A THESIS

ON

"EFFECT OF VARIOUS FILLERS ON PHYSICAL AND OPTICAL PROPERTIES OF AGRO-STRAW PAPERS"

Submitted in partial fulfillment of the requirements for the award of the degree of

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CERTIFICATE

This is to certify that the thesis entitled **"Effect of various fillers on physical and optical properties of agro-straw papers"** submitted by Ms. Neha Gupta in the partial fulfillment of the requirement for the award of the degree of *Masters of Technology* in *Material Science & Engineering* from the *School of Physics and Material Sciences, Thapar University, Patiala,* is a record of candidate's own work carried out by her under our supervision and guidance. The matter of this report has not been submitted in part or full to any University or institution for the award of any degree.

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Man's quest for 'Why and How of Things' is a signal event in the evolution of human civilization. The ceaseless endeavor and the faith in scientific temper have enabled him virtually to hitch his wagon to the stars. It has opened new vistas for him in the realms of knowledge, be in electronics or nuclear science. Every new device, a new result, brought to light in the laboratory, however, modest, contributes to the main stream of knowledge. It is a new step in ladder, which ultimately takes to the unknown dizzy heights. The project undertaken by me at A.B.I.L., a premier industry in the field of Paper, Towel and Chemicals is a step further in the same direction. It can by no means, be constructed as the solo performance of an individual, but is a result of coordinated efforts of the worthy and talented people engaged in the pursuit of scientific knowledge in the prestigious industry.

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Neha Gupta

CONTENTS

ABSTRACT

A method to incorporate fillers within pulp fibers has been the subject of extensive research. In the present study, our purpose was to study the effect of various fillers on the physical and optical properties of paper. Apart from this, a low cost environment friendly fiber could be developed which can be used to prepare low cost paper having high strength. Non-wood fibers have a long history as a raw material for papermaking. Environmental and population growth pressures are contributing to long range changes in forest land management practices which reduce harvest of wood for pulp and paper manufacture.

In general, paper contains cellulose, lignin, hemi-cellulose, various additives and fillers which can be modified by the processing techniques so as to obtain better properties. However, the various properties are interrelated and when a change is made to improve one property, some other property is often made poorer. Therefore, optimization of various properties with processing techniques is a way to get appropriate and desired properties of the end-products.

In the present study various type of fillers such as soapstone (SS), titanium oxide (TiO_2) and Hydex-P (HP, synthetic material) are used in acid paper to study their effect on the optical and physical properties of agro-based wheat straw papers. The samples are made by conventional processing techniques of papermaking. These samples were characterized by using various techniques viz. Tensile and Tear strength tester, Differential Scanning Calorimetry (DSC), X-Ray Diffraction (XRD) etc. It is observed that TiO_2 exhibits a minimum drop in strength properties i.e. breaking length and tear factor while maximum gain in optical properties and maximum strength drop is observed in Hydex-P. Both TiO_2 and Hydex-P exhibit gain in brightness and opacity but Hydex-P shows lowest filler retention.

CHAPTER 1

INTRODUCTION

The word paper comes from the Greek term for the ancient Egyptian writing material called papyrus (3000BC), which was formed from beaten strips of papyrus plants and is a commodity of thin material produced by the amalgamation of fibers, typically vegetable fibers composed of cellulose, which are subsequently held together by hydrogen bonding. Chinese Scholar, Ts'ai Lun made paper by grinding Mulbury bark, linen and hump in the first century. Rene de Reaumur in seventeenth century, made paper from the wastage of Paper Wasp insect. Keller in end of 18^{th} Century made Ground wood pulp. Finally, the full fledged paper making started in the beginning of 19^{th} Century at various places of the world.

The earliest efforts at mechanizing paper industry in our country dates back to the beginning of 19^{th} century. First paper mill was set up at Sarampur, West Bengal in 1812. At the beginning of 20^{th} century, India's production of paper was estimated as 19000 tonnes per year [1]. In India, the major players in paper industry are Andhra Pradesh Paper Mills Ltd., Hindustan Paper Corporation Ltd., Abhishek Paper Industries Ltd., Bhadrachalam Paperboards Ltd., Daman Ganga Ballarpur Industries Ltd. etc. Presently, paper includes a wide range of products with very different applications such as communication, cultural, educational, artistic, hygienic, sanitary, as well as storage and transportation of all kinds of goods. It's almost impossible to imagine a life without paper. Based on paper applications, the classification of papers is given below.

1.1 TYPES OF PAPER

There are a number of types of paper. Each type is endowed with some specific property preferred for a particular use. The paper is classified into following categories:

i) Cultural paper

a) Newsprint.

b) Printing and writing paper: Drawing, account book, bank bond, type-writing, white and color printing, litho, maplitho and offset printing paper.

ii) Industrial paper: Kraft paper, bag making, corrugated, wrapping and folding box paper.

iii) Structural paper: Wall paper, tissue paper and towel paper etc.

1.2 PAPER MANUFACTURING PROCESS

Papermaking is a tedious job which involves number of steps during the processing which give final shape to the paper. Various steps of paper manufacturing are shown in fig.1.1.

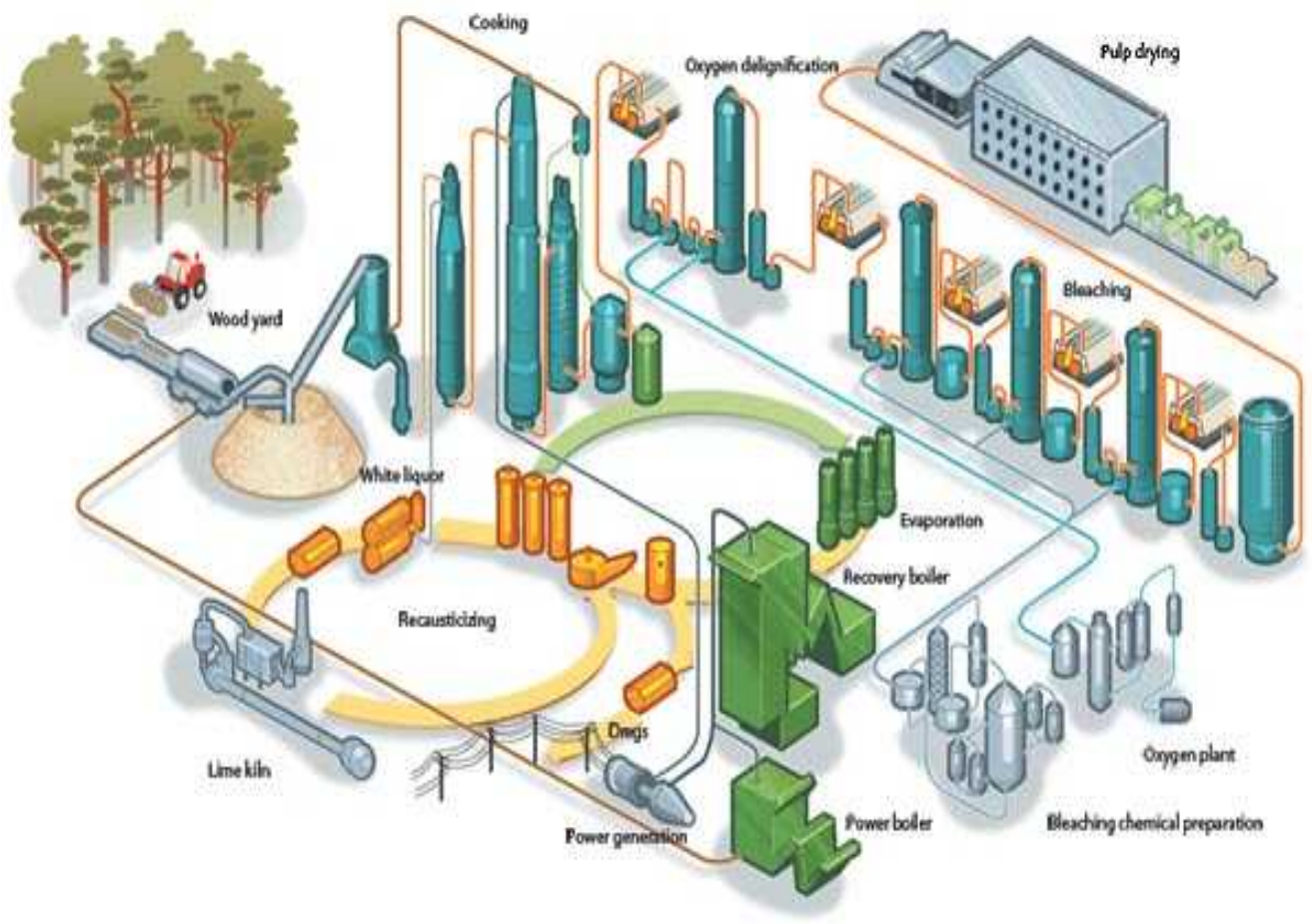


Fig. 1.1 Various steps of papermaking.

1.2.1 RAW MATERIAL PROCESSING

i) Forestry: Typically, trees used for papermaking are specifically grown and harvested like a crop for this purpose.

ii) Debarking, Chipping and/or Recycling: The logs are passed through a debarker, where the bark is removed. The logs are then sent to grinders, which break the wood

down into pulp by pressing it between huge revolving slabs. The pulp is filtered to remove foreign objects or waste materials.

1.2.2 PULPING

Wood chips are then pressure-cooked with a mixture of water and chemicals in a digester. Used paper is another important source of paper fiber. The paper is shredded and mixed with water. During this process, chemical reaction taking place is as follows:

NaOH + Wood ⟶ Pulp + Sodium Lignates

Wood or plant cell walls are composed of fibers bound together. During pulping, these fibers are separated from each other and carbohydrate surfaces, primarily cellulose or hemicellulose, are exposed. Hydrogen bonding between these carbohydrate surfaces gives paper its strength. Fibers can be separated chemically, mechanically or via a combination of the two: chemical pulping and mechanical pulping as shown in fig 1.2.

(i) Chemical Pulping

Mostly, chemical pulp is made using the Kraft process. The purpose of chemical pulping process is to break down the chemical structure of lignin and render it soluble in the cooking liquor, so that it may be washed from the cellulose fibers. Because lignin holds the plant cells together, chemical pulping frees the fibers and makes pulp. Chemical pulps tend to cost more than mechanical pulps, largely due to the low yield (40-50% of the original wood). The process preserves fiber length. Also, chemical pulps tend to make stronger paper. Another advantage of chemical pulping is that, the majority of the heat and electricity needed to run the process is produced by burning the lignin removed during pulping.

(ii) Mechanical Pulping

There are two major mechanical pulps, thermomechanical pulp (TMP) and groundwood. In the TMP process, wood is chipped and then fed into large steam-heated refiners where the chips are squeezed and fiberized between two steel discs. In the groundwood process debarked logs are fed in into the grinders where they are pressed against the rotating stones and are fiberized. Mechanical pulping does not remove the lignin, so the yield is very high (> 95%) but causes the paper made from this pulp to yellow and become brittle with time. Mechanical pulps have rather short fiber lengths which produce weak paper.

Although, large amount of electrical energy is needed to produce mechanical pulp, it costs less than chemical pulp. By mixing with water and applying mechanical action the hydrogen bonds in the paper can be broken and the fibers separated again.

Paper made from either chemical or mechanical pulp can also be recycled.

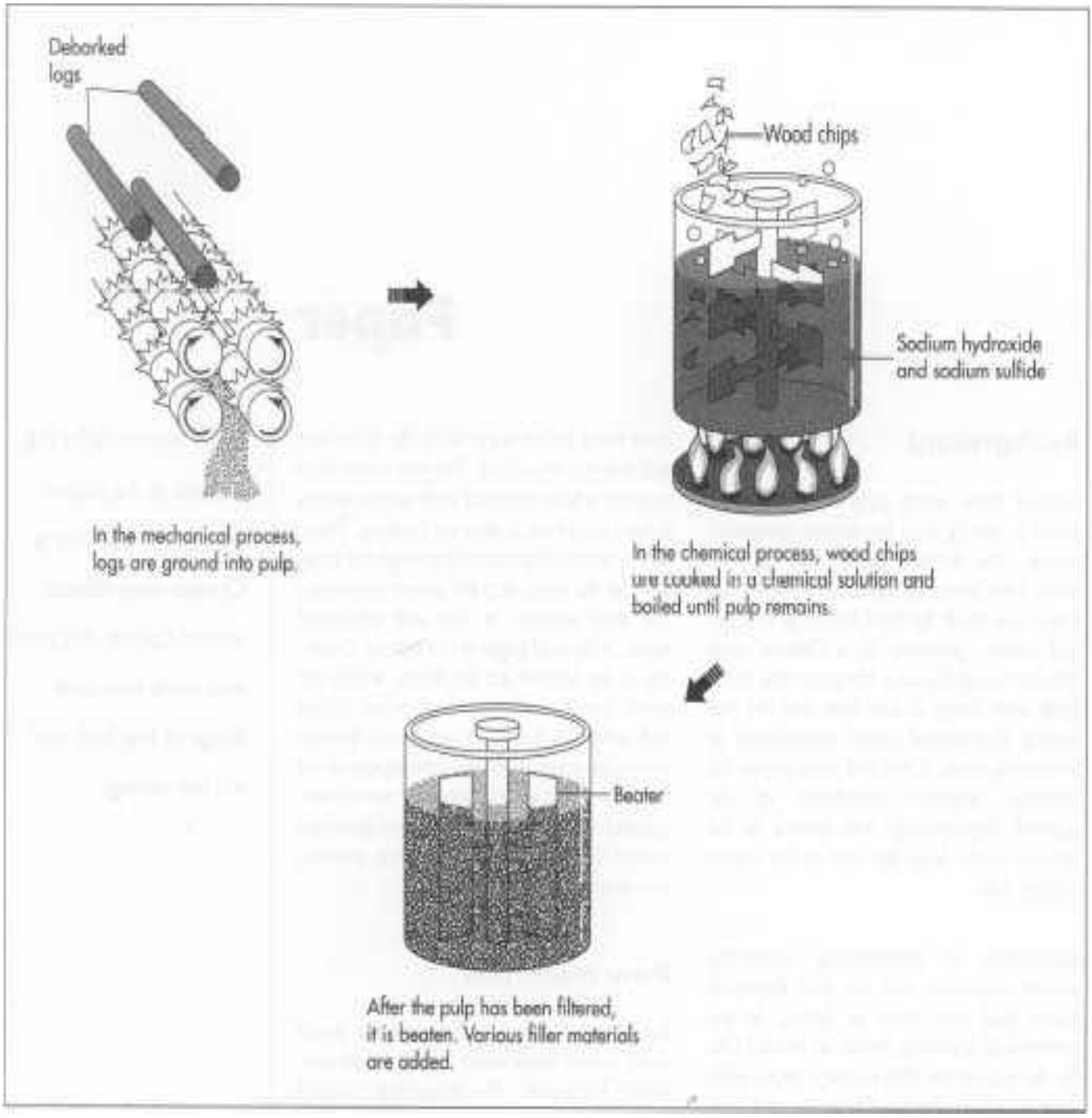


Fig 1.2 Mechanical and Chemical pulping process.

