods **[60]**.

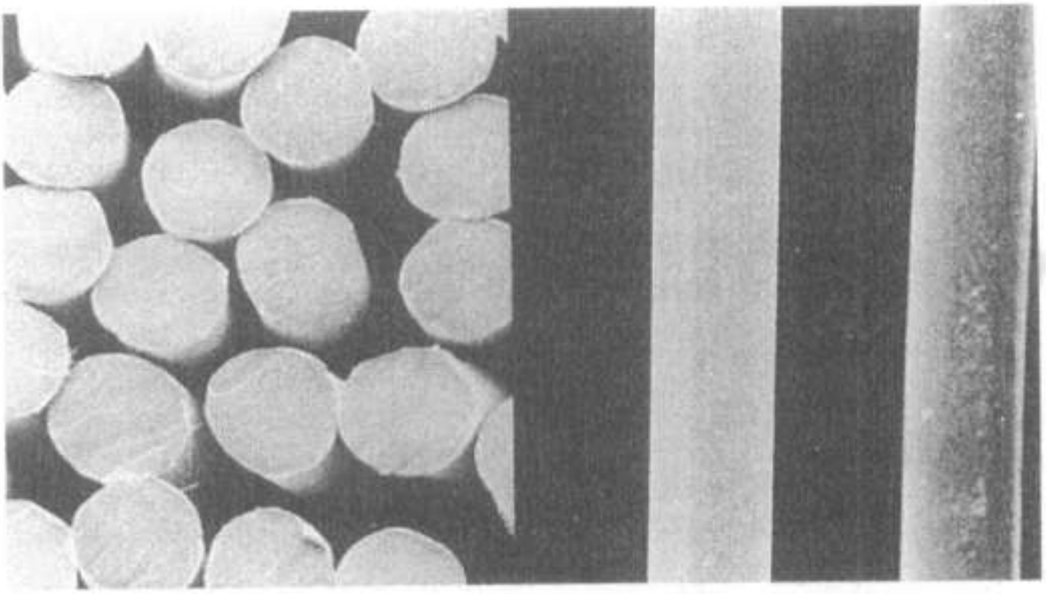

Figure 17: photomicrograph of nylon fiber : cross- sectional view (left) ; longitudinal view (right)

- **Physical**

- Color

Nylon fibers are transparent unless they have been delustered or solution dyed.

-Tensile strength

The strength, or tenacity, of nylon may be varied within limits by adjusting the manufacturing conditions. Fiber strength is increased in several ways. Drawing or stretching the fiber to align or orient the molecules strengthens the intermolecular forces. Chemical modifications of the fiber polymer increase the degree of polymerization, the length of the polymer chain. Some-tenacity fibers are produced by combining drawing with chemical modification. However, as a general category, high tenacity nylon has a tenacity of 6.5-9 g/denier for dry and 5.8-8.2 for wet, regular tenacity nylon has a tenacity of 4.0-7.0 g/denier, for dry and 3.7-6.0 for wet **[60]**.

-Absorbency

Nylon has low absorbency and absorbs only a small amount of moisture compared with most natural fibers **[71]**. Nylon is not as comfortable a fiber to wear as the natural fiber **[60]**.

● **Chemical**

- The action of acids

Dilute acids have little effect on nylon under the condition encountered in practical use. Hot mineral acids will, however, decompose nylon. The fibers disintegrate in cold concentrated acids **[71]**.

- The action of alkalis

Nylon has excellent resistance to alkalis. Nylon 6,6 can be boiled in strong caustic soda solution without damage **[71]**.

- Effect of organic solvents

Nylon dissolves in concentrated formic acid, phenol and cresol **[71]**.

- Effect of light

Nylon has low resistance to sunlight. Better resistance is achieved in end uses where sunlight exposure is a concern by using bright rather delustered fibers so that damaging energy is reflected and not absorbed. In addition, sunlight-resistance modifications of nylon are available **[60]**.