1.2.3 WASHING AND CLEANING

In this step, the chemical or mechanical pulp is washed, refined, cleaned and sometimes bleached so as to remove the unwanted materials. It is then turned to slush in the beater.

1.2.4 STOCK PREPARATION (Beating)

In beating process, the pulp is put through a pounding and squeezing process. Inside a large tub, the pulp is subjected to the effect of machine beaters. At this point, various filler materials can be added such as chalks, clays, or chemicals such as titanium oxide. These additives influence the various properties of the final product such as opacity, whiteness, strength, durability etc. Sizings are also added at this point. Sizing affects the way the paper reacts with various inks. A sizing such as starch makes the paper resistant to water-based ink (inks actually sit on top of a sheet of paper, rather than sinking in). Color dyes, coatings and other additives are mixed in, and the pulp slush is pumped onto a moving wire screen. Computerized sensors and state-of-the-art control equipment monitor each stage of the process.

1.2.5 PAPERMAKING/ DRYING:

As the pulp travels down the screen, water is drained away and recycled. The resulting crude paper sheet/web is squeezed between large rollers to remove most of the remaining water and ensure smoothness and uniform thickness. The semi-dry web is then run through heated dryer rollers so as to remove the remaining water. Waste water is carefully cleaned and purified before its release/reuse. Fiber particles and chemicals are filtered out and burned to provide additional power for the mill. After the paper web is produced, the water is removed from it, to create a usable product through pressing and drying. Pressing the sheet removes the water by force. Once the water is forced from the sheet, another absorbent material must be used to collect this water. On a paper machine this is called a felt. When making paper by hand, a blotter sheet is used. Drying involves using air and/or heat to remove water from the paper sheet. The paper may then undergo "sizing" to alter its physical properties for use in various applications.

1.2.6 PAPER FINISHING (CONVERTING AND PACKAGING)

Finally, the dried paper is wound onto large reels, where it will be further processed depending on its ultimate use. A slitter cuts the paper into smaller, more manageable rolls and the paper is ready for use. Paper is smoothed and compacted further by passing through metal rollers called calendars. A particular finish, whether soft and dull or hard and shiny, can be imparted by the calendars. The common papermaking process is given in fig.1.3.

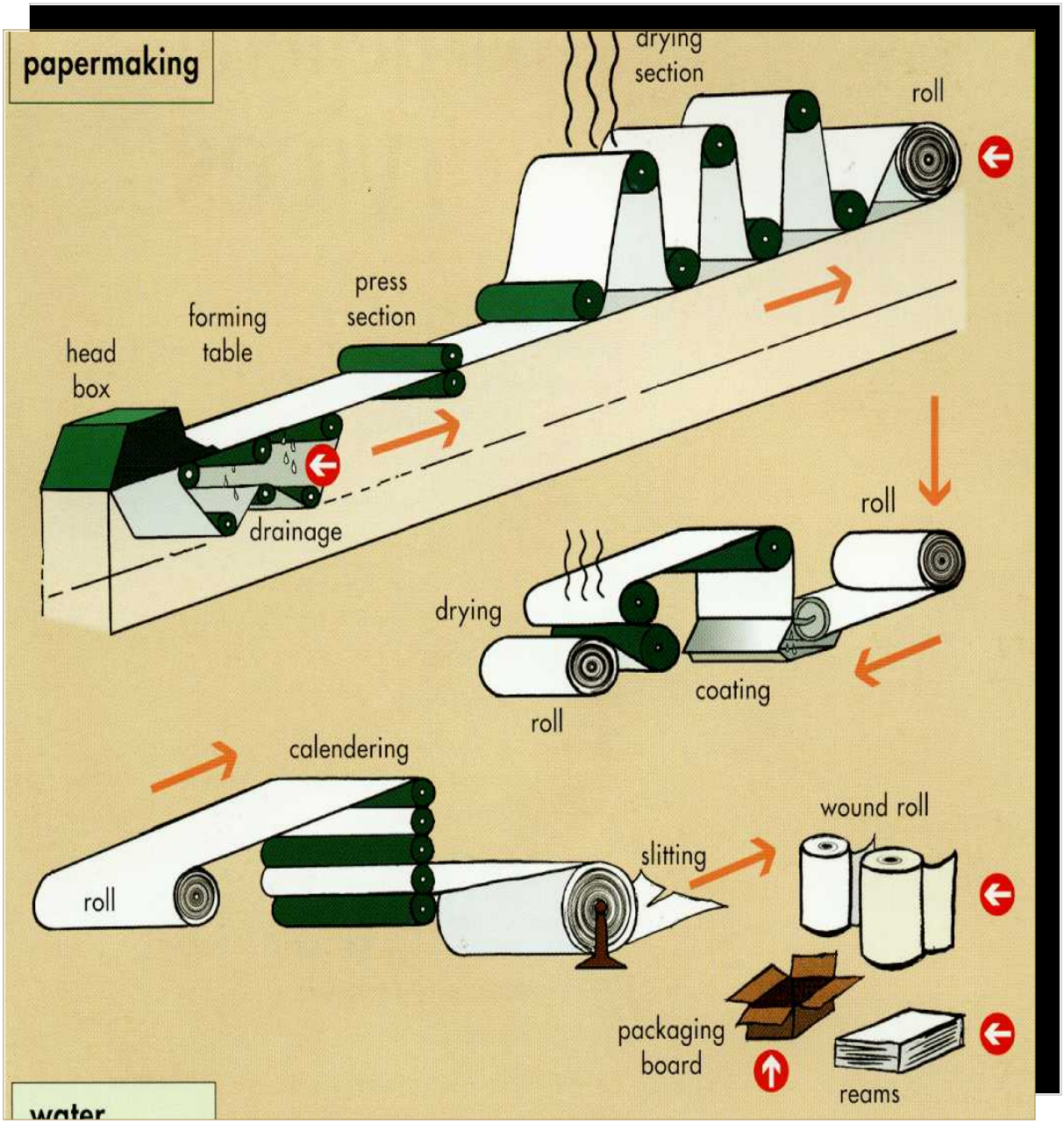


Fig.1.3 A typical paper making process

1.3 ROLE OF ADDITIVES IN PAPERS

Paper is often externally sized with various materials to increase their strength, resistance to picking and scuffing and resistance to undue penetration of water, organic solvents, oils, inks and various types of aqueous solutions as well as for improving their smoothness and optical characteristics. When sizing materials are applied to the surface of a web or sheet in order to cement the surface fibers to the body of the paper and to modify the sheet surface, the process is known as external or surface sizing; the latter process being quite distinct from an internal sizing process wherein sizing agents are admixed with the pulp slurry prior to its being converted into web or sheet form, to reduce penetration of aqueous and other fluid into the paper.

The various additives to paper stock can be classified into two groups [2]:

1. Functional additives: These additives are a component of paper and modify its properties e.g.:

- Fillers or pigments for increased opacity, brightness and printability of paper.
- Colored pigments for coloring of paper.
- Sizing materials for increased water resistance.
- Interfiber bonding agents, starches, gums and resins for increased strength.
- Wet strength resins for increased strength when wet.

2. Control additives: These additives are used to affect the performance of stock at wet-end of the paper machine e.g.:

- Retention and drainage aids.
- Pitch control agents.
- Deformers.
- Bacteriocides and slimicides or microbicides.

Various additives used are discussed below.

1.3.1 OPTICAL BRIGHTENING AGENT (OBA)

Optical Brightening Agents are chemicals which are used to purify and increase the visible whiteness or brightness of paper fibres. Optical brighteners work by absorbing light from the ultra violet end of the spectrum (invisible) and in turn giving off light in the visible range, usually toward the blue white range. This "shift" in the frequency of

light energy results in a whiter-brighter appearance to the product treated. These additives are designed to enhance the appearance of colors on papers. A white surface treated with an optical brightener emits more visible light than shines on it, making it appear brighter. The blue emitted hides the yellow and brown tones, making treated paper appear whiter. They do not change the color of the paper; they only fool the eye into seeing a whiter color. After being exposed to UV rays for a long period of time, OBA begin to lose their fluorescent quality, leaving only the natural base color.

1.3.2 STARCH

Since the beginning of papermaking, starch has been used as an important additive and adhesive in paper manufacture. It forms additional hydrogen bonding between starch and cellulose hydroxyl groups, which improve mechanical and surface properties of paper. Due to its chemical stabilities and good adhesive properties, starch is used in paper conservation for surface coating and as an adhesive between the original and the newly formed part. Starches do not affect much the structural and optical properties of paper, but have influence on the uniformity of the paper sheet, on some mechanical and some surface properties [3, 4]. Starch is relatively inexpensive but it doesn't always work and can cause the sheet more difficult to dry. Starch is a complex and valuable material. Chemically starches are polymers with repeating units of glucose joined through hemiacetal glycosidic bonds. Empirically, the formula is identical to that of cellulose, however starch repeating units are connected by α rather than β configuration which in solution results in a helical configuration of linear segments that have about six repeating units per turn. The ability of starch to aid in interfiber bonding is a function of the tendency of starch to form hydrogen bonds and its high molecular weight.

Highly dispersed starch is inefficient in the low-density sheet because it doesn’t contact two or more fibers at many points. In contrast, the larger granules in the poorly dispersed starch suspension are more effective in the low-density sheet because of their larger size, which causes them to bridge fibers. On the other hand, the highly dispersed starch is very effective in the high-density sheet where there is considerable fiber-fiber contact. Whereas coarsely dispersed granules are relatively ineffective because the granules don’t cover enough surface. In some cases, starches are added at the wet-end without being

cooked. Surface starches improve surface as well as internal strength and printability. A pictorial display of starch contributions to papermaking is presented in fig. 1.4.

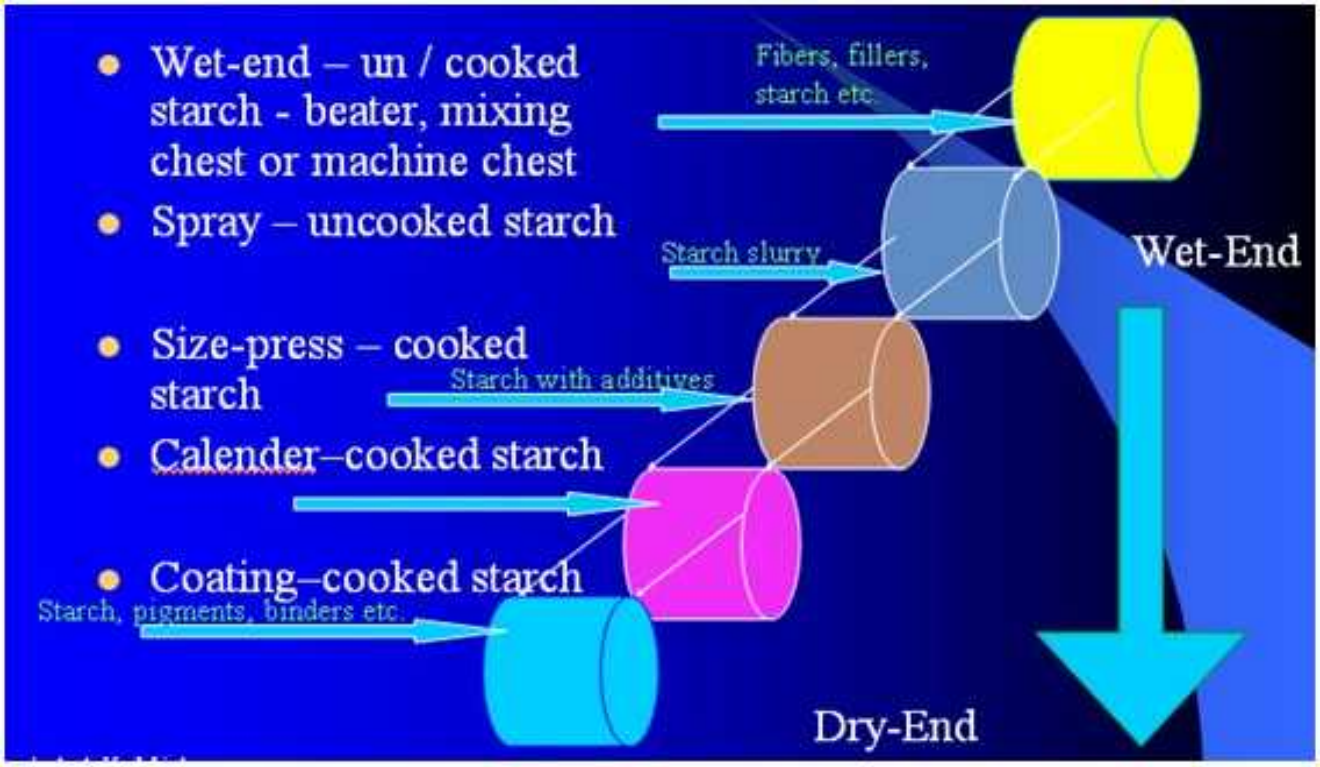


Fig 1.4 Starch application points in papermaking

1.3.3 DRY-STRENGTH ADDITIVES

The term "dry strength additives" refers to a variety of water-soluble polyelectrolytes. The term "dry strength resin" is most often used in connection with anionic copolymers of acrylamide [5]. The dry strength of paper depends on the strength and distribution of fibers within the sheet and the degree of interfiber bonding. Its main function is to increase the relative bonded area or strength per unit of bonded area between the fibers in a sheet of paper. Properties most likely to be favorably affected include internal bond strength and tensile strength.

1.3.4 ROSIN

Rosin is widely used as an internal sizing agent. It is obtained from softwood trees in three ways that yield three slightly different type of rosin: Gum rosin, wood rosin and tall rosin.

Rosin is an amber-colored complex mixture of compounds present in southern pine. Rosin consists of a group of closely-related diterpene acids. The major component of rosin is a family of triclinic acids called resin or rosin acids. The molecular structure of the most common diterpene acid, abietic acid is shown in fig 1.5:

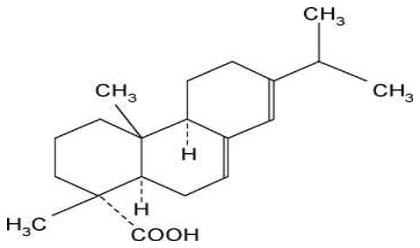


Fig 1.5 Molecular structure of abietic acid

Like alum, rosin has been added to papermaking stock in two different forms. One form of rosin is free acid rosin dispersion, known as rosin acid emulsion. The second form of rosin is produced by saponification to create a soluble, alkali metal soap, known as rosin soap. Rosin is a twenty-carbon organic acid, and is considered an amphipathic material because the compound contains both hydrophilic and hydrophobic parts [6, 7].

Figure 1.6 below shows the aliphatic and aromatic forms of rosin, as well as the hydrophilic and hydrophobic portions of both forms. The aliphatic form of rosin is abbreviated as designated by the parentheses in "(CH_2)", since the molecule actually contains twenty carbons.

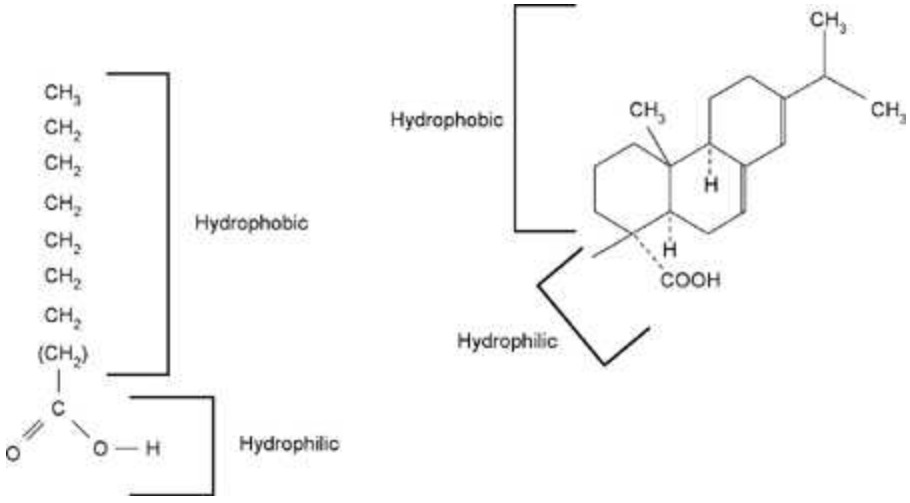


Fig1.6. Aliphatic (left) and aromatic (right) forms of rosin, showing the hydrophobic and hydrophilic portions of both forms.

1.3.5 RETENTION AID

In case of filled papers, the ideal situation would be to have each of the fibers coated with filler particles equally spaced along the fiber axis. The particles, singly or agglomerated should have a size about 1/2 the wavelength of light for maximum scattering and opacity. On the microfloc scale, if filler particles are flocculated before they adsorb onto the fiber, they act as a single large unit that drastically reduces the optical efficiency (scattering unit weight) of the filler. The addition of polymeric retention aids also affects the mechanical properties of the finished sheet. Increased filler content will act to debond the sheet and reduce dry strength. Greater polymer dosages will recover dry strength and even promote wet strength in some cases [8, 9]. It is known that the particles that pass through a 75μm hole (200 mesh) constitute fines fraction [10]. Those particles held back are considered to be the fiber fraction. These two fractions add up to 100% of the suspended solids regardless of chemical composition. There are two general aspects of fine particle retention: Mechanical entrapment and colloidal forces. Varieties of chemicals like natural polymers as carboxymethyl cellulose, starch and synthetic organic polymers give improved retention. Cationic starch may function effectively as retention aid for fillers, but overdose may impede the retention mechanism [11]. Excess causes problems probably because the colloid covers all the particles entirely and rate of floc formation is reduced.

1.3.5.1 EFFECT OF FILLER RETENTION AID ON PAPER PROPERTIES:

i) To enhance the water drainage during paper formation. Maximum water removal results in reduced energy consumption.

ii) Reduction of scattering coefficient i.e. opacity increase is less than that expected from increase in the ash content [12]. The distribution in optical efficiency, therefore not be greater than what would be expected from statistical reasons i.e. the likelihood of having adjacent filler-filler particles with less scattering will increase with an increase in amount of filler in the sheet. The optical efficiency is much better when alum is present in the system than when a cationic retention aid is used alone [13].

1.3.6 ALUM

Alum is a salt commonly used in papermaking. True (potash) alum is chemically a double salt of aluminum, or potassium aluminum sulfate (K_2SO_4. Al_2 $(SO_4)_3$. $24H_2O$). The papermaker's alum used today is not true alum, but either aluminum sulfate (A_{12} $(SO_4)_3$.$14H_2O$), ($A_{l2}(SO_4)_3$.$18H_2O$), or a mixture of these hydrates. It is soluble in water and while slightly alkaline in the dry form, it is decidedly acidic when dissolved in water. Alum has two major functions in papermaking: 1) to control pH; and 2) because of its flocculating ability, to retain other additives in the paper, notably the sizing agent. Aluminum is the active component in alum, and its properties are important to the sizing process. The aluminum ion has a high charge of +3, and a small ionic radius of 0.50ºA, which results in a high charge density.

CHAPTER 2

RAW MATERIALS

Half of the fiber used for paper today comes from wood that has been purposely harvested. The remaining material comes from wood fiber from sawmills, recycled papers**,** some vegetable matter and recycled cloth. Hence, the paper industry in India can be classified as forest based raw material, waste paper based, agro-residue based raw material. In the following section, more details of forest-based raw materials and agro-residue based raw materials are given.

2.1 FIBROUS RAW MATERIALS

Fibrous raw materials can be classified as wood based raw materials and non-wood based raw materials (Bagasse, Bamboo, Kenaf, Reed, Straw and Grasses).

Wood based raw materials are classified as: Soft woods (low density, long fibers as Spruce, Pine, and Birch etc) and hardwoods (high density, short fibers such as aspen, oak, walnut, poplar, acacia, eucalyptus etc). Paper made from soft wood is much stronger. This paper is ideal for making products like shipping containers that require superior strength. But the finish is rougher which is not good for writing, printing and many other uses. Now, hardwood trees (oaks, maples) are also used as an ideal raw material for pressing into fluting for corrugated case as well as printing and writing papers. These trees have wood with very short fibres. Paper made from these species is weaker than that made from softwoods, but its surface is smoother and therefore better to write and print.

2.2 MAIN COMPONENTS OF FIBROUS RAW MATERIALS

i) Cellulose

ii) Lignin

iii) Hemi Cellulose

iv) Extractives

i) Cellulose: Cellulose is a natural polymer, a long chain made by the linking of smaller molecules. Cellulose is a major component of wood. Cellulose fibers in wood are bound in lignin, a complex polymer. Paper-making involves treating wood pulp with alkalis or

bisulfites to disintegrate the lignin, and then pressing the pulp to matte the cellulose fibers together. Cellulose $(C_6H_{10}O_5)_n$ is a polysaccharide of beta-glucose and is formed by polymerisation of glucose molecules which make long flat regular chains.

The primary cell wall of green plants is made of cellulose; the secondary wall contains cellulose with variable amounts of lignin. Lignin and cellulose, considered together, are termed lignocellulose. It occurs naturally in almost pure form in cotton fiber. Cellulose is the major constituent of paper and textiles made of cotton, linen and other plant fibers; further processing can be performed to make cellophane, rayon, cigarette papers (transparent), and more recently Modal, a textile derived from beechwood cellulose. In micro fibrils, the multiple hydroxyl groups on the glucose residues hydrogen bond with each other, holding the chains firmly together and contributing to their high tensile strength. This strength is important in cell walls, where they are meshed into a carbohydrate matrix, helping in keeping the plant cells rigid.

ii) LIGNIN: Lignin (sometimes "lignen") is a chemical compound (complex, highly cross-linked amorphous aromatic polymer having no predetermined order) that is most commonly derived from wood and is an integral part of the cell wall of plants, especially in tracheids, xylem fibres and sclereids. Lignin is a co-polymer of phenylpropanes having high molecular weight which holds the fibers and the cellulose together. It has several unusual properties for being a biopolymer, such as having a network structure and lacking a defined primary structure. Lignin contains three different alcohol units: coniferyl alcohol (the primary constituent), p-courmaryl alcohol and sinapyl alcohol as shown below fig 2.1.

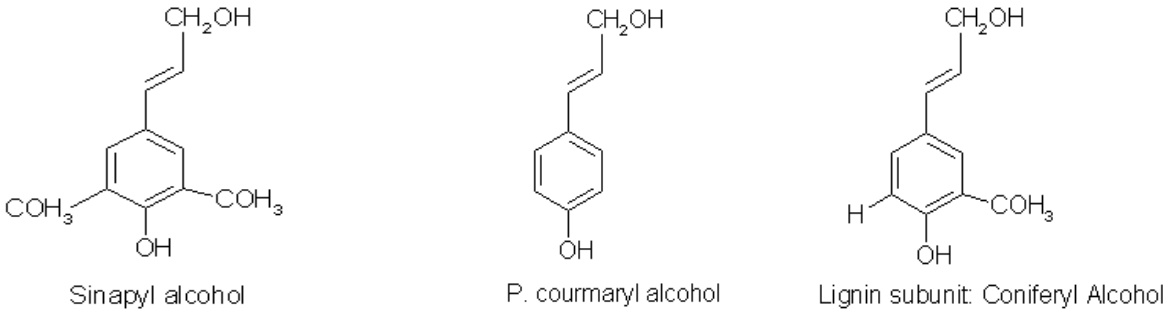


Fig 2.1 Structure of lignin

These monomers are polymerised by a reaction that results in a variety bonds between the units and side chains are added which can be more alcohol units or aldehydes (these vary between types of lignin in different plants). The binding is such that a random and unordered structure is formed, with each lignin molecule being different from another. Ether bonds within this structure give lignin its strength. It is formed with multiple reactions involving phenolic compounds (hydroxyl derivatives of aromatic hydrocarbons). The complexity of the lignin polymer is the main reason why it is so hard to degrade by enzymes. Because of the variety of units, a single enzyme cannot degrade it, yet for a microorganism it is not effective in terms of energy production to produce every enzyme needed to break each bond.

Lignin can be largely removed during pulping and the cost of low-lignin papers is higher than that of high-lignin or groundwood papers. Lignin is believed to contribute to the degradation of both papers and photographs. In nature it is very resistant to degradation, being held together with strong chemical bonds; it also appears to have a lot of internal H bonds. It is bonded in complex and various ways to carbohydrates (hemicelluloses) in wood [14].

iii) HEMICELLULOSE: Hemi-cellulose are any of a group of short-chain complex carbohydrates that, with other carbohydrates (e.g. pectins), surround the cellulose fibres of plant cells. In contrast to cellulose that is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base. Hemicellulose contains many different sugar monomers (glucose, xylose, mannose, galactose, rhamnose, and arabinose). In contrast, cellulose contains only anhydrous glucose. Hemicelluloses are important to the paper industry. In chemical wood pulps, hemicellulose is needed for satisfactory pulp quality. Its presence aids the swelling of the pulp, the bonding of the fibers, the bursting strength, tensile strength, tear resistance, folding endurance, opacity, and specific surface of the pulp sheet [15].

iv) EXTRACTIVES: The term extractives (terpenes, phenols, fatty acids, resin acids) refer to a large number of wood compounds which are soluble in organic solvents [16]. The accumulation of wood extractives in paper mills (forming the so-called pitch

deposits) results in interruptions in paper production (examples: machine downtime for wash ups, holes or dirt spots), low-quality pulp due to formation of spots, specks and other product defects [17]. Over the years, a number of additive methods have been used to minimize these problems. These include dispersion, fixation, encapsulation, stabilization, and absorption. Extractives removal increased the hydrophilicity and basicity of fibres and increased the adhesion between fibres and water [18, 19].

2.3 AGRICULTURAL RESIDUE BASED RAW MATERIALS

The use of agro residues, which is the major source of non-wood fibers in pulp and paper production, has shown an increasing trend in recent times due to ecological consideration as they prevent the denudation of forests [20]. It is also well known that non-wood materials can be delignified more easily than wood chips under alkaline conditions [21]. The severe depletion of forest raw material and the growth of agro-based paper mills have led to increased utilization of agricultural residue and other secondary raw materials which have now assumed a significant role in meeting the demand of cellulose fibers for paper industry. Most important among them are:

i) Bagasse: Bagasse is the solid fibrous material left after extraction of juices from sugarcane. A number of industries in India utilize bagasse as a part of raw material furnish. Bagasse in India is available abundantly in Western Uttar Pradesh, Maharastra, Haryana etc.

ii) Cereal straw: China, India and Taiwan are the major users of rice straw and wheat straw as a raw material. The main problems associated with the use of these materials are handling, transportation and storage.

iii) Grasses: Varieties of grasses, those are comparatively easy to pulp can be used for papermaking. Availability of adequate being the only limitation. The important varieties utilized in India are: Sabai grass and Elephant grass.

iv) Non-wood crop fiber such as jute, kenaf, cotton linters etc: India is a major producer of jute and hence the potential is immense. The major problems related to it are collection and transportation.

2.3.1 WHEAT STRAW

Non-wood fibers have a long history as a raw material for papermaking. Environmental and population growth pressures are contributing to long-range changes in forest land management practices, which reduce harvest of wood for wood products and for pulp and paper manufacture. Yet, excess straw often presents problems for subsequent field operations such as no-till seeding. Until recently, these fibers have been thrown away or burned. But disposal costs are rising. State bans on burning rice or wheat straw after harvest, for example, have spurred farmers to seek alternative uses of straw. Wood fiber prices have increased since 1991, a result of increased worldwide demand and a reduced cutting on some national forests resulting from environmental restrictions. Agricultural materials are bulky and expensive to transport. Therefore they often are processed near where the raw materials are located. Thus, straw might represent a significant fiber substitution opportunity. Straw makes excellent paper. Straw fibers are similar to hardwood fibers, and straw pulp can be used in most papers as a substitute for hardwood pulp. Because of the large quantity of straw available, and their tensile qualities, many types of agricultural straw are ideal for a wide array of products including paper, building materials, textiles and other fiber-based products. Due to the characteristics of straw fiber, straw pulp has good smoothness, opacity and stiffness, but is lacking in tear and burst strength. Pulp made from straw is best suited for corrugated medium, newsprint, printing and writing papers, and linerboard. Usually paper products are not made from 100% straw pulp, but are mixed with recycled or wood pulps, and could be mixed with other nonwoods.

Straw has a relatively small open cell structure and silica-rich epidermis. This is an advantage in that it allows for almost instantaneous liquor penetration, but creates a drawback in that the fiber has poor drainage characteristics. Due to high hemicellulose and fines content, straw has a good bonding ability. Many researchers find that straw pulp tends to bond better than wood. Papatheophanus notes that pulps with decreased hemicellulose have better mechanical properties. Compared to wood, straw is low in lignin, thus less time, energy and chemicals are required for cooking and bleaching. Somewhat higher in cellulose than wood, it is generally somewhat higher in yield.

Overall straw has a low bulk density. A comparison between wood fiber and straw fiber is given in table 2.1.

S.No.	Straw Fibers	Wood Fibers
1	Low Bulk	High Bulk
2	Low Opacity	High Opacity
3	High water uptake	Low Water Uptake
4	Low Oil Uptake	High Oil Uptake

Table 2.1 Comparison between straw and wood fibers

Wheat is a short fibre material, which means that it can be used in combination with other long fibre materials such as flax or spruce pulp to produce common paper types. Wheat, like most agricultural fibres, takes less than half the time to "cook" into pulp than wood, resulting in less energy being used in the pulping process. Wheat straw pulp is likely to be used in blends with wood pulps in proportions consistent with paper and board cost and performance specifications. Straw based raw materials show following properties:

- **i)** The high bond area associated with high paper density, results in relatively high tensile index despite the predominance of short fibers in wheat straw. Conversely, tear index is lower than most wood pulps as a result of the low average fiber length.
- **ii)** Straw pulp has a broader fiber length distribution than hardwood and a broader distribution in L/D (Runkel ratio) than hardwoods and softwoods.
- **iii)** The small fiber dimensions typical of cereal straw limit both the paper products strength and paper machine operating speeds [22, 23].

Wheat and rice straw is by far the most abundant non-wood fiber raw material. Straw yields short fiber pulp, similar to hardwood pulp. When properly processed, straw pulp can replace hardwood pulp in for e.g. Printing and writing paper with no noticeable loss in paper quality. Chemical pulping of straw poses no problems. Efficient and well-proven continuous digestors are available for delignification of straw by the soda process that

uses only NaOH in the cooking liquor. The high inorganic content of straw creates potential problems in conventional chemical recovery systems. Blends of straw and recycled paper or wood pulps can provide useful paper properties. However, one problem still needs to be resolved; the fiber from the wheat straw is short so it doesn't always provide the sturdiness needed for the printer's press.

2.3.1.1 THE SILICA PROBLEM: Serious problems are associated with recovery of sodium and energy from black liquor. In hardwood black liqour, the silica content is typically about 1kg/ton of dry solids, but in black liquor from the soda cook of wheat straw it is 40-60 kg and for rice straw even higher. The high content of silica in liquor contributes to the sharp increase in viscosity when liquor is evaporated and to scaling of heat exchangers in the evaporators. The silica forms hard deposits on the furnace walls of the recovery boiler and the low dry solid contents of the strong black liquor requires continuous burning of fuel oil in the boiler furnace [24].

2.3.1.2 CHALLENGES

i) Chemical Recovery: Wheat straw contains 4-10% silica as small crystals embedded in the straw, rice straw has an even higher silica content of 9-14%, and other cereals such as barley, oat and rye straw have 1-6% silica. Wood on the other hand, has a silica content of less than 1%. The silica dissolves during cooking to produce pulp and it is contained in the used cooking liquor (black liquor). Black liquor contains inorganic material used as the cooking chemical, and both inorganic and organic material removed from the fiber raw material (wood or nonwood) during cooking. All modern pulp mills include a chemical recovery process which treats the black liquor to recover the pulping chemicals, to use organic non-cellulose material (up to 50% of the original material before cooking) to generate energy for the pulp mill and to recycle process water. The problem with cereal straw is that its high silica content causes many problems in the chemical recovery process such as scaling (coating equipment with a glass like substance) which reduces the efficiency of some equipment and actually can plug it and increased viscosity which make it difficult to pump the black liquor at some parts of the recovery process. These problems make chemical recovery difficult, less efficient and more costly as compared to

recovery for black liquor from wood. Without recovery a pulping process is extremely polluting.

ii) Capacity: Another property very different from hardwood fiber is that the water retention capacity of straw fiber is much better than hardwood fiber. This poses a significant problem to the pulping engineer, because a large part of making pulp is separating fiber and water. In a pulping process, fiber goes through a number of wet processing steps in which water is added to the fiber followed by water removal. Each new liquid brings particular chemicals to the fiber, dissolves unwanted components from the fiber, and then takes those unwanted components away from the fiber when liquid and fibers are separated. Due to the high water retention capacity of straw fiber, each separation step requires about three times as much separation capacity as for hardwood processing (four times for rice straw). This means a significant increase in capital investment per ton of straw pulp versus hardwood pulp.

iii) Yield: Straw yields less pulp per ton of raw material than wood about 45% yield for straw versus 55% for wood, so a pulp plant has to buy more straw to produce the same amount of pulp.

iv) Density: Straw bales take about three times as much space as logs. So, transport is about three times as expensive. This limits the supply radius for a straw based pulp mill considerably. Also, the bales are bulky and are more difficult to handle than wood chips [25, 26].

CHAPTER 3

FILLERS AND ITS REQUIREMENTS

3.1 FILLERS

Fillers are generally white pigments that can be divided in two major categories:

i) Regular fillers: These have wide application and cost lower than that of cellulosic fiber, e.g. kaolin clay, ground calcium carbonate, talc, soapstone and precipitated calcium carbonate.

ii) Specialized fillers: These fillers usually have lower volume applications and costs are sometimes comparable with or even higher than cellulosic fiber as titanium oxide, composite pigments e.g. clay, titanium oxide, precipitated synthetic silica-silica oxides and precipitated silicate-aluminum silicate (PSS), aluminum trihydrate, Hydex-P. Inorganic fillers are applied primarily in printing and writing papers.

3.2 NEED OF FILLER

Increasing global competition, fiber shortages and environmental and ecological concerns force papermakers to constantly work to reduce production costs. The process of adding mineral matter to paper stock prior to the formation of sheet has been practiced since the ancient days of paper making. At first, this was considered a poor practice and any paper containing large amount of fillers was regarded as inferior. Today, the situation is quite different. The benefits of fillers are generally accepted and the addition of fillers such as clay, calcium carbonate and titanium oxide is regarded as an integral part of the paper making process. In fact, some paper qualities cannot be achieved without fillers. Mineral fillers increase the paper brightness, opacity and improve the paper's quality while having reduced costs by replacing fiber. However, filler loading has been limited to 15%-20% because higher levels cause a loss of sheet strength and bulk as well as "dusting" (unreacted superfacial filler particles come out of paper during printing creating problem in the printing machine) during printing. Fillers are highly desirable in printing papers where they increase the opacity, raise the brightness and generally improve the printing properties. The application of fillers is especially important when opacity is needed at a low basis weight and they are invaluable in packaging grades where low permeability should be combined with opacity for light protection of foodstuff. Fillers must be used in

almost all paper grades, but especially in those grades where the optical properties and printability are more important than strength.

3.3 PREPARATION OF FILLERS

Pigments either in form of slurry or dry powders is purchased. The pigment slurry is screened before being added to the stock and the addition of grit and other foreign matter to paper can thus be avoided.

Fillers generally disperse better in hot than in cold water. Normally, small amounts of dispersing agents are added to obtain a uniform particle size. Moreover, slurry may be prepared at higher percent solids if dispersing agents are used although the performance/ efficiency on paper machine are not significantly improved. Pigments as TiO_2 and silicoaluminates require vigorous agitation to avoid oversized particles that lower the scattering coefficient and may cause dusting in paper.

3.4 DISTRIBUTION OF FILLERS IN THE SHEET

The pigment in the sheet partly adheres to the fiber surface and is partly held by electrostatic forces, but it is also retained mechanically in the open space within the fiber network. The relative magnitude of these forces will vary according to the type of pulp, other chemicals used and numerous other factors. However, these forces are not strong enough to hold the filler immobilized in the sheet when it is exposed to the hydraulic forces required to give a high drainage rate. Most papers containing fillers are two-sided in the sense that thereby contains more pigment on the felt or top side than on the wire side. This may be a serious disadvantage for the user, especially with regard to the printing properties that are dependant on the amount of filler located at or near the paper surface.

3.5 FILLER ADVANTAGES

1. To increase surface smoothness.
2. To improve printability.
3. To improve paper optical properties (opacity, brightness etc). Small particle size and large specific surface area give good opacity. Filler to fiber interfaces scatter

little light because the refractive index (n') for most fillers is very near that of fibers (~1.55). The refractive indices of various medium are shown in table 3.1.

S.No.	Medium	Refractive Index
1	Air	1
2	Water	1.33
3	Paraffin	1.43
4	Linseed oil	1.48
5	Cellulose (sp. gr. 1.50)	1.53
6	China clay (sp. gr. 2.60)	1.55
7	Calcium carbonate (sp. gr. 2.60)	1.56
8	Asbestine	1.56
9	Gypsum(sp. gr. 2.30)	1.57
10	Talc(sp. gr. 2.70)	1.57
11	TiO_2 + Blance fixe(1:3)	1.89
12	Zinc sulphide (sp. gr. 4.00)	2.01
13	TiO_2 (Rutile) (sp. gr. 3.88)	2.70
14	TiO_2 (Anatase)	2.55
15	ATH (Alumina)	1.57
16	Starch	1.57
17	Fibers	1.53

Table 3.1 Refractive indices of various mediums

4. The light scattering surface of paper increases as bonding degree decreases. A narrow particle size distribution and low degree of agglomeration promotes light scattering. The average particle size of fillers varies from 2m to a few m. and is much smaller than fibers and fines.
5. To improve gloss and color.
6. To decrease the paper cost due to decreased paperweight.
7. Filler use provides faster machine speeds.
8. They are also effective at making paper thick, tight, and soft.
9. Improve softness and smoothness/finish particularly after calendaring.
10. Improve dimensional stability: Replacing relatively hydrophilic fibers by (hydrophobic) pigments makes a more dimensionally stable paper.

11. More rapid H_2O absorption and other liquid absorption i.e. beneficial effect on ink absorption and penetration (Clay particles are more readily wetted by ink than fibers and clay also produce more and finer capillaries in the sheet).

Fillers used to enhance paper properties are more expensive than pulp and so should be used sparingly, as excess use reduces their cost benefit like TiO_2, urea formaldehyde plastic pigments, aluminium trihydrate, calcined clay etc.

3.6 FILLER DISADVANTAGES

1. Increased amount causes a decrease in sizing. Normally, sizing is not affected until 10-15% filler is added but even a small amount of alkaline pigment ($CaCO_3$) may be harmful in this respect.
2. If pigments are higher than fibers; they tend to increase the specific gravity of the sheet. This means lower bulk and less stiffness, which may be a disadvantage on sheet fed printing press.
3. More filler use causes "dusting" which can be seen at calendar, rewinder or printing press which is caused due to weakening of the sheet structure. It can be prevented by increasing internal bonding through use of wet-end additives as starch.
4. Loss of strength will occur to the extent that a powdered mineral, which has no binding power, replaces the fiber substance. The effect of over 5% of loading is apparent in reduction of strength and this becomes serious when 20% is exceeded.
5. Loss of resistance to ink particularly writing inks.
6. If the loading is coarse in texture, abrasion of the printing surface (which is continually coming into contact with it) will occur.
7. Increased two sidedness, reduced rigidity and increased linting

Importance of moisture content of loading is that the papermaker doesn't wish to pay for water at price of the loading. At same time, a certain amount of moisture may be regarded as "natural' to the loading.

3.7 LITERATURE REVIEW ON FILLERS

The principal fillers used are:

1. Clay.
2. Calcium carbonate.
3. Talcum/ Soapstone.
4. Titanium oxide.
5. Blanc fixe.
6. Colored pigments.
7. Aluminium trihydrate.
8. Synthetic pigments (organic and inorganic type).
9. Hydex-P.
10. Synthetic sodium, aluminium, magnesium silicates.

Commonly used fillers alongwith properties in paper industry are shown in table 3.2.

S. No	Chemical Name	Used For	Specific Density	Other Characteristics
1	Silicate of Magnesia(Agalite or Talc)	It gives paper a greasy or soapy feel and enables it to take a high finish.	2.6 - 2.8	A natural fibrous form of talc, gray in color.
2	Barium Sulfate(Barytes)	Used as filler	4.2-4.5	-
3	Barium Sulfate(Blanc Fixe)	Used as a base for watercolor pigments and as a filler in paper.	4.2-4.5	Powdered barium sulfate
4	Precipitated Calcium Carbonate(Chalk (Precipitated))	Filler particularly with acidic sizing.	2.7-2.9	High Brightness & Opacity
5	Hydrated Silicate of Alumina (China Clay, Kaolin)	Filler, Coating	2.4-2.7	-
6	Calcium Magnesium Carbonate(Dolomite)	Filler, Coating	2.86	-
7	Calcium Carbonate(Lime Stone)	To make Lime Precipitated $CaCO_3$ is used as Filler and in Coating	-	-
8	Titanium oxide(Titania)	Filler to increase the opacity and brightness of paper. Used in coating also.	3.84-4.26	-

Table 3.2 Commonly used fillers in Paper Industry

3.7.1 CLAY

Clay meets most of the requirements (except high refractive index) and hence is admirably suited for filling. Clay pigments are used in magazine paper, book paper and other printing papers.

Clay is found in natural deposits and can be processed in various ways to give a variety of different qualities. Clay will not give same brightness improvement as $CaCO_3$ and TiO_2 but its overall good qualities combined with low price make it well suited for a number of paper grades. It is common to add 15-20% clay in printing paper and upto 35% in some grades [especially in cigarette tissue ($CaCO_3$) and in absorbent kraft paper and salmica paper (TiO_2)]. Kaolin clay can be divided into two types as hydrous and structured (calcined, chemical) kaolin clay.

Kaolinite is a mineral belonging to the group of aluminosilicates commonly referred to as "China clay" because it was first discovered at Kao-Lin, in China. Kaolin is white, soft, plastic clay mainly composed of fine-grained plate-like particles. In paper industry, it is used both as a filler in the bulk of the paper and to coat its surface. The principle use of kaolin in coatings is as TiO_2 extender. Partially calcined and delaminated grades generally provide the best extension, durability and dry hide. Water washed and delaminated clays are used in water-based coatings to control gloss, film integrity, durability, scrub resistance, covering power, suspension ability, flow and leveling. Various properties of clay are given below:

1. Non-abrasive with high whiteness and large surface area.
2. Soft and plastic nature.
3. Fine grained plate-like particles.
4. Remains chemically inert over a relatively wide pH range.
5. Low conductivity of heat and electricity.
6. High opacity and brightness.
7. Enhanced optical properties.
8. Improved printing characteristics and high gloss.
9. Reduction in amount of expensive wood pulp required.
10. Offers excellent covering when used as a pigment or extender in coated films and filling applications.

3.7.2 TITANIUM OXIDE (TiO_2)

TiO_2 pigments are white inorganic compounds and an oxide of titanium (TiO_2) also known as titanium oxide, titanic dioxide, titanic oxide, titania, rutile, anatase, or brookite. It occurs naturally in the rutile (tetragonal); anatase or octahedrite (tetragonal); and brookite (orthorhombic) crystalline forms. Brightness of TiO_2 pigments is 98% or more having particle size ranging between 0.3-0.35µm. To increase the efficiency of TiO_2, it is frequently mixed with other cheaper fillers as clay. In recent years, new synthetic pigments containing various proportions of alumina and SiO_2 have been suggested as extenders for TiO_2. TiO_2 pigments are inert; do not react with other materials, thermally stable, non-flammable and non toxic. Titanium oxide has a remarkably high refractive index and an exceedingly high reflectance. It offers maximum opacity or hiding power as well as imparts whiteness and brightness to the products in which it is used [27]. Various properties include:

1. Insoluble in water and most acids while soluble in hot concentrated sulfuric acid and alkalies.
2. Due to high R.I. and fine particle size, TiO_2 pigments show exceptionally high opacifying effect making it easy to read brochures and literature: titanium oxide particles increase opacity by scattering light.
3. Reduced show through after printing.
4. High price doesn't permit indiscriminate use. Therefore, TiO_2 is primarily used to produce high quality and high priced paper products.
5. Have a very high brightening effect.

The important property of titanium oxide particles is that, they increase opacity by scattering light. The efficiency of TiO_2 for light scattering is strongly dependant on the refractive index of the pigment relative to that of the surrounding medium and on the size of TiO_2 particles [28, 29]. Completely opaque waxing papers and gassine require a minimum of ~ 4-4.5%, airmail papers require ~9%, Bible paper and decorative laminates require ~15% TiO_2.

Their ability to scatter light depends on their being present in the sheet as separate particles, not clumps. This means that the TiO_2 product should be well dispersed before it is added. Premature mixing of titanium oxide slurry with alum or other cationic materials

should be avoided in order to minimize self-agglomeration of the pigment. Good optical efficiency usually can be achieved by first adding the pigment at a place where it becomes well mixed with the furnish, and then adding a retention aid. Even better optical efficiency can be achieved in some cases if enough highly charged cationic polymer is added before TiO_2, to create cationic sites on the surfaces of fibers and fines. The amount has to be optimized, since an excess of cationic polymer in the solution merely will agglomerate the TiO_2 to itself. However, it has relatively high abrasiveness, absorption of ultraviolet light which reduces the effectiveness of the fluorescent whitening agents. TiO_2 is more expensive than pulp and other mineral pigments like kaolin clay and $CaCO_3$, so it must be used as efficiently as possible. For paper applications, the cost effective approach is to optimize the use of non-TiO_2 components and then add TiO_2 as required to achieve target opacity.

Titanium oxide (TiO_2) exhibits two forms i.e. anatase and rutile. The rutile form is used in the manufacture of pigmented paper coatings, while the anatase form is used as a filler pigment in paper manufacture. Refractive index of rutile (2.70) is higher than refractive index of anatase (2.55). Both types (as used in papermaking) are important because of their whiteness, high brightness, and high refractive index (2.52 to 2.76), all of which results in a paper of improved brightness and opacity. Anatase is less expensive, but rutile is slightly more efficient in some applications.

1) Anatase is an excellent choice for filling of paper. It is economical, easily dispersed in water based systems, and an excellent opacifier. Untreated anatase provides over 98%+ pure TiO_2 with a refractive index of 2.55. This form is also good for use in interior paints, plastic filling, and highway marking paints. With the exception of highway paints, it is not recommended for exterior (weather exposed) applications.

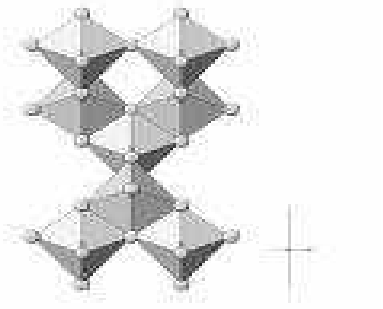


Fig 3.1 Anatase structure of TiO_2

2) Rutile provides superior "wet" opacity, which is useful in wet strength paper grades, waxed papers, and other saturated applications [30]. It is slightly more efficient than anatase with a refractive index of 2.70, but it is more expensive. Rutile is often provided as a "treated" product, which aids in easy dispersion in high solid coatings. Rutile has superior weather resistant characteristics for applications with exterior (outdoor) exposure or where long term light fastness is important. Rutile TiO_2 is an especially effective opacifier because of its high refractive index [31, 32]. The rutile crystalline form of TiO_2 has higher intrinsic scattering efficiency than the anatase crystal because of its higher refractive index (2.74 vs. 2.56) at the center of visible light spectrum. Efficiency is maximized by generating narrow particle size distributions near the optimum diameter. White pigment particles in filled papers are not surrounded completely by cellulose (refractive index ~1.45) but rather by cellulose and air (refractive index ~1). Rutile particles are more efficient in porous paper substrates, which are a mixture of cellulose and air [33].

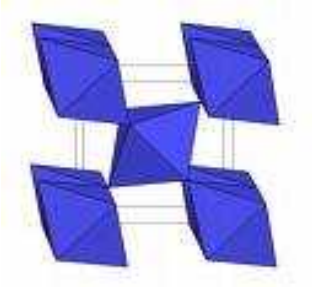


Fig 3.2 Rutile structure of TiO_2

3.7.3 CALCIUM CARBONATE ($CaCO_3$)

Fillers are always lower in cost than pulp. Papermakers have tried to maximize filler levels for decades. In paper manufacturing, the shift from an acid-based process to an alkaline one has revolutionized the use of these fillers. It has allowed calcium carbonate to replace wood-pulp and other pigments, while improving paper quality in terms of brightness, opacity, porosity and bulk. The alkaline process is actually used for fine printing and writing paper. Calcium carbonate is a chemical compound, with chemical formula $CaCO_3$. It comprises more than 4% of the earth's crust and is found throughout the world. Calcium carbonate is found naturally as the following minerals and rocks as

aragonite, calcite, chalk, limestone, marble and travertine. The brightness of [34] $CaCO_3$ is used in various printing grades, cigarette paper and Bible paper. Carbonates are available in two forms: Precipitated calcium carbonate (PCC) and Ground calcium carbonate (GCC).

1. Precipitated calcium carbonate (PCC)

The availability of low-cost precipitated calcium carbonate (PCC) fueled the rapid expansion of alkaline papermaking. PCC provides many benefits, including excellent brightness and opacity at significantly lower cost than the clay or fiber, it replaces. PCC has a very fine and controlled particle size, on the order of 2 µm diameter which is particularly useful in production of paper. PCC has the advantage of being less abrasive but is also more expensive than ground type (GCC). PCC is produced for applications requiring higher brightness, better TiO_2 extension, smaller particle size, greater surface area, lower abrasivity or higher purity [35]. Precipitated calcium carbonate (PCC) is a cost effective, high performance replacement for titanium oxide (TiO_2). Generally, PCC can displace 15-25% of the TiO_2 in a typical formulation and hence can cause significant raw material cost savings. PCC has excellent optical properties due to the small median particle size, controlled particle size distribution, and high brightness.

2. Ground calcium carbonate (GCC)

Dry-ground calcium carbonates are among the least expensive white fillers available. GCC pigments depend on whether its origin is chalk, limestone or marble. GCC provides benefits like increased brightness, reduced binder demand, excellent printability and whiteness and very good rheology. But it suffers from low ink holdout i.e. low print gloss values.

Difference between PCC and GCC is shown in table 3.3.

PARAMETERS	GROUND $CaCO_3$	PRECIPITATED $CaCO_3$
Particle shape	Irregular	Irregular
GE Brightness	91-95	95-98
Oil absorption	8-18	30-50
Medium P.S. (µm)	1-40	0.07-0.7
Hegman fineness	$0\text{-}7^{+}$	7^{+}
pH (10%)	9-10	9-10
Specific gravity	2.71	2.70
Refractive index	1.66	1.66
Mohs Hardness	3	3
lbs/solid gel	22.5	22.5

Table 3.3 Various parameters of GCC and PCC

3.7.4 TALC/ STEATITE/ SOAPSTONE

Soapstone is a soft rock which is made up mostly of the mineral talc. The word soapstone has been named probably due to its soapy feel. Steatite, talc and soapstone are the three terms used in trade for one and the same mineral. Steatite is designated to indicate a purer variety of compact and massive talc while the use of word soapstone is restricted to a slightly impure variety of steatite containing 50 to 80% talc. Talc traditionally an inert filler is now a versatile functional additive. The mineral's properties make it useful not only in its original role, but in paper coating and in the control of stickies and pitch as well. Talc is a sheet silicate mineral and is described as a hydrated magnesium silicate with a chemical composition $Mg_3Si_3O_{10}(OH)_2$, theoretically 31.7% MgO, 63.5% SiO_2, and 4.8% H_2O. It is a word derived form the greek word "talq" meaning pure which is a unique mineral. Talc has an extremely lamellar structure having high aspect ratio. Because of the platy nature of this special form of Talc, it is considered as reinforcing filler in many plastic applications. In its unprocessed form, it is a rock with a platelet microstructure consisting of hydrophobic planar surface and hydrophilic edges. That is, its planar surface has no affinity for water, while its edges do. Talc can occur virtually pure or in highly contaminated mixed mineral deposits.

The term talc covers a wide range of natural minerals, most of which are high magnesium silicates. Another term for talc is steatite and the natural occurrence of steatite is in soap-stone. Minerals commonly associated with talc, except soap-stone are tremolite [($CaMg_3(SiO_3)_4$)], serpentine [($3MgO.2SiO_2.2H_2O$)], anthophyllite, magnesite, mica and chlorite. Other impurities such as dolomite (Ca, $MgCO_3$), calcite ($CaCO_3$), iron oxide, carbon, quartz, and manganese oxide may also be present. Pure talc mineral is characterized by softness (1-2 on the Mohs scale), brightness in range 70% to 98% and hydrophobic surface properties. It is slippery/greasy in feel. Talc is inert in most chemical reagents, although it exhibits a marked alkalinity (typically pH 9.0 – 9.5). It is however soluble in hot concentrated phosphoric acid and have particle size ~1-10µm [36].

The higher aspect ratio of talc results in a more closed sheet and therefore lowers the porosity. The particle shape also contributes to greater smoothness and higher retention levels. The talc ore selected should be low in abrasive impurities. Even small amounts of hard minerals in paper fillers can increase the degree of wear on paper machine clothing and machinery. Its platy character, compressibility and hydrophobic/ oleophillic nature produces a sheet with improved smoothness and excellent ink adsorption. The inclusion of talc lowers the surface abrasivity of paper, allowing layers to slide past one another without premature rupture of ink capsules.

The calcium content may vary considerably from one source to another. High Ca talcs are the whitest, but Ca is harmful to sizing and certain dyes. For this reason, talc should be the last component added to furnish. Talc contributes to TiO_2 extension, suspension stability, flatting, chemical resistance, leveling, film integrity and weatherability. Since, it contains a variety of particle shapes and is lower in oil absorption, tremolitic talc provides easier dispersion, higher loading levels, less flatting and better dry hide than platy talc. It also provides better durability in exterior and traffic paints. Micronized platy talc is used for pitch adsorption in pulp and paper mills because of its low abrasion and its ability to preferentially wet oily materials in the presence of water. In paper and paper coatings, high purity, high brightness platy talc is used for TiO_2 extension and for improved gloss, opacity, brightness and ink holdout.

PARAMETERS	PLATY	INDUSTRIAL
Particle shape	Platy	Mixed; acicular, irregular, platy
GE Brightness	80-90	80-92
Oil absorption	25-55	20-40
Medium P.S. (µm)	1-15	2.7-13
Hegman fineness	3-6.5	0-7
pH (10%)	9.5	9.4
Specific gravity	2.75	2.85
Refractive index	1.6	1.6
Mohs Hardness	1-1.5	3.5
lbs/solid gel	22.6	23.7

Table 3.4 Parameters for various talc types

3.7.5 ALUMINA TRIHYDRATE

This is used as filler in fine printing papers as it increases opacity and brightness; and in paper coatings as it imparts brightness, gloss and high ink receptivity. It is also used for TiO_2 extension and gloss control in interior and exterior coatings. It have irregular particle shape with particle size ~0.25-0.26µm having brightness in range 93-100%. The refractive index is ~1.57.

3.7.6 BARITE

High brightness micronized barite is used as an extender to provide the weight and also have low binder demand for high loadings. It is used primarily to add weight in bristolboard, playing cards and heavy printing papers. It have irregular particle shape with particle size ~1-11µm having brightness in range 80-95%. The refractive index is ~1.64 and have a high specific gravity (4.6) which gives weight and body to the coated paper.

3.7.7 DIATOMITE

Diatomite used as white filler is flux calcined, milled, screened and air classified. Natural and flux calcined products are used in certain specialty papers as a light weight bulking agent, as a drainage aid, as an opacity binder and as a fiber dispersion aid. It have irregular particle shape with particle size ~4-20μm having brightness in range 85-90%. The refractive index is ~1.46.

Based on the literature review of various fillers we came to know very fewer studies have been done on the combination of various fillers. Due to this reason, various filers and their combination have been tried to study the effect of fillers on physical and optical properties of papers.

CHAPTER 4

EXPERIMENTAL TECHNIQUES

A brief detail about sample processing methodology which we followed during the course of investigation is presented in this chapter.

4.1 SAMPLE PREPARATION

Both straw pulp and wood pulp samples are taken from their respective chest storage areas and are measured with their respective consistency and °SR (Schopper–Riegler) for further calculations.

i) Consistency and ° SR measurement:

200 ml graduated flask is filled to the mark with the pulp (diluted and made upto 1000ml volume). The sample is then transferred to a Buchner funnel, into which it has fitted a circular filter paper. Suction is applied until no more water is removed, the residual pulp is washed a few times with a little distilled water and sucked dry between each wash. The paper and contents are finally dried in oven at 105°C.

ii) Volume of pulp to be taken is then calculated based on 95% straw pulp and 5% wood pulp. The mixture is then diluted and placed in the disintegrator (allowed to run for about 10 sec) and hence cleared for lumps. The desired chemicals/ additives are added herein only as shown in table 4.1.

			SAMPLES													
			1	2	3	4	5	6	7	8	9	10	11	12	13	14
S.No	PARAMETERS	NORMS	SP	SP+Additives	WP	SP(95%)+WP(5%)+Additives	10gm TiO2	10gm SS	10gm HP	5gm TiO2+5gm SS	5gm HP+5gm TiO2	5gmSS+5gmHP	6gm SS+4gm HP	7gm SS+3gm HP	8gm SS+2gm HP	9gm SS+1gm HP
1	Straw pulp		100%	100%		95%	95%	95%	95%	95%	95%	95%	95%	95%	95%	95%
2	Wood pulp				100%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%	5%
3	Soap stone (SS)							10gm		5gm		5gm	6gm	7gm	8gm	9gm
4	Hydex-P(HP)								10gm		5gm	5gm	4gm	3gm	2gm	1gm
5	TiO2						10gm			5gm	5gm					
6	OBA	3kg/ton, 1GPL		75ml		75ml	105ml	105ml	105ml	105ml	105ml	105ml	105ml	105ml	105ml	105ml
7	Starch	1.5kg/ton, 1%		3.75ml		3.75ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml
8	DSR 55	1.5kg/ton, 1%		3.75ml		3.75ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml
9	DSR 41	1.5kg/ton, 1%		3.75ml		3.75ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml	5.25ml
10	Rosin	20kg/ton/50%		1ml		1ml	1.4ml	1.4ml	1.4ml	1.4ml	1.4ml	1.4ml	1.4ml	1.4ml	1.4ml	1.4ml
11	Retention Aid (R.A.)	50gm/ton, 1GPL		1.25ml		1.25ml	1.75ml	1.75ml	1.75ml	1.75ml	1.75ml	1.75ml	1.75ml	1.75ml	1.75ml	1.75ml
12	Alum	As Such														

Table 4.1 Various chemical amounts taken for sample preparation

iii) Sheet machine container is then partially filled with water. Water is then allowed to run till is just above the wire level so that air below wire is driven off. Pulp slurry (250ml) is then taken and the water is turned so that level raises upto the mark. Perforated stirrer/ agitator is used to the stock well by moving up and down. Drain clock is then opened after ~10sec and the water is allowed to drain from sheet under suction. The cylinder is then tilted after drawing the water and the sheet is couched with help of filter paper and couch plate. Sheet is dried in hot air oven and taken its oven dried (O.D.) weight. The volume of pulp stock equivalent to 1.2gm of O.D. pulp is then calculated and prepared 8 samples in similar manner.

iv) The sheet of blotting paper is then peeled off the pate (when pulp sheet should adhere to it) and laid, with the pulp sheet uppermost on another piece of blotting paper on top of this, after which another pulp sheet and its supports of blotting paper may be added until a stack of 8 pulp sheets alternating with sheet plates is built up. Press the hand sheets in the standard press by raising pressure aprox. 3.5kgf/cm^2 in half minute and maintain it there for 5 min. Release the pressure and remove the cover and filter paper. The steel plates (to which the test sheets are now attached) are removed and the top plate is placed on a square of blotting paper (with the pulp sheet uppermost) and covered by another square which serves as a base for the next plate and pulp sheet and so on. The order of the sheets is thus reversed in the new stack and pressure is again applied but for only 2min.

v) The plates and attached pulp sheets are attached in perforated brass drying rings, which can be fitted into one another and are prevented from shrinkage by the fact that they are held all round the edge by the pressure of the ring higher up in the stack. The sheets are then dried with help of rapid dryer. The sheets prepared are then examined as discussed below.

4.2 EXAMINATION OF THE SHEETS/PAPER TESTING

Unequal internal strains are set up when the paper is dried on the paper machine because of increased tension in the machine direction produced by drying. Since, most papers are dried to a moisture content of about 3%, they tend to subsequently pick up moisture until the moisture content amounts to 5-9% (according to the humidity of the atmosphere in which they are placed). A logical preventive for such troubles is to add sufficient

moisture to the paper to bring it to a state in which it will neither gain nor lose moisture in the atmosphere in which it is to be used ("conditioning"). Hence, paper must be conditioned before the test in an atmosphere of standard humidity (50-65%) and temperature (27 ± 2°C). The tests are then carried out on paper as given below.

4.2.1 MEASUREMENT FOR GRAM SQUARE METER (GSM)

In the paper machine section, GSM is the main important quality measurement. Consistency and stock flow variation are the most commonly known sources of substance variation. For any system, the substance may be indicated as a function of side flow and consistency in following way:

GSM = weight of sheets (gms) x 50/ number of sheets taken [R & D standard, A.B.I.L.]

4.2.2 STRENGTH

Paper strength can be regarded as being a result of the strengths of individual fibers, plus the strengths of bonds between those fibers. Usually the bonds are weaker than the fibers themselves. In common with most paper testing methods strength tests differ from determinations of weight and thickness in that they don't measure a definite property of paper (i.e. Weight or thickness).

a. TENSILE STRENGTH: This test measures the tensile pull necessary to break a strip of paper. The breaking length is thus calculated from the following formulae:

Tensile Index (Nm/g) = Avg. Tensile Strength (N/m)/ Grammage (g/m^2)

Breaking Length (m) = Tensile index x 102

= Avg. Tensile Strength (N/m) x 66700 [R & D standard, A.B.I.L.]

This value may be regarded as the length of a strip of the paper that, if hanging freely from one end, will just support its own weight.

b. INTERNAL TEARING STRENGTH: The Elmendorf instrument is used for this test. It consists of a sector shaped plate hanging from its apex on a substantially frictionless bearing and free to swing in pendulum fashion in its own plane. Means are provided for holding the pendulum in a raised position with one edge vertical and for releasing it instantaneously. It will then swing to the same height on the other side of its normal

vertical position. The maximum arc through which the sector travels is indicated by a vertical pointer that is carried forward with the outward travel of the pendulum.

4.2.3 BRIGHTNESS, OPACITY AND COLOR TESTING

Color, brightness and opacity of the paper samples were measured using Lorentzen and Wettre (L&W) ELREPHO (S070) Spectrophotometer testing equipment. The instrument consists of an optical path containing the optics and photometer. The illuminant is a barium sulphate coated sphere, the light source and a pulsed xenon lamp. The reflectance measurement is made using a dual-beam-diode-array spectrometer. The reflectance is reported at 10nm intervals in the visible spectrum (400-700nm).

4.2.4 MEASUREMENT OF ASH CONTENT

The ash in paper may be derived from fiber, pigments used in filling, sizing agents, mineral matter in the fresh water, pigments used, metallic matter from piping and machinery, wastepaper if any used in the furnish. Normally, ash from unfilled and uncoated papers is not over 2%, although in rare cases it may be as much as 5%. It is usually light and fluffy in appearance. If the ash content is over 5% and is dense and compact in appearance, it may be taken as positive evidence that the paper is filled/coated with pigment. Printing papers for letterpress generally have an ash content of 15-25% because of the pigments used in filling. Mineral and organic suspended solids are determined by igniting the sheet in a platinum crucible in order to obtain the inorganic portion, which is represented by the residue. The organic portion is obtained by difference. The ash content is an approximate measure of the mineral salts and other inorganic matters present in all types and pulp grades.

Ash content (%) = ash weight x 100/ O.D. weight of sample.

a) INORGANIC CONSTITUENTS: These constitute the ash which remains after ignition of the paper. They are subdivided as follows:

1. Major: White pigments (loadings), colored pigments (coloring matters).
2. Minor: Mainly traces of mineral salts present as impurities and due to inadequate washing e.g. acidity, bleaching residues, metal and acid radicals.

b) ORGANIC CONTITUENTS: These are destroyed completely by ignition of the paper, although they may leave behind certain mineral constituents (e.g. inorganic bases from take colors, generally impurities).

1. Major: Cellulose (α- cellulose) and its related substances; lignin.
2. Minor: Substances added to the paper for special purposes (e.g. rosin size, dye stuffs, starch) or derived from impurities.

4.2.5 DIFFERENTIAL SCANNING CALORIMETRY

Differential scanning calorimetry (DSC) is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature [37].

DSC equipment consists of a furnace containing two identical crucibles, each of which rests on a thin plate located inside the measurement head as shown in fig 4.1. Any difference in temperature of the two specimens is caused by differences in mass, specific heat, heats of reaction, or phase transitions.

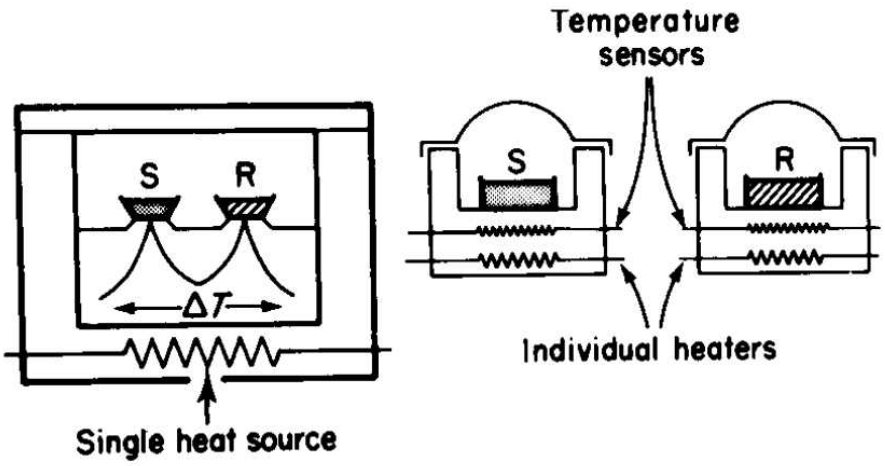


Fig. 4.1: (a) Heat flux DSC; (b) Power compensation DSC

Thermal response records are acquired for a standard material (usually sapphire) and an unknown under identical conditions. The ratio of the departure of the standard and unknown from the baseline is then used to calculate the specific heat of the unknown. There are two main types of differential scanning calorimeters: heat flux DSC and power compensation DSC. There are two pans as shown in fig 4.2. In one pan, the sample pan, you put your polymer sample. The other one is the reference pan. You leave it empty.

Each pan sits on top of a heater. The heating rate can be given as required in various atmospheres such as air, N_2, Ar etc. The automized system makes absolutely sure that the heating rate stays exactly the same throughout the experiment. So the heater underneath the sample pan has to work harder than the heater underneath the reference pan. It has to put out more heat. By measuring just how much more heat it has to put out is what we measure in a DSC experiment.

Fig 4.2 Sample holder of DSC

The present study of DSC measurement was carried out on selected samples so as to check their stability with respect to the temperature. These measurements are performed on LINSEIS (DSC L63) in the temperature range of room temperature (R.T.) to 350ºC at rate of 10ºC in presence of air.

4.2.6 X-RAY DIFFRACTION

Phase identification was carried out by X-rays diffraction using Rigaku model Geiger diffractogram with Cu Kα radiation (λ = 1.541Aº) obtained from copper target using an inbuilt Ni filter. The paper samples were loaded in the suitable sample-clamping device rotated by motor- driven goniometer. The X-ray diffractometer used in the present study consist of the X-ray tube mounted in a fixed position, the sample at the center of rotation and a detector mounted on to the goniometer such that it rotates in a circular arc around the sample. The mechanism was calibrated so the sample rotates at half the speed (scanning rate) of the detector so that the angle at which the X-ray beam impinges on the sample was the same as the angle from which the radiation was sensed by the detector. Angles were measured as 2θ, the filter or monochromatic and collimating slits were placed in the beam paths. As the sample and detector were rotated from nearly 0^0 (2θ) to near 180^0 (2θ), radiation sensed by the detector was amplified and recorded as a function of 2θ. After completion of the experiment the data in the form of angle Vs intensity has

been plotted and the exact peak position was located. Using these peak positions the interatomic planar distances (d) were calculated using Bragg's law:

$$n\lambda = 2d \sin\theta$$

The intensities (I) were normalized to 100% in each case. Identification of the crystalline phases was carried out by the comparison of the d-spacing and relative intensities obtained with those of reference material pattern compiled by the powder diffraction file.

CHAPTER 5

RESULTS AND DISCUSSIONS

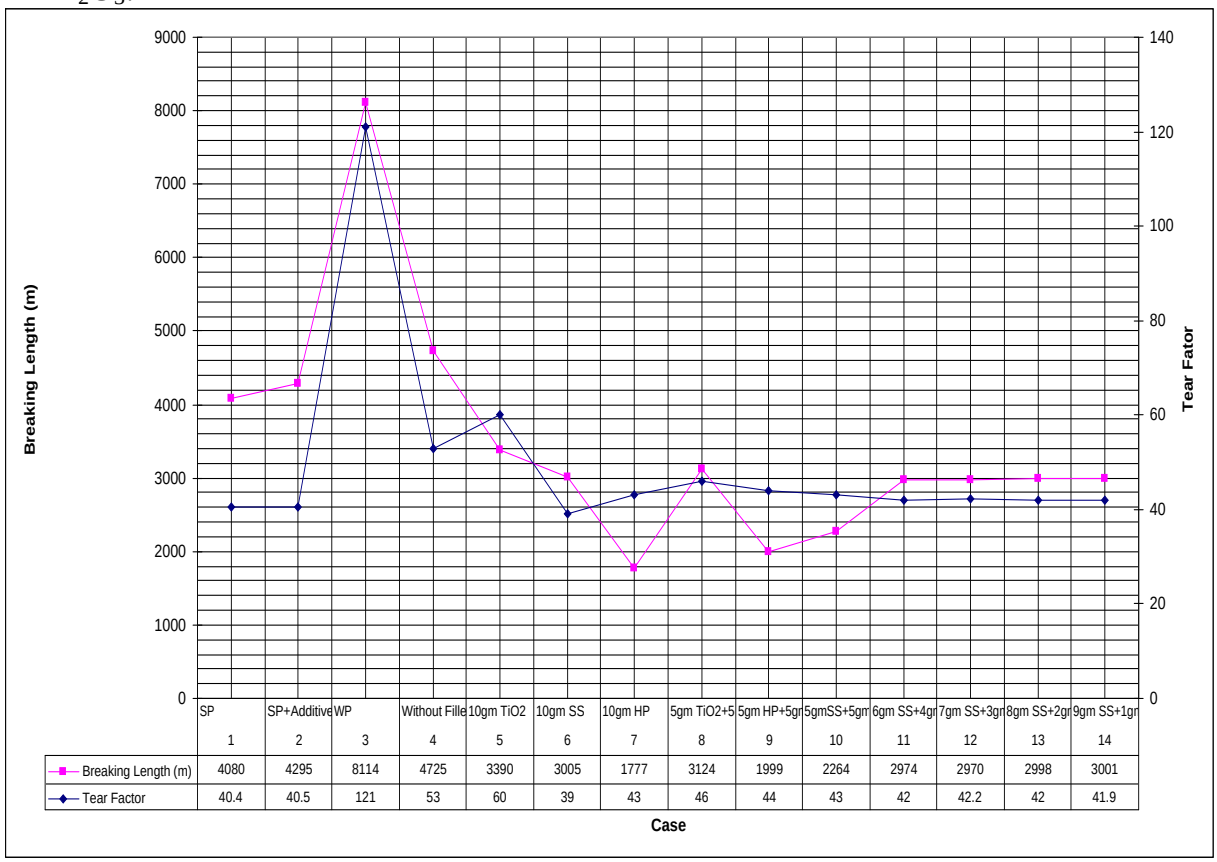
As prepared samples are tested by different techniques to find their physical and optical properties and also their suitability for end use applications. The results are summarized in table 5.1. The usual procedure is to plot each of the obtained values against the corresponding parameters and so to obtain a graphical representation of them in relation to one another.

S.N.o	Parameters	Unit of Measurement (UOM)	Test Results													
			1	2	3	4	5	6	7	8	9	10	11	12	13	14
			SP	SP+Additives	WP	SP(95%)+WP(5%)+Additives	10gm TiO2	10gm SS	10gm HP	5gm TiO2+5gm SS	5gm HP+5gm TiO2	5gmSS+5gmHP	6gm SS+4gm HP	7gm SS+3gm HP	8gm SS+2gm HP	9gm SS+1gm HP
1	GSM	(gm/m2)	59	59	59	61	60	60	60	60	62	62	60	61	60	61
2	Breaking Length	(m)	4080	4295	8114	4725	3390	3005	1777	3124	1999	2264	2974	2970	2998	3001
3	Tear Factor		40.4	40.5	121	53	60	39	43	46	44	43	42	42.2	42	41.9
4	L*		93	92	93	92	93.85	93	96	93.43	96	95	93.3	93	93	93
5	a*		-0.6	1	-0.4	0.5	0.23	0.5	1.3	0.18	0.8	1.2	-0.3	-0.3	-0.3	0.2
6	b*		4.3	0.4	2.1	1.8	2	1.6	-1.7	2.7	-0.7	-1.3	3.3	3.3	3.3	1.7
7	Yellowness		7.5	1.8	3.7	4	4.23	4	-2.3	5.5	0.8	-1.5	6.2	6.2	6	3.5
8	Brightness	(%)	80.7	82	84	82.7	85	83	87	82.2	87	86	85.7	85	84.1	83
9	Opacity	(%)	84	85	75	86	91	88	91	90	91	90.7	90	89	89	88
10	Scc/2		42.3	43.3	29.2	43.4	68.04	53	78	60.3	77.7	70	57	54.9	54	53.1
11	Kcc/2		0.8	1.04	0.5	1.07	0.91	1.05	0.6	0.9	0.61	0.8	0.95	0.9	1	1.03
12	Flourescence		0.3	5	1	3.3	3.61	4	6	3.6	4.4	5.95	4.5	4.47	4.07	3.9
13	Ash	(%)	3	4	2	3.6	17.3	20	16	19.2	17.3	17.5	17.1	17.3	18	19.9
14	Filler retention	(%)	10.5	14	7	13	61	70	56	67.4	60.7	61.4	60	61	63	69.7

Table 5.1 Physical and optical results of samples

It is observed that the strength of the samples decreases with increasing filler content as shown in fig 5.1. Wood pulp shows highest strength properties as compared to that observed for straw pulp. This is due to presence of longer fibers in wood pulp than straw pulp. Longer fiber exhibit higher strength than short fibers. On filler addition, in the straw pulp, highest strength property is observed on addition of TiO_2 while a minimum is observed in case of Hydex-P. Basically, strength highly depends on the nature of impurity and their particle size [38]. Similarly, a combination of TiO_2 and soapstone shows better strength properties compared to samples having more of HP which is a

synthetic anhydrous material. As mentioned above, the addition of TiO2 as filler enhance the strength. This is due to the structure of filler and their compatibility (chemical and mechanical bonding) with the matrix. The constituents of HP are NaO, MgO, SiO_2 and Al_2O_3.

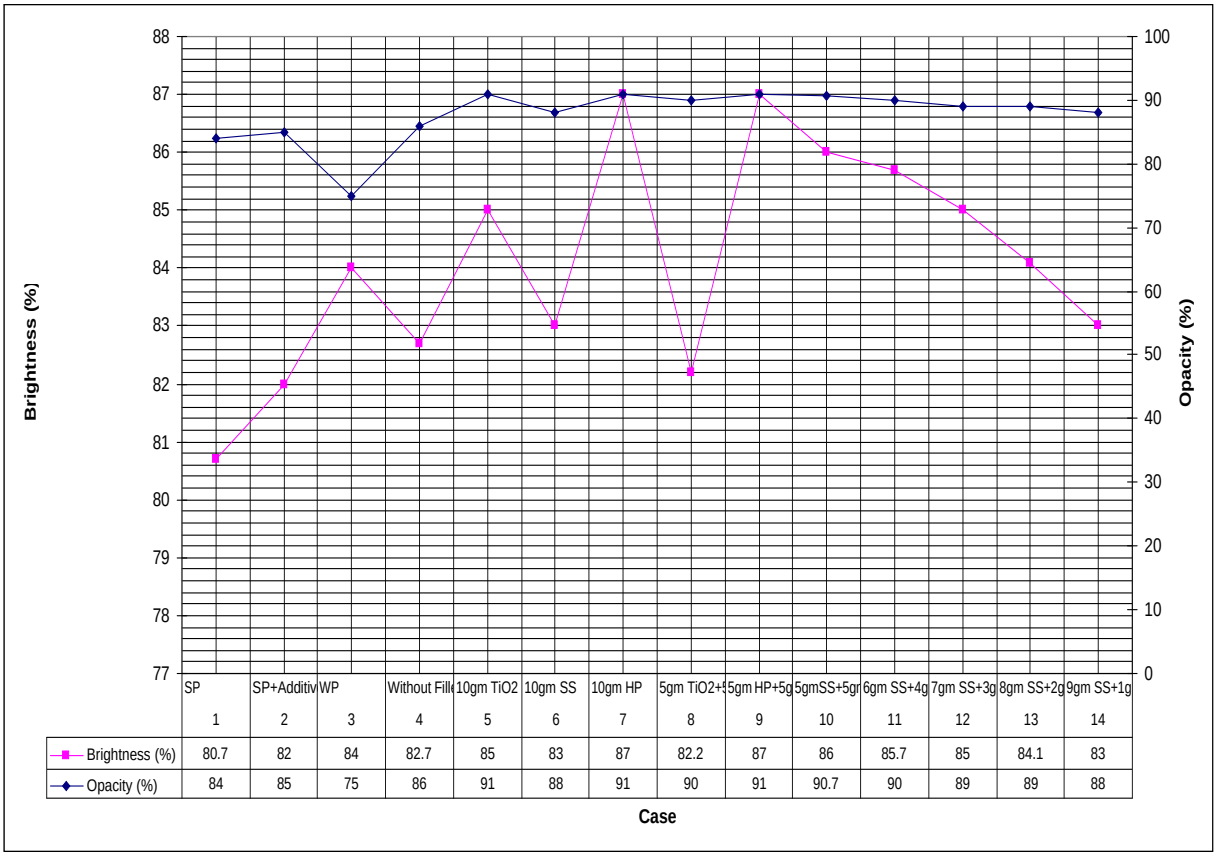


	SP	SP+Additive	WP	Without Fille	10gm TiO2	10gm SS	10gm HP	5gm TiO2+5	5gm HP+5gr	5gmSS+5gm	6gm SS+4gr	7gm SS+3gr	8gm SS+2gr	9gm SS+1gr
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Breaking Length (m)	4080	4295	8114	4725	3390	3005	1777	3124	1999	2264	2974	2970	2998	3001
Tear Factor	40.4	40.5	121	53	60	39	43	46	44	43	42	42.2	42	41.9

Fig 5.1 Effect of Breaking Length and Tear Factor of samples having various fillers

It is clear from fig 5.2 that wood pulp shows good brightness (84%) but at the same time, low opacity (75%) due to its open structure among the long fibers. As additives are added to the straw pulp, its optical properties increases since these block the pores present in the fibers which further increases the light scattering property of the sheet and hence its optical properties. On filler addition, sample containing 10gm Hydex-P (HP) shows highest optical properties while soapstone (SS) shows a minimum. Sheet containing both HP and TiO_2 shows highest optical properties and those containing TiO_2 and SS shows a minimum. Hence, samples containing more of Hydex-P are optimum for obtaining good optical properties, then TiO_2 and at last samples containing more of SS. This may be attributed due to the optimum particle size of HP as compared to TiO_2 and SS. Optimum

particle size means, the particle size of impurities which are present in the matrix are smaller than pores present. The small particle size of HP could be filled more densely into the pores present among the fibres. This may be the reason, to get better optical properties in HP filled samples.

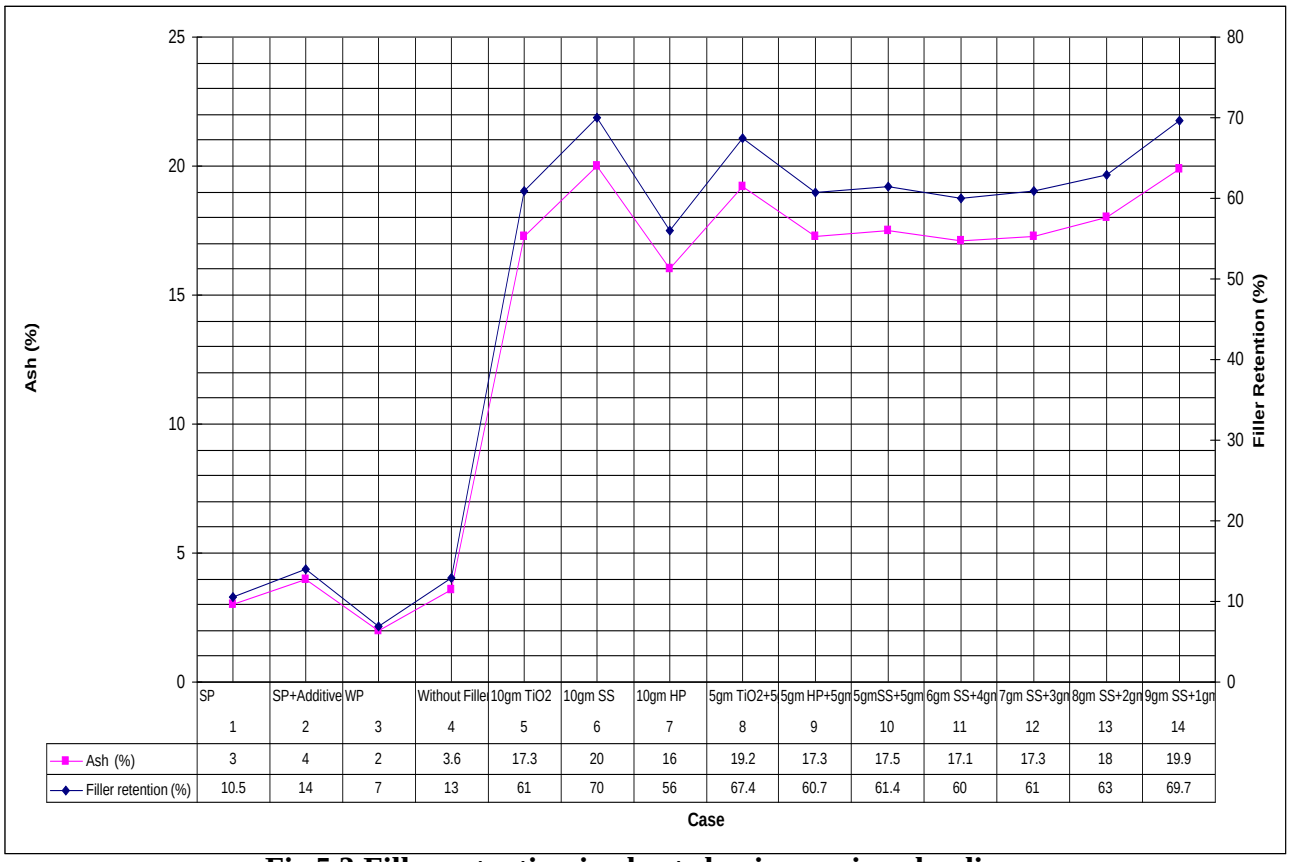


	SP	SP+Additiv	WP	Without Fill	10gm TiO2	10gm SS	10gm HP	5gm TiO2+5	5gm HP+5g	5gmSS+5gr	6gm SS+4g	7gm SS+3g	8gm SS+2g	9gm SS+1g
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Brightness (%)	80.7	82	84	82.7	85	83	87	82.2	87	86	85.7	85	84.1	83
Opacity (%)	84	85	75	86	91	88	91	90	91	90.7	90	89	89	88

Fig 5.2 Effect of Brightness and Opacity of samples having various fillers

Wood pulp shows minimum filler retention as can be seen in fig 5.3 due to long fibres present in it which are responsible for having gap in between the fibres, hence reducing filler retention in it. In other words, fillers come out easily as compared to the short fibers (straw pulp). However, with addition of fillers and other additives retention increases as more open pores present in fiber are filled up. If filler particle size is smaller than the pores present in the fibres then packing of the fillers in pores will be better. On filler addition, the observed filler retention is highest in case of samples containing more of SS and minimum in samples containing higher percentage of HP. On adding SS to TiO_2 the filler retention shows an increase compared to sample on addition of HP. Higher retentivity of SS in paper samples might be explained on the basis of compatibility of

both the materials. It seems that, the retentivity of the fillers might be explained on basis of the reactivity among matrix and fillers, availability of pores in the matrix and particle size of additives and fillers.



	SP	SP+Additive	WP	Without Fille	10gm TiO2	10gm SS	10gm HP	5gm TiO2+5	5gm HP+5gm	5gmSS+5gm	6gm SS+4gm	7gm SS+3gm	8gm SS+2gm	9gm SS+1gm
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ash (%)	3	4	2	3.6	17.3	20	16	19.2	17.3	17.5	17.1	17.3	18	19.9
Filler retention (%)	10.5	14	7	13	61	70	56	67.4	60.7	61.4	60	61	63	69.7

Fig 5.3 Filler retention in sheets having various loadings

Differential thermal analysis also called Differential Scanning Calorimetry (DSC) was carried out on samples 5(10gm TiO_2) and sample 12(7gm SS+ 3gm HP) to check their stability and phase transition in the temperature range of room temperature to 350ºC. The DSC curves of both samples are shown in fig 5.4 and fig. 5.5 respectively. In both the graphs, no endothermic and exothermic peaks were observed in the above mentioned temperature range. It is clearly indicated that there is no phase transition upto 240ºC. The decomposition of both the paper samples was started at ~240ºC and was completed at ~318ºC. However, the enthalpy is more in sample 5 as compared to sample 12. It means in sample 5, wherein 10gm TiO_2 was used as filler, additive is forming stronger bond as compared to sample 12. However, both the samples couldn't show any appreciable changes. Hence, it clearly indicates that fillers are not playing any role to change the thermal stability of the samples.

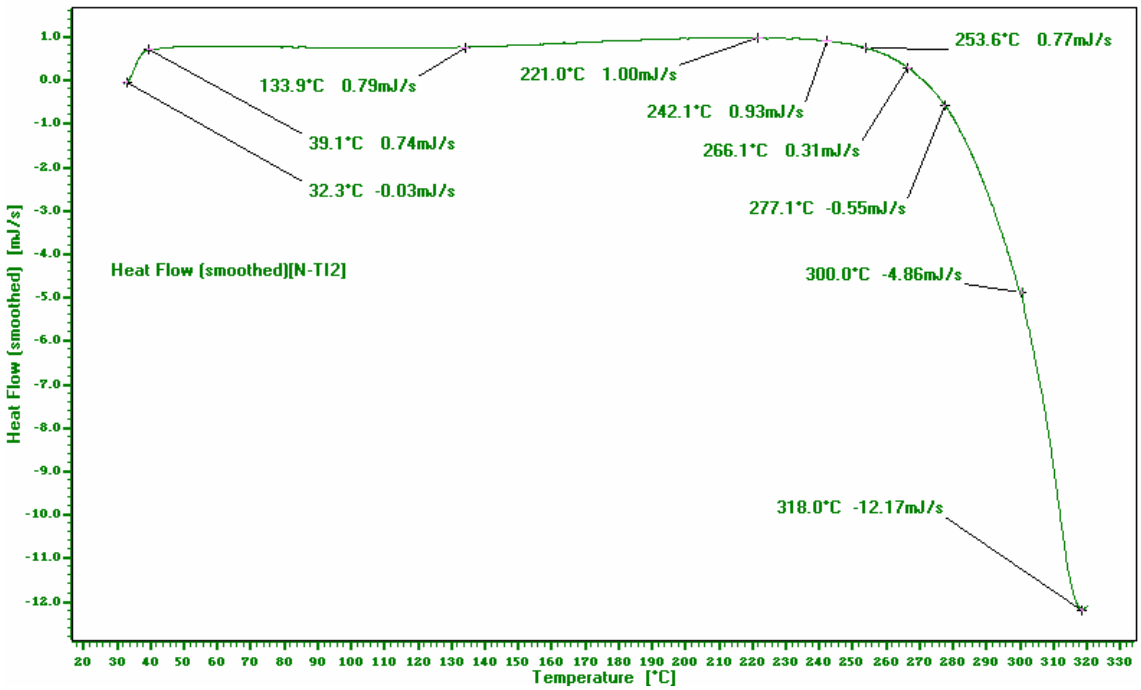


Fig 5.4 DSC curve of sample 5

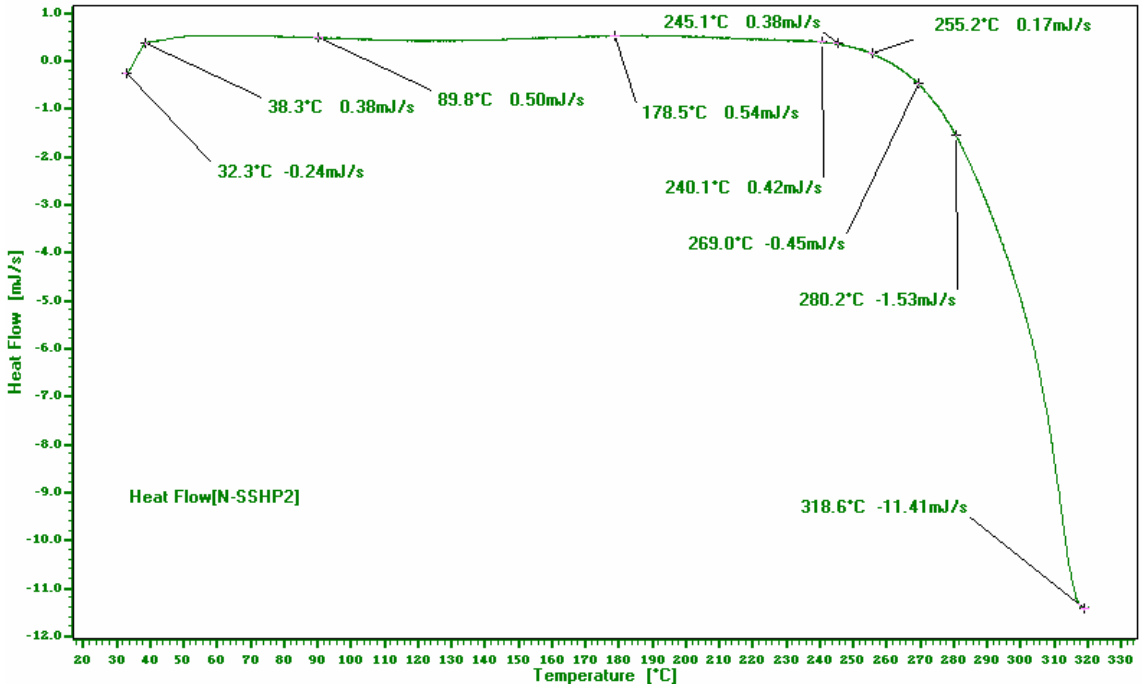


Fig 5.5 DSC curve of sample 12

X-rays diffraction (XRD) pattern was done on some selected samples to identify the various phases present and their effect on the physical properties of the samples. The sample selection for XRD analysis was based on the various additives and their effect on the properties. All the XRD patterns exhibit broad peaks at values of 2θ 20.5 to 24º. This broad peak in all samples is due to the presence of cellulose and hemicellulose. However, in case of sample 6 where we used 10gm SS, an additional peak was observed at 26.50ºC. On the other hand, when we decrease SS at the cost of HP, this particular peak disappeared from the XRD pattern as shown in fig 5.6 (b) and (c). In all three spectras (Fig 5.6 a, b, c) the most intense peaks were shifted at lower 2θ values without any change in their peak width. XRD pattern is also taken of sample 5(10gm TiO_2) and sample 9(5gm TiO_2+ 5gm HP) to compare their results with other samples.

Careful examination of XRD pattern as given in fig 5.6(d) indicates higher amount of amorphousness of this particular sample. Interestingly, this sample exhibit best optical properties (opacity and brightness) as compared to all other examined samples. On increasing the TiO_2 filler content at the cost of HP, the crystalline character of the samples increases. The broad peak also becomes sharper compared to that obtained in fig 5.6 (a), (b) and (c). Conclusively, the XRD patterns clearly indicate that the sample [as in fig 5.6(d)] wherein the amorphous behaviour is more pronounced & the optical properties shown are better due to proper amalgam between additive and straw pulp. Probably, filler bonding with matrix is better in case of sample 5 than sample 6 as shown in fig 5.6 (a) and (f). XRD patterns have also showed some unidentified peaks .The unidentified peaks might be attributed to the various additives present. As mentioned earlier, basically, the reactivity among the additives and matrix and their compatibility to each other and proper distribution of additives throughout the samples are very deciding factor to govern the physical and optical properties of present samples.

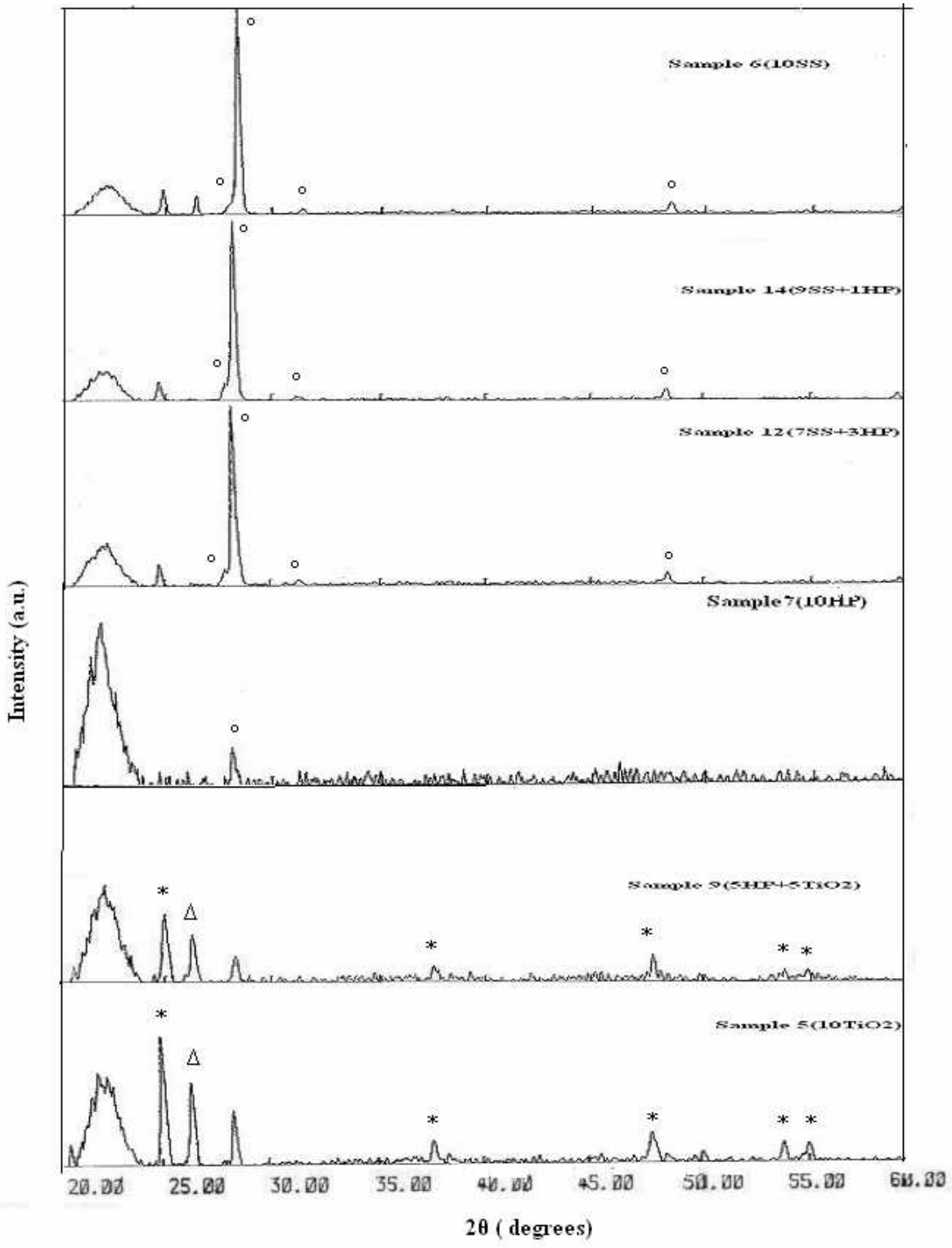


Fig 5.6 XRD plots for various samples viz: samples 6, 14, 12, 7, 9 and 5 as a, b, c, d, e and f respectively. Δ----TiO_2 (Rutile), *---TiO_2 (Anatase) and °----$Mg_3(OH)_2Si_4O_{10}$.

CONCLUSIONS

The following conclusions are drawn from the present study:

- **i)** Soapstone can be used as a filler for making high GSM paper (60 and above) as higher GSM supports the fiber. Hence, it can be used to prepare normal read and write papers.
- **ii)** In order to obtain high quality paper having high brightness and opacity, 1-2% of Hydex-P and TiO_2 can be used to replace soapstone and hence can obtain a lower GSM paper.
- **iii)** Among TiO_2 and Hydex-P, TiO_2 is preferred as filler as Hydex-P drastically affects (decreases) the strength of the paper.

By use of TiO_2 as filler a high degree of opacity is obtained without losing its strength. Unfortunately, the high cost of TiO_2 and Hydex-P fillers more than balances its advantage in this respect, except for high-grade papers.

FUTURE SCOPE OF WORK

During the study it is observed that Hydex-P (particle size 3-18µm) and its distribution in the paper sheet, highly affects both the strength and optical properties compared to TiO_2 and soapstone. Hence, the effect of particle size of fillers on paper properties can be studied. Also, effect of $CaCO_3$ (GCC) as a filler in replacement of TiO_2 and Hydex-P can be studied due to its low cost and better optical properties.

REFERENCES

[1] V.D. Khanilkar, Papermaker, Vol. 8, No. (12), P 32, Dec. (1998).

[2] J.E. Unbehend and K.W. Britt, Pulp and Paper, Vol. III, Chap. 17.

[3] S.E. Bruun, Starch, Papermaking Science and Technology, Book 11, Pigment coating and Surface Sizing of Paper, Finish Paper.

[4] Helsinki, Engineers Association and TAPPI, Finland, P 241-229, (2002).

[5] W.F. Reynolds and R.B. Wasser, Pulp and Paper, Vol. III, Chap. 13.

[6] Journal of Wood Science, Vol. 44, No. (2), March (1998).

[7] R.J. Kulick, Tappi, 60(10), 74(1977).

[8] K.W. Britt & J.E. Unbehend, unpublished results.

[9] W.F. Linke, Tappi, 45(4), 326(1962).

[10] C.E. Brandon, Pulp and Paper, Vol. III, Chap. 21.

[11] E. Wildemann, Wochenbl. Papierfabr., 99(1), 22(1971).

[12] O.Huber & J. Weigl, Das Papier, 26(10A), 545 (1972).

[13] Pulp and Paper, Vol. III, P 1539, Chap. 15.

[14] Ellen Mc Crady, Alkaline paper advocate, Vol. 4, No. (4), Nov (1991).

[15] reports.andritz.com/2003/index/technisches-glossar.htm

[16] Krista Koljonen, APPW, (2004).

[17] Wood Extractives Biocontrol (WEB) Project, European Project FAIR CT95-560, (1995-99).

[18] Sal Mirza, Guy Harvey, Martin Senechal and Stephane Ouellet, PAPTAC (2006).

[19] Wood in Our Future: The Role of Life-Cycle Analysis: Proceedings of a Symposium (1997).

[20] P.Marimuthu and G. Venkoba Rao, IPPTA Journal, Vol.15, No.(2), P 57, Apr.-June (2003).

[21] Jaakko Jantunen, Pperex, P 59, (2007).

[22] Extraction and characterization of original lignin and hemicelluloses from wheat straw, J. Agric. Food Chem., (2005).

[23] Straw's new horizons by Bertel Myreen, Pulp and Paper, P 23, Oct. (2000).

[24] Status of Pulp and Paper Industry in India: Handbook on Indian Pulp and Paper Industry, Chap. 1, (1998).

[25] Robert W. Hurter, P. Eng., TAPPI non-wood short course (1997).

[26] David C. Drown et al., Fertilizer Production from Wheat Straw Pulping.

[27] John H. KIungness, Fabienne Pianta, Mathew L. Stroika, Marguerite Sykes, Freya Tan and Said AbuBakr, Fundamental Advances in the Pulp and Paper Industry 99, Vol. 95, AIChE Symposium Series No. (322), (1999).

[28] Ross, W.D., Paint.Technol., 43 (563):51(1971).

[29] Ross, W.D., J. and EC Prod. Res, 13(1):45(1974).

[30] Houle, L.L., Boudreau, J. and Shukla, G., TAPPI (1990) Coating Conference Proceedings TAPPI PRESS, Atlanta, P 259.

[31] Kwoka, R.A., TAPPI (1990), Dyes, Fillers and Pigments Short Course Notes, TAPPI PRESS, Atlanta, P 21.

[32] Kwoka, R.A., TAPPI (1993), Coating Conference Proceedings TAPPI PRESS, Atlanta, P 133.

[33] Kwoka, R.A. and Logan, T.W., TAPPI J., 77(10): 136(1994).

[34] Peter Burri, Christian Naydowski, Daniel C. Spielmann and Ernest T. Swanson, TAPPI Journal, Vol. 80, No. (11), Nov. (1997).

[35] Canadian Pulp & Paper Association Meeting: Report, Vol.2, No.(1), Apr. (1989).

[36] Richard William, Papermaker, Vol. 8, No. (10), P 33, Oct. (1998).

[37] Dean, John A., The Analytical Chemistry Handbook, P 15.1–15.5, McGraw Hill, (1995).

[38] Raghvan et al.